Research article

Combined effects of plasticizers and D-lactide content on the mechanical and morphological behavior of polylactic acid

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A B S T R A C T

Nowadays, research into environmentally friendly, renewable materials is the focus of materials science. One of the best candidates for these purposes is polylactic acid (PLA), whose properties are determined mainly by its D-lactide content. PLA is often plasticized to achieve proper toughness. Our aim was to investigate the combined effects of plasticizers and D-lactide content on PLA. We investigated two different plasticizers: oligomeric lactide acid (OLA) and dioctyl adipate (DOA). An internal mixer was used to prepare the compounds, and then sheets were prepared by hot pressing. After mechanical and morphological analyses, we found that tensile strength and modulus of neat PLAs and PLA-OLA compounds decreased almost linearly with increasing D-lactide content. The mechanical properties of PLA-DOA compounds depended far less on D-lactide content than in the case of PLA-OLA compounds. Plasticizers promote the crystallization of crystallizable PLAs by their chain mobilizing effect—we obtained a higher crystalline fraction. The latter effect reduces the impact of the plasticizing effect of plasticizers in the product. The compatibility and dispersibility of plasticizers also have a significant effect on the properties of the materials. OLA is more compatible with PLA than DOA, which resulted in better plasticization, but caused more defects in the crystallites, thus reducing the crystalline melting temperature, and so the processing temperature of the compound containing plasticizers.

1. Introduction

In the early 21st century, a centralized policy was adopted in Europe with the goal of reducing the environmental burden of plastics, forcing the plastics industry to start developing biopolymers. A polymer can be called a biopolymer if it is either bipodegradable or can be produced from renewable sources, or both. Of course, it is more advantageous for sustainability when both conditions are fulfilled at the same time. It should be mentioned that biocompatible polymers are also often called biopolymers. Almost 40% of artificially produced polymers are used to make one-way packaging, leading to the generation and accumulation of large amounts of plastic waste in a short time. It means that biodegradable polymers as materials for packing applications may play a major role in the near future [1–4].

Polylactic acid has come into view as it may be produced from forage crops. It is biodegradable, i.e., the resulting waste can be

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composted, and its mechanical properties are close to poly(ethylene terephthalate) and polystyrene, which are popular packing materials [5]. Some properties of PLA make it difficult to use as a packaging material. These properties include relative rigidity [6,7], low strain at break, low impact resistance [8], and low glass transition temperature (in the range of application temperatures of the packaging materials) [9]. Another critical issue is that food packaging materials should often be transparent. Most types of commercial PLA are able to crystallize, which lowers the transparency, therefore crystallinity should be controlled by additives or the manufacturing parameters [10,11].

The isomerism of lactic acid provides an opportunity to influence the mechanical properties of the polymer during its synthesis by changing the ratio of the D-lactide and L-lactide content. Increasing the D-lactide content above 10% makes the PLA amorphous, which decreases the modulus and increases impact resistance, but tensile strength and heat resistance become lower. The most commonly used PLA types contain 95–99% L-lactide and have a crystalline structure, which can result in better strength properties, but in the case of fast cooling from the melt, their structure remains nearly amorphous after processing (e.g., extrusion, injection molding, compression molding or fiber spinning [12–15]), due to the slow crystallization of PLA. Overall not just the structure but also the processing parameters affect the product's transparency and mechanical behavior [16–18].

One way to modify the mechanical properties of PLA is to add a plasticizer to it, which can be smaller molecules, even lactic acid dimers or oligomers. Based on the lubricant theory, plasticizers reduce the intermolecular forces between the polymer chains [19]. To preserve the environmentally friendly nature of the material, the additive itself must also be environmentally friendly (e.g., produced from renewable sources, and the decomposition products released during degradation cannot be toxic or harmful). Lactide is an effective plasticizer for PLA, but a large drawback is its pronounced migration towards the surface, which makes it inappropriate for use in the food industry, as the amount of foreign substance that migrates into the food is limited by the European Union's regulations [20–26].

In the past few years, oligomeric lactide acid (OLA) has come to the fore due to its excellent compatibility with PLA (they have the same composition, they only differ in molecular weight) and because it can effectively increase the toughness of PLA. Another advantage is that its migration ability is relatively low. Burgos et al. [27] observed only one glass transition temperature in OLA-plasticized PLA, which proves their excellent compatibility. The presence of OLA decreased the tensile modulus and increased elongation at break, indicating a high improvement in toughness. Several other studies have confirmed the good toughening effect of OLA on PLA [28–31].

In addition to dimers and oligomers, we studied the plasticizing effect of numerous other additives on PLA as well. Dioctyl adipate (DOA) is one of the most promising plasticizers. It is the diester of 2-ethylhexanol and adipic acid. It increases the toughness of PLA, which results in higher elongation at break. At the same time, the drop in glass transition temperature (T_g) is moderate, which is advantageous for a wide range of applications. Another advantage of using DOA is that with the use of this additive even a ten-fold increase in impact strength can be achieved compared to neat PLA. The favorable change in properties is due to the relatively good chemical compatibility, as DOA contains ester groups. DOA is a favored plasticizer in the food industry, as its migration into food is very low [30,32,33].

As we have shown, the D-lactide content of PLA affects the crystalline fraction that forms in it and thus, its mechanical properties. It means that the effect plasticizers have on toughness may differ depending on the D-lactide content of the PLA. In this paper, we studied the combined effect of the D-lactide content of the PLA and the commonly used oligomer lactic acid and dioctyl adipate plasticizers on the mechanical properties and morphology of PLA.

2. Experimental

2.1. Materials and preparation

Different PLA grades produced by NatureWorks (Minnetonka, USA) were used in the experiments: Ingeo 4032D (1.4% D-lactide content), 2003D (4.3% D-lactide content), and 4060D (12.0% D-lactide content). These PLAs are recommended for extrusion; the melt flow index (MFI) is between 2 and 4 g/10 min. These PLAs have a density of 1.24 g/cm^3 and their glass transition temperature is between 55 and 65 °C [14].

We used Glyplast OLA2 (OLA2) oligomeric lactic acid (supplied by Condensia, Barcelona, Spain), and dioctyl adipate (DOA) (by

Table 1
The compositions of the materials produced.

Sample name	D-lactide content	PLA type	Additive type	Amount of additive
	%	–	–	wt.%
1.4%	1.4	Ingeo 4032D	–	0
4.3%	4.3	Ingeo 2003D	–	0
12.0%	12.0	Ingeo 4060D	–	0
1.4%_OLA2	1.4	Ingeo 4032D	OLA2	10
4.3%_OLA2	4.3	Ingeo 2003D	OLA2	10
12.0%_OLA2	12.0	Ingeo 4060D	OLA2	10
1.4%_DOA	1.4	Ingeo 4032D	DOA	10
4.3%_DOA	4.3	Ingeo 2003D	DOA	10
12.0%_DOA	12.0	Ingeo 4060D	DOA	10

HSH Chemie Kft.) as additives to increase toughness.

Before mixing, the PLA granules were dried for 6 h at 80 °C, according to the manufacturer's recommendation. We prepared the compounds with a Brabender Plastograph (Brabender GmbH & Co. KG, Duisburg, Germany) internal mixer with a 50 cm^3 mixing chamber at 190 °C. Rotor speed was 50 rpm, and the material fed in the mixer was 50 g (50 g PLA or 45 g PLA + 5 g plasticizer). The steps of mixing were the following. After heating the mixer, 45 g of PLA was mixed at 50 rpm for 1 min, then 5 g (10% by weight) OLA or DOA was added dropwise with a syringe to the PLA (~40–60 s), then mixed for additional 4 min. From the mixtures, 0.5 mm thick, 200 × 200 mm sheets were fabricated with a Teach-Line Platen Press 200E (Dr. Collin GmbH, Munich, Germany) hydraulic press. The maximum temperatures of the upper and lower plates were 190 °C. After the mold had been heated, the mixture was placed between the two press plates. Pressing time was 5 min at a pressure of 1 MPa. The designation and composition of the prepared samples are shown in Table 1.

2.2. Testing methods

The tensile tests were performed on a Zwick Z005 (Zwick GmbH & Co. KG, Germany, Ulm) tensile tester, according to EN ISO 527-1 and 527-3; tensile speed was 10 mm/min. At least five specimens were tested from each material.

Differential scanning calorimetry (DSC) was carried out on a TA Instruments Q2000 (TA Instruments, New Castle, USA) device. The temperature range was 0–200 °C, the heating and the cooling rate was 5 °C/min, and two heating scans were performed. The weight of the samples was around 6 mg, and the tests were performed in a nitrogen atmosphere (40 mL/min). We calculated the degree of crystallinity after cold crystallization (X_c) (Equation (1)) and the degree of crystallinity before cold crystallization ($X_{c'}$) (Equation (2)). ΔH_m [J/g] is the melting enthalpy, ΔH_{cc} [J/g] is the cold crystallization enthalpy of the polymer, and the theoretical melting enthalpy of 100% crystalline PLA (PLA$_{100\%}$) is 93 J/g [34].

$$X_c = \frac{\Delta H_m}{PLA_{100\%}} \bullet 100 \; [\%] \tag{1}$$

$$X_{c'} = \frac{\Delta H_m - |\Delta H_{cc}|}{PLA_{100\%}} \bullet 100 \; [\%] \tag{2}$$

To reveal the structure of the materials, we broke off smaller pieces of the samples under cryogenic conditions. The fracture surfaces of the samples were inspected with a JEOL 6380 LA (JEOL, Tokyo, Japan) scanning electron microscope (SEM) with an acceleration voltage of 10 kV. The samples were sputtered with a thin gold layer.

3. Results and discussion

3.1. Mechanical properties

The effect of plasticizers and their compatibility affects the mechanical properties of the mixtures [35]. The typical stress–strain curves are shown in Fig. 1. The results indicate that increasing D-lactide content decreases tensile strength. Both the increasing D-lactide content and the presence of the plasticizer have a plasticizing effect on the PLA. However, the impact of plasticizers is much more significant. The stress–strain curves show tensile strength (Fig. 2 a.), the tensile modulus (Fig. 2 b.), and strain at maximum force (F_{max}) (Fig. 3). The tensile strength and modulus of neat, unplasticized PLA are higher than those of the plasticized PLA samples, regardless of the type of plasticizer (OLA or DOA). Tensile strength and modulus decreased almost linearly with increasing D-lactide content in the case of neat PLAs. When plasticizers were added, mechanical properties worsened [36,37] because of the reduced intermolecular forces [19,38].

Regarding the compounds containing OLA, the decrease in strength shows a linear trend, similarly to the neat reference materials.
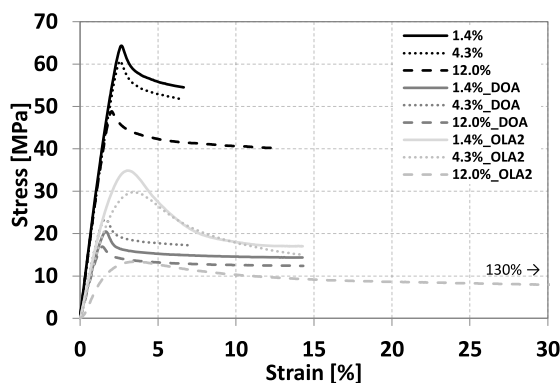

Fig. 1. The stress–strain curves of PLA with different D-lactide content and different type of plasticizers.
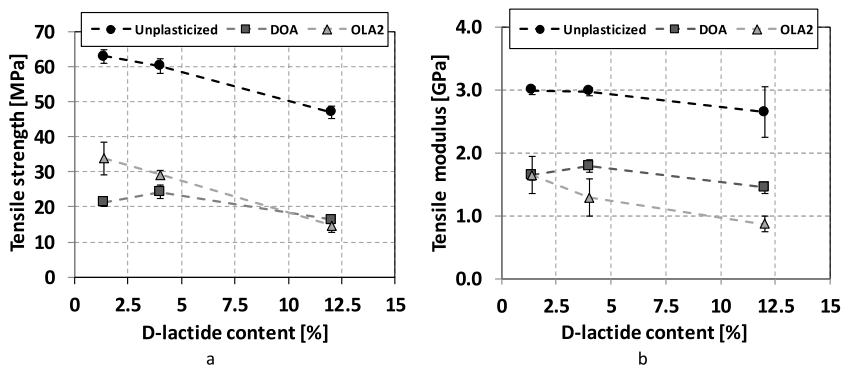
Fig. 2. The effect of plasticizers on the tensile properties of PLA as a function of the D-lactide content a) tensile strength, b) tensile modulus.
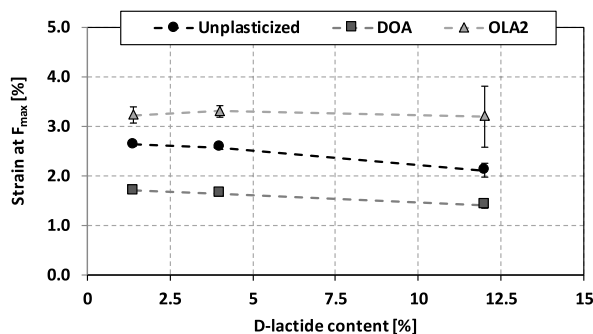

Fig. 3. Strain at maximum force for plasticized and unplasticized PLAs.

However, the modulus was around 1.5 GPa for the two PLA + OLA compounds with PLA containing less D-lactide and decreased significantly for only the compound with PLA containing 12.0% D-lactide (close to 1 GPa). However, the tensile strength and modulus of the unplasticized PLA and the PLA containing OLA worsened almost linearly with increasing D-lactide content; this correlation does not hold for DOA. The reasons for the differences can be explained with morphological changes.

A plasticizer's effectiveness is clearly reflected in the increase in strain at maximum force (Fig. 3). In this case, using OLA is particularly advantageous, as the strain at the maximum force of the PLA + OLA compounds increased compared to the PLA + DOA compounds and neat PLA. Plasticizers reduce the intermolecular forces between the polymer chains, and the decreased intermolecular forces enhance molecular chain mobility [19,38,39].

Although we expected increased strain at maximum force when using DOA, this did not happen. The reasons for this can also be explained with the effects of plasticizers on morphology.

Overall, in terms of tensile properties, OLA as a plasticizing additive is more advantageous than DOA. In the case of OLA, the drop in tensile strength is moderate, while the decrease of the tensile modulus is more pronounced, and OLA increased elongation at the maximum of the tensile curve.
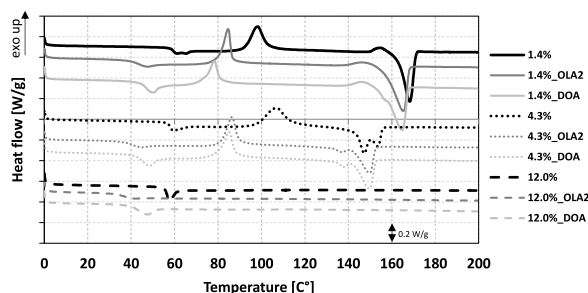

Fig. 4. 1st heat up DSC curves of the plasticized and unplasticized PLAs.

3.2. Differential scanning calorimetry

Differential scanning calorimetry was used to reveal the cross-effects of D-lactide content and the plasticizers on the glass transition temperature and crystalline properties. Fig. 4 shows the first heating curves. D-lactide content affects the crystallization tendency of polylactic acid. The melting peaks get smaller as D-lactide content increases, showing that the crystallization tendency of the polymer decreases [16]. Above 10% D-lactide content, the melting peak is not visible, showing that PLA has an amorphous structure [40]. The crystal melting temperature of polylactic acid is 165–185 °C, depending on the type of PLA [41]. The differences in melting temperature are caused by the different crystal modifications of PLA, for example, α, β, and γ [42]. Frackowiak et al. [43] explained that the crystals belonging to the lower crystal melting temperature are smaller in size and formed during the cold crystallization process. In contrast, the crystal types with higher melting temperatures formed during primary crystallization. A double melting peak—observed primarily for the 4.3% D-Lactide samples—means that these samples had both the disordered α' and the more ordered α crystalline form [42]. As expected, the glass transition temperature (T_g) of the pure PLA samples is between 55 and 60 °C [10]. Plasticizers, as expected, decreased the glass transition temperature (37–47 °C) because plasticizers have the ability to increase the mobility of the molecular chains [19,38]. PLA with 12.0% D-lactide content plasticized with OLA has the lowest T_g (37 °C). These results are in accordance with Roberto et al. [37]. For the samples that crystallize, both the cold crystallization (T_{cc}) peak (around 85 °C) and the crystalline melting (T_m) temperatures shifted towards lower temperatures [44] when plasticizers were added.

As indicated by the crystalline fraction ($X_{c'}$) that formed after the manufacturing process (Table 2), the presence of plasticizers helped crystallize the material during processing. The crystallizing effect of DOA was superior to that of OLA2. The decrease in the cold crystallization peak temperature also confirms the crystallization-promoting effect. It can be explained with the fact that the molecules become mobile enough to crystallize at lower temperatures. The decrease in T_g gives information about the interaction between plasticizers and PLA. OLA2 reduced T_g more, indicating a better interaction compared to DOA.

The cooling curves of DSC provide information on the effects of plasticizers and D-lactide content on crystallization. As Fig. 5 shows, neat PLA has a crystallization temperature (T_c) of 120 °C in the case of 1.4% D-lactide content and 94 °C in the case of 4.3% D-lactide content. The plasticizers reduced the peak crystallization temperatures for PLA with 1.4% D-lactide content to 115 °C, which means that they hampered crystalline nucleating, which is understandable because of the atactic structure of OLA2 and the different structure of DOA compared to PLA.

The area under the crystallization peaks of the PLA with 1.4% D-lactide content and its compounds increased when the plasticizers were added (Table 3). It means that the plasticizers enhanced the growth rate of the crystals, consistent with the above-mentioned chain mobilizing effect. Although the increase in Fig. 4 is hardly visible, the evaluation of the curves clearly showed a peak for the PLA with 4.3% D-lactide content; the results support the results described for the PLA with 1.4% D-lactide.

After cooling the polymer sample down, its thermal history is erased. We used the second heating curves to compare the inherent properties of the materials. Fig. 6 (second heating) shows that the cold crystallization peak disappeared for the mixtures containing 1.4% D-lactide, i.e., the cooling rate applied during cooling was adequate for maximal crystallization, which is also shown in the cooling curves. For both the first and the second heating, the presence of plasticizers increased the crystalline fraction (Table 4). Since OLA2 can be considered amorphous, it does not participate in the formation of crystallites, and so it may be integrated in the crystallite as a defect. A similar conclusion was reached by Tanrattanakul et al. [22]. These results suggest that plasticizers increased the chain mobility of PLA molecules, which positively affected crystallization, allowing the corresponding molecular parts to arrange more easily.

In Table 4, one can see that in the presence of plasticizers, the crystalline melting temperatures decreased significantly, in the same way as was observed in the first heating. Two effects can explain it: either the average crystallite size decreased or the number of defect sites in the crystallites increased. In the case of 1.4% D-lactide content in the cooling curve, the evaluated characteristics of the curves changed slightly. Based on these, the crystallization process was very similar in these cases, i.e., the increase in the number of defect sites may explain the lower crystal melting temperature. It is also supported by the change in the case of T_g, which suggests a strong interaction between PLA molecules and plasticizers, i.e., plasticizer molecules may remain in the crystallites during crystallization.

In the case of PLA containing 4.3% D-lactide, a double melting peak was measured for the first and second heating. Also, the α' (T_m) and α ($T_{m'}$) crystallites have the same melting temperature (Tables 2 and 4). In the presence of DOA, T_m and $T_{m'}$ are also the same. PLA containing 4.3% D-lactide plasticized with OLA2 also has a double melting peak, T_m is the same, but $T_{m'}$ decreased. This effect could be

Table 2
Thermal properties of plasticized and unplasticized PLAs determined by the 1st heat-up cycle.

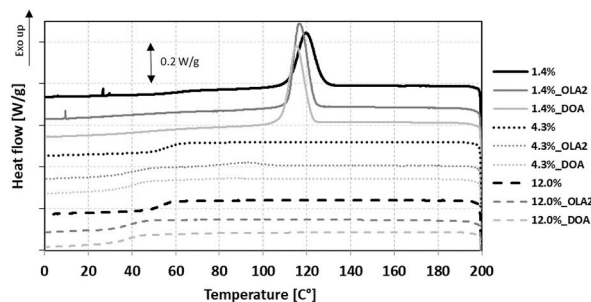| Sample name	T_g	T_{cc}	ΔH_{cc}	T_m	$T_{m'}$	ΔH_m	X_c	$X_{c'}$
	°C	°C	J/g	°C	°C	J/g	%	%
1.4%	60	98	27.8	168	–	28.0	30.1	0.2
1.4%_OLA2	43	85	26.9	165	–	33.5	33.6	7.0
1.4%_DOA	47	78	24.1	165	–	33.9	36.5	10.5
4.3%	57	107	27.4	147	154	26.2	28.2	0.9
4.3%_OLA2	40	87	24.3	140	150	24.8	26.7	2.6
4.3%_DOA	43	85	25.0	138	150	28.1	30.2	3.3
12.0%	57	–	0	–	–	0	0	0
12.0%_OLA2	37	–	0	–	–	0	0	0
12.0%_DOA	44	–	0	–	–	0	0	0

Fig. 5. Heat flow of the plasticized and unplasticized PLAs during cooling.

Table 3
Thermal properties of plasticized and unplasticized PLAs determined by the cooling cycle.

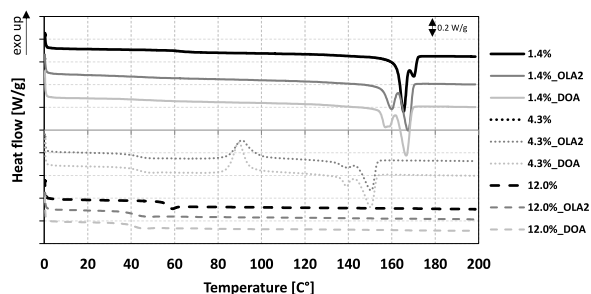| Sample name	T_g	T_c	ΔH_c
	°C	°C	J/g
1.4%	62	120	32.4
1.4%_OLA2	43	117	37.7
1.4%_DOA	44	115	38.7
4.3%	58	94	0.5
4.3%_OLA2	40	93	4.0
4.3%_DOA	40	85	1.4
12.0%	54	–	0
12.0%_OLA2	39	–	0
12.0%_DOA	38	–	0

Fig. 6. 2nd heat-up DSC curves of the plasticized and unplasticized PLAs.

Table 4
Thermal properties of plasticized and unplasticized PLAs determined by the 2nd heat up cycle.

Sample name	T_g	T_{cc}	ΔH_{cc}	T_m	$T_{m'}$	ΔH_m	X_c	$X_{c'}$
	°C	°C	J/g	°C	°C	J/g	%	%
1.4%	62	–	0	165	170	35.0	37.6	37.6
1.4%_OLA2	43	–	0	160	168	40.6	43.7	43.7
1.4%_DOA	46	–	0	157	167	41.4	44.5	44.5
4.3%	58	108	25.9	148	154	26.6	28.6	2.9
4.3%_OLA2	43	91	20.4	139	143	26.7	28.7	6.7
4.3%_DOA	44	90	24.4	139	150	28.6	30.8	4.5
12.0%	57	–	0	–	–	0	0	0
12.0%_OLA2	42	–	0	–	–	0	0	0
12.0%_DOA	42	–	0	–	–	0	0	0

related to the fact that the average crystallite size decreased or the number of defect sites in the crystallites increased. In the case of PLA containing 1.4% D-lactide, only one melting peak was detected during the first heating, with a lower peak temperature (T_m), meaning smaller crystallites.

On the other hand, during the second heating, the PLA containing 1.4% D-lactide was able to form crystallites, and their crystalline

melting temperature ($T_{m'}$) was higher. It can indicate that crystallites with higher crystalline melting temperature were created during the primary crystallization process [42]. If a plasticizer is present in the system, just like in the case of the PLA containing 4.3% D-lactide, $T_{m'}$ decreased.

A comparison of the DSC results with the results obtained in mechanical tests shows that with DOA, a higher crystalline fraction formed during manufacturing in PLAs with a low D-lactide content than with OLA2 and with unplasticized polylactic acid. This effect is reflected in the change of mechanical properties, since both modulus and tensile strength decrease slightly at the beginning. However, at 12.0% D-lactide content, no crystalline particles are detected in the material, so this compensatory effect is not present.

3.3. Morphology

Scanning electron microscopy can be used to show the material's behavior from the inhomogeneities in the material and the surface features that are formed during fracture. As shown in Fig. 7, there was no significant difference in the type of fracture (rigid or tough) between the materials without plasticizer, nor did the addition of OLA2 result in a significant behavior change. Due to the similar molecular structure of the PLA and OLA2, no inhomogeneity can be observed on the fracture surface, which refers to excellent compatibility. On the fracture surface of the PLA containing DOA, there are visible plasticizer phases, which is in accordance with the results of Martino et al. [44]. From their size, the quality of compatibility can be deduced. For DOA, the size of the plasticizer phases decreased with increasing D-lactide content as the plasticizer can best be incorporated in the amorphous parts of the PLA. Since we were able to deduce changes at the molecular level from the DSC studies, we can conclude that DOA was partially dispersed in the system. From a mechanical point of view, the presence of inhomogeneities should mainly affect strength. Therefore, the lowest strength values measured for PLAs containing DOA are related to the partial distribution of DOA. Due to their inhomogeneous structure, strain at maximum force is the smallest for compounds containing DOA.

4. Conclusions

We investigated the effects of plasticizers on the mechanical and morphological properties of polylactic acid with different D-lactide content. We showed that the tensile strength and modulus of neat, unplasticized PLA are higher than those of the plasticized PLA samples, regardless of the type of plasticizer (OLA or DOA). Tensile strength and modulus decreased almost linearly with increasing D-lactide content in the case of neat PLAs and for compounds containing OLA. For PLA compounds containing DOA, tensile strength and modulus were much less dependent on D-lactide content than for OLA. For crystallizable PLAs, plasticizers promote crystallization, which also affects mechanical properties. In the presence of plasticizers, the crystalline fraction that formed after post-crystallization increased significantly. In contrast, crystallization temperature decreased. This phenomenon can be explained by that
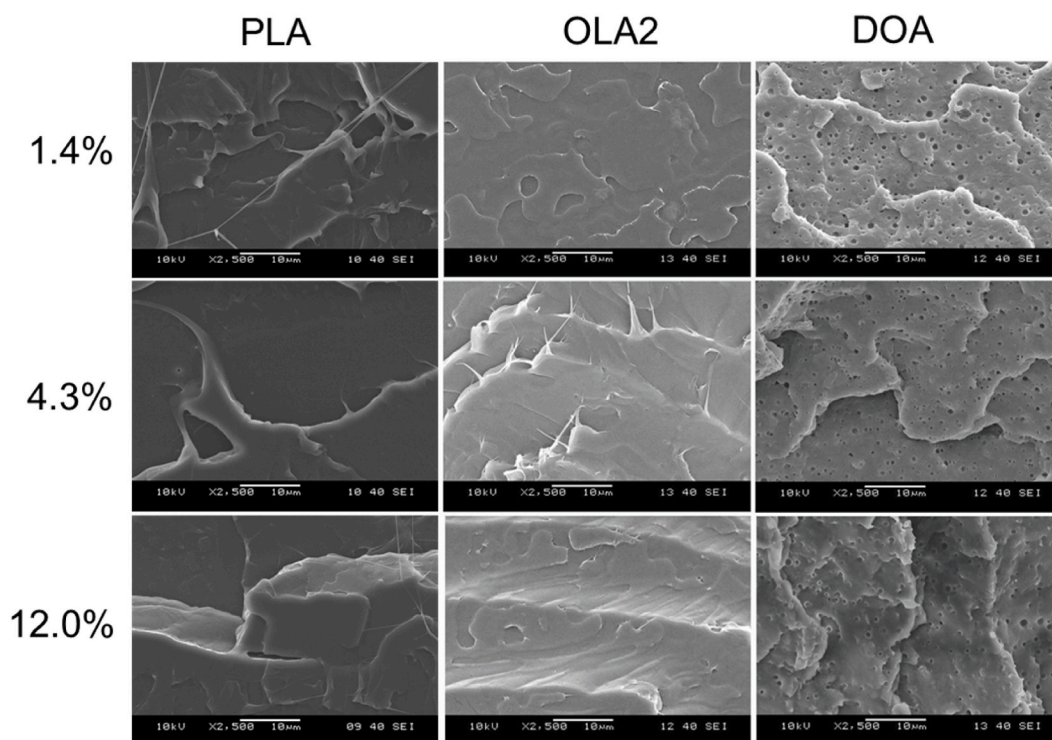

Fig. 7. SEM images of the plasticized and unplasticized PLAs.

molecules or parts of molecules are embedded as defect in the crystallites during crystallization. Scanning electron microscopy indicated that OLA2 formed a single phase with PLA. The DSC results showed that the dispersion of DOA was only partial. The inhomogeneous structure results in lower strength and lower strain at maximum force. Overall, it can be concluded that D-lactide content and plasticizers have a complex effect on the properties of the PLA since the plasticizers influence both the crystallization processes and the mechanical properties.

Author contribution statement

Katalin Litauszki: Conceived and designed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

Roland Petrény: Analyzed and interpreted the data; Wrote the paper.

Zsófia Haramia: Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data.

László Mészáros: Conceived and designed the experiments; Analyzed and interpreted the data; Wrote the paper.

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Data availability statement

No data was used for the research described in the article.

Declaration of interest's statement

The authors declare no competing interests.

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