

PLA PLASTICIZED WITH ESTERS FOR PACKAGING APPLICATIONS

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ABSTRACT. In this study, polylactic acid PLA was melt blended with bis(2-(2-butoxyethoxy)ethyl) adipate, tributyl citrate and/or sorbitan monooleate. The thermo-mechanical analysis of plasticized PLA highlighted an improvement in its behavior. Thus, the plasticization of PLA with the tested esters favored the lowering of its vitrification temperature and the bending resistance of the tested materials at room temperature varied in an area of interest for all the tested plasticizers. No significant difference was noted between the maximum flexural strengths and the elongation at deformation recorded at 25°C and those at 4°C for the three recipes. Also, the weight loss of PLA recipes in contact with water decreases in the presence of hydrophobic plasticizers.

Keywords: PLA, bioplasticizer, DSC analyses, vitrification temperature, flexural strength, water absorption

INTRODUCTION

Food packaging contributes significantly to environmental pollution. For this reason, plastic materials will need to be biodegradable to limit environmental pollution. They can be obtained from bio-renewable resources, usually called biopolymers, and have excellent mechanical and barrier properties. Thus, biopolymers are considered potential ecological substitutes for non-biodegradable and non-renewable materials currently used in food

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packaging [1-4]. Moreover, biopolymers are excellent polymer matrices that incorporate a wide variety of additives, such as antioxidants, antimicrobial agents, etc. [3,5]

Renewable biomass-based bioplastic packaging materials could be used as a sustainable alternative to petrochemical-based plastics [1, 7, 8]. Thus, polyhydroxyalkanoates like polylactic acid (PLA) are aliphatic biopolyesters with a potential for sustainable replacement of thermoplastic polymers based on fossil raw materials in developing smart packaging films [1,6].

Polylactic acid (PLA) is classified as safe by the United States Food and Drug Administration (FDA) for all food packaging applications. It has become increasingly interesting in the manufacture of biodegradable plastic materials due to its superior transparency and easy processability compared to other biodegradable polymers. Low resistance, hydrophobic character, relatively low crystallinity, limited thermal processability, lack of reactive functional groups along the polymer chain and high costs are the main limitations of this polymer in industrial applications [9-15].

Concerns to improve the performance of PLA are oriented towards the identification of effective plasticizers or additives. Numerous parameters such as solubility, polarity and structural compatibility are considered important and can influence the selection of effective plasticizers. In this context, the structural characteristics determine the compatibility of these plasticizers with PLA. A low compatibility of the plasticizer with PLA favors the migration of the plasticizer over time to the surface of the film, accelerating the aging of the plastic material. Also, the selection of the plasticizer must take into account the efficiency of the processing, the mechanical and thermal characteristics as well as water resistance. At the same time, the plasticizer must improve the flexibility and workability of the polymer. Usually the plasticizer lowers the glass transition temperature T_g of the polymer, it can improve the tear resistance and flexibility even at low working temperature [16].

Bis(2-(2-butoxyethoxy)ethyl) adipate (DBEEA) exhibits lower viscosity and volatility compared to the phthalate-type equivalent, good miscibility with polymers of relatively low polarity, maintains plasticity at low temperatures and improves strength polymers to heat. It also shows good stability when storing the plastic material and favorable properties of flexibility at low temperature.

The new technological solutions in the synthesis of acids and alcohols from renewable raw materials are the basis of the production of bioplasticizers that are an alternative to their phthalate counterparts. These substitutes, among others, include citric acid esters such as tributyl citrate, but migration of citrates from plasticized products can be a problem.

The use of a bioplasticizer with surfactant characteristics such as sorbitan monooleate was aimed at improving the compatibility of the plasticizers used in this study with PLA.

The objective of this study was to prepare and determine the thermo-mechanical properties and water absorption properties of PLA plasticized with bis(2-(2-butoxyethoxy)ethyl) adipate, tributyl citrate and/or sorbitan monooleate.

RESULTS AND DISCUSSIONS

The synthesized recipes were homogeneous and did not contain incorporated air bubbles, as can be seen in the images obtained with the scanning electron microscope in figure 1.

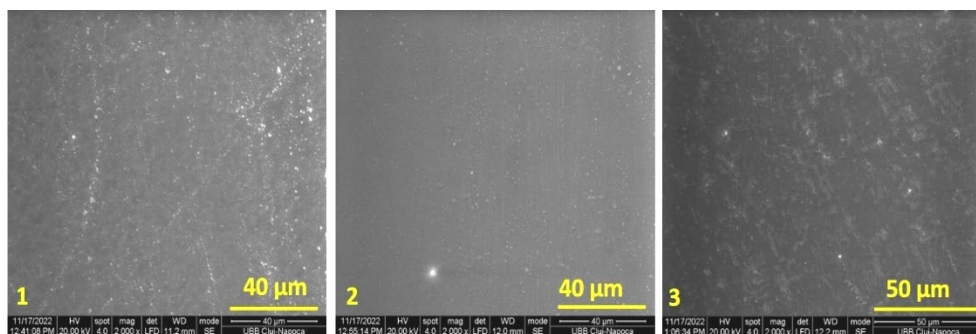


Figure 1. SEM images, at a magnification of x2000, on the surface of samples 1, 2 and 3.

The three samples have in their composition the same concentration of PLA (85%). Samples 1 and 2 contain the same type of bis(2-(2-butoxyethoxy)ethyl) adipate and sample 3 contains tributyl citrate. The concentration of Proviplast esters in sample 1 is higher (15%), while in samples 2 and 3 it is 11.5%. Also, samples 2 and 3 additionally contain an identical concentration of sorbitan monooleate (3.5%). In both cases, the surfaces of samples 2 and 3 are smoother than the surface of the sample without sorbitan monooleate (sample 1). The most homogeneous surface is observed in the case of sample 2, which contains the same type of Proviplast as sample 1 but in a lower concentration, having in addition sorbitan monooleate in its composition.

Differential scanning calorimetry (DSC) thermograms

The increase in temperature favors the appearance of some phase transitions, which involve a change in the thermodynamic properties of the recipe, as can be seen in figure 2. The characteristic temperatures of the DSC curves for the PLA-based formulations are shown in Tables 1.

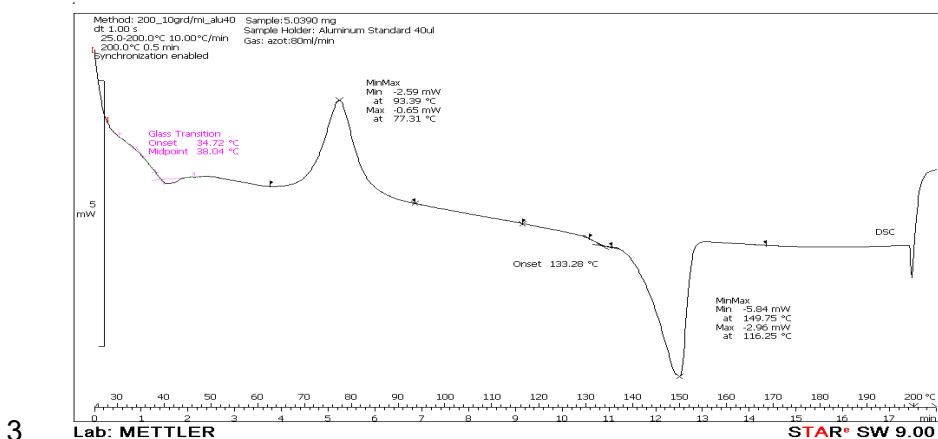
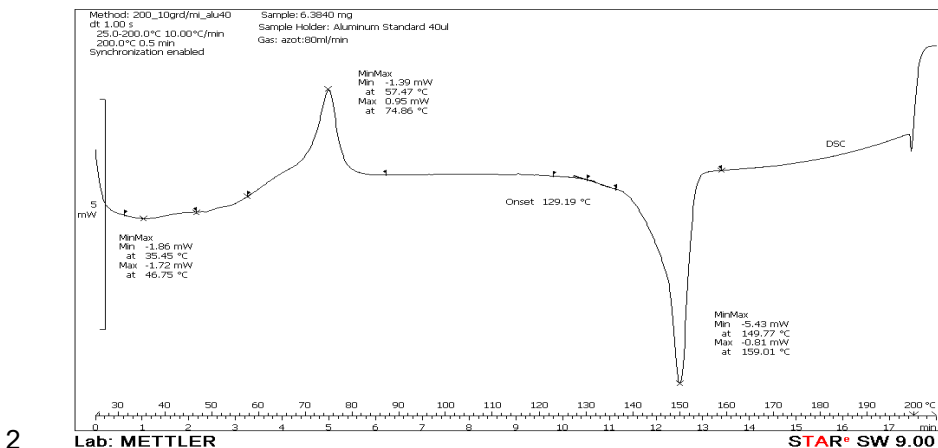
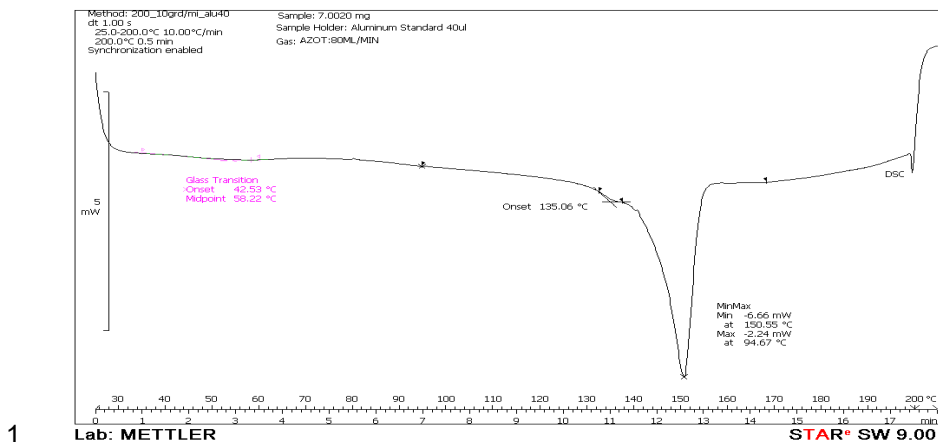


Figure 2. DSC curve of the samples

The transformations identified in the sample 1 DSC curve are:

- in the temperature range 25-80 °C an inflection point with the onset of the transformation temperatures 42.53°C with midpoint temperature values of 58.22 °C (probably the vitrification temperature);

- in the temperature range 80-200°C an endothermic process (probably melting) was identified, with the onset of the transformation temperatures of 135.06 and 150.55°C respectively;

The DSC analysis revealed that plasticizing of polylactic acid with bis(2-(2-butoxyethoxy)ethyl) adipate at a concentration of 15%, favors lowering the vitrification temperature to 58.22 °C and an endothermic transformation (probably soaking) at temperatures of 135.06 and 150.55°C respectively.

Table 1. Characteristic temperatures for samples.

Sample	DSC		The process type
	Temperature interval (°C)	Temperature transformation (°C)	
1	25-80	Onset 42.53 58.22	glass transition
	80-200	Onset 135.06 150.55	endothermic process
2	25-60	35.45	slightly endothermic process
	60-90	74.86	exothermic process
	90-200	Onset 129.19 149.77	endothermic process
3	25-70	Onset 34.72 38.04	Glass transition
	70-100	77.31	Exothermic process
	100-200	Onset 133.28 149.75	Endothermic process

The transformations identified in the sample 2 DSC curve are:

- in the temperature range 25-60 °C a weak endothermic process was identified, with transformation temperature values of 35.45 °C;

- an exothermic process has been identified in the temperature range 60-90°C, with transformation temperature values of 74.86°C;

- in the temperature range 90-200°C an endothermic process (probably melting) was identified at 149.77°C, with the onset of the transformation temperatures of 129.19°C.

The DSC analysis revealed that plasticizing of polylactic acid with dibutoxyethoxyethyl adipate at a concentration of 11%, in the presence of

fatty acid sorbitol esters, favor the appearance of endothermic transformations at temperatures of 35.45°C and 149.77°C respectively, as well as an exothermic transformation at temperature of 74.86°C.

The transformations identified in the DSC curve of the sample 3 are:

- in the temperature range 25-70°C has been identified an inflection point with the onset of the transformation temperatures 34.72 °C and midpoint of 38.04°C (probably the vitrification temperature);

- an exothermic process has been identified in the temperature range 70-100°C, with transformation temperature values of 77.31°C;

- in the temperature range 100-200°C an endothermic process (probably melting) was identified at 149.75°C, with the onset of the transformation temperatures of 133.28°C respectively.

The DSC analysis revealed that plasticizing of polylactic acid with tributyl citrate at a concentration of 11.5%, in the presence of sorbitan monooleate, favor lowering the vitrification temperature to 38.04 °C and the appearance of endothermic transformations at temperatures of 149.77°C as well as an exothermic transformation at temperature of 77.31°C.

Mechanical bending tests

Results of the flexural test at a temperature of 25°C and 4°C are shown in table 2.

Table 2. Results of the flexural test.

Samples	Load at Maximum Load (N)	Young's Modulus of Bending (MPa)	Flexural Rigidity (Nm ²)	Maximum Bending Stress at Maximum Load (MPa)	Maximum Bending Strain at Maximum Load (N/mm ²)	Elasticity (mm)
At a temperature of 25°C (± standard deviation).						
1	82.5997 ±11.95526	712.8231 ±221.145	0.01515 ±0.009	37.888 ±15.1216	0.3376 ±0.087	8.944 ±1.115
2	92.9024 ±14.1524	1007.1113 ±199.428	0.01902 ±0.005	44.8928 ±14.541	0.1385 ±0.025	4.985 ±0.956
3	83.3344 ±12.4241	1359.8934 ±183.655	0.01762 ±0.004	51.6224 ±19.5488	0.1240 ±0.045	5.200 ±0.848
At a temperature of 4°C (± standard deviation).						
1	56.6757 ±12.8744	613.8090 ±265.8041	0.01053 ±0.006	28.9162 ±12.4010	0.3680 ±0.0999	9.8264 ±2.154
2	116.2945 ±20.9986	1986.6484 ±310.5481	0.03223 ±0.009	61.709 ±23.48472	0.1535 ±0.08457	5.0036 ±2.212
3	126.9227 ±25.2554	1992.8465 ±298.5283	0.02963 ±0.011	72.1415 ±25.1585	0.1615 ±0.0514	5.5093 ±2.318

The flexural strength of the materials tested at room temperature varies from 37 MPa (for sample 1) to 51 MPa (for sample 3). Between samples 1 and 2, the highest resistance is represented by the sample that has the addition of sorbitan monooleate (sample 2). Comparing the last two mixtures (samples 2 and 3), the flexural strength is higher for the sample with tributyl citrate in the composition.

The highest mechanical resistance was supported by sample 3, followed by sample 2 and sample 1.

Results obtained depend on the test temperatures of the specimens were statistically investigated by the One-way Anova test. Comparing the results of the maximum strength recorded at 25°C with those at 4°C, there is no statistically significant difference between the three recipes ($p = 0.56946$). For sample 1, the differences between the two test temperatures for bending strength did not register statistically significant differences ($p=0.18682$), instead for samples 2 and 3, there were significant differences between the two investigation temperatures ($p= 1.25831E^{-2}$, respectively $p=5.49392E^{-6}$).

Comparing Young's modulus between the two temperatures, it can be seen that for all three investigated samples its value increases. Another characteristic that does not show significant statistical differences between the two temperatures was the elongation at deformation ($p=0.81302$), with the samples showing approximately the same elongation values.

The deformation curve of the three samples at 25°C and at 4°C are presented in figure 3.

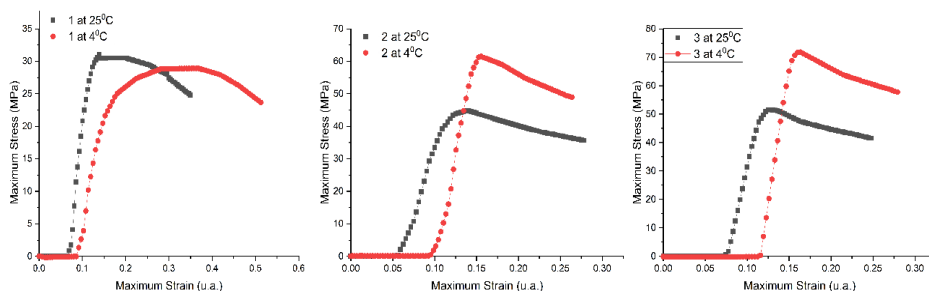


Figure 3. The deformation curve of samples at room temperature 25°C (on the shelf) and at 4°C (in the refrigerator).

From these graphs it can be seen that for all the tested mixtures, the decrease in temperature caused an increase in both the elastic modulus and the maximum load supported. These results are the expected ones, because the decrease in temperature reduces the flexibility of the polymer chain and

increases the stiffness of the material. However, the results regarding the differences in flexural strengths gave a different deformation curve depending on the composition of the mixtures. If for sample 1 the bending strength of the specimens is almost the same, it means that its composition is not influenced in any way by the storage conditions in the range of 4°C-25°C. For samples 2 and 3 we can deduce that the presence of sorbitan monooleate in their composition favors an increase in the resistance of the samples at low temperatures. The highest bending strength was obtained in sample 3 with tributyl citrate at 4 °C and then at 25°C.

Absorbed water can lead to the irreversible degradation of a polymer structure. Thus, effects such as: i) dimensional and mass changes (for example: swelling); ii) extraction of water-soluble components; iii) changes in mechanical performances (elasticity, tensile strength, impact resistance). The results of water absorption for sample 1, expressed as the weight percent variation of a sample, depending on the immersion time are given in Table 3. On the fourth day an increase in weight, with a maximum, is observed followed by a decrease in weight that is accentuated towards the end of the test period. The weight loss of the sample can be due both to the solubilization of the plasticizer in saline water and to the hydrolysis of the polymer and implicitly to the water solubilization of the depolymerization products.

Table 3. Absorption results (standard deviation) according to immersion time

Sample	Immersion time				
	1 day	4 days	7 days	13 days	p
1	0.23887 ±0.00346	0.3052 ±0.02533	0.29765 ±0.04716	-1.18723 ±2.09137	0.48375
2	0.29686 ±0.02033	0.42514 ±0.02016	0.49018 ±0.05765	0.46818 ±0.06286	0.0415
3	0.27519 ±0.01459	0.44846 ±0.0147	0.5198 ±0.01475	0.55038 ±0.02918	4.8942E ⁻⁴

The results of water absorption for sample 2, expressed as the weight percent variation of a sample depending on the immersion time, are given in Table 3. An increase in weight is observed with a maximum on the seventh day, followed by a decrease in weight to a value close to that of the fourth day. The weight loss of the sample is much lower than in the case of sample 1, probably due to the presence of the hydrophobic surfactant plasticizer.

This loss may be due to the solubilization of the citrate-type plasticizer in saline water.

For sample 3, an increase in the weight of the sample is observed throughout the test period. The absence of weight loss of the sample can be explained by the reduced solubility of the two plasticizers in saline water.

CONCLUSIONS

The aim of the study was the development of recipes based on PLA plasticized with two esters with different structures and polarities and which show low volatility, in the presence of a hydrophobic biosurfactant such as sorbitan monooleate.

The DSC analyses of the three recipes of PLA plasticized with two types of esters (an alkoxyated adipate and a citrate) in the presence of partial esters of fatty acids with sorbitol, highlighted the decrease in the vitrification temperature of PLA. Thus, if in the case of plasticization with bis(2-(2-butoxyethoxy)ethyl) adipate, the decrease in T_g is lower while in the case of plasticization with tributyl citrate in the presence of sorbitan monooleate, the decrease in T_g is more pronounced. Both endothermic and exothermic transformations were identified. For example, the endothermic transformations that occurred at temperatures higher than 150°C probably correspond to the melting of the recipes, and the exothermic ones located at temperatures above 75 °C may be due to recrystallization phenomena.

The flexural strength of the materials tested at room temperature ranges from 37 MPa to 51 MPa. The addition of sorbitan monooleate improves the bending strength of the tested materials. At the same time, the bending strength is higher for the PLA recipe containing tributyl citrate compared to the one containing bis(2-(2-butoxyethoxy)ethyl) adipate. There is no statistically significant difference between the results of the maximum strength recorded at 25°C with those at 4°C for the three recipes.

Comparing Young's modulus between the two temperatures, it can be seen that for all three investigated samples its value increases with temperature. Another characteristic that does not show significant statistical differences between the two temperatures was the elongation at deformation, the samples showing approximately the same elongation values. Water absorption tests in PLA recipes usually show a parabolic variation with the contact time, with maximum. The weight loss of the PLA recipes can be due both to the solubilization of the plasticizer in saline water and to the hydrolysis of the polymer and implicitly to the water solubilization of the depolymerization products. Weight loss is reduced in the presence of more hydrophobic plasticizers such as tributyl citrate.

EXPERIMENTAL SECTION

Materials

Reagents: Polylactic acid produced by NatureWorks LLC under the Ingeo® brand, with a vitrification temperature of 61.0°C, plastifiers: sorbitan monooleate-type Sarbosorb®, bis(2-(2-butoxyethoxy)ethyl) adipate (Proviplast® P01422 by Proviron) and tributyl citrate (Proviplast® 2604 by Proviron).

Preparation of polymer formulations

The experimental formulations based on PLA were processed in the melt on the Brabender Plastograph, at a temperature of 180 °C, 60 rpm and a mixing time of 30 minutes. The obtained PLA formulations were compression molded (hydraulic press: 120 kg/cm²) at 180°C into 1.0 mm thick sheets and were characterized by determining thermo-mechanical and water sorbtion properties. The composition of the PLA recipes is presented in table 4.

Table 4. Composition of PLA recipes

No. sample	Composition			
	PLA, %gr.	Bis(2-(2-butoxyethoxy)ethyl) adipate, %gr.	Tributylcitrate, %gr.	Sorbitan monooleate, %gr.
1.	85.0	15.0	0	0
2.	85.0	11.5	0	3.5
3.	85.0	0	11.5	3.5

Characterization of polymer formulations

The Scanning Electron Micrographs of the investigates samples were recorded by Inspect S- SEM microscope (FEI Company, Hillsboro, OR, USA).

PLA-based recipes were characterized by determining thermal properties, mechanical properties and the adsorptive properties of water.

The thermal performance of PLA blends for packaging applications was evaluated by Differential Scanning Calorimetry (DSC method). DSC thermograms were measured using a DSC calorimeter Mettler Toledo DSC 823e/700°C, under a nitrogen atmosphere.

The mechanical properties of plasticized PLA samples were made by determining the flexural strength. Flexural strength was achieved through the 3-point technique, reflecting the stiffness and resistance capacity of the materials to deformation or breaking, due to mechanical stress. For each investigated material, 20 rectangular specimens with the size of 2x2x25mm were made, which were subjected to flexural tests with the help of the universal mechanical testing machine Lloyd LR5k Plus (Lloyd Instrumente, AmetekIns, West Sussex, England), with the maximum allowed capacity of 5KN. The distance between the two fixed points is 20 mm, the loading force of the mechanical testing machine is 0.5 N and descends at a speed of 1 mm/minute, the data being processed using the Nexygen software (version 4.0).

The mechanical properties were recorded for two different storage temperatures of the specimens: 10 specimens from each batch were tested at a temperature of 25°C (the specific temperature of the packaging used on the shelf), and 10 specimens were kept for 24 h at a temperature of 4°C (optimal refrigerator temperature), for packages stored in refrigerated display cases.

Absorption is expressed as a percentage increase by weight of a test sample according to ASTM D57- Standard Test Method for Absorption of Plastics. The initial samples with the size of 20mm length, 10mm width and 3mm thickness are weighed with an analytical balance (Ohaus Explorer) obtaining $M_{initial}$. The samples are placed in 10% saline solution at a constant temperature of 23°C. At certain time periods (24h, 4, 7, 13 days), the samples are taken out of the immersion medium and weighed M_{final} .

The absorption percentage is calculated with the formula:

$$Ab = \frac{M_{final} - M_{initial}}{M_{initial}} \times 100$$

For each group of investigated samples, 4 weight percentage increase measurements were recorded.

The results obtained from both the bending and absorption tests were subjected to descriptive statistical analysis, using the Origin2019b program, to obtain the averages and standard deviations of each tested group. For the analysis of the temperature variables in the case of the bending test and the immersion time in the case of absorption, the One-Way Anova test was used, with a level of significance set at $\alpha = 0.05$.

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