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Mechanical Properties of Polylactide-Based Wrapping Films for the Food Industry

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Abstract

The aim of the work was to produce wrapping films made of biodegradable polymer PLA (polylactide) and its modification in the form of a polymer mixture with additions of aluminosilicate – montmorillonite and anti-bacterial concentrate – SilverBatch nanosilver; followed by analysis of selected mechanical properties of these films. The assessment of mechanical properties included checking the tensile strength, as well as assessment of the degree of deformation of the film due to force and of the value of Young's modulus measured. The results were analyzed statistically using such indicators as arithmetic mean and standard deviation.

Key words: packaging film, polymer, anti-bacterial additives.

Introduction

The basic procedure used to preserve the nutritional quality of food products is packaging. This treatment also allows to reduce losses and limit the amount of additives in food that extend its shelf life. The basic and most commonly used plastics for food packaging are as follows: PE – polyethylene, PP – polypropylene (OPP oriented variety), PS – polystyrene, PC – polycarbonate, PET – polyester, and PA – polyamide. Because PLA is obtained primarily from lactic acid, which can be made from renewable substances (such as potato, wheat and corn starch), it is a material accepted as GRAS (generally recognized as safe) by the Food and Drug Administration (FDA). For this reason, it is increasingly used to produce food and drink packaging [1].

As Carrasco et al. write, much attention has been paid to biodegradable polymers in recent years because of their wide range of applications in biomedical, packaging and agricultural fields [2, 3]. The most popular biodegradable polymers are as follows: poly(lactic acid) (PLA), polycaprolactone (PCL), poly(butylene adipate terephthalate) (PBAT) and polyhydroxybutyrate (PHB) [4-8]. Poly(lactic acid) is a linear aliphatic thermoplastic polyester. It gained popularity by being made from renewable resources and easily biodegradable. PLA has many good mechanical properties, good thermal stability, is easy to process, and has little impact on the environment (it is biodegradable). The problem with recy-

cling this material is related to its thermal stability [9]. Compared to commodity polymers (like PET, PS, i-PP), PLA often presents the highest mechanical properties but the lowest thermal resistance [2, 10, 11]. Also, this polymer presents some advantages like good processability in conventional industrial transformation equipment and biocompatibility.

PLA is often studied in terms of the possibility of creating a composite that combines this polymer with nanostructures, especially for food packaging applications. Youssef and El-Sayed, in their study, described concepts and future perspectives regarding the use of bionanocomposites, including PLA materials in food packaging [12]. In the light of promising participation in food packaging applications, the effect of the addition of cellulose nanocrystals (CNC) on the barrier properties as well as immigration efficiency of pure PLA and its bionanocomposites were investigated [13, 14]. Several studies have been performed involving the modification of PLA by adding montmorillonite (MMT) nanocomposite to it in various concentrations [15-19]. Numerous publications confirm that the addition of MMT to PLA film increases its mechanical strength [15-18].

Fortunati et al. [20, 21] produced PLA based high performance composites for packaging applications using an innovative combination of cellulose nanocrystals (CNC) and silver nanoparticles (Ag) in order to obtain multifunctional systems. A bactericidal effect of nanocomposites on *Staphylococcus aureus* and *Escherichia coli* was detected, suggesting that these systems offer good prospects for food packaging and sanitary applications, which require an antibacterial effect constant over time [22].

Purpose and scope of research

The purpose of the work was to produce degradable packaging films with antibacterial properties for the food industry and to determine their mechanical properties. Tests were conducted to check the tensile strength of the film tested. This particularly concerned checking the effect of bactericidal additives on the value of the force causing the film to break. The tests allowed verification of the suitability of the anti-bacterial phase film for packaging selected food products.

The scope of the work included the production of packaging film (polymer films and films with additives), checking the impact of selected food products on the film produced, assessment of mechanical properties of the materials tested, and analysis of test results obtained.

Materials and methods

Four types of materials in the form of film were prepared for research. The first film was made of PLA – INGEO 3251D polylactide, manufactured by NATUREWORK. It was the reference film. The polymer granulate was dissolved in a solvent, which was methylene chloride (dichloromethane), manufactured by the Avantor Performance Materials Poland company. The proportions of the ingredients were as follows: 5 g of 3251D polymer was dissolved in 50 ml of dichloromethane (CZDA, ACS, FP test). In addition to the original films, films with the following bactericidal additives: montmorillonite (MMT – Akros) and nanosilver (antibacterial concentrate – SilverBatch) were also prepared. Montmorillonite is a layered aluminosilicate obtained from volcanic mineral with a par-

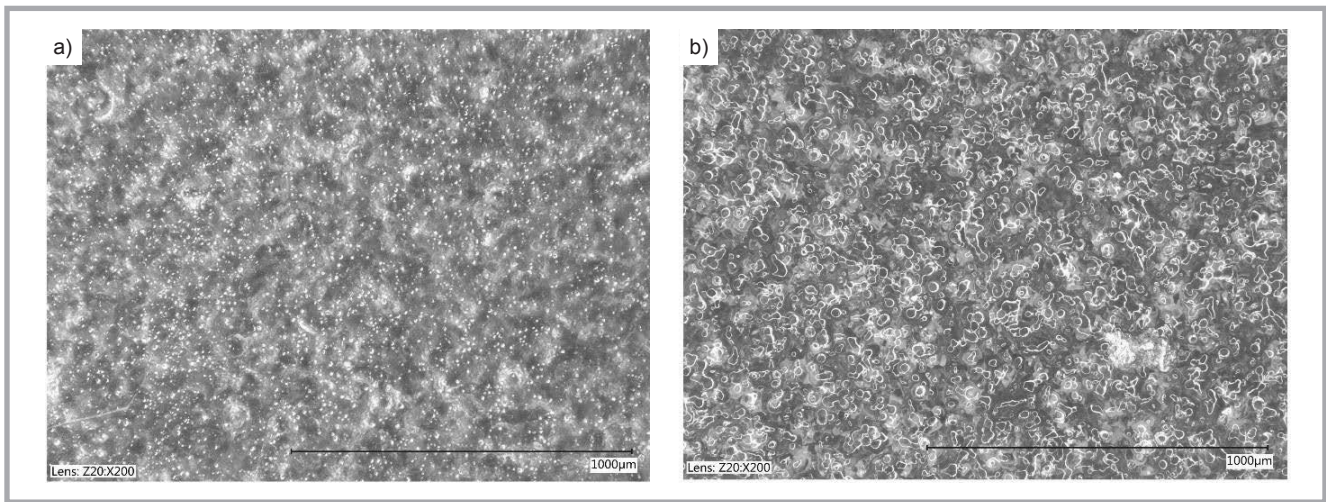


Figure 1. Microscopic photo of PLA (a) and PLA/MMT 4% (b) samples, before incubation (200x magnification)

ticle size from 100 to 150 nm. Silver-Batch antibacterial concentrate contains silver nanoparticles dispersed in the PLA polymer matrix with an average size of 5 nm. The choice of nano-additives was justified by numerous studies, confirming not only the bactericidal properties of these materials, but also their positive effect on the strength of the film. **Table 1** presents the components of the samples obtained together with a description of their preparation and the proportions of the substrates.

The solutions were poured into glass petri dishes. Finished film material was obtained after a week of convection drying at ambient temperature (ranging from 20 to 25 °C). The resulting samples were divided into three parts. One was left at ambient temperature, at which mechanical analysis was performed. The remaining samples were incubated at a temperature of 20-25 °C and 40 °C for 21 days. As the incubation medium, beet acid produced from beetroot boiled in water in the proportion of 1 kilogram of beetroot per 3 litres of water was used. The solution pH was identified by the use of electronic acidimetry and amount-

ed to 3.8. The films produced, based on the EN ISO 527-1: 2012 standard [15], were used to prepare samples for testing material strength. Each sample had the following dimensions: length 90 mm and width 5 mm. The film thickness measured was 0.14-0.16 mm.

Films are used to pack food of various pH. Usually these are neutral products (pH), but it happens that the film is also in contact with an acidic environment (pH < 7). Therefore, some of the films produced were treated with beet acid, which is a component of beetroot acid – a minimum of five samples of each material, both non-incubated and incubated at 20 °C and 40 °C. The film samples were immersed in beetroot acid for a period of 14 days and then dried.

The remaining samples were stretched. Tests were carried out on a ZWICK brand testing machine with a nominal force of 5 kN, in accordance with the methodology given in the EN ISO 527-1: 2012 standard, Plastics – Determination of mechanical properties at static stretching – Part 1: General principles. Tests for each sample were carried out in five series

(i.e. five tests for each material tested). During the analysis, results were eliminated that were found to be incorrect (error caused by machine operation or poor sample preparation). The distance between the machines jaws was 70 mm, and the fixed, constant speed of the traverse – 2 mm/min.

Material tensile strength tests were carried out on polymer and composite films. During the tests carried out on the testing machine, three mechanical parameters of the samples of the materials tested were determined: R_m – tensile strength, in MPa, $\varepsilon_{(F_{max})}$ – deformation at the maximum strength, in mm or % and E – Young's modulus, in GPa. Tensile strength is a parameter determining the stress, understood as the ratio of the largest tensile force obtained during a static tensile test of the material to the original cross-sectional area of the sample tested [16]. It is expressed by the following formula:

$$R_m = \frac{F_{max}}{S_0}$$

Where, R_m – tensile strength, F_{max} – maximum creeping force, S_0 – primary cross-sectional area of the sample tested. The deformation (ε), determined at the

Table 1. Components of the samples tested along with the method of their preparation.

No.	Working name of the sample	Sample components	Sample preparation method
1.	PLA – Basic sample	INGEO 3251D polymer – 5 g, methylene chloride – 50 ml	INGEO 3251D polymer in granular form was dissolved in methylene chloride. A magnetic stirrer was used to obtain a homogeneous material.
2.	PLA/2MMT – Sample with the addition of MMT 2% by mass	Polymer INGENO 3251D – 5 g, methylene chloride – 50 ml, MMT K10 – 0.1 g	Methylene chloride was mixed with MMT using an ultrasonic mixer. INGENO 3251D polymer granulate was dissolved in the solution prepared using a magnetic stirrer.
3.	PLA/4MMT – Sample with the addition of MMT 4% by mass	Polymer INGENO 3251D – 5 g, methylene chloride – 50 ml, MMT K10 – 0.2 g	Methylene chloride was mixed with MMT using an ultrasonic mixer. INGENO 3251D granular polymer was dissolved in the solution prepared using a magnetic stirrer.
4.	PLA/Ag – Sample with the addition of nanosilver SilverBatch 2% by mass	INGEO 3251D polymer – 5 g, methylene chloride – 50 ml, SilverBatch – 0.1 g	Methylene chloride was mixed with INGENO 3251D polymer and SilverBatch nanosilver using a magnetic stirrer.

maximum force (F_{max}), is expressed as the ratio of the elongation of the material (l) to the initial length (l_0):

$$e_{F_{max}} = \frac{l}{l_0}$$

Young's modulus is a quantity determining the elasticity of a material. The Young's modulus of most materials depends on two factors: the interatomic stiffness and bond density per unit area. Polymers exhibit strong covalent and weak hydrogen bonds at the same time, i.e. Van der Waals bonds (0.5 ÷ 2 N/m). Poor bonds allow the significant deformation of polymers, causing a decrease in the value of the E module of these materials to the level of 1 GPa [23].

Results

Analysis of material microstructure properties after the application of fillers

Observations of the microstructure of the films produced were aimed at assessing their homogeneity and comparing the impact of the additive introduced on the construction of the film. **Figure 1** shows microscopic photos of an example sample of the film produced.

Analysis of computer images showed that the film made from the material without additives is definitely more uniform and smooth than samples of PLA film with bactericidal additives. The addition of MMT and nanosilver to the film increased the unevenness of its surface. Evidence of this are the visible pores and crystallites of the material on samples made of a mixture of PLA and bactericidal fillers MMT (**Figure 1**).

Analysis of mechanical properties

In **Figures 2-4**, presented are average values of the parameters tested, with the standard deviation marked for all samples (i.e. PLA, PLA/2MMT, PLA/4MMT, PLA/Ag) before incubation and after incubation at a temperature of 20 °C and 40 °C.

Test samples of basic PLA showed similar tensile strength, in the range <25.01; 49.66> MPa. The smallest deformation of the material at the maximum force was 0.73%, and the largest 2.66%. The deformation of samples incubated before stretching was definitely less than that of the samples before incubation. Young's modulus for all samples tested is in the range <2.2; 3.6> GPa, which cor-

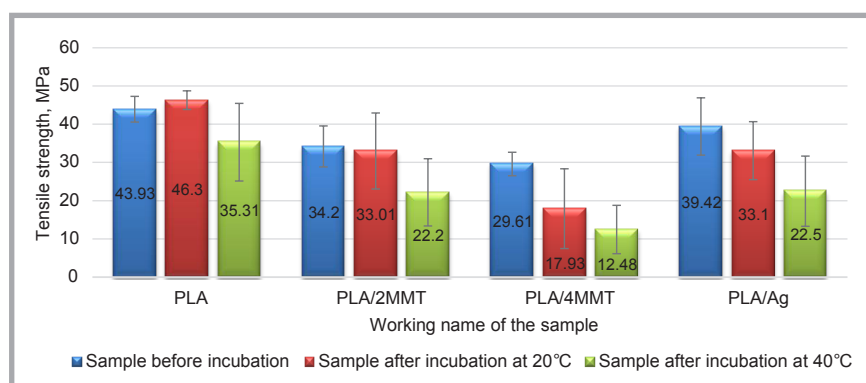


Figure 2. Average values of tensile strength for all samples tested before and after incubation.

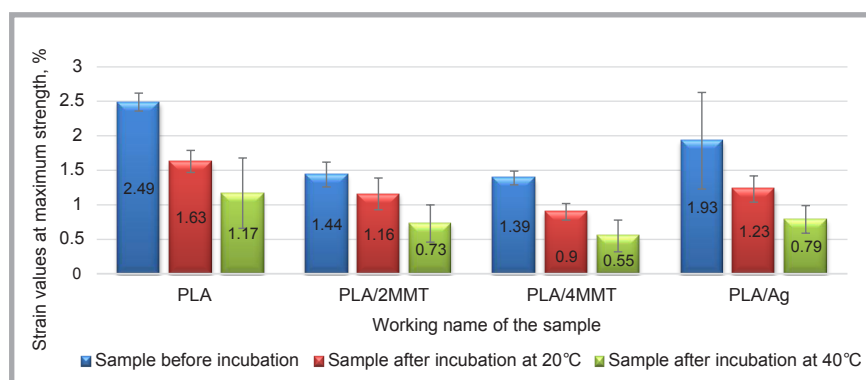


Figure 3. Average strain values at maximum strength for all samples tested before and after incubation.

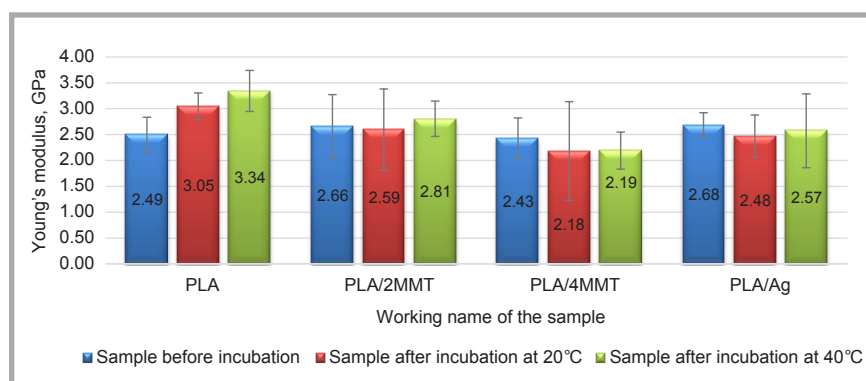


Figure 4. Average values of Young's modulus for all samples tested before and after incubation.

responds to the Young's modulus values characteristic for plastics, such as polyethylene terephthalate (PET), for which it is 2.0-2.5 GPa, and polystyrene (PS), ranging 3.0-3.5 GPa. The average value of tensile strength for the PLA sample before incubation was close to 44 MPa, the value of which increased by less than 2.3 MPa (approximately 5.8%) for the sample incubated at 20 °C, but decreased by about 9 MPa (20.5% change) for that incubated at 40 °C. The largest deformation was shown by the sample before incubation, and its average value decreased with incubation at 20 °C and incubation at 40 °C. The mean values of Young's modulus for the basic sample were in the range from 2.5 to 3.3 GPa. It should

be noted that all values determined for a 95% confidence interval indicate relatively small deviations, excluding values for samples incubated at 40 °C. For example, analysis of the results showed that with a probability of 95%, the tensile strength of the test material after incubation at 40 °C is in a range with wide limits – <10.11; 60.52> MPa. This result may be due to the low sample population or the occurrence of defects associated with the secondary agglomeration of particles during the air drying process.

The PLA/2MMT samples tested (polymer with 2% MMT) showed similar tensile strength before and after incubation at a temperature of 20 °C. The val-

ues of strength obtained were in the range <16.65; 45.42> MPa, with the minimum value (and the second lowest) obtained for the sample incubated at 40 °C. The smallest strain was 0.56 and the largest – 1.71. Similar to basic PLA samples, higher strain values were noted for non-incubated samples. Young's modulus for all samples tested is in the range <1.7; 3.7> GPa. It is worth noting that for the test samples with a 2% MMT addition, the deformation value was lower than for those without the addition of this material. However, it is less resistant to stretching.

The average tensile strength for the PLA/2MMT sample before incubation was just over 34 MPa, the value of which slightly decreased for the sample incubated at 20 °C, and decreased significantly (i.e. by about 12 MPa) for that incubated at 40 °C. The largest strain was recorded for the sample before incubation, and its average value decreased with incubation at 20 °C and 40 °C. The mean Young's modulus values for the PLA/2MMT sample were in a narrow range <2.7; 2.8> GPa. As with the basic PLA sample, all values determined for a 95% confidence interval indicate relatively small deviations, excluding those for samples incubated at 40 °C. For example, analysis of the results showed that with a probability of 95%, the tensile strength of the test material after incubation at 40 °C is in a range with very wide limits – <0.39; 44.01> MPa for the standard deviation 8.79. This result is probably due to the fact that the nanocomposites from which the films were made were not monodisperse. The degree of homogenisation of the materials significantly affected the results of mechanical properties (the samples were mixed only mechanically, hence the homogenisation of the filler in the matrix could not be sufficient).

In the PLA/4MMT samples tested (polymer with 4% MMT), a greater variation in tensile strength results was observed. The highest values were obtained for samples before incubation, and the lowest after incubation at 40 °C. Values for incubated samples were almost twice lower than for non-incubated ones. The smallest value of strain at stretching was at the smallest force – 0.29%, and at the highest – 1.46%. These values are lower than for PLA and PLA/2MMT samples. As with samples without additives and those with 2% MMT, pre-incu-

bation samples had greater material strain than incubated ones, with samples incubated at 40 °C having the least strength. Young's modulus for all types of materials tested is in the range <1.5; 3.5> GPa. As in the case of samples with the addition of 2% MMT, this value was lower than for samples without the addition of this material, and its range is larger, covering the ranges characteristic for most plastics (including PP, PET & PS). The average tensile strength values for material with 4% MMT were lower than for material without or with 2% MMT. The reason for this may be better homogenisation of the PLA/2MMT solution. In addition, a higher concentration of MMT powder caused greater agglomeration of the particles, which reduced the strength of the resulting film. The average value of tensile strength for the PLA/4MMT sample before incubation was less than 30 MPa, the value of which decreased by almost half for the sample incubated at 20 °C, and significantly for that incubated at 40 °C. The highest strain value was shown by the sample before incubation, the average value of which decreased with incubation at a temperature of 20 °C and 40 °C; but these values were much lower than for the materials previously discussed. The average Young's modulus values for the PLA/4MMT sample were in a narrow range: <2.2; 2.4> GPa. This range is close to that for polyethylene terephthalate (PET), which is <2; 2.5>. Similar to the basic PLA sample and the other samples discussed above, all values determined for a 95% confidence interval indicate relatively small deviations, excluding those for samples incubated at 40 °C.

In the materials tested from the PLA/Ag group (polymer with 2% addition of nanosilver), a greater diversity of tensile strength results was also observed. The highest values were obtained for samples before incubation, and the lowest – after incubation at 40 °C. Values for incubated samples were almost four times lower than for unincubated samples, where the smallest strain was 0.54% and the largest 1.48%. Similar to the samples without additives and those with a 2% and 4% addition of MMT, samples before incubation were characterised by a greater strain of the material than those incubated. Young's modulus for all samples tested is in the range <1.8; 3.3> GPa. As in the case of samples with a 4% MMT addition, the range of Young's modulus recorded for

the samples tested includes ranges characteristic for most plastics (including PP, PET & PS). The lowest tensile strength was recorded for the PLA/4MMT sample (polymer with 4% MMT) incubated at 40 °C, and the highest for the PLA sample (polymer without additives) incubated at 20 °C. The smallest strain created using the maximum force was also noted for the PLA/4MMT sample incubated at 40 °C, and the highest for the PLA sample incubated at a temperature of 20 °C. One of the PLA/4MMT samples tested was characterised by the lowest Young's modulus value, and the highest was exhibited by one of the PLA/2MMT samples tested (polymer with 2% MMT).

A statistical analysis of the results was performed for more accurate inference. The arithmetic mean and standard deviation were calculated for the range of parameters tested at a 95% confidence interval. The average tensile strength for the PLA/Ag sample before incubation was almost 40 MPa (nearly 10 MPa higher than for the PLA/4MMT sample), the value of which decreased by almost 7 MPa for the sample incubated at the lower temperature, and almost twice for that incubated at the higher temperature. The highest deformation value was shown by the sample before incubation, whose average value decreased with incubation at 20 °C and at 40 °C. The mean Young's modulus values for the PLA/Ag sample were in a narrow range: <2.5; 2.7> GPa, which is between the range of Young's modulus of polyethylene terephthalate (PET), which is <2; 2.5> and that of Young's modulus for polystyrene, which is <3.0; 3.5>. Contrary to the results for PLA, PLA/2MMT and PLA/4MMT samples, there were no such large deviations of values determined at a confidence interval of 95% as before. It can therefore be concluded that the film with the addition of nanosilver was characterised by better particle homogenisation.

Figures 5-7 show examples of static stretching diagrams of test material samples made by use of the testing machine. The maximum of the curve on the graph signifies the R_m value, i.e. the tensile strength. The horizontal displacement of curves in *Figures 5-7* was used to obtain better legibility.

The graphs of strength characteristics of incubated samples, especially those incubated at 40 °C, are almost linear. Such characteristics of the graph indicate

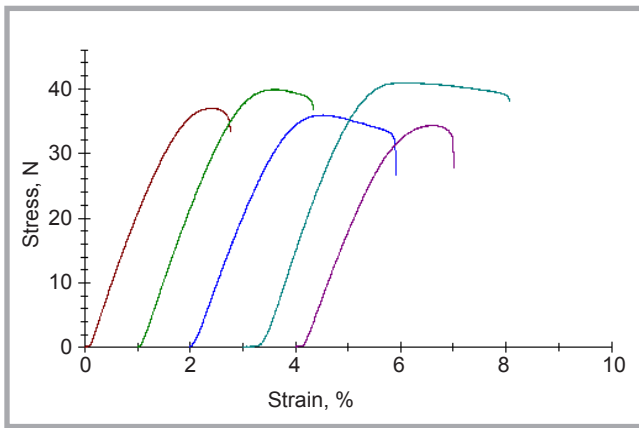


Figure 5. Graph of static stretching of PLA stock samples before incubation.

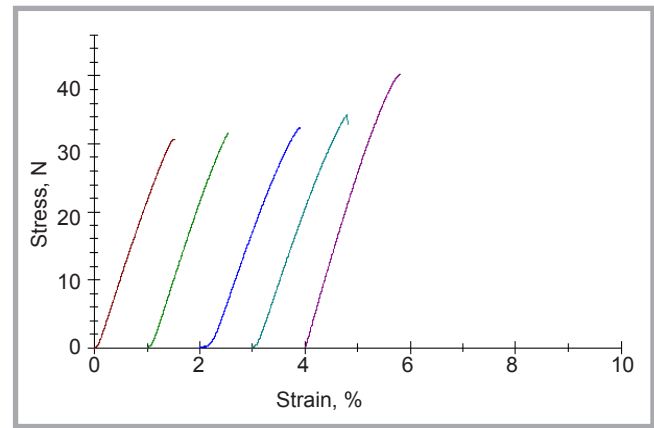


Figure 6. Graph of static stretching of PLA stock samples after incubation at a temperature of 20 °C.

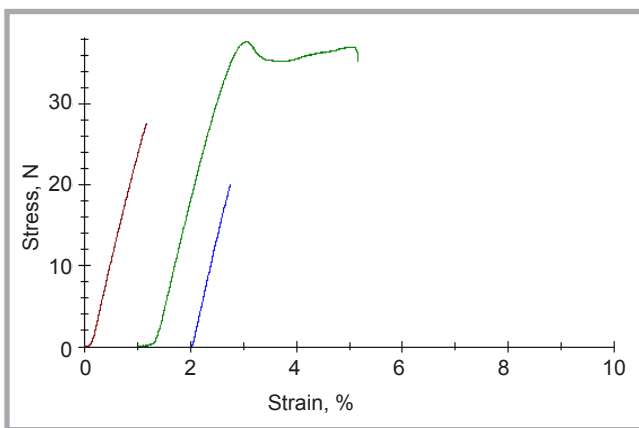


Figure 7. Graph of static stretching of PLA stock samples after incubation at 40 °C.

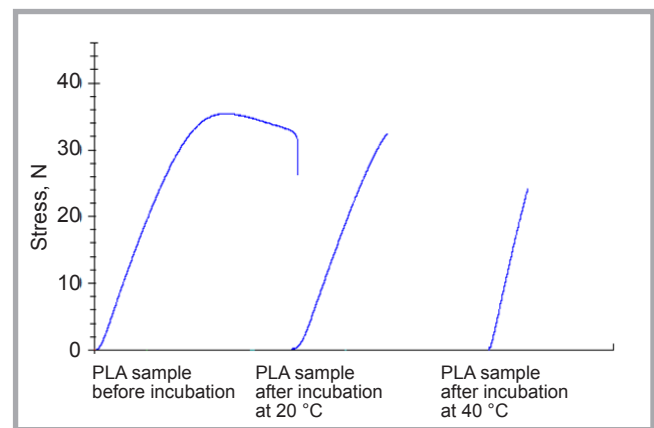


Figure 8. Comparison of static stretching characteristics of the PLA stock sample before incubation, and after incubation at 20 °C and 40 °C.

greater fragility of the material, which thus breaks faster. Plots of non-incubated samples have a non-linear pattern, which means that they were more ductile – as a result of the force, the material first stretched, underwent plastic deformation, and only later broke. **Figure 8** is a graph that shows the strength characteristics of a selected sample before and after its incubation at 20 °C and at 40 °C.

Analysing the graph (**Figure 8**), it can be seen that incubation of the film at 20 °C did not affect the course as clearly as incubation at a temperature of 40 °C. Therefore, the incubation process at higher temperature directly reduced the plasticity of the film, which is confirmed by the analysis of static stretching characteristics of the remaining samples.

■ Conclusions

The analyses carried out allowed us to formulate two main conclusions. Firstly, testing the strength of the material using a testing machine showed that non-in-

cubated samples displayed significantly higher plasticity than for incubated samples. The material incubated at 40 °C was the most fragile. Secondly, the film without bactericidal additives had the highest average tensile strength, while the lowest was shown by the film with 4% MMT. For incubated samples, the average tensile strength value for films with 4% MMT was almost twice lower than that recorded for films with 2% MMT and 2% nanosilver (SilverBatch). However, the results concern a solvent casted film.

Well-dispersed, homogeneous composites are characterised not only by good antibacterial properties but also by better (compared to basic materials) mechanical properties [24, 25]. Therefore, it should be assumed that the deterioration of mechanical properties in the films tested may be associated with the insufficient homogenisation of additives in the polymer matrix. Nanometric MMT particles in a heterogeneous solution tend to re-agglomerate the particles, which directly affects the formation of micromet-

ric particles in the material. The level of homogenisation of solutions containing SilverBatch was also not satisfactory, which was confirmed by photos of film microstructures containing nanofillers. The unsuccessfully carried out dispersion resulted in finally obtaining heterogeneous nanocomposites, which, in turn, significantly weakened the final material.

Based on the research carried out, it should be stated that among the four materials for packaging food products analysed, the most useful should be the film without bactericidal additives, not incubated. Films with the addition of MMT and nanosilver showed less strength, but their undoubted advantage may be the bactericidal action, which would prolong the product's durability. Regardless of the composition, it was shown that contact with liquids, especially at elevated temperatures, can reduce shelf life and change the characteristics of packaging materials. This is especially important if the packaging should ensure the long-term safe storage and protection of the

product. Therefore, research should be extended to determine the safe time of use of packaging films, assuming minimal strength and microbiological analysis, which would allow to determine the effectiveness of the use of antibacterial agents.



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