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Thermo-mechanical characterization of plasticized PLA: Is the miscibility the only significant factor?

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Abstract

PLA is a widely used polymer which has received much attention in the last decade because of its originating from renewable resources and its potential biodegradability. PLA fulfils the packaging industry's requirements for most of the rigid objects but the polymer needs to be plasticized to be used as soft films. In this work, agreed plasticizers for food contact were melt mixed with L-PLA and then, the glass transition, melting, crystallization and mechanical properties of the blends were investigated. The experimental results were compared to the predicted results found through empirical interaction parameters and Fox equations. Molecular scale miscibility is assumed in the amorphous phase whatever the plasticizer. The mobility gained by the PLA chains in the plasticized blends yields crystallization, which is the driving force for various scale phase separations.

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Keywords: PLA; Plasticization; Mechanical properties

1. Introduction

Research in biodegradable polymers has received increased attention in recent years because of their wide application in environmental friendly packaging. The most popular and biodegradable polymers are aliphatic polyesters, such as polylactic acid (PLA), polycaprolactone (PCL), poly(butylene adipate terephthalate) (PBAT) and polyhydroxybutyrate (PHB).

PLA has a number of interesting properties including biodegradability, good mechanical properties, and processability. For these reasons PLA is an interesting candidate for producing biodegradable packaging materials. However, low deformation at break and high modulus have limited applications of PLA to the rigid thermoformed packaging industry [1]. One important requirement for packaging materials such as films is high flexibility at room temperature, transparency, and low crystallinity. Barrier properties are also relevant for these applications.

So, attempts to improve the mechanical properties for packaging applications have focused on food contact agreed plasticizers or polymers. PLA has been blended with a number of polymers such as poly(hydroxybutyrate) [2,3], poly(vinylacetate) [4], poly(ethylene oxide) [5–9] and polysaccharides [10–13]. These polymer blends generally exhibit phase separation in the whole or part of the composition range.

Plasticizers are widely used to improve processability, flexibility and ductility of polymers. In the case of semi-crystalline polymers like PLA, an efficient plasticizer has to reduce the glass transition temperature but also to depress the melting point and the crystallinity [9]. Lactide monomer, for instance, is a good candidate to plasticizing PLA but it tends to migrate to the material's surface causing a stiffening of the films in time. The most common plasticizers used for PLA are poly(ethyleneglycol) [9,14–20] and citrate [21–24].

Among the more representative results, Younes and Cohn [9] showed that microphase separation occurs at a given composition depending on the molecular weight of PEG (1500 and 35,000 g/mol). Hu et al. [18] demonstrated that the glass transition temperature of PLA–PEG (8000 g/mol) followed the empirical Fox equation but the blends were not stable in time and phase separation was observed. Another work described PEG (1500 g/mol), glucosemonoesters and partial fatty acid esters blended with PLA at 2.5, 5, and 10 wt%. It was claimed that fatty acid ester is a good plasticizer with a strong hindrance of the crystalline phase development [17]. Nijenhuis et al. [15] explained that the poor long-term stability of blends between PLA and PEG was due to slow crystallization of PEG.

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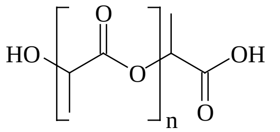
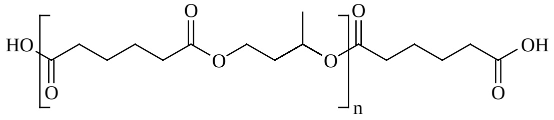
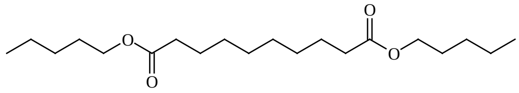
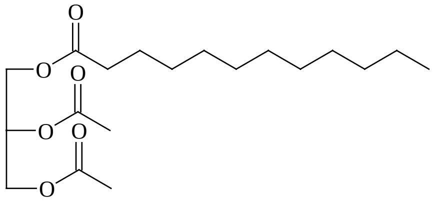
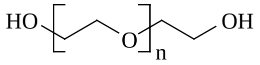
Table 1
Chemical formula of PLA and plasticizers

Name		M_w (g mol^{-1})	Chemical formula
Poly(lactic acid)	PLA	74,000	
Poly(1,3-butanediol)	PBOH	2100	
Dibutyl sebacate	DBS	314	
Acetyl glycerol monolaurate	AGM	358	
Poly(ethyleneglycol)	PEG	200 400 1000	

Plasticization of PLA with citrate provides materials, which exhibit the same properties as those with PEG, and long-term phase separations have also been observed [22,24]. Moreover, the choice of plasticizers to be used as modifiers for PLA is limited by technical and legislative [European directive 2002-72-CE] requirements of the application in food packaging.

The objectives of the present study are to determine thermal and mechanical properties of PLA with PEG and several other oligomeric plasticizers that can be used in food packaging. Moreover, glass transition and melting behavior are discussed in light of traditional polymer blend approaches and the mechanical performances assessed for blends containing 10, 20, and 30% of plasticizers.

2. Materials and methods

2.1. Materials

PLA 4042D was purchased from Cargill-Dow, and consists of 92% L-lactide and 8% D-lactide units. The molecular weight is 74,000 g mol^{-1} with polydispersity index of 2 and a density of 1.25 g cm^{-3}. Its glass transition temperature is about 54 °C and melting temperature 155 °C (Table 1).

All the plasticizers were chosen for their being food-contact approved. PBOH was obtained from Bayer. AGM, DBS and the PEGs (molecular weight 200, 400, and 1000 g mol^{-1}) were purchased from Sigma–Aldrich.

2.2. Blending conditions

The plasticizers were blended to PLA at 10, 20, and 30% w/w. Higher plasticizer content was studied but the results are not reported here since the mechanical properties are only very poor. An opened mixer (Brabender, 50 EHT) controlled by a Lab-Station driven by the BRABENDER Software Winmix was used. Blending temperature was 180 °C and blending time 15 min and blade rotation speed was 30 rpm. The blends were then extracted from the blender and molded into plates of $20\times 20\times 0.8$ cm^3 from which tensile test samples were cut.

2.3. Differential scanning calorimeter

Thermograms were obtained from a Perkin–Elmer Pyris 1 differential scanning calorimeter (DSC) using the Pyris V 3.0 software under Windows NT 4.0 for data collection and treatment. Calibration was done with indium and tin in the temperature range [+15 to +350 °C]. The base line was checked every day. Aluminum pans with holes were used and the samples' mass was approximately 10 mg. All samples were first heated to 200 °C for 5 min to get rid of thermal history. All the temperatures measured at the peak maximum (T_c, T_m) are determined with an accuracy of less than ±0.5 °C. Non-isothermal crystallization and melting temperatures, respectively, T_c and T_m, and glass transition temperature T_g, were determined at ±20 °C min^{-1} heating/cooling rates. Melting enthalpies were determined using constant integration limits.

2.4. Mechanical measurements

The static tensile experiments were performed on the MTS Synergie RT1000 testing apparatus for comparing with the above tensile impact results. The loading speed was 1 mm min^{-1} for pure PLA and 10 mm min^{-1} for plasticized PLA.

Table 2
Solubility parameter δ and interaction parameter χ between PLA and plasticizers

	δ ($MPa^{0.5}$)	χ/PLA
PLA	23.1	–
PEG 200	23.5	0.0
PEG 400	22.5	0.1
PEG 1000	21.9	0.5
PBOH	21.3	2.3
AGM	18.5	1.5
DBS	17.7	3.7

3. Results and discussion

3.1. Solubility parameter calculation

In order to assess the compatibility between two molecules, several methods can be used to calculate the solubility parameter. This parameter (δ) has been calculated using the methods of Hoy [25–27]. For the polymers used, the determination of solubility parameter was based on the average molecular weight.

Interaction parameter χ has been obtained using Eq. (1) [27]:

$$\chi = \frac{V_1}{RT}(\delta_1 - \delta_2)^2 + B \qquad (1)$$

The terms B corresponds to entropic component (between 0.3 and 0.4) and a value of 0.34 is generally used for non-polar systems. In Table 2, δ was calculated for PLA and plasticizers. Interaction parameter χ was obtained using Eq. (1), without entropic component because of the large polarity of the component used.

Grulke [27] stated that blends with $\chi < 0.5$ can be considered as miscible ones and no phase separation is expected and, therefore, only one glass transition temperature has to be found. From the results summarized in Table 2, the PLA/PEGs should exhibit only one glass transition temperature, whereas PBOH, AGM and DBS/PLA blends might be non-miscible with PLA and exhibit two distinct glass transition temperatures. Nevertheless, polarity, H-bond and particularly the crystallinity of PLA, which are not taken into account in the Hoy approach might modify the prediction of miscibility of these systems.

3.2. Thermal analysis of miscibility

Miscibility is generally stated when only one glass transition temperature is recorded on the DSC traces of polymer blends. However, phase separation yielding very little domains of less than 20 nm will not be detected by this technique. Miscibility also yields some changes in crystallization and melting temperatures with the decreasing of the integrated enthalpies.

Thermograms of pure PLA and PLA/plasticizers 90/10 (w/w) are shown in Fig. 1. At room temperature, all the blends are amorphous and present only one glass transition temperature. A crystallization exotherm (cold crystallization) and a subsequent melting peak are observed for PLA/PEG blends. The glass transition temperature of PLA is decreased with all the plasticizers used. Only the pure PLA is very weakly crystallized because it presents a melting endotherm at 154 °C with an enthalpy of 0.5 J g^{-1} in comparison to thermodynamical melting enthalpy of 94 J g^{-1} for fully crystalline PLA [28]. The PEGs promote an important crystallization of PLA whereas DBS, PBOH and AGM induce only weak crystallization.

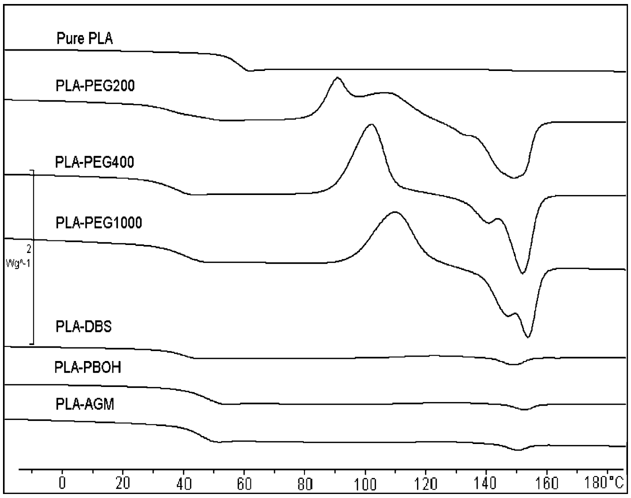


Fig. 1. Thermograms of PLA/plasticizers 90/10 (w/w) heated at 20 °C min^{-1} after cooling at 20 °C min^{-1}.

Table 3 summarizes the glass transition temperatures of pure components and blends with PLA. The glass transition temperature of pure plasticizers were obtained with tests at low temperature (−120 °C). For the blends, it was obtained using a cycle from −100 to 200 °C. For PEGs, blends with 20 and 30% for PEG 200 and blends with 30% for PEG 400 cannot be analyzed because of the macroscopic phase separation of the two components that occurs during cooling. For others blends, only one glass transition temperature is observed above 0 °C, which lets us suppose that all the blends are miscible. This point is discussed later with comparison between theoretical values (Fox equation) and experimental values. This is in total contradiction with the prediction made in Table 2 since PLA/PEG was expected to be miscible and the other blends were not. Therefore, crystallinity of PLA should play a significant role on the miscibility. Moreover, the Hoy approach assumes a constant interaction parameter with the blend composition, which is also not true.

One can assume that for PLA/PEG systems the large enhancement of the crystallinity of PLA is the major cause for the phase separation above 20% of plasticizer. On the other hand, the improvement of miscibility observed for the other plasticizers is mainly due to the dipole/dipole interactions, which are not accounted for in the Hoy model calculations.

Several theoretical and empirical equations are used to estimate the glass transition temperature of miscible blends.

Table 3
Glass transition temperature of pure components and of blends between PLA and plasticizers

Components	Glass transition temperature (°C) (±1 °C) of PLA blends						
	100%	10%		20%		30%	
		T_{g_1}	T_{g_2}	T_{g_1}	T_{g_2}	T_{g_1}	T_{g_2}
Pure PLA	59.2	–	–	–		–	
PEG 200	−81.8	35.8	n.o.	–	–	–	–
PEG 400	−65.7	37.1	n.o.	18.6	−50.2	–	–
PEG 1000	−81.0	40.2	n.o.	22.4	−62.7	29.9	−68.9
PBOH	−64.7	47.6	n.o.	30.1	−48.5	29.4	−45.0
AGM	−82.0	45.8	n.o.	24.3	−65.8	12.9	−56.9
DBS	−81.7	39.9	n.o.	26.1	−66.9	29.2	−56.5

T_{g_1} corresponds to the PLA rich phase and T_{g_2} corresponds to the plasticizer rich phase (n.o., not observed).

Among them, Fox equation is the most widely used for systems in which weak interactions dominate [29]

$$\frac{1}{T_g} = \frac{w_1}{T_{g_1}} + \frac{w_2}{T_{g_2}} \tag{2}$$

where T_g is the glass transition temperature of the blends, and T_{g_1} and T_{g_2} are those of the blends' components. w_1 and w_2 are the weight fractions.

For contents higher than 20% of plasticizer it is clear that all the blends present a limit of miscibility and the glass transition temperature reach reaches a plateau value. In Fig. 2(a)–(c), for composition lower than 30% of plasticizers, PLA/PEGs measured glass transition temperatures are consistent with Fox equation. A low deviation is observed for DBS (Fig. 2(e)) and a higher one for PBOH and AGM (Fig. 2(d) and (f)). According to the Fox relation, PLA plasticized with PEGs should be totally miscible in the whole composition range. These values correspond to the calculations of the interaction parameter, which yield low PEG/PLA interaction parameter. Nevertheless, experimentally a second glass transition temperature is observed for contents higher than 20% of plasticizers (Table 3). This lower temperature T_{g_2} corresponds to high plasticizer content phase. The phase separation is induced by the PLA crystallization, which is enhanced for low PEG molecular weight. Indeed, PEG200 yields macroscopic phase separation for 20%, PEG400 for 30% whereas PEG1000 only yields microscopic demixtion.

The other plasticizers deviate more severely from the Fox relation and yield higher interaction parameters as well. However, even though these blends do not lead to total molecular scale miscibility between PLA and plasticizers, they can offer satisfying compatibility as will be assessed by tensile tests.

Table 4 summarizes melting enthalpies and temperatures of pure components and of PLA/plasticizers. Pure PLA exhibits low melting endotherm, percentage of crystallinity was calculated using heat of fusion of 94 J g^{-1} and is about 0.5% in the raw pellets material [28]. The melting endotherm of PLA shifts to low temperatures with all the plasticizer and composition. It clearly appears that low PEG molecular weights induce a decrease in the PLA melting point as already noticed by Younes and Cohn [9]. They explained this decrease by a lower capacity the short chains of PEG have to crystallize and their high mobility, which are powerful enough to plasticize PLA chains. Similarly, the enthalpy of melting increases for the lower PEG molecular weight, which can explain the macroscopic phase separation observed for PEG200 and 400.

PBOH, AGM and DBS also induce a decrease in melting points. Nevertheless, a very low degree of PLA crystallinity is obtained with PBOH, AGM and DBS at 10% whereas PEG allows crystallinity to reach values generally observed for fully crystallized PLA (55 J g^{-1}) [9].

In order to compare the miscibility between PLA and plasticizers, the Flory–Huggins relation can be used [30]:

$$\frac{1}{T_m} - \frac{1}{T_m^0} = -\frac{RV_2}{\Delta H_m V_1} \chi_{12} \phi_1^2 \tag{3}$$

where T_m and T_m^0 are the equilibrium melting points of PLA in blends and neat crystallizing polymer. The subscript '1' indicates the non-crystallizing component (plasticizer) and '2' the crystallizing PLA. V_1 and V_2 are the molar volume of the repeat units. ΔH_m is the heat of fusion of PLA and ϕ_1 is the volume fraction of plasticizer.

Using interaction parameters calculated, miscibility at molecular level between PLA and PEG ($\chi_{12} < 0.5$) is expected from Eq. (3) to induce a strong decrease in the melting point of crystalline polymer. This is only a qualitative approach since the experimental T_m values are not true equilibrium melting points. As observed in Table 4, the PEGs increase the crystallinity ratio for all blend compositions and the most efficient ratio is 10%. We can, therefore, suppose that PEG can yield a higher mobility of PLA chains and promote its crystallization kinetics.

However, other plasticizers also yield a decrease of melting point despite their higher interaction parameters. Nevertheless, we can notice from Table 4 an important difference in the melting enthalpy for blends containing 10% of plasticizers according to their nature. From Eq. (3) one can observe that a low value of ΔH_m can compensate a high value of χ. This would explain the rather close T_m observed, no matter the plasticizer under study.

As in Table 4, a strong decrease in crystallization temperature is observed for PLA blended with PEGs (Table 5).

In the presence of plasticizer, PLA crystallization temperature decreases strongly with PEGs, particularly with the

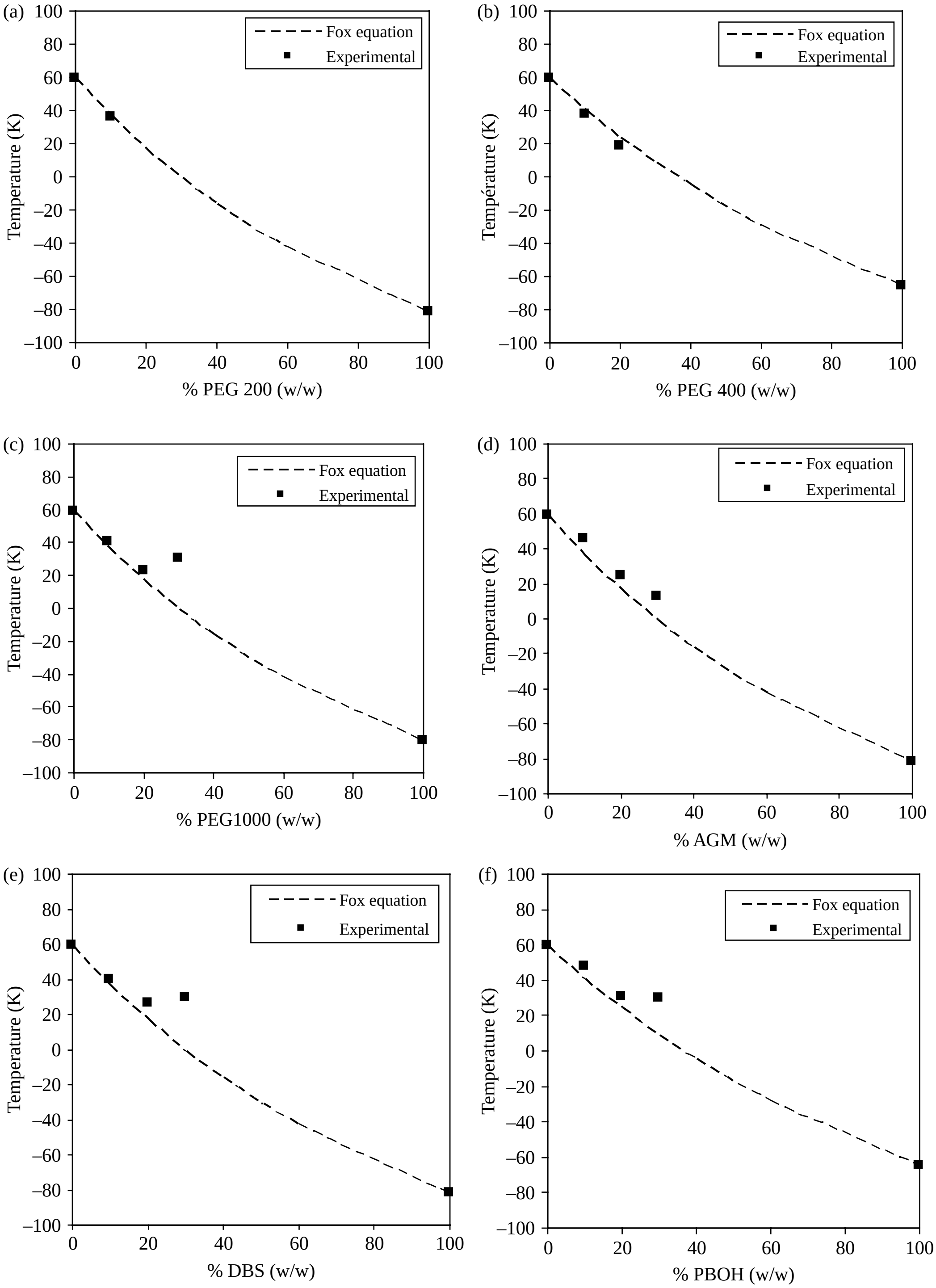


Fig. 2. Glass transition temperature of PLA/plasticizers. The dash line represents the Fox equation. (a), PEG 200/PLA; (b), PEG 400/PLA; (c), PEG 1000/PLA; (d), AGM/PLA; (e), DBS/PLA; (f), PBOH/PLA.

shortest PEG chains; this indicates a higher mobility of PLA macromolecules. This enhancement of the PLA molecular mobility is claimed to be the major factor acting on the crystallization kinetic of this polymer. PBOH, AGM and DBS are less efficient than PEG to promote crystallization at relatively low temperature. A high molecular scale miscibility is, therefore, required to achieve the strong enhancement of PLA chain mobility.

3.3. Mechanical properties

Results of static tensile experiments are summarized in Tables 6–8. From a general viewpoint, plasticizers are improving the ductile character of PLA, which is the expected effect. In Table 6, tensile modulus experiments show a strong decrease for plasticizer content higher than 20%. The PEGs provide lower tensile modulus than the other plasticizers.

Table 4
Melting temperature and enthalpies of pure components and melting temperature and enthalpies for PLA in PLA/plasticizers blends

%Plasticizer	100%		10%		20%		30%	
	T_m (°C)	ΔH_m (J g^{-1})	T_m (°C)	ΔH_m (J g^{-1})	T_m (°C)	ΔH_m (J g^{-1})	T_m (°C)	ΔH_m (J g^{-1})
Pure PLA	154.0	0.5	–	–	–	–	–	–
PEG 200	–	–	148.0	34.1	–	–	–	–
PEG 400	6.9	113	150.8	32.4	142.4	44.6	–	–
PEG 1000	39.8	149.4	153.0	32.1	150.6	38.6	149.3	41.3
PBOH	−15.5	1.8	152.5	1.3	151.9	23.9	151.0	34.3
AGM	−8.3	71.9	150.3	1.6	146.6	29.3	143.4	31.4
DBS	−6.9	160.8	148.8	2.2	144.2	32.3	143.4	32.0

PLA melting enthalpies are normalized by the PLA content in the blends.

Table 5
Crystallization temperatures of pure components and of PLA/plasticizer blends during heating at a rate of 20 °C min^{-1}

	100%		10%	20%	30%
	T_c (°C)	ΔH_c (J g^{-1})	T_c (°C)	T_c (°C)	T_c (°C)
PEG 200	[a]	[a]	90.6	–	–
PEG 400	[a]	[a]	102.2	61.8	–
PEG 1000	[a]	[a]	110.0	87.4	–
PBOH	−26.1	1.7	128.5	110.4	98.2
AGM	[a]	[a]	126.0	99.3	67.8
DBS	[a]	[a]	122.5	78.2	85.4

[a] Only classical crystallizations are observed for pure plasticizers.

Nevertheless, PEG 200 can be blended to PLA at a content of 10%, PEG 400 at 20% and PEG 1000 at 30%. For higher contents, the material becomes brittle because of a lack of cohesion between the separate phases. This was already noticed from the T_g measurements and ascribed to a macroscopic crystalline induced phase separation between the components of the blend. The tensile modulus results correlate quite well with the T_g measurements as seen in Fig. 3. The efficiency of the plasticizer is, therefore, related to the molecular level miscibility which is higher in the case of PEG than for other molecules.

As shown in Table 7, strain at break increases with the increase of the plasticizer content but the optimum is reached at 20% for PEG whereas 30% can be added for the other products. The cohesion of the blends at high deformations is higher for PBOH, AGM and DBS plasticizers than for PEG. The mechanisms responsible for the ultimate mechanical characteristics are not the same as those for the elastic modulus. The strain at break is mainly governed by the cracks propagation, which is retarded in biphasic materials with controlled domain size and distribution. The fracture energy can be dissipated at the interfaces and in the high mobility domains which tend to delay the final rupture of the material.

At 20%, the most efficient plasticizer is the AGM that reduces elastic modulus values from 2840 to 35 MPa. Moreover, the strain at break is the highest with AGM added at 10 or 20% (8). PBOH and DBS yield better mechanical properties than PEGs and the obtained materials are not brittle. Whatever, the nature of the plasticizer, the glass transition temperature reached for miscible systems correlates well with the measured modulus as shown in Fig. 3. This is ascribed to the predominant mechanism of plasticization of the miscible amorphous phase whatever the blend even though a crystalline phase is present in various proportions according to the plasticizer nature as shown previously.

When plasticizers (PBOH, AGM and DBS) are blended higher for 30% to PLA, tensile modulus or strain at break are stable in comparison to 20% and the stress at break is slightly reduced. In light of these results, the most efficient plasticized formulations are AGM, PBOH and DBS at 20 to 30% according to the mechanical requirements. Long-term stability of the blends will be studied in a forthcoming paper.

Table 6
Tensile modulus (MPa) of pure PLA and plasticized PLA

	0%	10%	20%	30%
PEG 200	2840 ± 50	1700 ± 100	–	–
PEG 400	2840 ± 50	1920 ± 53	630 ± 20	–
PEG 1000	2840 ± 50	1970 ± 120	290 ± 50	420 ± 40
PBOH	2840 ± 50	2350 ± 50	350 ± 20	300 ± 50
AGM	2840 ± 50	2240 ± 100	35 ± 5	107 ± 25
DBS	2840 ± 50	2000 ± 80	430 ± 50	370 ± 35

Table 7
Strain at break (%) of pure PLA and plasticized PLA

	0%	10%	20%	30%
PEG 200	3.0 ± 0.3	2.0 ± 0.6	–	–
PEG 400	3.0 ± 0.3	2.4 ± 0.3	21.2 ± 2.3	–
PEG 1000	3.0 ± 0.3	2.7 ± 0.3	200.0 ± 12.5	1.5 ± 0.2
PBOH	3.0 ± 0.3	3.0 ± 0.1	302.5 ± 32.0	390.0 ± 35.0
AGM	3.0 ± 0.3	32 ± 2.1	335.0 ± 2.3	320.0 ± 21.0
DBS	3.0 ± 0.3	2.3 ± 0.2	269.0 ± 6.0	333.0 ± 9.5

Table 8
Stress at break (MPa) of pure PLA and plasticized PLA

	0%	10%	20%	30%
PEG 200	64.0±1.5	30.0±4.1	–	–
PEG 400	64.0±1.5	39.0±3.0	16.0±0.3	–
PEG 1000	64.0±1.5	39.6±5.0	21.6±0.4	4.7±0.2
PBOH	64.0±1.5	56.3±1.9	30.2±1.1	25.2±1.8
AGM	64.0±1.5	52.1±4.0	27.1±3.1	17.9±1.2
DBS	64.0±1.5	39.2±4.0	23.1±0.9	18.3±0.5

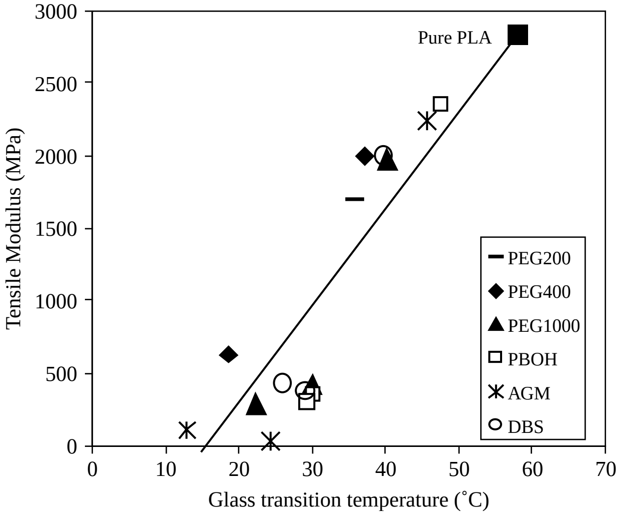


Fig. 3. Tensile modulus vs glass transition temperature of plasticizers/PLA blends.

4. Conclusion

Plasticizers blended with PLA lowered the glass transition temperature and modified the melting and crystallization characteristics. The PEGs are the most efficient for the T_g reduction and it clearly appears that for compositions higher than 20% of plasticizer, all the blends present a limit of miscibility and the glass transition temperature reaches a plateau value.

In this composition range, the glass transition temperature is in good agreement with the calculated interaction parameters: PEGs exhibit lower interaction parameters with PLA than other plasticizers and yield better fit with Fox relation. No strong differences are observed between PEG and other plasticizers on the T_m since it can be deduced from Flory Huggins equation that the interaction parameter is balanced by the enthalpy of melting.

Mechanical characteristics of these materials showed a decrease in modulus and stress at break. Nevertheless, the PLA blended to PEGs becomes very brittle as a function of plasticizer content and molecular weight. So, PEGs induce a decrease in cohesion of these materials that were shown by a very low stress at break. The more efficient plasticizers are PBOH, AGM and DBS that give mechanical characteristics that can be consistent with soft packaging applications.

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