

EVALUATION OF THE EFFECT OF CASTOR OIL-BASED EXPERIMENTAL ADDITIVES ON PLA/STARCH FOILS

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Biodegradable packaging materials are attracting more and more interest nowadays, the primary driving force of which is the generation of enormous amounts of plastic packaging waste. The aim of this study was to investigate the effect of two castor oil-based experimental additives on the properties of foils made from incompatible biodegradable polylactic acid (PLA) and native starch (10-50 wt%). Differential Scanning Calorimetry (DSC) measurements and tensile tests were used. It was found that increasing the starch content affected the crystallization of PLA in the blends. Furthermore, since the additives did not significantly change the glass transition temperatures, the additives did not affect the mobility of PLA chains. Regarding the tensile tests, the tensile strength of the 60:40 PLA:starch longitudinal sample could be increased by approximately 10 and 6 MPa at 25 and -25 °C, respectively, when additives were introduced.

Keywords: biopolymers, starch, polylactic acid, castor oil, PLA/starch foils

1. Introduction

As a result of the widespread use of plastics, plastic pollution is becoming a growing problem [1]. In 2021, the amount of plastic produced globally was estimated to be 390.7 million tons, a significant proportion of which originated from fossil-based sources (90.2%) [2]. Approximately 40% of this was utilized in the packaging industry, while the food packaging market is growing exponentially in developing countries [3]-[4]. In 2020, the amount of packaging waste generated per inhabitant in the EU was estimated to be 177.9 kg, of which 19.4% was plastics [5]. Less than 30% of plastic waste in the EU is recycled, some of which is exported to non-EU countries to be treated [6]. Although there is no effective way to recycle and reuse food waste mixed with synthetic plastics, plastic packaging is indispensable as the increase in the amount of food waste as a result of eliminating the packaging could be more environmentally threatening than the plastic packaging itself. Furthermore, being light, it is more energy efficient to transport plastic packaging than food waste [3],[7]. In November 2022, new packaging regulations were proposed throughout the EU, e.g. clear labelling, promoting reuse and recycling, as well as switching to bio-based, biodegradable and compostable plastics [8].

Although the global production of plastics is dominated by non-degradable, fossil-based polymers [9], bioplastics can potentially provide a green solution in light of the negative environmental impacts, strict environmental protection regulations as well as increasingly important ecologically supportive monetary policies and capital investments [10]-[13]. Due to their stable carbon-hydrogen bonds and complex polymer structure, fossil-based plastic waste is not biodegradable, it only breaks down into pieces over a long period of time, resulting in many negative consequences [14]-[15]. In order to protect the ecosystem, in addition to introducing proper waste management, the complete or partial replacement of traditional food packaging with bioplastics is crucial, however, many obstacles have to be overcome [3-4, 15]. Nevertheless, concerns about waste disposal and the increasing costs of crude oil extraction have made biodegradable polymers economically attractive [9]. In 2020, 2.1 million tons of bioplastics were produced worldwide, 47% of which were used for packaging [7]. The basic role of packaging materials is to protect food or packaged products from external influences and damage [16]. Although the demand for biodegradable packaging materials is basically driven by its biodegradable nature, the packaging material must exhibit suitable mechanical and thermal properties as well as processability in addition to protect products by inhibiting the diffusion of water

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vapor, atmospheric gases and lipids which can change the properties of the packaged products (taste, color, nutritional content) [3-4, 17-19].

Because of their hydrolyzable ester bonds, polyesters play a dominant role as biodegradable plastics [9]. Among others, biopolyesters like polylactide, polyhydroxyalkanoates and polycaprolactone can function as biodegradable packaging [3]. Polylactic acid (PLA), which can be easily processed by traditional methods, e.g. thermoforming or injection molding, has a high molecular weight and exhibits favorable mechanical, thermal and barrier properties, which can be further enhanced by blending it with plasticizers or other polymers [4,18,20]. PLA is an aliphatic polyester, pseudoplastic and non-Newtonian fluid that behaves as a classical flexible polymer chain in all compositions above its melting point [4],[20]. It is brittle with a tensile strength of approximately 32 MPa, a Young's modulus of 2.3 GPa and an elongation at break of about 5% [4]. The rigidity of PLA as well as its poor thermal resistance, limited gas barrier properties and high expense are bottlenecks in the packaging industry [9]. PLA is often blended with starch to increase its biodegradability and reduce feedstock costs [9]. Starch is a renewable polysaccharide that is attractive given its biodegradability and abundance [4,15,18]. However, as a packaging material, it can only be used in its natural state to a limited extent since its poor solubility, thermal decomposition, high retrogradation, moisture sensitivity, hydrophilic nature and unfavorable mechanical properties have to be compensated for by softening, chemical modifications or mixing it with other polymers [4,7,14,18].

2. Experimental

The aim of the experiment was to produce foils from PLA and starch with suitable tensile properties (Figure 1). However, due to the limited miscibility between starch and PLA, it was necessary to improve their mechanical properties. As a result, the synthesis of additives was required to process blends. Castor oil was added to maleic anhydride in the presence of the initiator di-tert-butyl peroxide with and without xylene as a solvent. The main properties and reaction parameters of our vegetable oil-based additives were presented in one of our previous papers [22]. It was found that the optimal temperature for the reaction was 140 °C and high acid number values were measured regardless of whether a solvent or solvent-free technique was applied. Over the course of this work, an impact assessment of 2 castor oil-based additives was performed. The difference between them was that one additive was synthesized in the presence of a solvent while the other was not. Therefore, in this study, the main goal was to compare the effect of the two additives based on differential scanning calorimetry (DSC) measurements and tensile properties of PLA/starch composites. To carry out the impact assessments, PLA/starch films were produced with the following compositions: 90/10, 80/20, 70/30, 60/40 and

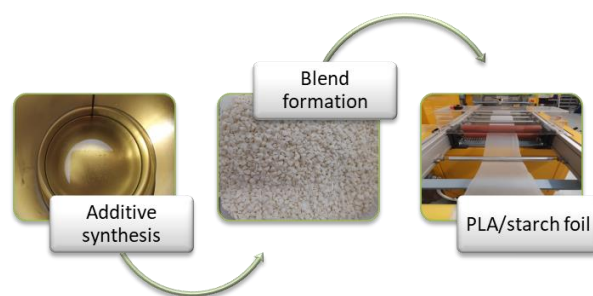


Figure 1: Sample production

50/50. Additive-free PLA/starch foils were examined as references. The temperature profile of 180-160 °C and an extrusion screw speed of 125 1/min were used during foil production. Afterwards, 10 x 2 cm test specimens were cut out and 5 parallel measurements taken.

2.1. Materials

Ingeo™ Biopolymer 4043D-type commercial PLA was supplied by NatureWorks LLC (USA), while the corn starch was provided by Hungrana Bioeconomy Company (Hungary). The vegetable oil used to synthesize the additives was castor oil with a molecular weight of 933 g/mol supplied by Alfa Aesar (USA).

2.2. Methods

DSC is effective for monitoring the physical and chemical changes resulting from the phase transformation of substances as well as exothermic and endothermic phenomena [23]. To analyze changes in the behavior of films made of PLA and starch, DSC measurements were taken using a DSC 214 Polyma instrument. 10 mg samples were weighed into an aluminum crucible and the measurements made in a nitrogen atmosphere with a heating/cooling rate of 10 °C/min. The measurements were taken over the following four stages: heating the specimens from 20 to 200 °C, tempering them at 200 °C for 3 min, cooling them down to 20 °C and finally reheating them to 200 °C, the second heating stage. The tensile properties of PLA/starch films were followed by an Instron 3345 Universal tensile testing machine at a crosshead speed of 75 mm/min and three parallel measurements were taken at both 25 and -25 °C.

3. Results and analysis

3.1. DSC evaluation

The second heating stage was taken into account, since the first one was used to eliminate the thermal history of the sample [23]. The main properties, e.g. the glass transition temperature (T_g), cold crystallization temperature (T_{cc}) and melting point (T_m) were determined by integrating the individual peak areas into enthalpies of cold crystallization and melting.

Table 1: Glass transition temperatures and degrees of crystallinity of PLA/starch blends

Compositions of PLA/starch blends	T_g , (°C)	X_c , (%)
PLA/10% starch	59.8	2.35
PLA/10% starch/CO-MA-140/xylene	58.7	2.22
PLA/10% starch/CO-MA-140/no xylene	58.3	3.01
PLA/20% starch	60.2	2.92
PLA/20% starch/CO-MA-140/xylene	60.0	4.37
PLA/20% starch/CO-MA-140/no xylene	58.1	1.90
PLA/30% starch	59.5	2.95
PLA/30% starch/CO-MA-140/xylene	60.1	4.01
PLA/30% starch/CO-MA-140/no xylene	59.2	3.06
PLA/40% starch	59.8	3.39
PLA/40% starch/CO-MA-140/xylene	59.2	3.57
PLA/40% starch/CO-MA-140/no xylene	59.0	3.49
PLA/50% starch	58.4	3.44
PLA/50% starch/CO-MA-140/xylene	59.5	3.10
PLA/50% starch/CO-MA-140/no xylene	59.0	1.98
PLA	59.9	2.16

The degree of crystallinity (X_c) was calculated by the following equation [24]:

$$X_c = \frac{\Delta H_m - \Delta H_{cc}}{\omega \cdot \Delta H_m^0} * 100 \quad (1)$$

where ω denotes the weight fraction of PLA in the blends, ΔH_m is the enthalpy of melting, ΔH_{cc} is the enthalpy of cold crystallization and ΔH_m^0 is the enthalpy of fusion of 100 % PLA taken into account with a value of 93 J/g [24]. DSC is excellent for determining polymer compatibility if the glass transition temperatures of the pure components can be sufficiently differentiated [25]. In heterogeneous systems, the sample exhibits two T_g values, i.e. two phases [26]. The miscibility and compatibility of polymer blends are best determined by examining the glass transition temperature, which can

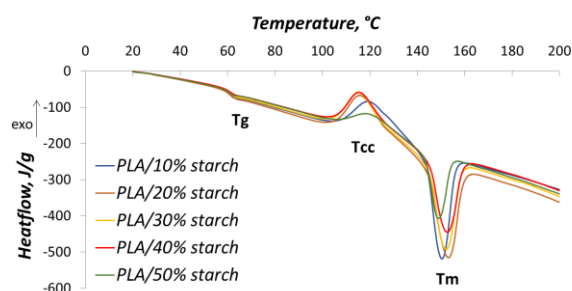


Figure 2: Thermograms of additive-free PLA/starch films

vary widely depending on the composition of the compatible system but is always somewhere between the T_g values of the pure components [25],[27].

The thermograms of the second heating stages of the reference PLA/starch foils can be found in Figure 2. The relevant T_g values and degrees of crystallinity are presented in Table 1. The glass transition temperature of virgin PLA was 59.9 °C, and those of the blends containing starch were very similar, between 58.4 and 60.2 °C to be exact, so the incorporation of starch into the PLA matrix did not have a significant effect on T_g . Furthermore, a single T_g value on the DSC curve is an indirect indication that the components are compatible [28]-[30]. However, as a result of molecular complexity, certain nanostructures may have a locally heterogeneous composition and a certain degree of segregation or partitioning can be experienced, in which case T_g appears as a single broad transition [27]. In light of the cold crystallization, the composites composed of 10 and 50% starch exhibited elongated cold crystallization peaks, perhaps caused by the slow and weak crystallization behavior. The melting points are also relevant if the polymers are partially crystalline [30]. T_m values fell within the range of 148.8-152.8 °C, while that of virgin PLA was 151.1 °C, so the starch had almost no influence on T_m .

By comparing the degree of crystallinity of additive-free films in Table 1, it can be established that X_c value rises by increasing the starch content, so starch affects the crystallization process of PLA in blends [28].

Figure 3 shows the effect of the additives on the DSC results, which was examined using five types of films with differing starch contents of 10-50%. In the case of samples containing 10 and 20 % starch, T_g decreased slightly in the presence of both types of additives (Table 1). However, taking into account all the tested samples, no notable changes were observed, so the additives did not influence the chain mobility of PLA. Larger differences were observed in the cold crystallization peaks. In almost all cases, the T_{cc} values increased compared to the additive-free reference samples. Regarding the degrees of crystallinity, no clear correlation could be established with the presence of the additives. Only in the case of samples containing 30 and 40% starch increased X_c in the presence of either additive; in the case of the samples containing different proportions of starch, this parameter depended on the type of additive present. The degree of crystallinity

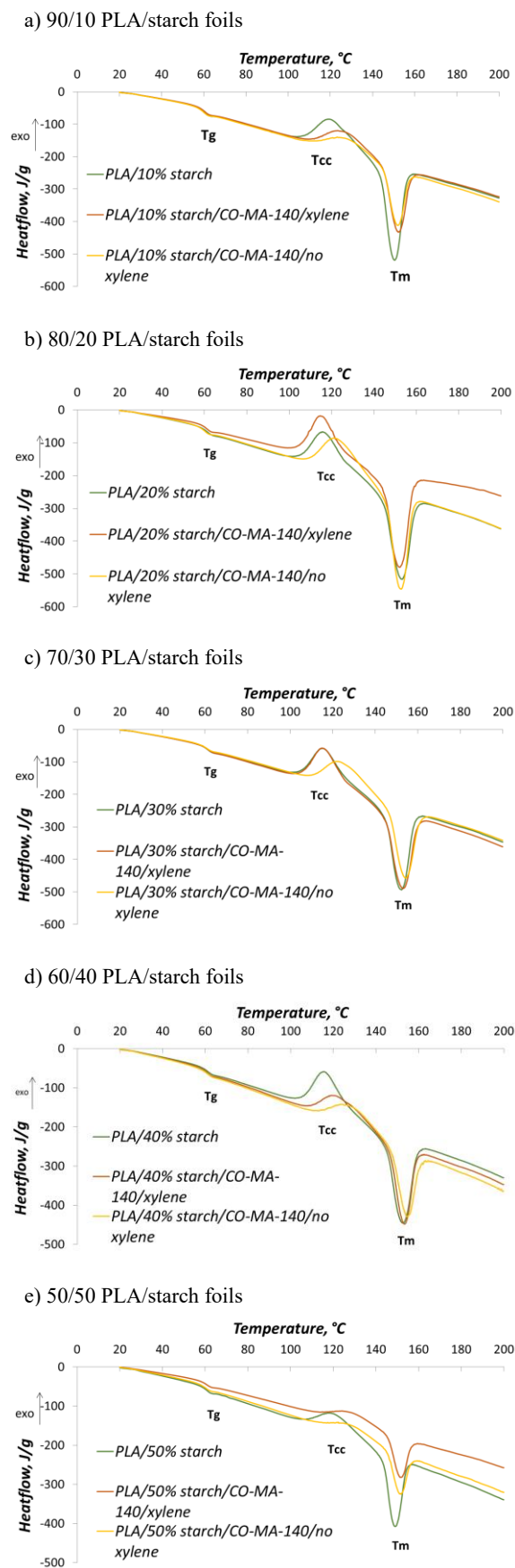


Figure 3: Thermograms of 90/10 (a), 80/20 (b), 70/30 (c), 60/40 (d) and 50/50 (e) PLA/starch foils in the presence and absence of castor oil-based additives

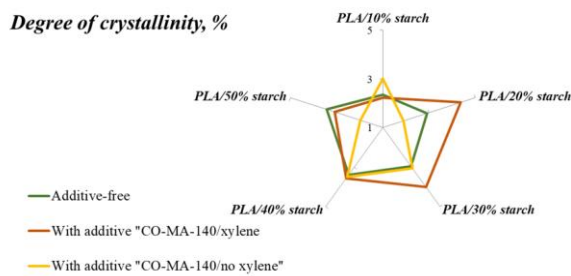


Figure 4: Comparison of the degrees of crystallinity between the different PLA/starch compositions

increased in the presence of the solvent-free additive with the exception of the 80/20 and 50/50 blends, while in the case of the other additive, X_c increased apart from when the 90/10 and 50/50 blends were used.

Figure 4 shows how the degree of crystallinity changed in the case of all the tested samples. Comparing the results, it can be observed that the additive in the presence of the solvent (highlighted in brown) had the greatest effect on the X_c for samples with 80/20 and 70/30 PLA/starch compositions.

3.2. Tensile tests

The tensile tests (tensile strength and elongation at break) of foil samples were studied on both longitudinal and transverse samples. The samples were tested at both 25 and -25 °C. The tensile strength values at 25 °C and -25 °C in both directions can be seen in Figure 5, which in almost all cases decreased as a result of using additives regardless of the temperature and direction.

Considering the longitudinal samples, the tensile strength increased at both temperatures in the case of the 80/20 and 60/40 PLA/starch compositions containing additives synthesized by the solvent technique, but the increase was not significant. In the case of the 60/40 composition, compared to the reference sample, the tensile strength of the longitudinal specimen increased by approximately 10 and nearly 6 MPa at 25 and -25 °C, respectively, after the additive was added.

Examining the transverse samples, it was observed that at room temperature, the additives slightly increased the tensile strength of the samples containing 40 and 50% starch but not at -25 °C. The decrease in tensile strength could be the result of the plasticizing effect of the additives.

Figure 6 shows the elongation at break values at 25 and -25 °C in the longitudinal and transverse directions. Regarding the longitudinal samples, at both temperatures the elongation at break values decreased as a result of using additives except for the 90/10 specimen. Taking into account the effect of the starch content, it can be concluded that the foils with 80/20 and 70/30 compositions exhibited the highest elongation at break values in both directions. Overall, based on the results, it is clear that the elongation at break was not increased due to the presence of additives, except for in a few cases where this increase was insignificant.

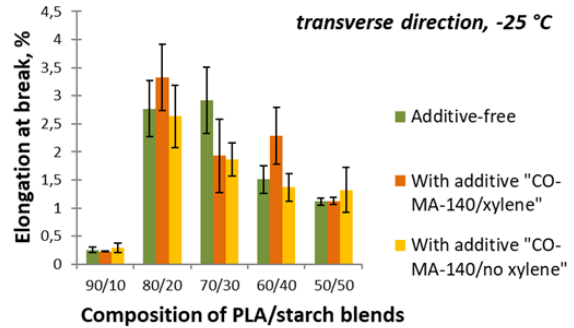
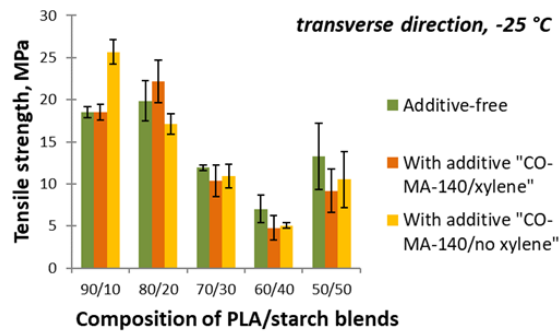
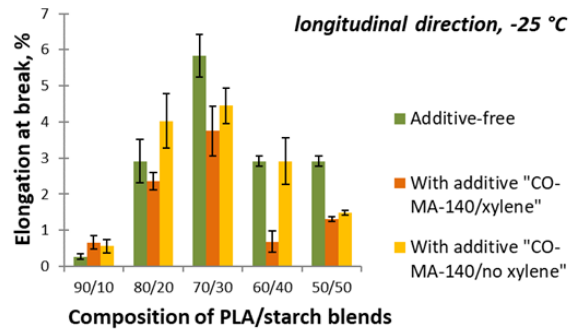
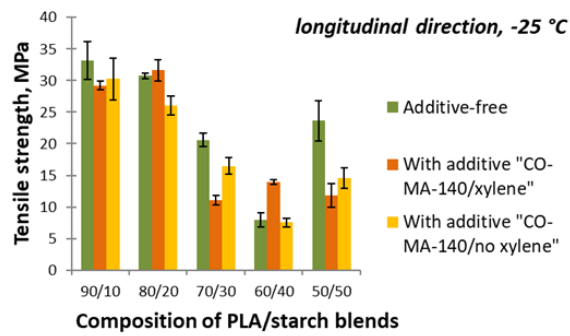
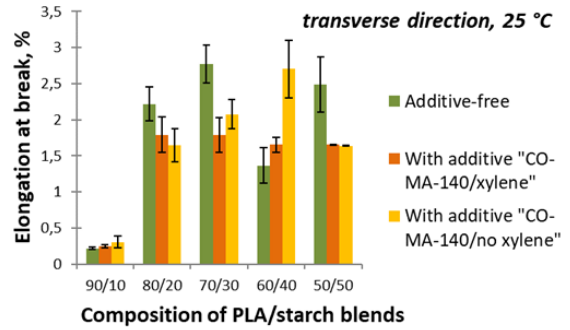
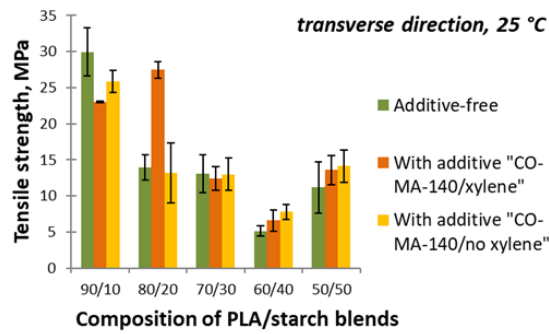
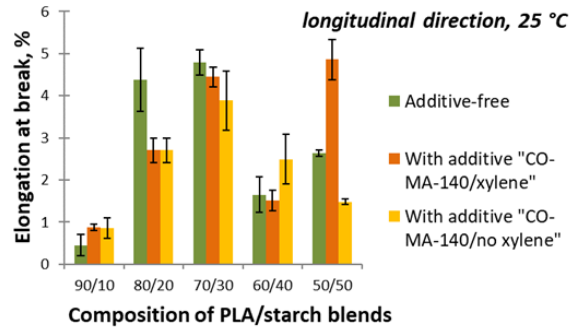
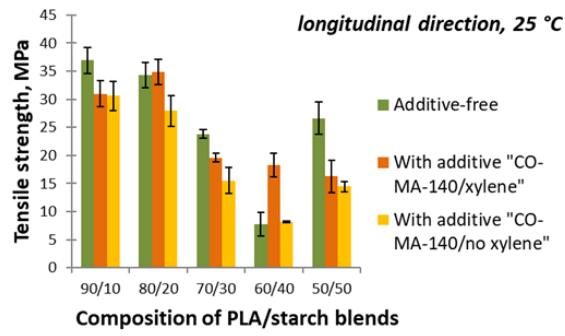


Figure 5: Tensile strength of PLA/starch foils at 25 and -25 °C

Figure 6: Elongation at break of PLA/starch foils at 25 and -25 °C

4. Conclusions

The aim of the study was to investigate the effect of castor oil-based additives produced using two techniques on the properties of PLA/starch films. The impact tests were studied through tensile tests and DSC analysis. Based on the DSC tests, it was established that as the starch concentration was increased, the degree of crystallinity of PLA in the blends also increased. Considering the glass transition temperatures of the doped and non-doped reference samples, no significant changes could be measured, which led us to conclude that the additives had no effect on the chain mobility of PLA. Based on the results of the tensile tests, it was established that, with the exception of a few cases, both the tensile strength and elongation at break decreased in the presence of the additives.

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