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Polylactide (PLA) designed with desired end-use properties: 1. PLA compositions with low molecular weight ester-like plasticizers and related performances

Marius Murariu[1], Amália Da Silva Ferreira[1], Michaël Alexandre[2] and Philippe Dubois[1]*

[1]Center of Innovation and Research in Materials and Polymers (CIRMAP), Laboratory of Polymeric and Composite Materials, University of Mons-Hainaut and Materia Nova Research Center, Place du Parc 20, 7000-Mons, Belgium
[2]Center for Education and Research on Macromolecules (CERM), B6a, University of Liège, Sart-Tilman, 4000-Liège, Belgium

Polylactide (PLA) is an attractive candidate for replacing petrochemical polymers because it is biodegradable and produced from annually renewable resources. Characterized by high tensile strength, unfortunately the brittleness and rigidity of PLA limit its applicability. For a great number of applications such as packaging, fibers, films, etc., it is of high interest to formulate new grades with improved flexibility and better impact properties. In this objective, a specific PLA grade (L/D isomer ratio of 96:4, high molecular weight) was melt-mixed with selected plasticizers: bis(2-ethylhexyl) adipate (DOA), glyceryl triacetate (GTA), and tributyl *O*-acetylcitrate (TBAC). Their effect on the molecular, thermal, and mechanical properties of PLA was investigated for content up to 20 wt% plasticizer and the results were correlated with a particular attention to the relationship between property and application. Using the solubility and interaction parameters, a tentative evaluation of the product that could act as the most effective plasticizer for PLA has been performed and the obtained results have been corroborated with the materials physical properties. Excellent mechanical performances were obtained using the plasticizer having the lowest molecular mass (GTA) and the best interaction parameter. In relation to plasticizer amount/nature, the glass transition temperature of PLA (62°C) is decreased by plasticizing by more than 30°C, whereas better impact properties and lower stiffness are measured. The optimal formulations targeted to the final applications are clearly characterized by specific end-use properties: improved crystallization rates (PLA-DOA); high elongation at break and tensile strength (PLA-GTA, PLA-TBAC), medium to high impact properties (PLA-DOA, PLA-GTA) compositions. Copyright © 2008 John Wiley & Sons, Ltd.

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INTRODUCTION

The market for biodegradable polymers is growing every year and important demands can be expected for those applications where biodegradability offers clear advantages for customers and the environment. Polylactide (PLA) is undoubtedly one of the most promising candidates for further developments since it is not only biodegradable but also produced from annually renewable resources, like sugar beets or corn starch.[1–6] Because PLA has been recently considered as an alternative in replacing petrochemical polymers, there is a strong demand to extend the range of PLA properties. Suppliers claim that using the right additives PLA performances can be made comparable to those of PS, PET, PE, flexible PVC, etc. and it can replace these or other non-biodegradable resins in many applications (cast, blown, and oriented films; fibers and nonwovens; blown, thermoformed, and injection molded rigid products, etc.).

PLA is characterized by excellent optical properties and high tensile strength but unfortunately, it is rigid and brittle. Since for many applications, such as packaging or textile fibers, rigidity, and low ductility of PLA limit its utilization, there is a general interest to formulate new grades with improved flexibility, ductility, and higher impact properties, while the tensile strength performances are maintained at the optimal level required by a given application. In this main goal, a large number of investigations have been made to improve PLA properties via plasticization but due to a great number of variables, e.g. nature of PLA matrix, type, and optimal percentage of plasticizer, thermal stability at the processing temperature, etc., unfortunately some times poor mechanical properties have been reported or the relationship between the thermo-mechanical properties and molecular parameters has not been considered enough. In this context,

Correspondence to: P. Dubois, Center of Innovation and Research in Materials and Polymers, Laboratory of Polymer and Composite Materials, University of Mons-Hainaut, 20, Place du Parc, 7000 Mons, Belgium
E-mail: philippe.dubois@umh.ac.be

it is important to note that an inadequate choice of the plasticizer can lead to PLA mixture that is not miscible, to migration of the plasticizer, to degradation of the polyester matrix and/or of the plasticizer along processing, etc.

Typically, amounts from 10 to 20 wt% plasticizers are required to provide a substantial reduction of the glass transition temperature (T_g) of the PLA matrix and adequate mechanical properties. The preferred plasticizer for PLA can be any biodegradable product, sufficiently nonvolatile, with a relatively low molecular weight to produce a desired decrease in Young's modulus value and increase in impact strength. It is well-known that for instance the monomer, lactide itself, is considered as one of the best plasticizers for PLA,[7–9] but it has the disadvantage to migrate very rapidly at the polymer surface. Excessive volatility can lead to fouling of the process equipment, which is observed when PLA with high content of lactide is processed. Therefore, different plasticizer systems have been studied to find out other alternatives: glucose monoesters and partial fatty acid esters,[9] lactic acid oligomers,[8,10] glycerol esters,[11–13] citrates,[7,13–15] citrate oligoesters,[15] citrate oligomers,[16] dicarboxylic esters,[7,17] and even higher molecular weight plasticizers like poly(ethylene glycol),[9,14,18,19] poly(propylene glycol),[20] etc.

In general, it has been accepted that the addition of a reasonable amount of plasticizer (e.g. 15–20 wt%) into PLA matrix leads to improved flexibility properties whereas for smaller percentages, especially up to 10 wt%, some "anti-plasticizing" effects in relation to the mechanical properties can be recorded.[9]

On the other hand, the choice of plasticizer used as a modifier for PLA is limited by the legislative or technical requirements of the application[15,16] and in this context its selection becomes more difficult. The nature of the plasticizer can strongly influence the final properties of the products, where the impact and/or crystallization properties are required to be higher than a critical value (e.g. in injection-molded parts, plastic containers, fibers, films, etc.).

The main objectives of the present study were to determine means of plasticizing a high molecular PLA matrix with a specific L/D isomer ratio (96:4) designed for processing by extrusion and thereby to propose a new insight in the preparation of plasticized grades with desired end-use properties, mainly for packaging and textile fiber applications.

Among the multitude of low molecular weight plasticizer systems, after a preliminary selection (not discussed here), three products, i.e. bis(2-ethylhexyl) adipate (DOA), glyceryl triacetate (GTA), and tributyl O-acetylcitrate (TBAC), were mixed together with PLA via melt-compounding technology and the performed compositions were fully characterized to evidence the improvements/modifications obtained by plasticization.

EXPERIMENTAL

Materials

Poly(L,L-lactide), commercial name "Galastic", was kindly supplied by Galactic S.A. This grade is typically designed for extrusion and thermoforming applications due to a high molecular weight and a reduced fluidity in the molten state. Characteristics of PLA are as follows: number average molecular weight, $M_{n(PLA)} = 74\,500$, index of polydispersity, $M_w/M_n = 2.0$, L/D isomer ratio of 96:4, MFI (190°C, 2.16 kg) = 6.6 g/10 min.

Glyceryl triacetate (molecular mass: 218.2, density: 1.16 g/cm^3, boiling point: 259.0°C)—GTA, known as "Triacetin" (Acros Organics), DOA (molecular mass: 370.6, density: 0.93 g/cm^3, boiling point: 374.4°C), known as "dioctyl adipate"—DOA (Acros Organics) and TBAC (molecular mass: 402.5, density: 1.08 g/cm^3, boiling point: 418.2°C)—TBAC (Aldrich) were used as low molecular weight ester-like plasticizers.

Melt-blending procedure and sample preparation for characterization

Before processing by melt-bending, PLA was dried during 4 hr at 80°C under vacuum. Various amounts of plasticizer, between 5 and 20% (by weight), dried first at 80–100°C for 1 hr under vacuum, were mixed together with PLA pellets at 190°C (moderate mixing with cam blades) by using a Brabender bench scale kneader (3 min premixing at 30 rpm—speed that allows preventing an excessive increase in torque and the protection of the device during melting of PLA, followed by 3 min mixing at 60 rpm). Plates (3 mm thickness) were then made by compression molding at 190°C by using an Agila PE20 hydraulic press. The material was first pressed at low pressure for 240 sec (three degassing cycles), followed by a high-pressure cycle at 150 bar for 150 sec. The samples were then cooled under pressure (50 bar). Specimens for tensile and Izod impact testing were made from plates by using a milling machine or by cutting (samples characterized by low T_g), in accordance with ASTM D 638-02a norm (specimens type V) and ASTM D 256-A norm (specimens $60 \times 10 \times 3$ mm^3), respectively.

Characterization

Size exclusion chromatography (SEC)

Isolation of PLA from the prepared compositions for molecular weight parameters determination was carried out by first dissolving the samples in chloroform. Then, the catalyst residues were removed by liquid–liquid extraction with a 0.1 N HCl aqueous solution and PLA was recovered by precipitation in an excess of heptane. After filtration and drying, PLA solutions were prepared in THF (10 mg polymer/5 ml solvent). Molecular weight parameters (number average molar mass, M_n, and polydispersity index, M_w/M_n) of neat PLA and PLA extracted from the plasticized compositions were determined by size exclusion chromatography (SEC) using the procedure described elsewhere.[21]

Differential scanning calorimetry (DSC)

DSC measurements were performed by using a DSC Q200 from TA Instruments under nitrogen flow. Procedure (Fig. 1): first heating with a ramp of 10°C/min from room temperature up to 220°C to discard any anterior thermal history, ramp of 10°C/min down to −10°C, second heating scan from −10 to 220°C with a ramp of 10°C/min. The start temperatures of DSC cycles were carefully selected to assure a difference of 50–60°C compared to the events of interest (e.g. glass transition or melting temperatures). The first
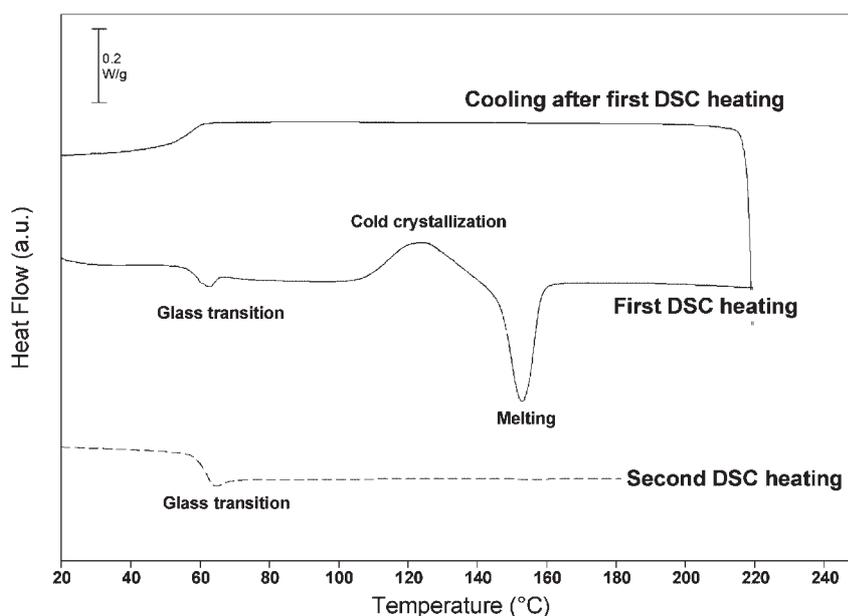
Figure 1. DSC traces to illustrate the experimental procedure and PLA behavior during first and second heating cycle.

heating scan followed by controlled cooling was performed to assure a similar thermal history of the samples. In order to limit PLA thermal degradation upon measurement, no plateau was maintained at 220°C.

The events of interest, i.e. the glass transition temperature (T_g), crystallization temperature (T_c), enthalpy of cold crystallization (ΔH_c), melting temperature (T_m), and melting enthalpy (ΔH_m) were determined from the second scan. As remark, when multiple endothermic peaks were found, the peak temperature of the largest endotherm was taken as melting temperature. For calculating the degree of crystallinity, the exothermic effect of cold crystallization has been taken into account when it was recorded. The degree of crystallinity was determined by considering a melting enthalpy of 93 J/g for 100% crystalline PLA.[22]

Thermogravimetric analyses (TGA)
TGA were performed by using a TGA Q50 (TA Instruments) with a heating ramp of 20 °C/min under air flow, from room temperature up to 600°C (platinum pans, 60 cm³/min air flow rate).

Mechanical testing measurements
Tensile testing measurements were performed by using a Lloyd LR 10 K tensile, compression and flexion-testing bench in accordance to the ASTM D 638-02a norm (specimens type V) at a speed rate of 10 mm/min. To have comparative information about PLA and plasticized compositions, it was preferred to determine the tensile stress performances in the same conditions of testing, even though PLA matrix is brittle and smaller speeds of testing can be more appropriate.

Notched impact strength (Izod) measurements were performed by using a Ray-Ran 2500 pendulum impact tester and a Ray-Ran 1900 notching apparatus, in accordance to the ASTM D 256 norm (Method A, 3.46 m/s impact speed, 0.668 kg hammer). All mechanical tests were carried out by

using specimens previously conditioned for at least 48 hr at 20 ± 1°C under a relative humidity of 45 ± 5% and the values were averaged over five measurements.

Scanning electron microscopy (SEM)
The samples were broken at liquid nitrogen temperature to observe by SEM analysis the morphology of plasticized samples. SEM analyses of the fractured surfaces of PLA and PLA-20% plasticizer blends were performed by using a scanning electronic microscope Philips XL at an accelerated voltage up to 20 kV and various magnitudes. The SEM was equipped for both secondary electron (SE) and backscattered electron (BSE) imaging.

RESULTS AND DISCUSSION

Theoretical prediction of plasticization efficiency

The selection of a plasticizer to be used in a specific PLA composition requires the consideration a many criteria: compatibility, low volatility, resistance to migration, and extraction during service life, lack of toxicity, etc. Another important key criterion is the plasticizer efficiency that is determined by finding how much plasticizer must be added in the polyester matrix for giving a required level of mechanical or physical response. One can assume that this efficiency is mostly related to the chemical structure of the plasticizer molecule and to its compatibility with the polymer matrix. From a molecular perspective, the plasticizer must be miscible with the polymer and characterized by similar intermolecular forces. It has been generally observed that the most effective plasticizer closely resembles to the polymer and it is characterized by solubility parameters close to those of the polymers.[23,24]

The compatibility of a plasticizer depends on both components (polymer and plasticizer) and for such a system it can be described in terms of polymer–liquid miscibility by

using the thermodynamic properties of polymer–liquid systems. By using the corresponding solubility parameters of the components, polymer and plasticizer, and by applying standard thermodynamic procedures [25–27], it is possible to estimate the polymer–solvent (plasticizer) interaction parameter, χ_T, which is modeled as the sum of entropic and enthalpic components (eqn 1):

$$\chi_T = \chi_s + \chi_H \qquad (1)$$

where χ_H is the enthalpic component and χ_s the entropic component that is usually taken to be a constant between 0.3 and 0.4; $\chi_s = 0.34$ being often used.[25,26] The enthalpic component can be related to the Hildebrand parameters according to

$$\chi_H = [V_{sol}(\delta_{sol} - \delta_{polymer})^2]/RT \qquad (2)$$

in which V_{sol} denotes the molar volume of the solvent (plasticizer), R the general gas constant, T the absolute temperature in Kelvin, δ_{sol} and $\delta_{polymer}$ are the solubility parameters of solvent/plasticizer and polymer, respectively.

Substituting eqn 2 into eqn 1 gives χ_T (eqn 3):

$$\chi_T = 0.34 + [V_{sol}(\delta_{sol} - \delta_{polymer})^2]/RT \qquad (3)$$

Equation 3 permits only positive values for the interaction parameter. Since the Flory–Huggins criterion for complete solvent–polymer miscibility is $\chi_T < 0.5$, the enthalpic contribution must be small and the solubility parameters of the solvent and polymer must be similar or their difference very small.[25] On the other hand, the molar volume of the plasticizer can also affect miscibility and phase equilibrium.

In Table 1 the interaction parameter (χ_T) for the three selected molecules was obtained using eqn 3 ($R = 8.314$ J/ mol K; $T = 298$ K). For calculation of χ_T, the values of the solubility parameters based on Hoy or Hansen approach were obtained from published data.[15,23–25,27,28] By analyzing the interaction parameters (χ_T), from the results summarized in Table 1, it is possible to predict a theoretical order of miscibility and plasticization efficiency as follows: GTA > TBAC > DOA.

In general, it is considered that the blends characterized by low χ_T values, i.e. $\chi_T < 0.5$, can be considered as miscible blends and no phase separation is expected, therefore, only one glass transition temperature has to be found.[25,26] It is reasonable to conclude that the theoretical predictions can be relative because the solubility parameter may only be representative for a given polymer since variations in compositions, crystallinity, polarity, etc. can lead to changes in the values of the interaction parameters.

On the other hand, from the results presented in Table 1, phase separation can be expected for the PLA-DOA blends that might be immiscible or only partially miscible where

PLA could incorporate only a certain amount of plasticizer before being saturated.

Indeed, from SEM pictures of the cryofractured surfaces (Fig. 2A–C) of PLA compared to PLA-plasticizer (20%) compositions it can be seen that in agreement with the theoretical prediction of plasticizer efficiency, addition of 20% TBAC or GTA into PLA leads to compositions in which the plasticizer tends to be rather homogeneously dispersed (Fig. 2B and C, respectively), whereas for PLA-DOA compositions (Fig. 2D), phase separation is clearly observed from the formation of regular small spherical voids throughout the whole sample.

Moreover, from the SEM picture performed in back scattering electron (BSE) mode (Fig. 3) the presence of quite well-dispersed spherical voids with diameter of 1–2 μm or less, indicating the presence of phase-separated DOA, is clearly evidenced. In this context, it can be assumed that for the PLA-DOA blends the PLA matrix became saturated with the plasticizer at a certain concentration and phase separation occurred. On the other hand, these morphology analyses allow some insights in the interpretation of tensile testing results (mechanical testing section), since the introduction of immiscible (or partially miscible) phase into PLA can affect the mechanical properties, i.e. the tensile strength, to a larger extent.

Modification of PLA molecular characteristics by plasticizer addition

In many cases, but not in all, the mixing of PLA with additives and/or plasticizers is followed by an important decrease in the molecular weights, with negative impact on the thermo-mechanical properties. Hydrolysis reactions of ester linkages may occur depending on residual water content into the polymer matrix and/or plasticizer leading to a reduction of the molar masses. Minimizing moisture content by intensively drying all components represents a first step to reduce the losses by hydrolysis and to preserve the polyester molecular weight as high as possible. On the other hand, the degradation in PLA during processing in the presence of plasticizers with ester groups can also be due to potential transesterification reactions leading to a decrease of PLA molecular weights.

Table 2 shows the effect of plasticizer amount on PLA molecular weight parameters after melt-blending under moderate mixing conditions and as determined by SEC (experimental accuracy of ±10%). As a remark, the unprocessed PLA is a thermally stable high molecular weight polymer for which the processing conditions only slightly affect the number average molar mass. The number average molecular weight (M_n) decreases from 74 500 to

Table 1. Solubility parameter δ and interaction parameter χ_T between PLA and plasticizers

Component of system	Molecular weight (g/mol)	Molar volume[a] (cm³/mol)	δ (MPa^0.5)	χ_T/PLA
PLA	74 500	—	20.1	—
DOA	370.6	394.4	17.6	1.33
TBAC	402.5	372.6	19.2	0.46
GTA	218.2	187.9	20.1	0.34

[a]Source ChemSpider™ Beta (www.chemsspider.com).
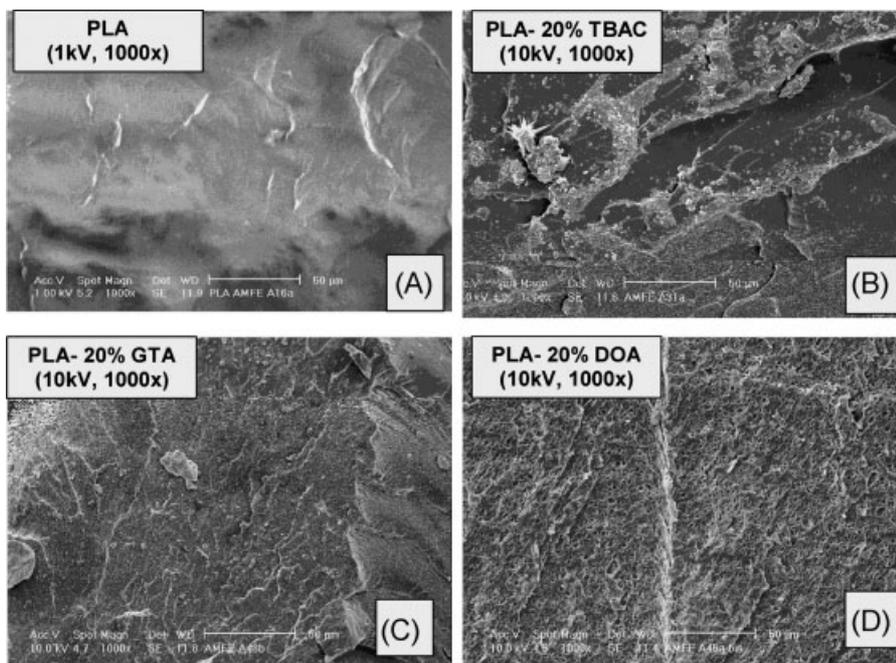
Figure 2. SEM pictures of the fractured surfaces of PLA (A) compared to PLA-20% plasticizer compositions (B-TBAC; C-GTA; D-DOA).

64 000 in the worst case. The molecular characterization allows concluding that, under adequate processing conditions, melt-blending of PLA with TBAC, GTA or DOA does not induce any substantial drop of PLA molar masses by thermal degradation or hydrolysis of the polyester chains, whereas the polydispersity index is poorly affected by the amount and nature of the plasticizer.

Plasticized compositions: evaluation of thermal properties

Since the glass transition temperature T_g is an excellent indicator of polymer structure and chain mobility,[29] plasticizing efficiency has therefore been evaluated by the decrease in T_g as a function of plasticizer concentration. DSC analysis seems to be one of the most preferred methods to

measure T_g and highlight the effect of the plasticizer in PLA compositions with increasing molecular mobility.[14]

On the other hand, in semi-crystalline PLA the plasticizers are incorporated primarily into the amorphous part. An increase in crystallinity degree over time can induce phase separation and segregation or migration of the plasticizer.[30] By considering all these aspects, the melt-blending of a mostly essentially amorphous PLA with adequate plasticizers can lead to more homogeneous materials that allows to maintain their main physical and mechanical properties during utilization and/or aging (as confirmed by ageing studies to be presented in a forthcoming paper).

DSC measurements confirm the poor ability of PLA matrix (4% content of D isomer) to crystallize. On the other hand, it comes out that addition of DOA as a plasticizer in PLA (Table 3 and Fig. 4A) promotes an important crystallization exotherm (cold crystallization), whereas for GTA and TBAC, under the investigated DSC procedure, crystallization
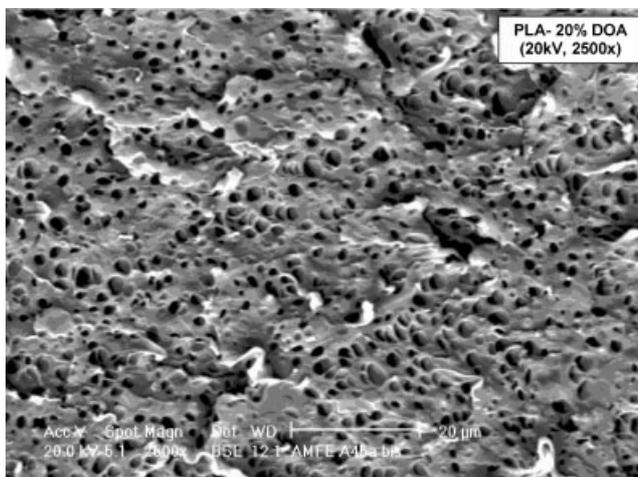
Figure 3. SEM picture of the fractured surface of PLA-20% DOA compositions in BSE mode (20 kV, magnitude 2500X).

Table 2. Evolution of PLA molecular weights and polydispersity indices upon melt-blending with the plasticizers

Sample composition (%, by weight)	Polydispersity index	$M_{n(PLA)}$ (g/mol)
PLA (granules)	2.1	74 500
PLA-processed	2.2	64 000
PLA-10% DOA	2.0	68 000
PLA-15% DOA	n.d.	n.d.
PLA-20% DOA	2.2	67 000
PLA-10% GTA	2.1	66 000
PLA-15% GTA	2.1	70 000
PLA-20% GTA	n.d.	n.d.
PLA-10% TBAC	2.1	66 000
PLA-15% TBAC	2.1	65 000
PLA-20% TBAC	2.0	67 000

n.d.—not determined.

Table 3. DSC data on PLA and PLA-DOA compositions (second heating, ramp of 10°C/min)

Sample (%, by weight)	T_g (°C)	T_c (°C)	ΔH_c (J/g)	Crystallinity from cold crystallization[a] (%)	T_m (°C)	ΔH_m[b] (J/g)
PLA (granules)	62	—	—	—	—	—
PLA-processed	62	—	—	—	153	0.1
PLA-5% DOA	49	—	—	—	151	1.3
PLA-10% DOA	45	97	28.2	30.3	151	30.1
PLA-15% DOA	45	110	27.2	29.2	144	27.9
PLA-20% DOA	45	110	29.9	32.2	144	32.6

[a]Increase due to cold crystallization.
[b]Initial crystallinity of samples was less than 2.5% as calculated by substracting ΔH_c from ΔH_m.

behavior is not practically evidenced (Fig. 4B and C, respectively). So, contrary to TBAC or GTA, heating of PLA-DOA compositions at approximately 100°C (Fig. 4A) promotes an important increase of crystallinity degree likely due to chains mobility and maybe nucleation from phase-separated DOA inclusion (shown in hereunder). Interestingly enough, this enhancement of crystallinity by more than 30% represents a property of interest for film and fiber applications.

As far as T_g is concerned, as observed in Table 3, addition of 10, 15, or 20% DOA leads to PLA compositions characterized by similar values (~45°C) more likely attesting for partial miscibility, while T_m are slowly decreased with the amount of plasticizer. In other words, above a certain content in DOA (at about 5%), on can assume that saturation in this partially miscible plasticizer is reached in the polyester matrix, yielding phase-separated microdomains (as shown in Fig. 3) able to nucleate the crystallization of the polyester chains.

As far as the other two plasticizers are concerned and whatever the plasticizer content, the shape of DSC traces remains the same for the PLA-GTA blends (Fig. 4B) where no crystallinity can be detected, whereas the PLA-TBAC blends (Fig. 4C) display a very limited crystallinity (less than 2%). Similarly to PLA-DOA compositions, all these blends are characterized by only one T_g, the value of which is significantly decreased by comparison to the neat PLA matrix ($T_g = 62$°C). It should be noted that the decrease in T_g is quite well correlated with the plasticizer content for the PLA-GTA and PLA-TBAC formulations: T_g values of PLA plasticized with 10 and 20% GTA are detected at 48 and 29°C, respectively, whereas the addition of 10 and 20% TBAC leads to T_g's at 44 and 38°C, respectively.

Finally, from DSC measurements it comes out that the more pronounced decrease of T_g has been recorded by adding 20% of GTA plasticizer into PLA ($T_g = 29$°C), whereas the same relative content in TBAC and DOA only leads to T_g's at 38 and 45°C, respectively. It is also important to point out that the lowest recorded T_g is obtained for the plasticizer having the smallest molecular weight (GTA) and therefore, the theoretical prediction of plasticizing efficiency is confirmed: GTA > TBAC > DOA.

In relation to the thermal stability, due to the volatility of the plasticizers, a decrease in thermal properties of plasticized formulations compared to the neat polymer is not surprising. Indeed, Fig. 5A and B show the TGA traces of PLA-DOA and PLA-TBAC compositions compared to neat PLA and the respective plasticizer (DOA or TBAC). The results are consistent with the vaporization temperature of plasticizers upon TGA conditions and a steady evolution in the decrease of stability of the plasticized compositions that is quite well correlated with the amount of plasticizer. A similar behavior was found for the PLA-GTA compositions (TGA traces not shown here). Because GTA is characterized by a relatively higher volatility by comparing to DOA or TBAC, a higher decrease in the thermal stability of PLA-GTA compositions can be assumed and as consequence the PLA-GTA blends could be recommended for applications where the temperature and residence time in processing conditions are more limited. In this context, it is important to point out that other direction of research concerning the improvement of thermal properties of plasticized compositions by utilization of polymeric plasticizers is under current investigation and will be the object of a future contribution.

Modification of mechanical properties by plasticization

Because a low molecular weight plasticizer behaves like a solvent when mixed with a polymer, it leads to the decrease in the macromolecular chains cohesion—well correlated on plasticizer percentage, and to reduction in tensile strength properties (lower stiffness and increased impact strength). Actually the main goal of plasticizer addition into PLA matrix is to decrease its rigidity while polymer strength properties are maintained at the optimum level.

Neat PLA below its T_g, e.g. at room temperature, is typically characterized by low elongation and impact values, together with high tensile and flexural moduli. Since the most important modifications of tensile properties by plasticization have been observed at relatively high percentage of plasticizer (10–20%), these effects are more discussed here as result of their key importance for practical applications.

As summarized in Table 4, addition of plasticizers leads to an expected decrease in tensile strength and Young's modulus, while the strain at break is characterized by an important increase with respect to the neat polyester. The studied neat PLA has a maximum tensile strength of 66 MPa, while the plasticized compositions are characterized by an important reduction of tensile strength performances, and generally, this decrease is well correlated with the percentage of plasticizer. Interestingly enough, the maximum tensile strength values of PLA compositions containing 10 and 20% DOA (29 and 21 MPa, respectively) are lower than values recorded for PLA-GTA (38 and 24 MPa, respectively) and
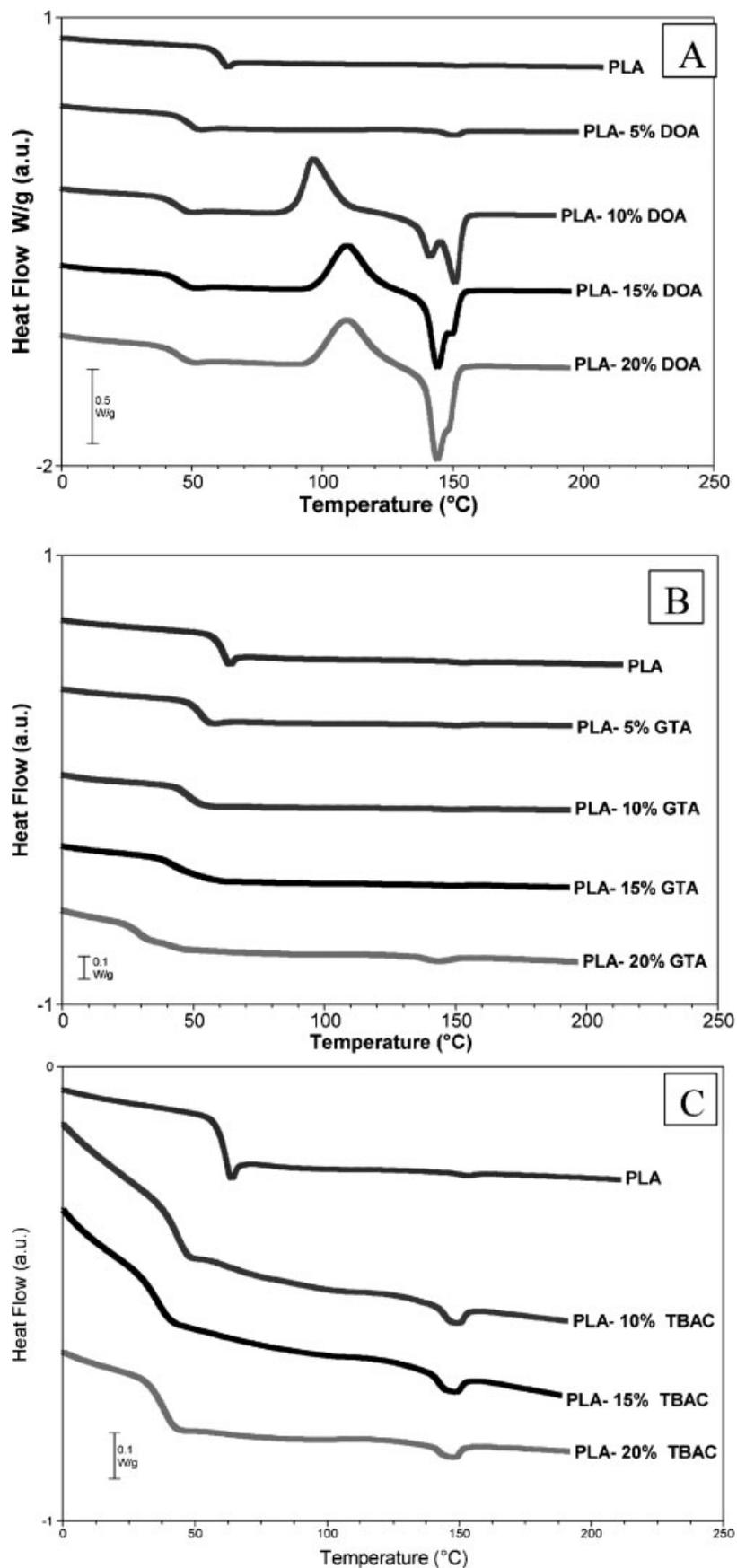
Figure 4. DSC measurements of neat PLA compared to plasticized PLA compositions: (A) PLA-DOA; (B): PLA-GTA; and (C) PLA-TBAC (second heating with ramp of 10°C/min). This figure is available in color online at www. interscience.wiley.com/journal/pat
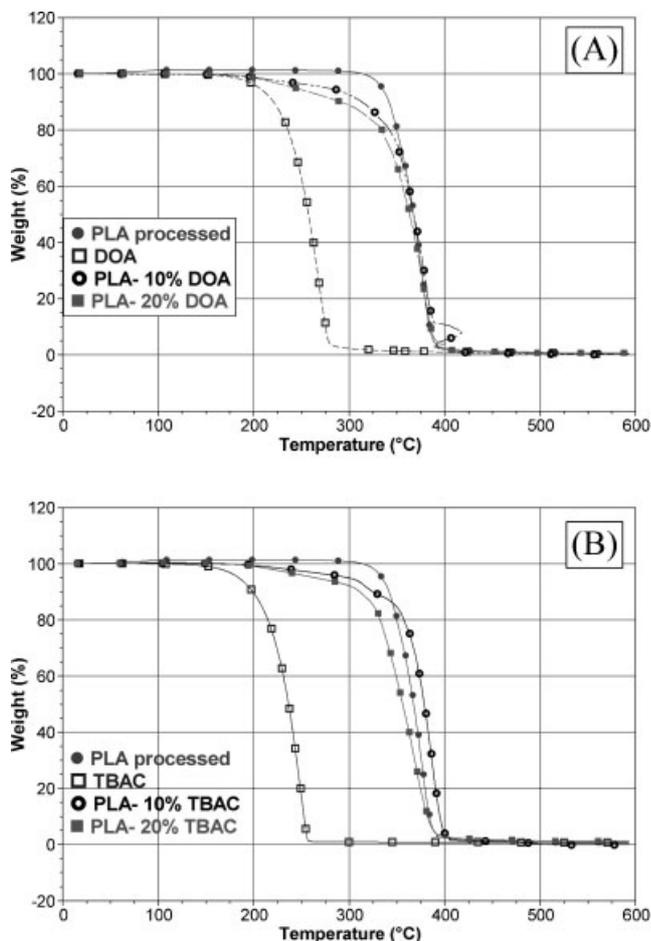
Figure 5. TGA traces of neat PLA compared to plasticizer and plasticized PLA compositions: (A) DOA and PLA-DOA compositions (B) TBAC and PLA-TBAC compositions (under air flow, ramp 20°C/min). This figure is available in color online at www.interscience.wiley.com/journal/pat

PLA-TBAC (51 and 30 MPa, respectively) compositions at the same percentage in plasticizer. In this context, PLA-TBAC and PLA-GTA compositions can be considered as more attractive for applications where good tensile strength properties are required. On the other hand, the stress–strain diagrams (not shown here) shows that the great majority of specimens are characterized by brittle behavior at lower

plasticizer percentages, i.e. up to 10%, and ductility for higher plasticizer percentages (15–20%).

It should be noted that the PLA compositions with 15% TBAC or GTA are characterized by remarkable values of both tensile strengths at yield and at break, and due to these properties they are interesting for applications where good tensile properties are looked for. By further increasing the percentage of TBAC or GTA up to 20%, the cohesion between the polyester chains is much decreased and a drop off of the tensile strength values is finally recorded.

On the other hand, in contrast to the progressive decrease in the tensile strength, the nominal strain at break is largely increased by the plasticizer, in direct relation to its nature and relative content. The compositions with 15–20% TBAC or GTA are clearly characterized by higher elongation at break and homogeneity (lower SD values) with respect to the compositions with similar percentage of DOA, therefore, they are potentially interesting for applications requiring high ductility. It is also important to point out that the highest elongation for an amount of 20% plasticizer was obtained for GTA as determined via tensile testing.

The decrease in rigidity for the plasticized compositions is well evidenced by lower Young's modulus values. Interestingly, the PLA-(10–20%) DOA blends are characterized by a similar Young's modulus more likely confirming the initial assumption that PLA can incorporate only a given amount of DOA as plasticizer. On the other hand, the decrease in Young's modulus depends on the nature and percentage of plasticizer and, in agreement with the evolution of the elongation at break, the same order of efficiency is recorded: GTA > TBAC > DOA.

Figure 6 shows pictures of neat PLA and PLA-(20%) DOA, TBAC, and GTA specimens as recovered after tensile testing, which confirm the differences between the starting brittle PLA and the plasticized compositions characterized by much higher elongation at break. One can also point out that the PLA-20% DOA specimens are characterized by stress whitening and opacity well evidenced in the region of deformation. This behavior was explained by Jacobsen et al.[9] by formation of voids in similar way like in filled composites where debonding occurs at the interface. By comparison, the occurrence of such debonding between the polyester matrix and the phase-separated DOA inclusions can also be assumed. Another explanation can arise from the modification of crystallization due to the energy of mechanical

Table 4. Mechanical properties of PLA and plasticized PLA compositions (standard deviations are given in brackets)

Compositions (%, by weight)	Tensile strength at yield (MPa)	Tensile strength at break (MPa)	Young's modulus (MPa)	Nominal strain at break, (%)[a]
PLA	66 (2)	65 (3)	1020 (100)	11 (3)
PLA-10% DOA	29 (2)	21 (2)	720 (90)	36 (5)
PLA-15% DOA	22 (1)	17 (1)	710 (50)	77 (44)
PLA-20% DOA	21 (1)	16 (2)	670 (120)	78 (33)
PLA-10% TBAC	51 (1)	44 (2)	970 (70)	11 (4)
PLA-15% TBAC	37 (1)	35 (1)	590 (50)	221 (8)
PLA-20% TBAC	9 (1)	30 (1)	270 (20)	317 (4)
PLA-10% GTA	38 (3)	35 (3)	760 (140)	8 (2)
PLA-15% GTA	31 (5)	29 (2)	590 (110)	223 (19)
PLA-20% GTA	—	24 (1)	10 (3)	443 (13)

[a]Gauge length of 25.4 mm.
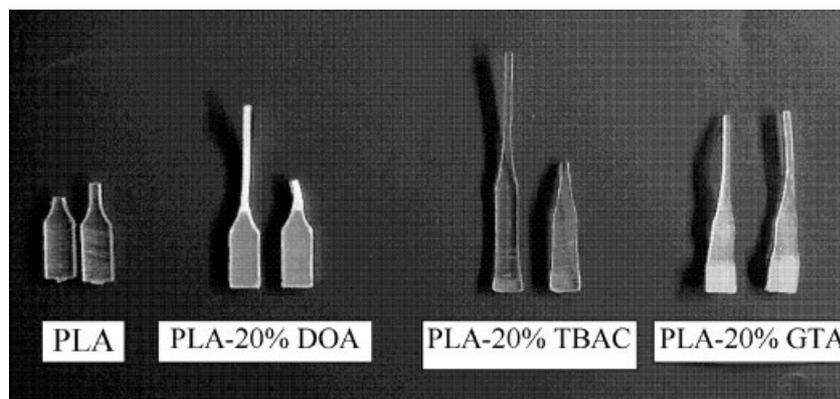
Figure 6. Pictures of PLA and plasticized PLA specimens to illustrate their aspect after tensile testing.

drawing,[23] assumption that can be in agreement with the result of DSC characterization, i.e. the existence of cold crystallization for these samples.

Regarding the impact properties, it might be interesting to use PLA compositions in applications where medium to high impact values are looked for and as consequence it is important to have information about their behavior at the higher deformation rates applied during impact solicitation. Because some differences exist between tensile and impact procedures, in particular concerning the deformation rates, it has been found in some cases that materials with high elongation at break can be characterized by relatively weak impact values. On the other hand, it is important to note that for plasticized compositions with low content in plasticizer (e.g. less than 10%) a decrease in impact strength has sometimes been reported, explained by a disturbance created by the plasticizer molecules into PLA matrix.[9] In this study, such an ''antiplasticizing'' effect has been observed especially for the addition of small quantities of DOA, i.e. 5% (Fig. 7), while the increase in plasticizer fraction up to 20% leads to a surprisingly 11-fold increase of impact strength (Izod) with respect to neat PLA, while the fracture is characterized by a ''hinge break''.

It was already concluded that addition of up to 20% GTA into PLA leads to stronger plasticizing effects within the polyester matrix (decrease of Young's modulus, high elongation at break, etc.). These improvements are also correlated with very attractive impact performances (Table 5), where 20% of GTA results in a sample that do not initiate any break. Interestingly enough, in relation to the impact performances, for a plasticizer content up to 20%, the order of efficiency is GTA > DOA > TBAC.

Pictures of PLA and highly plasticized PLA samples (Fig. 8) summarize the main conclusions after the impact

Table 5. Notched impact strength-Izod measurements of PLA and plasticized PLA compositions as function of the plasticizer percentage (standard deviations are given in brackets)

Plasticizer	Percentage by weight				
	0[a]	5	10	15	20
TBAC	2.6 (0.2)	2.5 (0.2)	2.4 (0.4)	2.6 (0.4)	4.6 (1.3)
GTA	2.6 (0.2)	3.4 (1.1)	2.7 (0.3)	Partial break	No break

[a]Neat PLA.
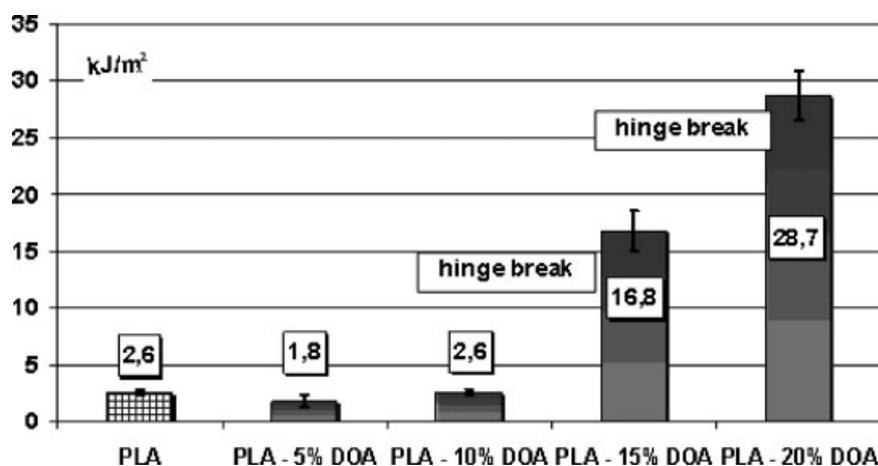
Figure 7. Notched impact strength-Izod measurements of neat PLA and PLA-DOA compositions. This figure is available in color online at www.interscience.wiley.com/journal/pat
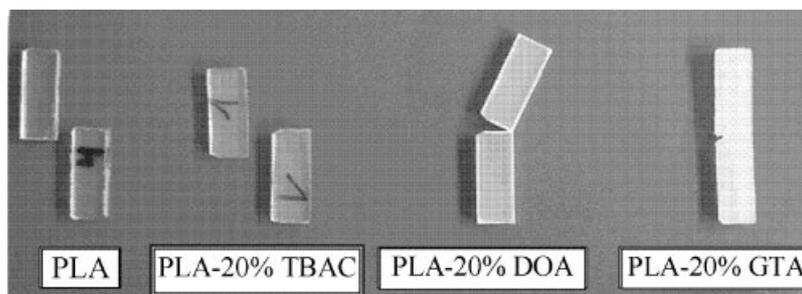
Figure 8. Pictures of PLA and plasticized PLA specimens performed to illustrate their behavior during impact testing.

testing: brittle behavior and break for both PLA and PLA-20% TBAC specimens, compared to ''hinge break'' observed for PLA-20% DOA and non-break of PLA-20% GTA specimens. By considering the impact strength performances, the PLA-20% DOA and GTA compositions appear more appropriate for applications where medium to high impact properties are required.

Finally, it is believed that optimized compositions can be obtained targeted to the desired end-use product characteristics by a perfect correlation between the chemical nature of the plasticizer, its relative content and the type of PLA used as polymer matrix.

CONCLUSIONS

To reduce the PLA brittle behavior and to improve its ductility, three selected plasticizers (DOA, TBAC, and GTA) have been mixed with a specific PLA grade for extrusion (high molecular weight, L/D isomer ratio of 96:4). The effect of plasticizer addition on the PLA molecular, thermal and mechanical properties has been evaluated. Accordingly, melt-blending of PLA with TBAC, GTA, or DOA does not lead to important drop of molecular weights whereas a regular decrease in thermal stability correlated with the plasticizer amount/volatility has been evidenced. DSC analysis has been used to evaluate the plasticizer efficiency by studying the decrease in T_g of PLA matrix (initial value: 62°C). The lowest T_g (29°C) was noticed for the addition of 20% of the plasticizer having the lowest molecular mass (GTA) and the best interaction parameter, whereas as resulting from SEM analyses, PLA plasticized with 20% of DOA displayed phase separation and relatively limited decrease in T_g.

Addition of up to 20% plasticizer into PLA leads to a progressive decrease of Young's modulus and to increased ductility in the following order of efficiency: GTA > TBAC > DOA. The best impact performances were obtained by addition of up to 20% GTA into PLA matrix, where specimens could not be broken. Surprisingly, addition of TBAC even up to 20%, does not lead to good enough impact strength. The results of the study allow formulating PLA grades with desired end-use properties as follows:

- flexibility and improved crystallization rates: PLA-DOA compositions;
- high elongation at break and tensile strength properties: PLA-GTA and TBAC compositions;

- medium to high impact properties: PLA-DOA and PLA-GTA compositions.

A detailed investigation to outline the comparative properties of PLA plasticized with low molecular weight and polymeric plasticizers is under current investigation and will be the object of a future contribution.

LIST OF ABBREVIATIONS

PLA	polylactide and poly(L,L-lactide)
GTA	glyceryl triacetate
DOA	bis(2-ethylhexyl) adipate
TBAC	tributyl O-acetylcitrate
T_g	glass transition temperature
T_c	crystallization temperature
ΔH_c	enthalpy of cold crystallization
T_m	melting temperature
ΔH_m	melting enthalpy

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