

Study of compostable materials for the production of transparent food containers

Giulia Cappiello^{1,a*}, Daniele Rocco^{2,b}, Clizia Aversa^{1,c}, and
Massimiliano Barletta^{1,d}

¹Università degli Studi Roma Tre, Dipartimento di Ingegneria Industriale, Elettronica e Meccanica, Via della Vasca Navale 79, 00146 Roma (Italy)

²Sapienza Università degli Studi di Roma, Dipartimento di Ingegneria Meccanica e Aerospaziale, Via Eudossiana 18, 00184 Roma (Italy)

^agiulia.cappiello@uniroma3.it, ^bdaniele.rocco@uniroma1.it, ^cclizia.aversa@uniroma3.it
^dmassimiliano.barletta@uniroma3.it

Keywords: Biobased materials, Extrusion, Thermoforming

Abstract. The aim of this work is to develop a new class of transparent containers for food packaging relying on bioderived polyesters and additives. Usually, transparent containers are manufactured using different plastic materials to achieve mechanical strength, thermal resistance, printability, good visual appearance. Yet, these containers cannot be recycled, being made by multiple polymers. This makes the management of their end-of-life troublesome. In contrast, bioderived polyester can be composted or recycled. In the present study blends of polylactic acid PLA with N,N'-ethylene(bis-stearamide) were processed by a co-rotating twin-screw extruder. The compounds were reprocessed by cast extrusion to make transparent films. Fine dispersion of ethylene(bis-stearamide), EBS, in PLA resulted in increased crystallinity, mechanical strength and thermal resistance, without compromising the transparency of the extruded films. The films were thermoformed to get the containers, whose thermo-mechanical performance were assessed.

Introduction

Currently, there is growing interest in technological solutions that can reduce the environmental footprint resulting from the use of fossil-sourced plastics. This interest has increased significantly since 2019, thanks to EU Communication COM 2019/904, in which a ban on the use of fossil-sourced plastics for single-use products was established. [1] Alternative strategies to the use of fossil-derived plastics are therefore necessary to enable the packaging sector to exceed the regulatory limits. One such strategy of particular interest is biobased and compostable bioplastics. There are already compostable materials on the market that are used in the food packaging sector, but it is currently particularly difficult to make compostable and transparent products [2]. Biopolymers have received considerable research attention due to their biodegradable nature and at the same time less environmental impact than their non-biodegradable petroleum-based counterparts. [3] Among the most promising biopolymers is polylactic acid PLA, which can only be composted in an industrial context. The behavior of compostable materials is defined by the EN 13432 standard, when disposed in an industrial composter [4] PLA is a material derived from renewable sources and represents a viable solution to the problem of food waste disposal [5]. PLA has mechanical properties and physical properties comparable to some petroleum-based polymers, such as polystyrene (PS) and poly (ethylene terephthalate) (PET), due to its high elastic modulus. However, further improvements are needed to achieve the accuracy and repeatability required for industrial applications. To improve the properties of bioplastic materials, it is necessary to mix them with other biopolymers or process additives and fillers that opacify or colour the final formulation [6].

For industrial applications, biopolymers such as PLA are often blended with mineral fillers, talc, to increase the overall mechanical properties of the blend. This totally decreases the transparency of the film produced [7]. To obtain a transparent, compostable film with high mechanical properties at the same time, it is necessary to choose additives that do not compromise its transparency. The present article is part of this contest and aims to study possible compostable, transparent formulations that can be used in the food packaging sector. PLA applications are limited by several factors, such as low glass transition temperature, low thermal resistance and brittleness. In the literature, there are several studies where attempts are made to improve these properties with additives, but the transparency is compromised [8] [9] [10]. The present study is devoted to the engineering of PLA blends with N,N'-ethylene(bis-stearamide and the thermal and physical properties associated with these formulations were evaluated. Blends of PLA polylactic acid with N,N'-ethylene (bis-stearamide) were processed by a co-rotating twin-screw extruder to make pellets and subsequently reprocessed by cast extrusion to obtain transparent films. The films were thermoformed to obtain containers, whose thermo-mechanical performance was evaluated.

Materials and methods

Materials. Luminy poly(lactic acid) (PLA) grades L175 and LX175 (Total Corbion PLA _Stadhuisplein, NS Gorinchem, The Netherlands) were chosen as the base polymers for the preparation of all formulations. PLA L175 and LX175 have a high molecular weight with an MFI of 8 g/10 min, suitable for the thermoforming process. Two PLA grades have a different -D isomer content, the LX175 grade has a higher -D isomer content of approximately 3%. This parameter affects the crystallization kinetics of the material and consequently the degree of transparency. As a clarifying nucleating agent, EBS EVIWAX 140 (Eigenmann & Veronelli S.p.A., Milan, Italy) is included in the formulations. EBS EVIWAX 140 is an active organic nucleating agent for PLA especially during heating heat treatments, based on N,N'-ethylenebis(stearamide) and is also used for its action as a process release agent [11].The table shows the formulations designed for this study.

Table 1 Composition of the blends

Materials	L [%wt.]	LX [%wt.]	LE [%wt.]	LXE [%wt.]
PLA L175	99		99	
PLALX175		99		99
EBS			1	1

EBS has low molecular weight and flexible hydrocarbon segment with the existence of polar amide groups (-CONH-) in the molecular structure of EBS make it compatible with some of the polar polymer such as PLA [12].All the materials involved in this study are safe for direct food contact and have the relevant manufacturer's certification, although the food contact compliance of the final formulations developed needs to be reassessed.

Processing. The LE and LXE materials, without any drying treatment, were extruded through the Leistritz ZSE 27 IMaxx 27 twin-screw corotating extruder used to mix the formulations. This machine consists of 10 thermoregulated zones where the temperature can be customised for each formulation. The temperature profile is set to be parabolic within the extrusion barrel (up to T9), as shown in Table 2. The head temperature is increased by 10-15 degrees. The head temperature is increased by 15°C, compared to T9, to prevent obstructions from passing through the die. The temperature profiles adopted for each material are shown below and are based on the melting temperature of the high melting material present in the formulation. The temperature profile used must be higher than the melting temperature of the materials in order to obtain a polymeric melt. [6] [7].

Table 2 Profile temperature for reative extrusion of LE, LXE blend

Materials	T _{S1}	T _{S2}	T _{S3}	T _{S4}	T _{S5}	T _{S6}	T _{S7}	T _{S8}	T _{S9}	T _{S10}
	[C°]	[C°]	[C°]	[C°]	[C°]	[C°]	[C°]	[C°]	[C°]	[C°]
LE	160	175	180	185	185	190	190	185	190	190
LXE	140	155	165	175	175	170	170	170	175	175

The maximum temperature of the thermal profile is set 10-15 °C higher than the melt temperature in the vicinity of the powder dosing zone (zone 4) to facilitate the incorporation process of the powder additive and the melt polymer. The operating parameters were set respectively at 230 rpm for the screw speed and a melting pressure at 33 bar. This process resulted in top-quality pellets that were dried for 4 hours at 65°C. Films were then made using a cast Minicast Plus extruder, manufactured by EUR.EX.MA. XTR 20. The operating parameters used for sheet extrusion are listed in the following tables.

Table 3 Operating parameters for cast extrusion of the films

Materials	Speed [rpm]	Thickness [mm]	T ₁ [°C]	T ₂ [°C]	T ₃ [°C]	T ₄ [°C]	T _{sx} [°C]	T _c [°C]	T _{dx} [°C]
L	135	400	195	195	195	195	197	195	197
LE	140	400	195	195	195	195	197	195	197
LX	155	400	190	190	190	190	192	190	192
LXE	170	400	190	190	190	190	192	190	192

The films were thermoformed using a machine called Formech 450DT. A ribbed rectangular tray suitable for food packaging and preservation was chosen as the mould. The operating parameters for the process are given in Table 4.

Table 4 Operating parameters for thermoforming process

Materials	Residence time [s]	Film temperature [°C]
L	25	160
LE	28	167
LX	22	138
LXE	32	138

The final manufactured products are shown in the following images.

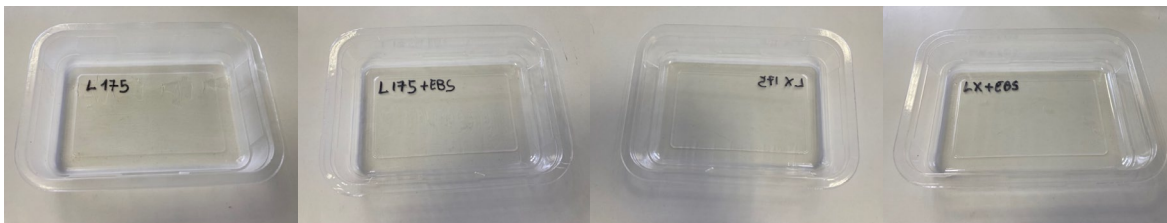


Figure 1 Final transparent products

Thermal characterization. The thermo-rheological properties of the manufactured compounds were characterized through DSC analysis, using a calorimeter DSC3 (from Mettler Toledo). Measurement was conducted under a nitrogen atmosphere, according to ASTM D-3418-15. The crystallization behavior of the solid samples was explored by heating/cooling the samples between 20 °C and 190 °C, at heating/cooling rates of 10 °C/min. Glass transition, cold crystallization and melting temperature (T_g , T_{cc} and T_m) such as ΔH_m and ΔH_{cc} were determined from second heating scan. The crystallinity degree (X_c) was calculated from the second scan as reported in Eq (1):

$$X_c = \frac{\Delta H_m - \Delta H_{cc}}{\Delta H_{mo} * (1 - m_f)} \times 100. \quad (1)$$

Where ΔH_m and ΔH_{cc} are the enthalpies of melting and cold crystallization, respectively. ΔH_{mo} is enthalpy of melting for a 100% crystalline PLA sample.

Haze test. This test method involves the evaluation of specific light transmission and light scattering properties of planar sections of translucent or transparent plastic materials. The test was performed in accordance with ASTM D 1003 - 00. A UV-Vis-NIR Spectrophotometer V-670 equipped with a single-beam integrating sphere ISN-723 (Jasco, Inc., Easton, MD, USA) was used. The spectral bandwidth is 5 nm. To proceed with the Haze calculation, it is necessary to take several measurements in different configurations to calculate transmittance values. Haze value can be calculated using the following equation:

$$\text{Haze [\%]} = (T_d / T_t) * 100. \quad (2)$$

where T_d is the diffuse transmittance and T_t is the total transmittance.

Thermal stability test. Thermal stability is evaluated through tests were carried out on the prototype trays to assess their thermo-mechanical resistance to contact with hot liquids. Specifically, 200 ml of a hot liquid (water) was poured into the thermoformed trays at a temperature of 65°C to assess any deformation. The test was repeated three times for each sample and the observation time was set at 5 minutes. This test is considered passed if the product does not show any deformation in its geometry after the observation period. In order to evaluate the dimensional parameters at the end of each test, the treated tray was inserted into a new one to see if they matched.

Mechanical characterization. The Izod impact test is a standard method approved by ASTM to determine the notch toughness of a material. Toughness is the ability of the material to absorb energy and deform plastically before fracture. Toughness, which exactly represents the energy absorbed by the specimen during impact, measured in Joules, is:

$$K = F_p(H-h). \quad (3)$$

Where K is the hardness of the notch, H and h are the final and initial heights of the pendulum respectively, and F_p is the force-weight of the pendulum. The test is performed in accordance with ISO 180. The specimens used for this type of test are rectangular and were moulded with an injection moulding machine RAY-RAN, equipped with a heatable cylinder with a capacity of 57 cm³ at a temperature of 190°C.

Results and discussion

From the DSC thermal characterization, the graphs corresponding to the second heating scan for the four formulations are shown. From the curves, it was possible to visualize and calculate the change-of-state temperatures and crystalline fraction index of PLA present in each formulation.

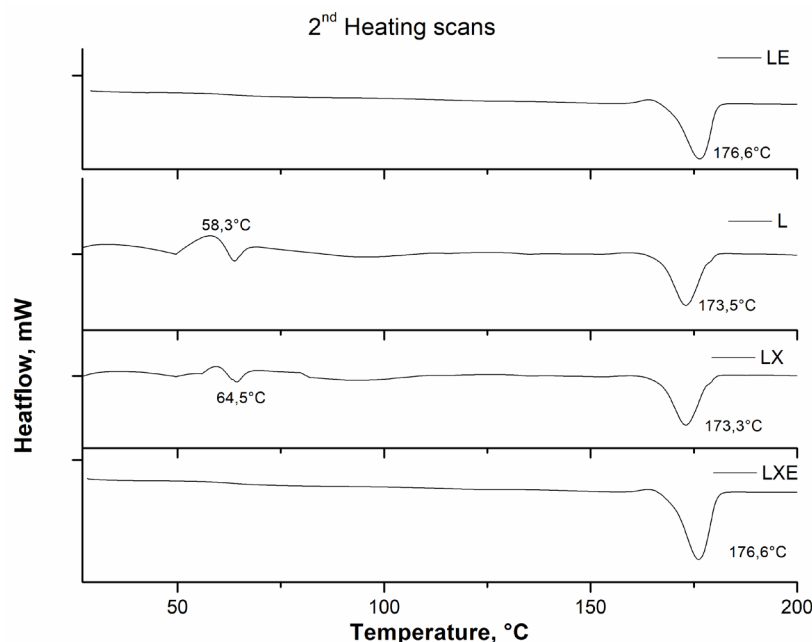


Figure 2 DSC scans for the transparent films

From the three scans performed, the parameters shown in Table 5.

Table 5 DSC results

Samples	L	LX	LE	LXE
Tg [°C]	58,3	64,5	-	-
Tc (PLA) [°C]	156,31	154,51	158,4	160,2
Tm (PLA) [°C]	173,5	173,3	176,6	176,6
Xc PLA [%]	14,3	27,1	28,9	41,2

EBS with both PLA L175 and LX175 increased the crystalline fraction. as evidenced by the decreased degree of disorder in the amorphous region of the crystalline fraction, due to the presence of EBS acting as a nucleant and promoter of PLA crystallization [13].

The crystalline fraction is an important parameter affecting the physical properties of a PLA film. According to a study by Mohanty et al., [11], increasing the crystalline fraction in a PLA film can improve its tensile strength, but at the same time reduce its deformability. However, the addition of a compatibilizer such as EBS could have a significant effect on the crystalline fraction of the film. According to research by Li et al., [9], EBS can promote the crystallization of PLA and increase its crystalline fraction, leading to higher mechanical strength of the film. Furthermore, EBS can also affect the morphology of the crystalline fraction of PLA, as observed by Dong et al., [14], who reported that the addition of EBS can increase the crystal size of PLA. In conclusion, the addition of EBS can positively influence the crystalline fraction of a PLA film, improving its

mechanical properties. However, it is also important to consider the side effects that may result from changing the morphology of PLA crystals, e.g. in terms of transparency or permeability of the film. For this reason, the transparency of extruded films has been evaluated with the Haze test. The haze test showed slightly less transparency in the formulations with EBS, but overall, the values were all below 10%.

Table 6 Haze results

Materials	T_t [%]	T_d [%]	Haze [%]
L	92.8	2.9	3.1
LE	92.6	5.2	5.6
LX	92.0	4.2	4.6
LXE	92.0	5.9	6.4

This result agrees with studies of Liu et al., [12], in which the addition of EBS to PLA led to an increase in the Haze value, due to the formation of compatible microphases between PLA and EBS. Specifically, the Haze value increased from 5.5% of the pure PLA film to 15.8% of the PLA-EBS film, with 10% by weight of EBS. Similarly, Wu et al., [15], also reported that the addition of EBS to PLA led to an increase in the Haze value of the film. Specifically, the Haze value increased from 1.7% in the pure PLA film to 4.4% in the PLA-EBS film to 5% by weight of EBS. The formation of compatible microphases between PLA and EBS refers to the creation of localized regions within the material, the two polymer phases tend to form homogenous microspheres or microstructures that can help improve certain properties of the composite material, such as mechanical strength or transparency. The compatibility between polymers depends on their chemical properties, such as polarity, molecular weight and molecular morphology, and the mixing conditions used to prepare the composite material. When polymers are compatible, they tend to mix homogeneously, forming a uniform polymer blend with improved physical and mechanical properties compared to individual polymers [16]. To assess the thermal stability of the formulations, a test at 70°C and 100°C was carried out on the thermoformed products. In particular, the deformation of the trays was assessed, using hot water, after an observation time of 5 minutes. After the test at 70°C, the trays in L and LX appeared visibly deformed, while those in LXE and LE showed no changes from their initial shape. The test repeated at 100°C also resulted in the deformation of all trays. PLA is known to have good thermal resistance, with a glass transition temperature (T_g) of approximately 60-65 °C. However, the addition of EBS to PLA increases the thermal resistance of the composite material. For example, Wu et al. showed that adding 10 wt% EBS to PLA can increase the T_g of the composite material up to 80 °C, [15]. Adding EBS to PLA can also improve the thermal stability of the material by reducing the thermal degradation rate of PLA [9]. However, the effect of EBS on thermal resistance also depends on the amount of EBS present in the formulation. Some studies have shown that a high amount of EBS can reduce the thermal resistance of the composite material. For example, another study reported that the addition of 30 wt% EBS to PLA can reduce the T_g of the composite material to about 57 °C [12]. In general, the addition of EBS to PLA can improve the thermal resistance of the composite material at low percentages but can reduce the thermal resistance at high percentages of EBS. Therefore, LXE and LE formulations compared to L and LX are optimal from a transparency-thermal resistance perspective. Despite the various transformation processes, the thermal properties of the final product remain optimum. The addition of EBS at 1 %wt. creates the right balance between transparency, thermal stability and mechanical properties of the formulation. From a mechanical point of view, an Izod characterization test was performed. The addition of EBS to PLA can affect the impact strength of the composite material.

Table 7 Izod results

Samples	Impact energy accumulated [J]	Impact Strength [kJ/m²]
L	2,89	70,6
LX	2,94	73,5
LE	4,75	103,32
LXE	5,84	114,50

In this case, an increase in the impact strength of PLA after the addition of EBS of approximately 60 % is observed. The LXE formulation is the most impact resistant as it contains a higher concentration of D isomer than the respective LE. These values agree with other studies. For example, Wang et al. showed that the addition of 5% by weight of EBS to PLA can increase the impact strength of the composite material by 60% compared to pure PLA [10]. Furthermore, Chen et al. reported an increase in the impact strength of PLA with the addition of EBS at 10 wt% [8]. However, when the percentage of EBS is more than 10%wt., it can reduce the impact strength of the composite material at high EBS percentages. For example, Liu et al. reported that the addition of 30% by weight of EBS to PLA can reduce the impact strength of the composite material by 50% compared to pure PLA [12]. In general, the effect of EBS on impact strength depends on the amount of EBS present in the formulation. The formation of compatible microphases between the PLA and EBS, which can promote the dissipation of impact energy and improve the toughness of the composite material [17]. The formation of a fibrillar structure of EBS in the PLA matrix can act as a bridge between the phases and improve the toughness of the composite material [8] [18].

Conclusion

In this study, four compostable formulations were proposed as suitable for interesting applications in transparent food packaging. Formulations engineered with EBS were found to be suitable for thermoforming processes, which is the most adopted production technique. Experimental results showed that the inclusion of EBS within the formulation allowed for a combination of transparency, thermal and mechanical resistance of the bioplastic blends used. The experimental results showed that the correct concentration of EBS in the evaluated formulations leads to the production of an excellent quality compound through the reactive extrusion process using a co-rotating twin-screw extruder. The good quality of the plastic films made the thermoforming process possible to produce products (food trays) with an excellent finish. The PLA-based compounds LX175 and EBS showed both good thermal and mechanical resistance, not deforming plastically under the action of a hot liquid (water) at 70°C. The L175 and EBS system showed higher transparency but lower impact strength. This behaviour is dictated by the different structure of the two formulations the compatibility between the chosen grade of PLA and EBS can improve the interaction between the two phases and increase the toughness of the composite material. The experimental results obtained are also influenced by the type of processing and the processing parameters used. The result obtained derives from a rational design of the formulation aimed at achieving thermal characteristics comparable to those of the fossil materials currently used. As future studies are planned to further improve the thermal performance of the product (>100°C) to extend its applicability.

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