

The Potential of an Itaconic Acid Diester as Environmentally Friendly Plasticizer for Injection-Molded Polylactide Parts

Juan Ivorra-Martinez,* Miguel Angel Peydro, Jaume Gomez-Caturla, Teodomiro Boronat, and Rafa Balart

This work reports on the use of dibutyl itaconate (DBI) as an environmentally friendly plasticizer for polylactide (PLA) with different proportions of DBI in the 2.5–20 wt% (weight content) range. A co-rotating twin-screw extrusion process followed by injection molding is employed for the manufacturing of the samples. The results show that the plasticized PLA formulation with 10 wt% DBI offers the most balanced overall properties, with a noticeable increase in the elongation at break from 4.6% (neat PLA) up to 322%, with a tensile modulus of 1572 MPa, and a tensile strength of 23.8 MPa. In the case of 15 and 20 wt% DBI formulations, PLA reaches the saturation point with no more increase in the elongation at break and a clear decrease in the tensile modulus. DBI also decreases the glass transition temperature (T_g) from 61.3 °C (neat PLA) down to 23.4 °C for plasticized PLA formulation containing 20 wt% DBI, thus showing the high plasticization efficiency of DBI.

(PHAs), being poly(3-hydroxybutyrate) (PHB) a very promising biobased and biodegradable polymer.^[3] Despite these developments, poly(lactide) (PLA) is, by far, one of the most promising polyesters.^[4] PLA is obtained from renewable resources from starch-rich compounds and offers biodegradation. In addition, it shows a reasonable price compared to PHAs and other biobased polyesters. For these reasons, PLA is currently being used in the food packaging industry.^[5] Moreover, PLA is a widely used standard material in 3D printing and in the manufacturing of medical devices, since it is a biocompatible and resorbable polymer.^[6–9] PLA is synthesized through biomass hydrolysis followed by fermentation, which produces lactic acid that is then converted into lactide, and subsequently,


into poly(lactide) by ring-opening polymerization (ROP).^[10] Although its use provides the aforementioned advantages, there are some drawbacks mainly related to a high stiffness and a brittle behavior attributed to a T_g (glass transition temperature) above room temperature (close to 60 °C).^[6–8]

To minimize this brittleness, several approaches have been explored. One technical solution is the use of plasticizers.^[11,12] Another approach is blending PLA with other ductile polymers with or without compatibilizers.^[13–15] Several researches have been carried out to obtain PLA with improved toughness by blending it with different biodegradable polymers such as poly(ϵ -caprolactone) (PCL), poly(butylene succinate) (PBS), poly(butylene adipate-co-terephthalate) (PBAT) or thermoplastic starch (TPS).^[16–19] The main drawback when using blends is a remarked poor miscibility between PLA and the other polymer in the blend. This phenomenon leads to phase separation, which in turn, has a negative effect on the final mechanical properties. To overcome this situation, compatibilizers are often used to improve the load transfer between the polymer phase involved.^[20–22] Ding et al. reported manufacturing of PLA blends with PBAT (70/30 respectively), with an interesting increase in the elongation at break from 6% (neat PLA) up to 30% for the uncompatibilized blend. The use of monomethoxy poly(ethylene glycol)-poly(lactide) di-block copolymers (MPEG-PLA) improved compatibility/miscibility between PLA and PBAT so the elongation increased up to 296%.^[23] The use of plasticizers is reported as the simplest and most economical method to improve the ductility of PLA. In addition, plasticizers also contribute to better processability.^[7,24] There are many plasticizer families with

1. Introduction

Plastics Europe's annual report showed a 50.7 million tons plastic total demand in 2019, from which 50% corresponded to several grades of polyethylene (PE) and polypropylene (PP). Among the most common uses for these polymers, the most popular one is the manufacture of packaging with a total share of 39.6%.^[1] As a result, a large amount of polymer wastes is generated, leading to severe environmental issues that have led to an increased interest in the development of polymers from renewable sources and potential biodegradation (or disintegration in controlled compost soil).^[2] In the last decade, important advances have been carried out on the development of polyesters obtained from bacterial fermentation or poly(hydroxyalkanoates)

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interesting plasticization properties. These plasticizers offer a wide range of molecular weights, nonetheless, the use of plasticizers with lower molecular weight results in a better plasticizing effect.^[5,10] When plasticizers are added to PLA, the mobility of the polymer chains increases due to the reduction of the interactions between them.^[25] The main problem that arises when plasticizers are used, is the possibility of plasticizer migration, being especially critical in those situations in which the plasticized polymer is in contact with food. This property highly depends on the compatibility of the plasticizer with the polymeric matrix. The use of high molecular weight plasticizers substantially reduces this migration phenomenon.^[7,26] As a result of the modifications involved when a plasticizer is introduced into a polymer matrix, the most relevant one is the improvement of the ductile behavior as the elongation at break and the impact strength. Moreover, some physical properties like the tensile strength, tensile modulus, hardness and storage modulus are reduced due to the lower interaction between the polymer chains.^[7,27] At the same time, the introduction of a plasticizer also promotes modifications on the thermal properties. Arrieta et al. reported that plasticization of PLA films with 15 wt% limonene allowed to reduce the T_g of neat PLA by 30 °C; accordingly to this decrease in T_g , plasticized PLA with limonene (15 wt%) resulted in a highly ductile polymer with an elongation at break of 150% which was remarkably higher than that of neat PLA film (1.5%).^[28] T_g of PLA is close to 60 °C, which provides a rigid and fragile behavior at room temperature, attributed to a low chain mobility state. The introduction of a plasticizer promotes a reduction in T_g close to room temperature, so that an enhancement of the polymer chain mobility is achieved, allowing to improve the ductile properties of the mixture.

Nowadays, the most commonly used plasticizers in the polymer sector are petrochemically-derived. Among the different families, phthalates have been, with difference, the most used plasticizers in polymers, such as poly(vinyl chloride) (PVC). Phthalates have also given good plasticization properties to PLA.^[29] Nevertheless, the increasing concern about environment has acted as the leading force for the development of environmentally friendly plasticizers. In fact, phthalates have been increasingly substituted by other families such as sebacates, adipates, epoxidized vegetable oils (EVOs), citrates, among others, which are obtained from renewable resources.^[27,30,31] Isosorbide diesters also offer interesting plasticization properties compared to traditional phthalates as Yang et al. have reported. They obtained very promising plasticization properties on PLA by using isosorbide dioctanoate (SDO) (20 wt%), compared to conventional dioctyl terephthalate (DOTP). The best outcome in this case was obtained with SDO plasticizer with an elongation at break of 281% while the phthalate-based plasticizer only provided an elongation at break of 104%.^[32]

As a result of an increasing environmental concern, plasticizers from natural resources are gaining special attention in PLA industry. In particular, the use of renewable raw materials and their biodegradability are of great interest.^[33] Some of these environmentally friendly plasticizers with interesting plasticization properties on PLA, are epoxidized soybean oil (ESO), epoxidized palm oil (EPO), lactic acid oligomer (OLA), citrate oligoesters, malonate oligomers, triacetate, citrate esters, glycerol, adipates and poly(adipates), among others.^[26,33] Itaconic acid (IA) is a biological molecule obtained by fermentation of citric acid.^[34] Ita-

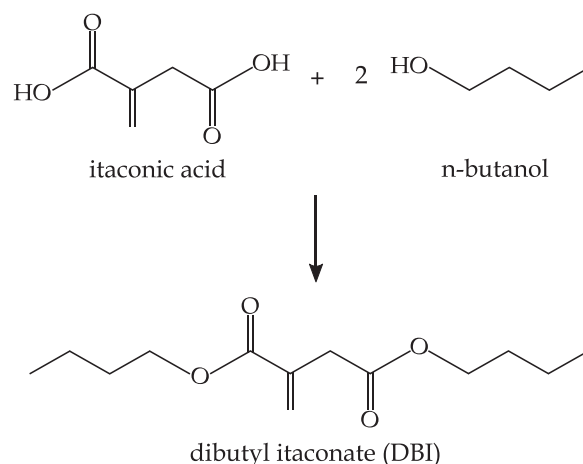


Figure 1. Scheme of the reaction of itaconic acid (IA) and *n*-butanol to give dibutyl itaconate (DBI).

conic acid could be used as a biobased building block for the polymer industry. Ma et al. reported interesting plasticization properties provided by itaconic acid-4-propylguaiaicol ester (IPE) to poly(vinyl chloride) films.^[35] Wu et al. reported the synthesis of methyl succinic acid (MSA) by direct hydrogenation of itaconic acid. Then, they copolymerized MSA with 1,4-butanediol to give a polymeric plasticizer, namely poly(butylene 2-methylsuccinate) (PBMS).^[36] The esterification of itaconic acid with *n*-butanol produces dibutyl itaconate (DBI) (**Figure 1**), which proves to have great applicability as a plasticizer, lubricant, adhesive, crosslinker, and so on. Its dual functionality (ester and carbon-carbon double bond) offers a wide range of possibilities in the polymer industry as a biobased building block for polymers, copolymers, chemical modification of polymers macromolecules and hydrogels.^[37–39]

The novelty of this work relies on the evaluation, for the first time, of the potential of a diester of itaconic acid, namely DBI, as a plasticizer in PLA formulations with improved toughness and ductile properties. Plasticized PLA formulations with different DBI proportions in the 2.5–20 wt% range were obtained by a co-rotating twin screw extrusion process followed by injection molding to manufacture standard test samples. The processing conditions for the injection molding stage were set according to a prior capillary rheology study which allowed to define optimum processing temperatures. In order to measure the final properties of the obtained materials, mechanical, thermal, thermo-mechanical, fracture morphology and X-ray diffraction tests were carried out.

2. Experimental Section

2.1. Materials and Solubility

PLA grade PURAPOL L130 from Total Corbion PLA (Gorinchem, The Netherlands) with a minimum L-isomer content of 99% and a melt flow index of 16 g/10 min (ISO 1133-A 210 °C/2.16 kg) was used in this study. Dibutyl itaconate was supplied by Sigma-Aldrich S.A. (Madrid, Spain), main properties are summarized in **Table 1**.

Table 1. Some thermal and physicochemical properties of dibutyl itaconate (DBI).

CAS number	2155-60-4
Molecular weight	242.31 g mol ⁻¹
Ester content	96%
Appearance	Transparent colorless liquid at 25 °C
Refraction index	n ₂₀ /D 1.444
Boiling point	284 °C
Density	0.985 g mL ⁻¹ at 25 °C
Viscosity	5.6 mPa s
Acid index (itaconic acid)	Max 0.1%
Water solubility	Very low
Surface tension	0.035 N m ⁻¹ at 25 °C

2.2. Theoretical Approach to Solubility

The solubility parameter (δ) is crucial to achieve a correct dispersion of the additive in the polymeric matrix. The solubility parameters of both DBI and PLA were calculated following the Hoftyzer–Van Krevelen group contribution method. The solubility parameter (δ) contained different contributions: dispersive forces (δ_d), polar forces (δ_p), and hydrogen bonding (δ_h) as seen in Equation (1). Each of these parameters was obtained from the contribution of each of the molecular groups of the molecule given by D.W. van Krevelen et al. and K. te Nijenhuis et al.^[40] Additionally, the molar volume (V_m) was obtained from the ratio between the molar mass (M_m) and the density (ρ).

$$\delta = \sqrt{\delta_d^2 + \delta_p^2 + \delta_h^2} (\text{MJ m}^{-3})^{0.5} \quad (1)$$

Where:

$$\delta_d = \frac{\sum F_{di}}{V_m} (\text{MJ m}^{-3})^{0.5} \quad (2)$$

$$\delta_p = \frac{\sqrt{\sum F_{pi}^2}}{V_m} (\text{MJ m}^{-3})^{0.5} \quad (3)$$

$$\delta_h = \frac{\sqrt{\sum E_{hi}}}{V_m} (\text{MJ m}^{-3})^{0.5} \quad (4)$$

The group contribution method proposed by Hoftyzer and Van Krevelen provided the characteristic molar attraction constants for each chemical group for both the dispersive (F_{di}) and the polar (F_{pi}) contributions, allowing a rather accurate estimation of δ_d and δ_p , respectively, as indicated in Equations (2) and (3). Nevertheless, the F -method cannot be applied to the calculation of δ_h . As indicated by Hansen, the hydrogen bonding energy E_{hi} per structural group was almost constant and it was useful to estimate δ_h as shown in Equation (4). The three solubility coordinates can be plotted in a 3D-space with axes δ_d , δ_p , and δ_h , each one with the corresponding units of a solubility parameter, that is, $(\text{MJ m}^{-3})^{0.5}$. The more similar the solubility parameter coordinates of the plasticizer ($\delta_{d \text{ DBI}}$, $\delta_{p \text{ DBI}}$, and $\delta_{h \text{ DBI}}$) to those of PLA ($\delta_{d \text{ PLA}}$, $\delta_{p \text{ PLA}}$, and $\delta_{h \text{ PLA}}$), the better solubility/miscibility will be

Table 2. Summary of the plasticized poly(lactide) (PLA) formulations with dibutyl itaconate (DBI) according to the weight content (wt%).

Code	PLA [wt%]	DBI [wt%]
PLA	100	0.0
2.5DBI/PLA	97.5	2.5
5DBI/PLA	95.0	5.0
10DBI/PLA	90.0	10.0
15DBI/PLA	85.0	15.0
20DBI/PLA	80.0	20.0

obtained. The geometrical 3D distance between the solubility parameters was a simple way to quantify how close is DBI to PLA in terms of their solubility parameter coordinates. As a 3D-space was considered, the solubility threshold (maximum distance to allow miscibility) of a particular polymer was defined as the maximum distance from the center, which was represented as a spherical region in this 3D-space, with the center located in the corresponding solubility parameter coordinates of the polymer. If the solubility parameter coordinates of a particular plasticizer fell inside this spherical region, the plasticizer was miscible with the polymer. Otherwise, miscibility will be restricted. This threshold distance was characteristic of each polymer and was referred to as the radius of the solubility sphere, R_0 , with units $(\text{MJ m}^{-3})^{0.5}$. The region in which a plasticizer is miscible, was obtained by means of a thermodynamical difference that allowed to give miscible mixtures and took a value of $R_0 = 10.7 (\text{MJ m}^{-3})^{0.5}$ for PLA.^[11,41] Thus, plasticizers inside PLA sphere will be miscible, while those outside will not. To quantify the distance between the base polymer (PLA) and the plasticizer (DBI), a parameter R_a was defined as the geometrical distance between both solubility parameters as proposed by the Hansen solubility parameters (HSP) theory (Equation (5)). The constant 4 in this equation allowed obtaining spherical solubility regions instead of spheroidal regions.

$$R_a = \sqrt{4(\delta_{d \text{ DBI}} - \delta_{d \text{ PLA}})^2 + (\delta_{p \text{ DBI}} - \delta_{p \text{ PLA}})^2 + (\delta_{h \text{ DBI}} - \delta_{h \text{ PLA}})^2} \quad (5)$$

The ratio between R_a and R_0 allows determining the relative energy difference (RED) according to Equation (6). When values close to zero are obtained, a miscible mixture is achieved. Values higher than 1 stand for the plasticizer is outside the sphere defined by the PLA and the resulting blend is immiscible.^[11,42]

$$\text{RED} = \frac{R_a}{R_0} \quad (6)$$

2.3. Processing of Plasticized PLA Formulations with DBI

PLA was dried at 60 °C for 48 h in a dehumidifying dryer MDEO from Industrial Marsé, (Barcelona, Spain) to remove any residual moisture avoiding the hydrolysis. The necessary amount of each component was weighted and then premixed in a zipper bag according to the compositions proposed in Table 2. The premixed materials were then fed into the main hopper of a co-rotating

Table 3. Summary of the optimized temperature profiles for the injection molding process of PLA and plasticized poly(lactide) (PLA) formulations with dibutyl itaconate (DBI).

Code	Zone 1 [°C] (hopper)	Zone 2 [°C]	Zone 3 [°C]	Zone 4 [°C] (injection nozzle)
PLA	210	205	200	195
2.5DBI/PLA	205	200	195	190
5DBI/PLA	200	195	190	185
10DBI/PLA	195	190	185	180
15DBI/PLA	185	180	175	170
20DBI/PLA	175	170	165	160

twin-screw extruder from Construcciones Mecánicas Dupra, S.L. (Alicante, Spain). This extruder had a screw diameter of 25 mm with a length-to-diameter ratio (L/D) of 24. The extrusion process was carried out with a residence time of 1 min in all cases. The temperature profile, from the hopper to the die was set as follows: 185–180–175–170 °C. The different compositions were extruded and subsequently pelletized using an air-knife unit.

After the extrusion process, the pellets were stored in the dehumidifying dryer to avoid moisture absorption. Standard samples were obtained with the 270/70 injection molding machine from Mateu&Solé (Barcelona, Spain) with 3 min as an average residence time. The introduction of the plasticizer induced a significant viscosity change of the base PLA polymer. To enhance processing of specimens of plasticized PLA formulations some adjustments in the temperature profile had to be done, since the viscosity was dramatically reduced by increasing DBI content. These temperature profiles were obtained from a capillary rheology study that allowed optimizing temperatures to provide similar viscosity, which is a key factor in processing plasticized polymer formulations. Therefore, the lubrication effects provided by DBI allowed to decrease the temperature profile thus preventing DBI loss. Similar changes in processing temperatures have been proposed by Lascano et al.,^[43] in plasticized PLA formulations with oligomers of lactic acid (OLA), since the decrease in viscosity produced by the plasticizers made processing impossible by injection molding without adjusting the temperature profile to obtain similar viscosities in all compositions. The temperature profiles considered for the processing of the injection molded samples are summarized in Table 3.

2.4. Material Characterization

2.4.1. Mechanical Properties

Tensile tests were carried out in a universal testing machine ELIB 50 from S.A.E. Ibertest (Madrid, Spain) on injection-molded specimens (ISO 527-2:2012 type 1B shape). A 5-kN load cell was used, and the cross-head speed was set to 20 mm min⁻¹. Shore hardness was measured in a 676-D durometer from J. Bot Instruments (Barcelona, Spain), using the D-scale, on injection-molded samples with 4 mm thickness, (ISO 868:2003). Impact behavior was also studied on injection-molded rectangular samples (ISO 179:2010 type 1 shape) by the Charpy impact test with a 6-J pendulum from Metrotec S.A. (San Sebastián, Spain). Samples were

notched with a 0.25 mm radius “V”-notch type. All tests were performed at room temperature, and at least five specimens of each formulation were tested to obtain the corresponding parameters. The obtained results were averaged and the standard deviation was calculated.

2.4.2. Morphology

Fractured tensile test samples were subjected to a sputtering process with gold–palladium alloy in a SC7620 sputter coater from Quorum Technologies Ltd. (East Sussex, UK). Samples were placed in the vacuum chamber of a ZEISS ULTRA 55 field emission scanning electron microscope (FESEM) from Oxford Instruments (Abingdon, UK). The working distance was set to 4 mm and the acceleration voltage was 2 kV.

2.4.3. Thermal Properties

Differential scanning calorimetry (DSC) was used to assess the main properties of the plasticized PLA formulations with DBI. In particular, the melting temperature (T_m), the cold crystallization temperature (T_{cc}), melting enthalpy (ΔH_m), cold crystallization enthalpy (ΔH_{cc}), and the degree of crystallinity χ_c (%) were obtained from DSC runs. The degree of crystallinity was obtained with the Equation (7) where w represents the weight fraction of PLA and ΔH_m^0 is the melt enthalpy of a theoretically fully crystalline PLA, which was considered as 93 J g⁻¹ as reported in literature.^[44]

$$\chi_c (\%) = \frac{\delta H_m - \delta H_{cc}}{\delta H_m^0} \cdot 100 \quad (7)$$

DSC runs were collected in a modulated heat flow DSC model Q2000 from TA Instruments (New Castle, DE, USA) with nitrogen atmosphere (66 mL min⁻¹) and a sample weight between 5 and 7.5 mg. The dynamic DSC runs were performed into three stages. First a heating cycle was performed to erase the thermal history from 30 to 200 °C at 10 °C min⁻¹. Then, a controlled cooling step was carried out down to -40 °C with a cooling rate of -10 °C min⁻¹. Finally, a second heating cycle was performed up to 240 °C at 10 °C min⁻¹. The main parameters of thermal degradation, namely the onset degradation temperature ($T_{5\%}$, obtained at a mass loss of 5%), the maximum degradation rate temperature (T_{deg}), and the residual weight (%), were obtained in a thermogravimetric TG-DSC2 thermobalance from Mettler-Toledo (Columbus, OH, USA). Samples with an average weight of 6 mg were placed into alumina crucibles and subjected to a single dynamic heating program from 30 to 700 °C at a heating rate of 10 °C min⁻¹ in air atmosphere. Additionally, a quantification of the DBI mass loss related to processing conditions, was obtained in isothermal thermogravimetric analysis (TGA) conditions at the maximum working temperatures in each temperature profile (see Table 2, zone 1). The heating rate to reach the desired isothermal temperature was 100 °C min⁻¹; once the target temperature was reached, the mass loss as a function of time was recorded for a total time of 40 min. All thermal tests were carried out in triplicate.

Table 4. Summary of the poly(lactide) (PLA) and dibutyl itaconate (DBI) solubility parameters according to the Hoftyzer–Van Krevelen group contribution method and the relative energy difference (RED).

	δ_d [MJ m ⁻³] ^{0.5}	δ_p [MJ m ⁻³] ^{0.5}	δ_h [MJ m ⁻³] ^{0.5}	δ [MJ m ⁻³] ^{0.5}	R_a	RED
PLA	15.3	8.4	11.0	20.7	-	-
DBI	15.1	2.8	7.6	17.1	6.6	0.62

2.4.4. Thermomechanical Properties

Dynamic mechanical thermal analysis (DMTA) was carried out in a Mettler–Toledo DMA1 (Columbus, OH, USA) in single cantilever mode. Samples with dimensions 20 × 6 × 3 mm³ were used for DMTA characterization. The maximum dynamic deflection was set to 10 μm and the frequency for the sinusoidal deformation was set to 1 Hz. Regarding the heating cycle, tests started at −100 °C and samples were heated up to 100 °C with a heating rate of 2 °C min⁻¹. To evaluate the dimensional stability, a thermomechanical analyzer (TMA) Q400 from TA Instruments (New Castle, DE, USA) was used. Rectangular samples sized 10 × 10 × 4 mm³ were subjected to a heating cycle from −20 to 100 °C at a heating rate of 2 °C min⁻¹ and a constant load of 20 mN. The coefficient of linear thermal expansion (CLTE) of the plasticized PLA formulations was determined as the slope in the plot of the expansion versus temperature. All tests were carried out in triplicate.

2.4.5. Rheological Properties

The rheological properties of PLA and plasticized PLA formulations were obtained using a capillary rheometer Thermo-Haake from Rheofixer (Baden-Wurtemberg, Germany). This was equipped with a capillary of 1 mm diameter and a length-to-diameter (L/D) = 10. The tests were performed according to ISO-11443. All materials were dried at 60 °C for 48 h in a dehumidifying dryer MDEO from Industrial Marsé, (Barcelona, Spain) to replicate the same residual moisture used in the processing by extrusion/injection molding. All tests were carried out five times to obtain reliable results.

3. Results and Discussion

3.1. Theoretical Approach to Solubility between PLA and DBI

Table 4 shows the results obtained for each of the solubility components and the total solubility parameter. In all cases, similar values are shown for both components, which leads to the assumption that there may be solubility between both materials. Additionally, the relative energy difference (RED) was found to be 0.62, which indicates that there may be solubility between PLA and DBI. For a plasticized PLA with derivatives of levulinic acid and valeric acid it was possible to observe a positive effect on the final properties showing that a plasticization process had taken place. For these plasticizers, the RED values obtained were comprised between 0.5 and 0.7,^[45] thus being in a similar range to that obtained in this work.

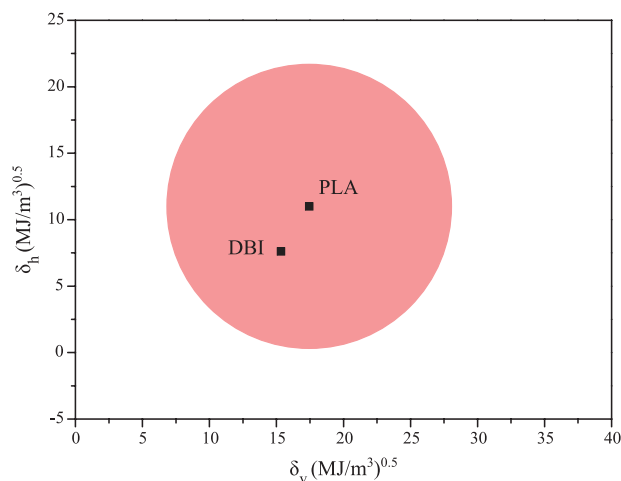


Figure 2. Bagley's solubility diagram for poly(lactide) (PLA) and dibutyl itaconate (DBI) where the $\delta_v = (\delta_d^2 + \delta_p^2)^{0.5}$.

As observed in **Figure 2**, the Bagley's diagram also suggests that DBI has solubility with PLA. The red sphere indicates the solubility region of PLA, and the δ coordinates of DBI fall into this region, thus indicating DBI is a good plasticizer for PLA, proved to its solubility with PLA. This theoretical approach has also been conducted with other linear polyesters such as poly(3-hydroxybutyrate) (P3HB) to assess its solubility with different organic solvents.^[46] Ramos et al. confirmed that the theoretical results were in agreement with the experimental results, thus suggesting the usefulness of the theoretical approach to select the appropriate solvent.

3.2. Effect of DBI on the Rheological Properties of Plasticized PLA Formulations

In spite of the fact that some polymers show a shear-thickening (dilatant) behavior, such as cornstarch in water, almost all polymer melts show a shear-thinning behavior, which is the typical non-Newtonian or pseudoplastic behavior, characterized by a decrease in viscosity with rising the shear rate. Osswald et al. studied the rheology of different grades of poly(ethylene) (PE) and poly(propylene) (PP), and characterized their pseudoplastic behavior.^[47] Depending on the processing technique, the applied shear rate is different. For example, the shear rate used in an injection-molding process is usually comprised between 100 and 10 000 s⁻¹, while lower shear rates of 10–1000 s⁻¹ are typically employed in extrusion processes.^[48] Plasticizers usually provide a decrease in viscosity due to their lubricant effect on polymer chains. Therefore, it is useful to study the effects of DBI on the rheology of plasticized PLA formulations, as it allows to define the proper temperature profiles for optimizing the injection molding process. Once a polymer reaches a low viscosity state due to high temperatures or plasticizer addition, a leakage from the cavity of the mold occurs and as a result, burrs appear. To minimize this effect, the working temperatures were reduced, considering that the polymer flow must be enough to completely fill the mold.

In a first attempt to analyze the rheological behavior of PLA with DBI, a temperature of 210 °C and a shear rate range between 100–10 000 s⁻¹ were selected, being this a usual working temperature for a PLA, and a usual shear rate for an injection molding process. The results obtained by capillary rheometry are shown in **Figure 3**. As seen in Figure 3a, not all materials could be tested under these conditions because the resulting viscosity at 210 °C was critically reduced and the equipment was not able to record the pressure generated to obtain the corresponding viscosity values. As Yoo et al. proposed, PLA viscosity can be modified with the working temperatures,^[49] so the behavior of the formulations proposed can be controlled during the manufacturing by the programed temperatures. Figure 3a shows plasticized PLA formulations with DBI at a constant temperature of 210 °C. Due to a reduction in the interaction of the polymer chains as a result of the plasticizer introduction, a remarkably lower viscosity was measured.^[50] Sun et al. have reported similar decrease in viscosity of chitosan and zein protein mixtures by increasing the amount of different plasticizers.^[51] Since viscosity plays a key role in injection molding, to get similar rheological behavior in all the plasticized PLA formulations, an iterative process was carried out to obtain the optimum temperatures for the injection molding process. The resulting curves and temperatures are shown in Figure 3b. The differences that emerge by the modification of the working temperatures can be also seen in Figure 3c, while a dramatic decrease of Eta-zero was observed at 210 °C, the iterative process carried out to optimize de working temperatures allowed to reduce the variations that arise with increasing plasticizer content.

3.3. Effect of DBI on the Mechanical Properties of Plasticized PLA Formulations

The addition of DBI into the PLA polymeric matrix had a remarkable effect on the final mechanical properties of the considered PLA/DBI formulations as proven by **Table 5** and **Figure 4**. First, the effect of the increase in plasticizer proportion over the stiffness of the material was studied. In this case, unplasticized PLA showed a tensile modulus of 4076 MPa and the addition of 2.5 wt% DBI decreased the tensile modulus by 3.1%, which suggests some plasticization. The effect of DBI on the stiffness was most noticeable at a DBI content of 10 wt% leading to a remarkably lower tensile modulus of 1572 MPa, as it was expected. This tensile modulus is within the range of some commodities such as high-density poly(ethylene) (HDPE) with tensile modulus ranging from 600 to 900 MPa and poly(propylene) (PP) with moduli comprised between 900 to 2000 MPa.^[52,53] In fact, the tensile modulus in plasticized PLA with 10 wt% DBI is similar to poly(propylene). This decrease in stiffness provided by the DBI plasticizer can be explained by different theories such as the lubricity, the gel and the free volume theories.^[54] One of the most known phenomena about the introduction of plasticizers in polymers is that they promote a reduction in the attraction forces between the chains of the polymer (hydrogen bonding, van der Waals forces, and so on). As a result, the movement of the polymeric chains requires less energy.^[55] In samples containing 15 and 20 wt% DBI, a remarkable decrease in the tensile modulus was observed, resulting in 58.5 MPa for the 20DBI/PLA.

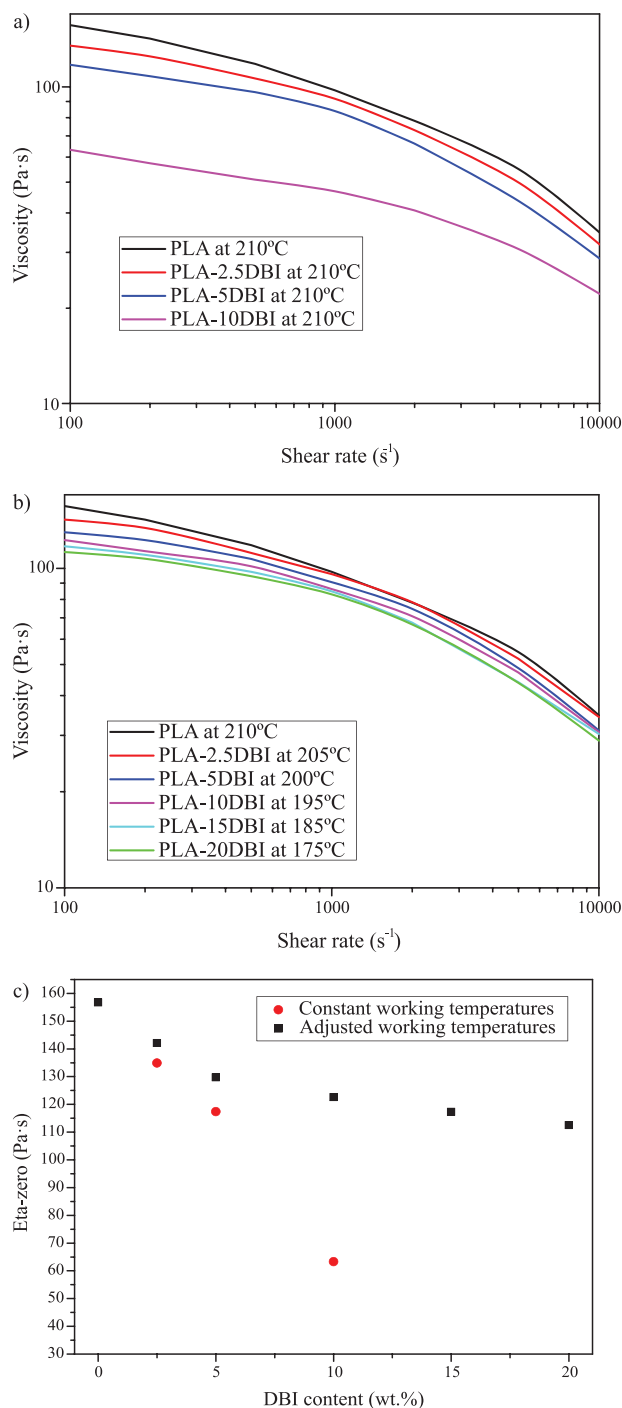


Figure 3. Rheological behavior of neat PLA and plasticized PLA formulations with different dibutyl itaconate (DBI) content: a) viscosity versus shear rate at a constant temperature of 210 °C, b) viscosity versus shear rate after iteration process to give similar viscosity profile, and c) Eta-zero versus DBI content.

Table 5. Summary of mechanical properties of neat PLA and plasticized PLA formulations with different dibutyl itaconate (DBI) content: tensile modulus (E), maximum tensile strength (σ_{\max}), elongation at break (ϵ_b), Shore D hardness, and impact strength.

Code	E [MPa]	σ_{\max} [MPa]	ϵ_b [%]	Shore D hardness	Impact strength [kJ m^{-2}]
PLA	4076 ± 34	55.0 ± 1.8	4.6 ± 0.5	81.0 ± 1.2	4.8 ± 0.2
2.5DBI/PLA	3949 ± 90	46.2 ± 1.7	3.2 ± 0.4	83.3 ± 1.0	4.8 ± 0.2
5DBI/PLA	3460 ± 50	44.4 ± 1.8	3.1 ± 0.4	81.5 ± 0.9	5.4 ± 0.2
10DBI/PLA	1572 ± 63	23.8 ± 0.4	322 ± 17	75.6 ± 1.1	7.7 ± 0.4
15DBI/PLA	162 ± 9	16.9 ± 0.8	263 ± 9	58.2 ± 1.8	nb
20DBI/PLA	58.5 ± 2	15.0 ± 0.1	262 ± 7	50.3 ± 0.6	nb

*nb: no break was observed even on "V"-notched specimens.

These results suggest that plasticized PLA formulations with more than 10 wt% DBI have a tensile modulus value similar to thermoplastic poly(urethane) (TPU). For example, Bueno-Ferrer et al. developed different formulations of biobased thermoplastic poly(urethanes) (TPU) with tensile modulus ranging from 0.7 to 11.1 MPa.^[56] Kumar et al. obtained similar results by plasticizing PLA with 30 wt% of a polymeric plasticizer, namely poly(ethylene glycol) (PEG) with a measured tensile modulus of 140 MPa.^[57] Similar decrease in stiffness can also be achieved by blending PLA with poly(ϵ -caprolactone) (PCL). In this sense, Mittal et al. reported on PLA/PCL blends with a tensile modulus of 866 MPa by blending PLA with 50 wt% PCL.^[58]

The most surprising effect of DBI on mechanical properties is the drastic increase in elongation at break it provides. PLA is usually characterized by a brittle behavior.^[6] As a result, a very low elongation at break (4.6%) is obtained for unplasticized PLA. The addition of small amounts of plasticizer (up to 5 wt% DBI) promoted a decrease in elongation at break, resulting in values between 3.1% and 3.2%. This effect has been observed when other plasticizers are used in small amounts in several polymers, and this phenomenon is known as anti-plasticization.^[59] Nevertheless, plasticized PLA with 10 wt% DBI shows a considerable increase in the elongation at break up to values of 322%, which is clear evidence of the high plasticizing potential that DBI can provide to PLA. This exceptional plasticization effect exerted by DBI provides to PLA is observed in Figure 4a which gathers the characteristic stress–elongation curves of neat PLA and plasticized PLA formulations, together with the broken specimens after the tensile test (Figure 4b). For the 15 and 20 wt%, the elongation at break is not increased which is related to PLA reaching the saturation point due to plasticizer introduction as observed by Ferri et al. in plasticized PLA with 5 phr (parts by weight of plasticizer per 100 weight parts of base polymer) octyl epoxy stearate.^[60] Xuan et al. reported plasticized PLA formulations with elongation at breaks comprised between 446% and 643% with 20 wt% of different plasticizers derived from levulinic acid.^[61] The results obtained with DBI are much better than the ones obtained with other biobased plasticizers such as those derived from chemically modified vegetable oils. Orue et al. reported an interesting increase in elongation at break up to 25% in PLA blends with 20 wt% vegetable oil-derived plasticizers.^[62] Thus, the obtained results suggest that esters from bioderived itaconic acid could

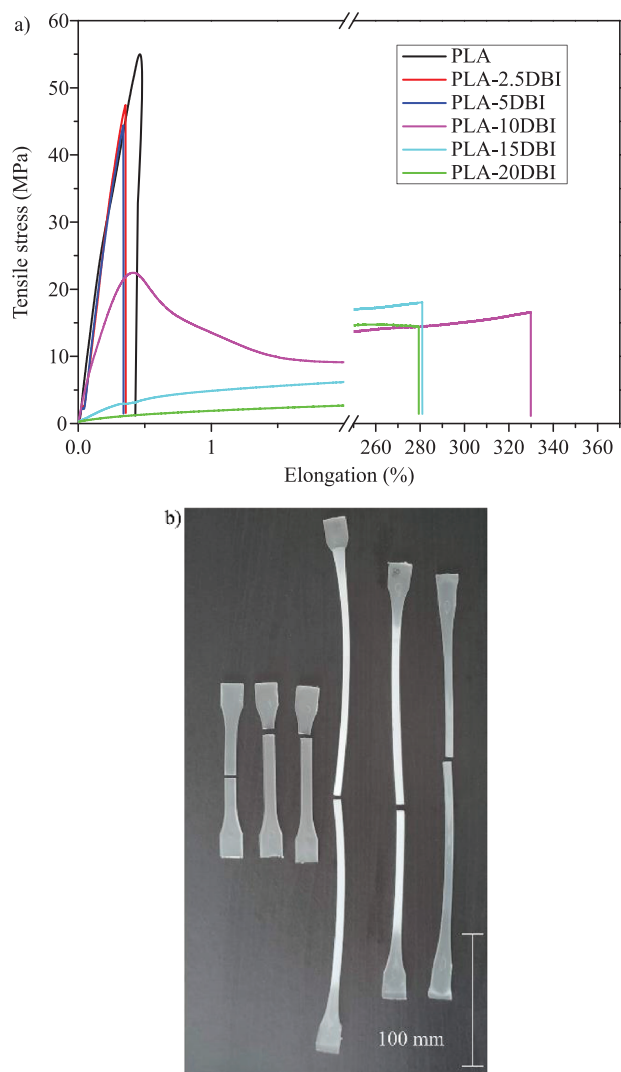


Figure 4. a) tensile stress versus elongation plots for neat PLA and plasticized PLA formulations with different dibutyl itaconate (DBI) content; b) appearance of PLA/DBI specimens after the tensile test (left neat PLA and right 20DBI/PLA) (scale bar = 100 mm).

represent a feasible technical solution for achieving effective PLA plasticization.

Regarding tensile strength, a clear decreasing trend as a function of the amount of plasticizer was obtained, which is also a typical plasticization effect. Tian et al. observed this behavior in PLA films plasticized with triethyl citrate (TEC) and glycerol triacetate (GTA), while Singh et al. reported this same tendency in poly(vinyl alcohol) (PVA) films plasticized with sorbitol.^[63,64] The effect of DBI on the internal structure of the base PLA polymer resulted in a reduction of the intermolecular forces between PLA polymer chains, resulting in a reduction of the maximum tensile strength.^[55] Neat PLA is characterized by a tensile strength of 55.0 MPa, while plasticized PLA with 10 wt% DBI shows a tensile strength of 23.8 MPa, which represents approximately half the value of neat PLA. It is important to bear in mind that the tensile strength of most commodities is comprised in the 20–35 MPa range.^[65] Therefore, plasticized PLA formulations

containing 10 wt% DBI provide balanced mechanical properties, similar to those of poly(olefins). As expected, a higher amount of plasticizer resulted in a decrease in tensile strength down to 15.0 MPa (20 wt% DBI).

The appearance of the tensile specimens after the tensile test is shown in Figure 4b. It is clearly seen that for a DBI content of 10, 15, and 20 wt%, the elongation at break is much higher than that of neat PLA or plasticized PLA formulations with low DBI content. This is indicative of a positive contribution of DBI toward the obtention of high ductile PLA materials. The whitening in the deformed region is promoted by the formation of voids during the tensile test as proposed by Chieng et al.,^[66] as well as a preferential PLA polymer chain alignment during axial deformation.

Additionally, Table 5 shows the hardness results of the PLA-based materials as a function of the amount of DBI plasticizer content. As expected, since hardness is a resistant mechanical property, it follows the same tendency observed for the tensile modulus and tensile strength. The addition of small amounts of DBI does not vary Shore D hardness, maintaining values around 80. 10 wt% DBI plasticized PLA formulations show a remarkable difference in Shore D values in relation to neat PLA, decreasing the hardness from 81.1 down to 75.6. As the proportion of DBI is increased, Shore D hardness further decreases down to 50.3 for the sample containing 20 wt% DBI. These results are in agreement with those reported by Bouti et al. on PLA plasticized with epoxidized sunflower oil.^[67]

As it has been stated, PLA is a rather brittle polymer with low toughness. Plasticization usually leads to improved toughness. It is important to bear in mind that toughness is related to the ability for energy absorption during deformation–break. Therefore, toughness is related to both tensile strength and elongation at break. Accordingly, toughness can be estimated by the area under the stress–strain curve. As observed in a qualitative way in Figure 4a, the area under the stress–strain curve increases with increasing DBI content, except from plasticized PLA formulations with 2.5 and 5.0 wt% DBI, which show an evident lower area than neat PLA. Table 4 also gathers the values of impact strength for neat PLA and its plasticized formulations with DBI. As expected, DBI has a positive effect on impact strength over PLA for plasticized formulations with 10, 15, and 20 wt%. In fact, the plasticized specimens with 15 and 20 wt% DBI did not break due to a stiffness reduction. Despite the area under the stress–strain curves suggest lower toughness for low DBI content (5 wt% or lower), these materials offer good behavior in impact conditions. This phenomenon may be promoted by the higher degree of crystallinity that DBI provides, as proposed by Lin et al.^[68] The low impact strength of neat PLA (4.8 kJ m^{-2}) is improved as the DBI content increases, with values of 7.7 kJ m^{-2} for plasticized PLA with 10 wt% DBI. These results are in total accordance with those reported by Jiao et al. on PLA plasticized with 20 wt% PEG.^[69] In this case, DBI provided similar results with lower concentration.

3.4. Effect of DBI on the Morphology of Plasticized PLA Formulations

Figure 5 shows the morphology of tensile test fractured samples of neat PLA and plasticized PLA/DBI blends. The introduction

of DBI showed visual changes in the morphology of plasticized PLA formulations. The flat fracture surface of neat PLA (Figure 5a) is representative of a brittle behavior, implying low plastic deformation.^[66] On the other hand, as the DBI content increases, a clear change in the surface morphology is detected, indicated by a rougher surface, ascribed to plastic deformation. This phenomenon occurred even on specimens with low DBI contents (5 wt% or lower) although, as it has been mentioned above, they showed slightly lower ductile behavior. A clear plasticization effect is noticed in Figure 5d for the 10DBI/PLA with a fracture surface with high roughness. Due to the improved elongation at break and, subsequently, ductility, ridges and tears emerged on the fracture surface.^[70] This morphology was not observed in plasticized formulations with 15 and 20 wt% DBI. In fact, their characteristic fracture morphologies show great roughness, but are smoother than the plasticized material with 10 wt%. Similar findings were reported by Ahmad et al. in PLA formulations plasticized with 10 wt% TEC. Moreover, they observed some phase separation at high TEC concentrations.^[71] In this case, phase separation is not observed by FESEM, but the morphologies of plasticized formulations with 15 and 20 wt% DBI suggest less plastic deformation that led to lower elongation at break values.

Despite the elongation at break results suggest a PLA structure saturation due to an excessive amount of plasticizer, no phase separation evidence was observed in all plasticized PLA formulations, which is representative of a miscible mixture. This demonstrates the theoretical solubility results previously analyzed. The absence of phase separation is good for the system since phase separation phenomena derived from polymer structure saturation can exert a negative effect on mechanical properties as reported by Rojas et al.^[72] It is also worthy to note that the morphology of plasticized PLA formulations with high DBI content (i.e., 20 wt%), show presence of voids at high magnification (Figure 5). This phenomenon is usual when plasticizers are introduced, as reported by Celebi et al. and Iglesias et al.^[73,74]

3.5. Effect of DBI on Thermal Properties of Plasticized PLA Formulations

Plasticization of PLA with DBI resulted in a noticeable change in the thermal properties of the resulting materials. These changes were assessed by differential scanning calorimetry (DSC) (Figure 6) and the main results from the second heating step are gathered in Table 6.

One of the most relevant thermal parameters affected by the presence of a plasticizer in a polymer is the glass transition temperature (T_g). In fact, the efficiency of the plasticizer can be assessed by a decrease in T_g it can provide to the base polymer. Below the glass transition temperature, a polymer is in a glassy state characterized by highly restricted chain mobility. Above the glass transition temperature, the polymer chains adopt a high mobility state, which provides increased ductility.^[27,75,76] Unplasticized PLA has a T_g of $61.3 \text{ }^\circ\text{C}$ as observed by DSC.^[77] The decrease in the T_g is significant in plasticized PLA formulations containing 5, 10, 15, and 20 wt% DBI. The progressive increase in the amount of DBI into the PLA matrix leads to a noticeable decrease in T_g down to values of $23.4 \text{ }^\circ\text{C}$ for a DBI content of 20 wt%. This suggests good plasticization efficiency, with a remarkable

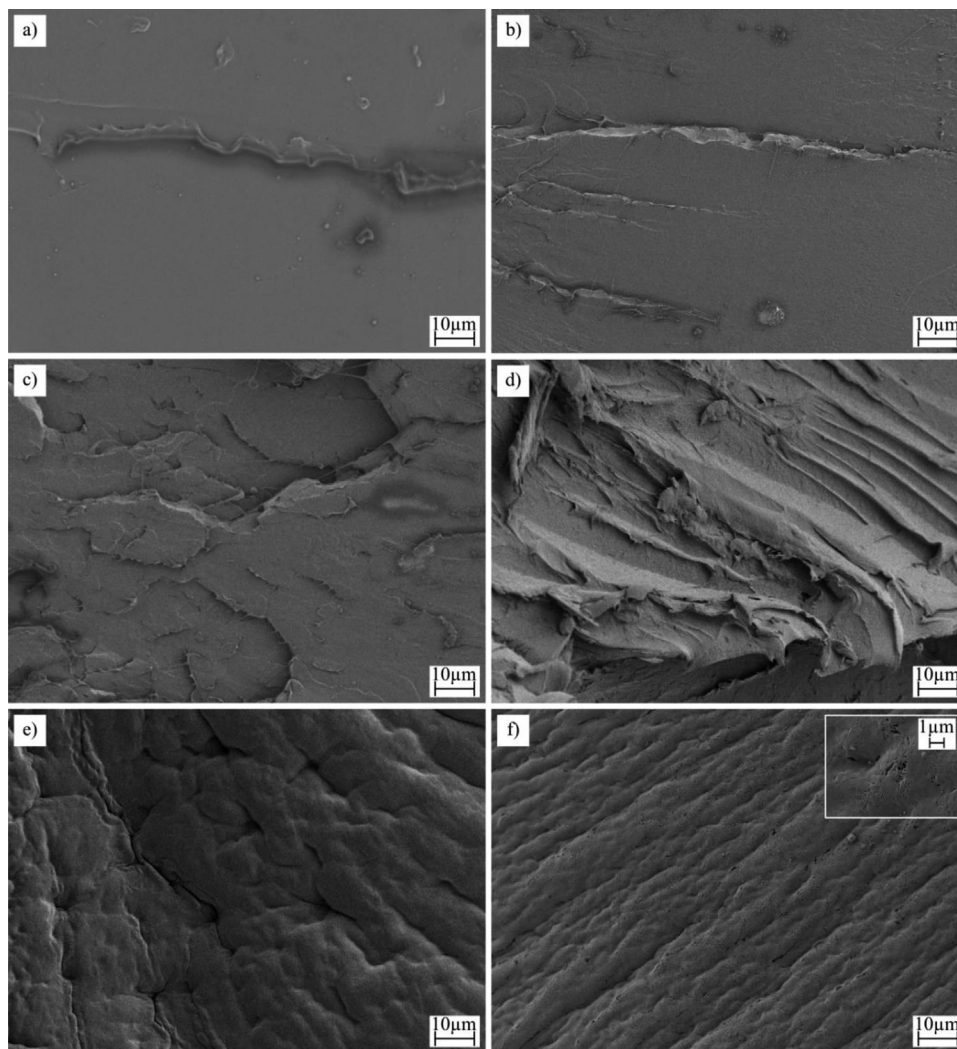


Figure 5. Field-emission scanning electron microscopy (FESEM) images of the fractured surfaces from tensile tests taken at 500 \times and inset at 5000 \times . a) PLA, b) 2.5DBI/PLA, c) 5DBI/PLA, d) 10DBI/PLA, e) 15DBI/PLA, and f) 20DBI/PLA (scale bar = 10 μm in all images except the inset scale bar = 1 μm).

increase in chain mobility in the amorphous PLA domains.^[78] As observed in mechanical characterization, plasticized PLA formulations with 15–20 wt% DBI show a low stiffness behavior. This is in agreement with the low T_g values obtained by DSC. Similar changes in T_g were reported by Harte et al. with different citrate ester plasticizers with results suggesting that despite a decrease in T_g is related to an increase in chain mobility, there is not a direct relationship with mechanical properties.^[79] Muller et al. work focused on the use of amorphous and semicrystalline PLA grades to obtain mono- and bilayer films with several plasticizers. They reported the influence of cinnamaldehyde in several bilayer PLA-based films and the effect of this plasticizer on mechanical performance.^[80] As the DSC curve for neat PLA used in this study suggests, this is a semicrystalline PLA with a low degree of crystallinity grade as the small melting peak suggests, thus indicating low tendency to crystallize. Nevertheless, the only addition of 2.5 wt% DBI leads to a remarkable change in the thermal behavior with the appearance of a well-defined cold crystallization process with a peak located at 115.1 $^{\circ}\text{C}$. This suggests that

DBI clearly favors crystallization. As the DBI content increases, the crystallization peak is moved to lower temperatures, reaching a minimum of 77.7 $^{\circ}\text{C}$ for the plasticized PLA formulation containing 20 wt% DBI. Choin et al. observed a similar effect when polyethylene glycol monoacrylate (PEGA) was used as plasticizer in PLA by reactive extrusion (REX), resulting in a crystallization peak temperature of 85.2 $^{\circ}\text{C}$ for a PEGA content of 20 wt%.^[81] Ferri et al. reported the same phenomenon on plasticized PLA with maleinized linseed oil (MLO) plasticizer.^[82] With regard to the melting peak temperature, neat PLA has a melt peak located at 168.7 $^{\circ}\text{C}$. As the DBI content increases, a decrease down to 160.9 $^{\circ}\text{C}$ is observed. Hassouna et al. also observed this phenomenon with PEG plasticizer on PLA with a melt peak temperature decrease from 154 $^{\circ}\text{C}$ down to 150 $^{\circ}\text{C}$ for the plasticized PLA with 20 wt% PEG and 10 wt% maleic anhydride-grafted-PLA.^[83] Regarding the normalized enthalpies, as the DBI content increased, the cold crystallization enthalpy (ΔH_{cc}) decreases while the melt enthalpy increases, thus indicating an increased crystallinity as shown in Table 6.

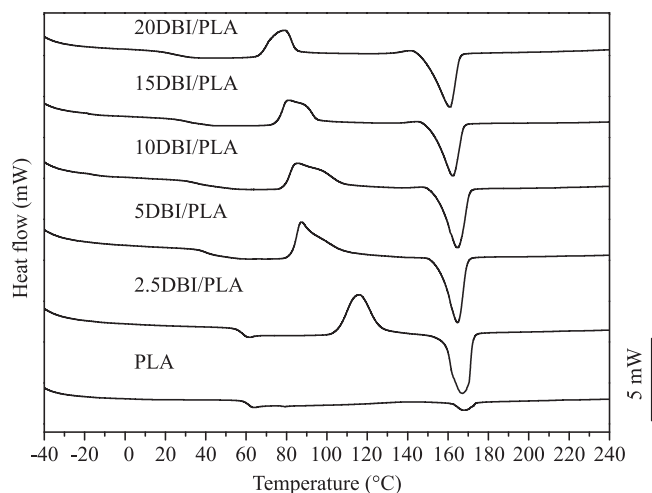


Figure 6. Differential scanning calorimetry (DSC) thermograms of the second heating step for neat PLA and plasticized PLA formulations with different dibutyl itaconate (DBI) content (scale bar = 5 mW).

The neat PLA used in this study has very low degree of crystallinity ($\chi_c\%$) of 4.5%. Unlike other commercial PLA grades, which are more crystalline, as reported by Muller et al. that used a semicrystalline PLA with a $\chi_c\%$ of 27%. The degree of crystallinity is highly dependent on the polymer structure and the thermal cycle.^[80] As shown by Table 6, the degree of crystallinity shows an increasing trend as a function of the amount of DBI, reaching values up to 24.5% for a plasticized PLA formulation containing 20 wt% DBI, this results are also in accordance with those obtained for XRD analysis provided in Supporting Information. The crystallization of PLA was promoted by the introduction of different additives that enhance the formation of crystallization nuclei. Choi et al. managed to promote PLA crystallization by using up to 10 wt% PEG on PLA. Higher amounts of PEG plasticizer resulted in a saturation of the plasticizer in the polymer structure and hence, the degree of crystallinity decreased.^[81] Gumus et al. reported a clear increase in PLA crystallinity by the addition of nanoclay particles that act as heterogeneous nucleant.^[77]

TGA allows to evaluate thermal degradability through studying the mass loss with temperature. This mass loss is usually attributed to polymer chain scission at high temperatures and evaporation of low molecular weight compounds such as plasticizers. A comparison of the mass loss (wt%) curves is shown

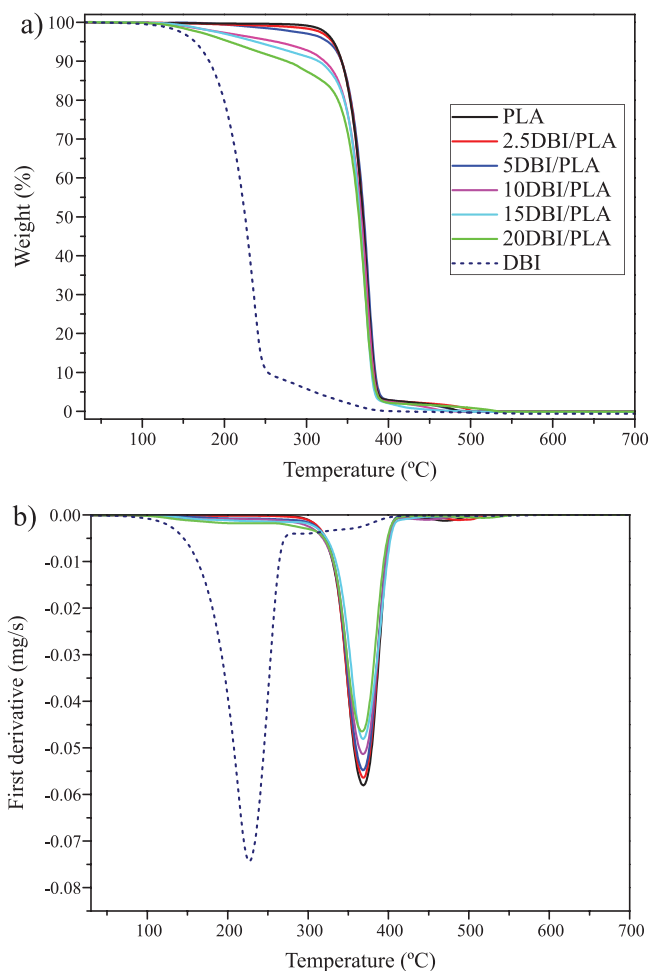


Figure 7. Thermogravimetric analysis (TGA) of neat PLA, DBI, and plasticized PLA formulations with different dibutyl itaconate (DBI) content: a) weight loss curves versus temperature; b) first derivative (DTG) curves versus temperature.

in **Figure 7** while the main characteristic parameters are gathered in **Table 7**. As seen in **Figure 7**, DBI is a volatile substance that evaporates at temperatures below than the PLA starts to decompose. Despite the boiling point of DBI is 284 °C, a 5% mass loss ($T_{5\%}$) is obtained at relatively low temperatures of 164.9 °C with the maximum mass loss rate temperature (T_{max}) located at

Table 6. Summary of thermal properties of neat PLA and plasticized PLA formulations with different dibutyl itaconate (DBI) content: glass transition temperature (T_g), cold crystallization peak temperature (T_{cc}), melting peak temperature (T_m), normalized cold crystallization enthalpy (ΔH_{cc}), normalized melting enthalpy (ΔH_m), and degree of crystallinity ($\chi_c\%$).

Code	T_g [°C]	T_{cc} [°C]	T_m [°C]	ΔH_{cc} [J g ⁻¹]	ΔH_m [J g ⁻¹]	$\chi_c\%$
PLA	61.3 ± 2.3	-	168.7 ± 1.3	-	4.2 ± 0.2	4.5 ± 0.3
2.5DBI/PLA	58.2 ± 4.1	115.1 ± 1.4	166.8 ± 1.4	32.5 ± 1.3	37.8 ± 0.9	5.8 ± 1.2
5DBI/PLA	40.0 ± 1.3	87.3 ± 1.0	164.9 ± 1.7	22.2 ± 1.5	28.7 ± 0.8	7.2 ± 1.1
10DBI/PLA	35.2 ± 2.3	84.8 ± 1.5	164.5 ± 2.0	23.1 ± 0.9	34.0 ± 1.4	13.0 ± 1.9
15DBI/PLA	31.4 ± 2.2	80.8 ± 1.9	162.1 ± 2.1	20.9 ± 0.7	35.0 ± 1.3	17.8 ± 1.5
20DBI/PLA	23.4 ± 3.4	77.7 ± 1.7	160.9 ± 1.9	16.6 ± 0.8	34.8 ± 1.2	24.5 ± 1.9

Table 7. Summary of thermal degradation properties of neat PLA, DBI, and plasticized PLA formulations with different dibutyl itaconate (DBI) content: temperature at 5% mass loss ($T_{5\%}$), temperature at the maximum mass loss rate (T_{\max}), and residual weight at 700 °C.

Code	$T_{5\%}$ [°C]	T_{\max} [°C]	Residual weight [%]
PLA	333.4 ± 1.3	368.6 ± 0.4	0.7 ± 0.2
2.5DBI/PLA	332.2 ± 1.1	368.1 ± 0.6	0.6 ± 0.2
5DBI/PLA	326.4 ± 1.3	368.3 ± 0.5	0.4 ± 0.2
10DBI/PLA	262.8 ± 1.3	368.5 ± 0.7	0.5 ± 0.2
15DBI/PLA	226.3 ± 1.2	368.8 ± 0.8	0.3 ± 0.2
20DBI/PLA	206.8 ± 1.4	364.7 ± 0.7	0.5 ± 0.2
DBI	164.9 ± 1.7	227.3 ± 1.4	0.3 ± 0.3

227.3 °C. These results agree with those reported by Richard et al. on octyl itaconate, with a characteristic mass loss onset temperature of 200 °C. In addition, they observed an increase in the mass loss onset as the length of the alkyl chain coupled to itaconic acid increased.^[84] As a result of the high thermal sensitivity that DBI possesses, processing of PLA specimens with DBI is critical since the typical processing temperatures for PLA are between 180–200 °C. For this reason, as indicated previously, the temperature profile for both the extrusion and injection molding was adjusted to avoid DBI loss. In spite of the fact that some DBI plasticizer was expected to be lost during processing, the overall effects on mechanical and thermal properties imply exceptional plasticization properties. Similar effects were reported by Arrieta et al. on plasticized PLA with limonene a high volatile compound. Despite the mass loss onset being very low (around 100 °C), limonene provided good plasticization properties to PLA films processed at 170 °C. These films offered an elongation at break of 165% for a limonene content of 20 wt%.^[28] The same phenomenon was reported by Jimenez and coworkers in plasticized PLA formulations with poly(hydroxybutyrate) and several plasticizers, namely PEG, and acetyl tributyl citrate (ATBC). They reported processing of these PLA-based blends at 180 °C. This temperature can cause some plasticizer loss during processing. They quantified this loss of about 0.5 wt% after 1 min at 180 °C, and 1 wt% after 6 min. Despite this slight plasticizer loss, the overall plasticizer efficiency was still very high as supported by the remarkable increase in elongation at break.^[85]

As seen in Figure 7, PLA thermal degradation (decomposition by chain scission) is characterized by a single mass loss process with a $T_{5\%}$ of 333.4 °C and a T_{\max} of 368.6 °C. Obviously, the TGA thermograms of plasticized PLA formulations with different DBI content show two overlapped mass loss steps, one corresponding to DBI evaporation, and a second one directly related to PLA decomposition. As the DBI content increases, the $T_{5\%}$ of the plasticized PLA formulations decreases due to the high volatility of DBI. The maximum mass loss rate, mainly attributable to the PLA chain scission, did not change in a remarkable way, showing values around 368 °C. A similar mass loss behavior was reported by Sessini et al. for plasticized PLA formulations with a bio-based polyether plasticizer derived from limonene.^[86] With regard to the residual mass, it was comprised in a very narrow range of 0.3–0.7% for all developed compositions. Battezzatore et al. obtained a residue of 1% at 800 °C on neat PLA.^[87]

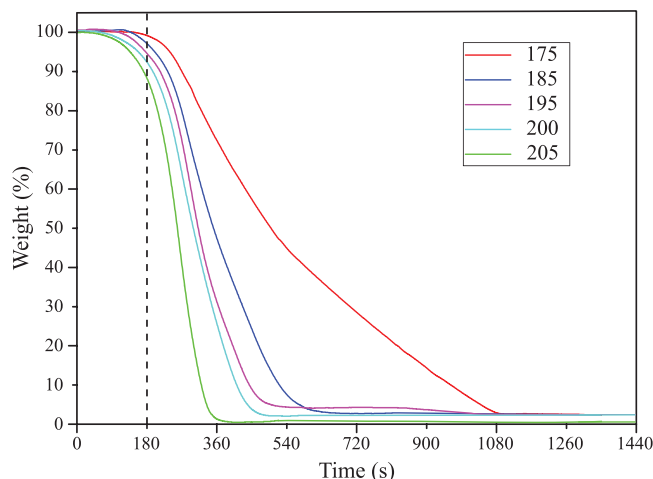


Figure 8. Thermogravimetric analysis (TGA) of DBI in terms of weight loss curves versus time for different isothermal temperatures.

Since the mass loss of the DBI due to its volatility is related to both exposure to high temperatures and time, the most aggressive thermal conditions used in the processing by injection molding were reproduced in isothermal conditions, to give a quantitative estimation of the lost plasticizer during processing. To this end, isothermal TGA curves for DBI, at different temperatures were programmed and the mass loss was recorded as a function of the time (Figure 8). Depending on the isothermal temperature scheduled, the plot evolution of the mass loss versus time is rather different.

As it was expected, the loss of the plasticizer as a result of its high volatility was reduced when the temperature of the isothermal profile was decreased, thus showing the importance of the rheological characterization, which allowed to reduce the processing temperatures, thus preventing the plasticizer from volatilizing. During the extrusion process, PLA/DBI formulations were exposed to a maximum temperature of 185 °C with a residence time of 1 min. Under these conditions, the mass loss related to DBI volatilization is almost negligible as indicated by Figure 8 (blue line). With regard to the injection molding process, the residence time is close to 3 min (dashed line in Figure 8). By considering the maximum temperatures of the corresponding temperature profile (see Table 3, zone 1), it is possible to quantify the maximum plasticizer loss. For plasticized PLA formulations with 2.5 wt% DBI, the maximum temperature these formulations had to withstand was 205 °C. At this isothermal temperature and residence time (green line in Figure 8), the DBI loss is 11.5%. Despite the nominal content was 2.5, the actual DBI content was 2.2 wt% as suggested by the isothermal volatilization curves of DBI. As the isothermal temperature decreased, the corresponding percentage of DBI lost was remarkably reduced, thus leading to the following nominal (actual) DBI contents: 2.5DBI/PLA (2.2 wt% DBI), 5DBI/PLA (4.6 wt% DBI), 10DBI/PLA (9.4 wt% DBI), 15DBI/PLA (14.5 wt% DBI), and 20DBI/PLA (19.8 wt% DBI). Despite this slight plasticizer loss, the mechanical and thermal characterization confirmed exceptional plasticization properties of DBI.

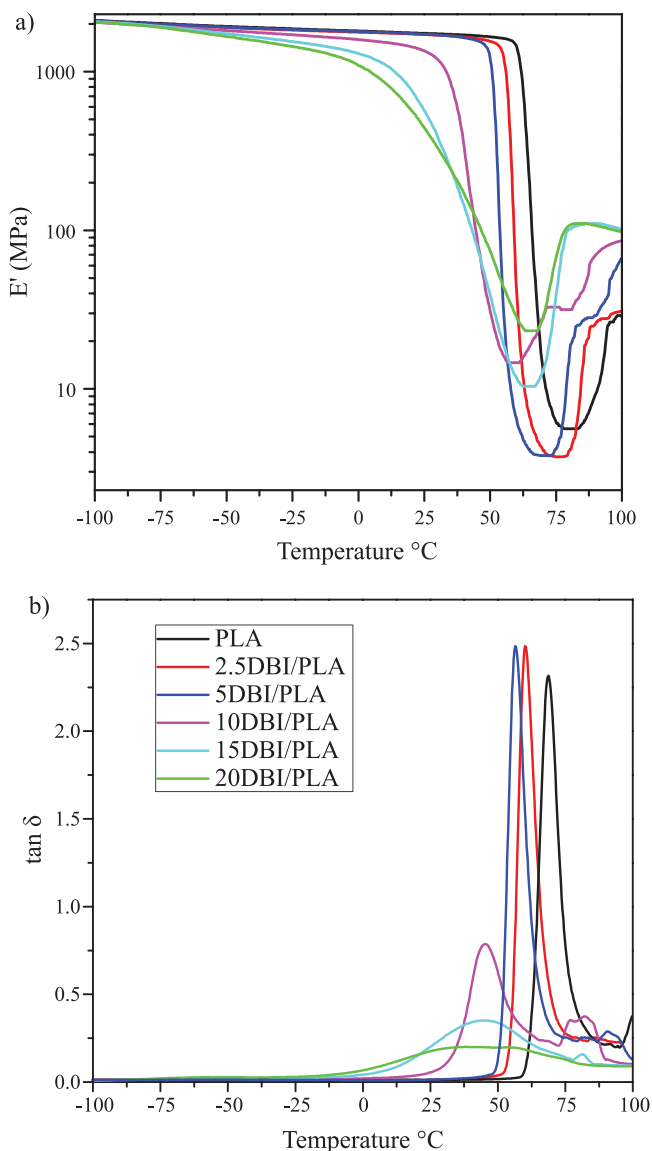


Figure 9. Dynamic mechanical thermal analysis (DMTA) curves of neat PLA and plasticized PLA formulations with different dibutyl itaconate (DBI) content: a) Storage modulus (E') versus temperature; b) dynamic damping factor ($\tan \delta$) versus temperature.

3.6. Effect of DBI and Temperature on Dynamical–Mechanical and Dimensional Properties of Plasticized PLA Formulations

A comparative plot of the storage modulus (E') and the dynamic damping factor ($\tan \delta$) is shown in **Figure 9a,b**, respectively. The DMTA curve for neat PLA shows the typical α -relaxation process, attributed to its glass transition temperature (T_g). This is distinguished by the decrease of E' by three orders of magnitude. Below its T_g , PLA behaves as a rigid and stiff polymer since only local rotational and vibrational motions are allowed (mainly related to secondary relaxation processes such as the γ - and β -relaxations). Once the glass transition temperature T_g is surpassed, long-range translational coordinated molecular motions of PLA chains can occur and this leads to a considerable softening.^[88,89] In spite

Table 8. Summary of the dynamic mechanical thermal analysis (DMTA) properties of neat PLA and plasticized PLA formulations with different dibutyl itaconate (DBI) content.

Code	T_g [°C]	Tan δ peak height	Tan δ peak FWHM ^{a)} [°C]	E' at -20 °C [MPa]	E' at 25 °C [MPa]
PLA	68.7 ± 1.2	2.34	7.92	1855 ± 25	1748 ± 13
2.5DBI/PLA	62.0 ± 1.1	2.54	8.01	1820 ± 31	1722 ± 16
5DBI/PLA	56.7 ± 1.3	2.51	8.41	1832 ± 20	1714 ± 21
10DBI/PLA	45.3 ± 1.4	0.79	16.83	1686 ± 27	1353 ± 14
15DBI/PLA	44.5 ± 2.1	0.34	47.52	1510 ± 29	563 ± 10
20DBI/PLA	39.7 ± 2.2	0.20	85.15	1388 ± 15	437 ± 12

^{a)} FWHM stands for the full-width at half-maximum taken from the $\tan \delta$ peak.

of the fact that several methods exist to estimate the glass transition temperature by using the storage modulus (E'), the loss modulus (E''), or the dynamic damping factor ($\tan \delta$), the use of $\tan \delta$ to assess the T_g is the most widely employed methodology. Using the $\tan \delta$ criterion, neat PLA is characterized by a T_g of 68.7 °C and, as observed by DSC, this value is remarkably moved down to values of 39.7 °C for the plasticized PLA formulations containing 20 wt% DBI. Although the T_g values obtained by DMTA ($\tan \delta$ criterion) are higher than those observed by DSC, the obtained values follow the same decreasing tendency. Plasticizers have a remarkable effect on the storage modulus, as well as on the dynamic damping factor (Figure 9b). The $\tan \delta$ peak for neat PLA has a very narrow peak with a maximum value around 2.30, while plasticized formulations show a broader peak with noticeably lower $\tan \delta$ values. For example, the $\tan \delta$ peak maximum for the plasticized PLA formulation with 10 wt% DBI is close to 0.8 and, as noticed in Figure 9b, the peak is broader than that of neat PLA (see **Table 8**). A similar phenomenon was reported by Maiza et al. on plasticized PLA formulations with ATBC and TEC with a remarkable decrease in the peak height related to $\tan \delta$.^[30] Additionally, Shirai et al. showed that plasticization of PLA-thermoplastic starch blends with diethyl adipate (DEA), led to a T_g ($\tan \delta$ peak) above 36 °C, which was higher than the room temperature. Despite this, at room temperature the material exhibited highly ductile behavior as observed in the PLA/DBI system. They concluded this was due to the fact that the $\tan \delta$ peak was wide enough to allow PLA/TPS blend to behave as a ductile material at 25 °C.^[90] It is worthy to note the decrease of T_g ($\tan \delta$ peak criterion) with increasing the DBI content in plasticized PLA formulations (**Table 8**). The $\tan \delta$ peak height also decreases, but the peaks corresponding to highly plasticized PLA formulations show a broader peak, measured through the full-width at half-maximum (FWHM) which changes from 7.92 °C up to 85.15 °C with 20 wt% DBI. Maiza et al. also reported this peak widening with increasing the content of different biobased plasticizers in PLA formulations.^[30] Even with T_g values above room temperature (calculated from $\tan \delta$ peak maximum), these formulations exhibit an extremely high ductile behavior since the glass transition relaxation occurs in a broader temperature range.^[89] Similar findings have been reported by Quiles-Carrillo et al. in plasticized PLA formulations by reactive extrusion with acrylated epoxidized soybean oil (AESO).^[44] As it has been observed by DSC, neat

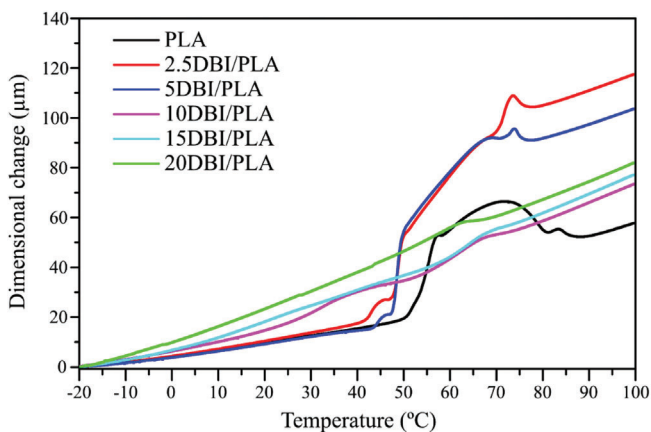


Figure 10. Comparative plot of dimensional change versus temperature obtained by TMA corresponding to neat PLA and plasticized PLA formulations with different dibutyl itaconate (DBI) content.

PLA shows a very low degree of crystallinity, being mainly amorphous, thus, the cold crystallization process is quite smooth. As the DBI content increases, the cold crystallization phenomenon is more evident, and this is confirmed by the increase of the storage modulus in the temperature range comprised between 60–90 °C, depending on the DBI content as observed by DSC. Agüero et al. observed this cold crystallization phenomenon in PLA subjected to several reprocessing stages in a more noticeable manner since thermal degradation during processing reduces molecular weight, thus allowing short chains readily to increase the crystallinity.^[91]

Regarding dimensional stability, the CLTE was obtained from the slope of the dimensional change versus temperature curve obtained by TMA. **Figure 10** shows representative TMA curves of neat PLA and plasticized PLA formulations with increasing DBI content. These TMA curves show different regions. By taking neat PLA as the reference curve, three different regions are detected. At low temperatures (below 50 °C) a linear relationship is noticed. At high temperatures (above 90 °C) a linear relation between the dimensional change and temperature is also evident. The third region is that comprised between 50–90 °C in which, the glass transition occurs. Moreover, the shrinkage due to the cold crystallization is overlapped in this temperature range. Due to this overlapping, it is not easy to accurately assess the glass transition temperature from these TMA curves. Usually, T_g is calculated as the interception between the extrapolation of both linear regions below and above the T_g , but due to the overlapping of the glass transition process and the cold crystallization, an accurate T_g value cannot be obtained from these TMA plots. The dimensional stability was measured by calculating the CLTE below and above T_g . Neat PLA has a CLTE of $58.3 \mu\text{m m}^{-1} \text{ }^\circ\text{C}^{-1}$ which is in agreement with the values reported by Balart et al. for neat PLA, around $78 \mu\text{m m}^{-1} \text{ }^\circ\text{C}^{-1}$.^[92] As the DBI content increases, the free volume does so, and this results in increased CLTE up to values of $149.9 \mu\text{m m}^{-1} \text{ }^\circ\text{C}^{-1}$ for the plasticized PLA formulation containing 20 wt% DBI (**Table 9**).

The cold crystallization occurs in the 60–90 °C. During cold crystallization, PLA chains mobility is increased to give a more packed structure which in turn leads to a shrinkage process

Table 9. Summary of the coefficient of linear thermal expansion (CLTE) and the total dimensional change over the test of neat PLA and plasticized PLA formulations with different dibutyl itaconate (DBI) content, obtained from TMA.

Code	CLTE -20 to 0 °C [$\mu\text{m m}^{-1} \text{ }^\circ\text{C}^{-1}$]	CLTE 90 to 100 °C [$\mu\text{m m}^{-1} \text{ }^\circ\text{C}^{-1}$]	Dimensional change [μm]
PLA	58.3 ± 1.3	155.7 ± 2.2	57.3 ± 1.2
2.5DBI/PLA	56.7 ± 0.9	180.2 ± 2.6	117.7 ± 2.7
5DBI/PLA	52.3 ± 1.2	168.0 ± 2.4	108.8 ± 2.6
10DBI/PLA	79.6 ± 1.5	201.8 ± 3.2	74.4 ± 1.8
15DBI/PLA	87.3 ± 2.1	209.1 ± 3.8	77.9 ± 1.4
20DBI/PLA	149.9 ± 2.3	202.5 ± 3.7	81.9 ± 1.5

which is evidenced by a dimensional contraction. It is important to bear in mind that all samples were obtained by injection molding with a fast-cooling process which inhibits crystallization. As seen in **Figure 10**, the plasticized PLA formulations with lower degree of crystallinity (χ_c %) are more sensitive to the cold crystallization at moderate temperatures and, subsequently, the observed shrinkage is more intense. Plasticized PLA with a higher amount of DBI did not show a noticeable shrinkage due to the greater ease of crystallization during processing as it has been confirmed by DSC. The ability of PLA to shrink is a common phenomenon; Nasrin et al. and Agüero et al. reported this shrinkage during the TMA test on PLA.^[91,93] Additionally, Espinach et al. observed this phenomenon in PLA composites with leached chemical fibers.^[94] Despite T_g and the cold crystallization are overlapped, the cold crystallization (shrinkage) is observed in the temperature range of 75 to 90 °C. As observed by DSC, by increasing the DBI content the cold crystallization moves to lower temperatures of about 65 °C.

Once the cold crystallization process is finished, the dimensional change follows a linear tendency again and, therefore, it is possible to obtain the CLTE in this region. Below the T_g , only rotational and vibrational motions of long chains are allowed, while above the T_g , translational motions of long chains are possible, and these lead to a remarkably higher CLTE of $155.7 \mu\text{m m}^{-1} \text{ }^\circ\text{C}^{-1}$. In a similar way as below T_g , as the DBI increases the CLTE also does up to values around $200 \mu\text{m m}^{-1} \text{ }^\circ\text{C}^{-1}$ for plasticized PLA formulations with 10, 15, and 20 wt%. This trend was also reported by Espinach et al. on fiber-reinforced PLA composites.^[94]

During the injection molding process, the polymer is progressively cooled inside the mold. This involves that the higher the CLTE value of the material, the more intensely the resulting injection-molded part will shrink. A constant pressure must be applied in order to avoid the shrinkage of the injection-molded parts while PLA is still in the melt state, thus avoiding the formation of sink marks.^[95–97]

4. Conclusions

DBI has shown high plasticizing efficiency over PLA formulations processed by extrusion and subsequent injection molding. DBI addition led to a remarkable decrease in viscosity and hence, the temperature profile during injection molding had to be adjusted to lower temperatures as suggested by capillary rheology

characterization, which in turn, prevented the plasticizer from volatilizing. A remarkable increase in ductile properties was achieved with DBI leading to an elongation at break of 322% for 10DBI/PLA sample, which was considerably higher than the elongation at break of neat PLA (4.6%). Higher DBI content on plasticized PLA formulations did not promote an increase in the elongation at break. In addition, the tensile strength and the tensile modulus were reduced. The tensile strength changed from 55.0 MPa (neat PLA) down to values of 23.8 MPa for 10 wt% DBI which is similar to most commodities. Differential scanning calorimetry showed two main effects related to DBI addition. On the one hand, a decrease in the glass transition temperature (T_g) was observed with increasing DBI content from 61.3 °C (neat PLA) to values of 23.4 °C with a DBI content of 20 wt%. On the other hand, the degree of crystallinity increased with DBI content, and the cold crystallization process of PLA was moved to lower temperatures. Similar tendency was observed by DMTA. Despite the slight mass loss undergone by DBI during the processing of plasticized PLA formulations with DBI due to its volatility, the plasticization efficiency is very good compared to other biobased plasticizers such as ATBC and TEC and broadens the potential of bio-derived itaconic acid and its esters as environmentally friendly plasticizers in PLA formulations.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

biobased materials, dibutyl itaconate, injection molding, plasticizers, polylactide

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[1] PlasticsEurope, Plastics—the facts 2020: An analysis of European plastics production, demand and waste data. <https://www.plasticseurope.org/en/resources/publications/4312-plastics-facts-2020>, (accessed: January 2022).

- [2] D. Li, Y. Jiang, S. Lv, X. Liu, J. Gu, Q. Chen, Y. Zhang, *PLoS One* **2018**, *13*, e0193520.
- [3] L. Argiz, R. González-Cabaleiro, Á. Val Del Río, J. González-López, A. Mosquera-Corral, *Sci. Total Environ.* **2021**, *763*, 142944.
- [4] A. Djukić-Vuković, D. Mladenović, J. Ivanović, J. Pejin, L. Mojović, *Renewable Sustainable Energy Rev.* **2019**, *108*, 238.
- [5] L. Aliotta, A. Vannozzi, L. Panariello, V. Gigante, M.-B. Coltelli, A. Lazzeri, *Polymers* **2020**, *12*, 1366.
- [6] Y. Wang, Y. Qin, Y. Zhang, M. Yuan, H. Li, M. Yuan, *Int. J. Biol. Macromol.* **2014**, *67*, 58.
- [7] A. Enumo, Jr., I. P. Gross, R. H. Saatkamp, A. T. N. Pires, A. L. Parize, *Polym. Test.* **2020**, *88*, 106552.
- [8] M. Mihai, M. A. Huneault, B. D. Favis, *Polym. Eng. Sci.* **2010**, *50*, 629.
- [9] J. Ivorra-Martinez, M. A. Selles, S. Sanchez-Caballero, T. Boronat, *J. Appl. Res. Technol. Eng.* **2021**, *2*, 6.
- [10] J. Gálvez, J. P. Correa Aguirre, M. A. Hidalgo Salazar, B. V. Mondragón, E. Wagner, C. Caicedo, *Polymers* **2020**, *12*, 2111.
- [11] B. Brüster, Y. O. Adjoua, R. Dieden, P. Grysan, C. E. Federico, V. Berthé, F. Addiego, *Polymers* **2019**, *11*, 1363.
- [12] B. W. Chieng, N. A. Ibrahim, Y. Y. Then, Y. Y. Loo, *Polymers* **2017**, *9*, 204.
- [13] E. Sritham, P. Phunsombat, J. Chaishome, *MATEC Web Conf.* **2018**, *192*, 03014.
- [14] I. N. H. M. Haneef, Y. F. Buys, N. M. Shaffar, N. A. Haris, A. M. A. Hamid, S. I. S. Shaharuddin, *Polym. Eng. Sci.* **2020**, *60*, 2876.
- [15] I. Fortelny, A. Ujcic, L. Fambri, M. Slouf, *Front. Mater.* **2019**, *6*, 206.
- [16] S. Wachirahuttapong, C. Thongpin, N. Sombatsompop, in *12th Eco-Energy and Materials Science and Engineering Symp., EMSES 2015* (Eds: B. Plangklang, H. Ohgaki, S. Pivsa-Art), Elsevier, New York **2016**, pp. 89–198.
- [17] S. Su, R. Kopitzky, S. Tolga, S. Kabasci, *Polymers* **2019**, *11*, 1193.
- [18] L. C. Arruda, M. Magaton, R. E. S. Bretas, M. M. Ueki, *Polym. Test.* **2015**, *43*, 27.
- [19] A. Przybytek, M. Sienkiewicz, J. Kucińska-Lipka, H. Janik, *Ind. Crops Prod.* **2018**, *122*, 375.
- [20] J. J. Koh, X. Zhang, C. He, *Int. J. Biol. Macromol.* **2018**, *109*, 99.
- [21] S. Su, M. Duhme, R. Kopitzky, *Materials* **2020**, *13*, 4897.
- [22] R. Muthuraj, M. Misra, A. K. Mohanty, *J. Appl. Polym. Sci.* **2018**, *135*, 45726.
- [23] Y. Ding, W. Feng, D. Huang, B. Lu, P. Wang, G. Wang, J. Ji, *Eur. Polym. J.* **2019**, *118*, 45.
- [24] B. N. Jung, D. H. Kang, J. K. Shim, S. W. Hwang, *J. Vinyl Addit. Technol.* **2019**, *25*, 109.
- [25] J. A. da Silva, C. Dalmolin, W. M. Pachekoski, D. Becker, *J. Appl. Polym. Sci.* **2018**, *135*, 46745.
- [26] N. Burgos, V. P. Martino, A. Jiménez, *Polym. Degrad. Stab.* **2013**, *98*, 651.
- [27] R. N. Darie-Niță, C. Vasile, A. Irimia, R. Lipșa, M. Râpă, *J. Appl. Polym. Sci.* **2016**, *133*, 43223.
- [28] M. P. Arrieta, J. López, S. Ferrándiz, M. A. Peltzer, *Polym. Test.* **2013**, *32*, 760.
- [29] P. Jia, H. Xia, K. Tang, Y. Zhou, *Polymers* **2018**, *10*, 1303.
- [30] M. Maiza, M. T. Benaniba, G. Quintard, V. Massardier-Nageotte, *Polimeros* **2015**, *25*, 581.
- [31] K. Gzyra-Jagięła, K. Sulak, Z. Draczyński, S. Podzimek, S. Gałęcki, S. Jagodzińska, D. Borkowski, *Polymers* **2021**, *13*, 3651.
- [32] Y. Yang, Z. Xiong, L. Zhang, Z. Tang, R. Zhang, J. Zhu, *Mater. Des.* **2016**, *91*, 262.
- [33] Y. B. Tee, J. Wong, M. C. Tan, R. A. Talib, *BioResources* **2016**, *11*, 1518.
- [34] X. Huang, M. Chen, X. Lu, Y. Li, X. Li, J. J. Li, *Microb. Cell Fact.* **2014**, *13*, 108.
- [35] Y. Ma, Z. Kou, P. Jia, J. Zhou, *Chem. Pap.* **2021**, *75*, 5515.
- [36] Y. Wu, Q. Xie, C. Gao, T. Wang, C. Wang, *Polym. Eng. Sci.* **2014**, *54*, 2515.

- [37] V. K. Gupta, S. Sood, S. Agarwal, A. K. Saini, D. Pathania, *Int. J. Biol. Macromol.* **2018**, *107*, 2534.
- [38] W. Li, Z. Zhang, L. Wu, Q. Liu, X. Cheng, Z. Xu, *Int. J. Biol. Macromol.* **2021**, *181*, 291.
- [39] K. M. Zia, A. Noreen, M. Zuber, S. Tabasum, M. Mujahid, *Int. J. Biol. Macromol.* **2016**, *82*, 1028.
- [40] D. W. van Krevelen, *Properties of Polymers*, Elsevier, New York **2012**.
- [41] S. Abbott, in *Poly(Lactic Acid)* (Eds: R. Auras, L.-T. Lim, S. E. M. Selke, H. Tsuji), Wiley, Hoboken, NJ **2010**, pp. 83–96.
- [42] A. Ruellan, A. Guinault, C. Sollogoub, V. Ducruet, S. Domenek, *J. Appl. Polym. Sci.* **2015**, *132*, 42476.
- [43] D. Lascano, G. Moraga, J. Ivorra-Martinez, S. Rojas-Lema, S. Torres-Giner, R. Balart, T. Boronat, L. Quiles-Carrillo, *Polymers* **2019**, *11*, 2099.
- [44] L. Quiles-Carrillo, N. Montanes, J. M. Lagaron, R. Balart, S. Torres-Giner, *Polym. Int.* **2018**, *67*, 1341.
- [45] W. Xuan, K. Odellius, M. Hakkarainen, *Eur. Polym. J.* **2021**, *157*, 110649.
- [46] A. F. Ramos, M. Muñoz, A. Espinosa, I. O. Cabeza, N. Moreno-Sarmiento, *J. Chem. Technol. Biotechnol.* **2020**, *95*, 1657.
- [47] N. Rudolph, T. A. Osswald, *Polymer Rheology: Fundamentals and Applications*, Carl Hanser Verlag, Munich **2014**.
- [48] C. Y. Khor, Z. M. Ariff, F. C. Ani, M. A. Mujeebu, M. K. Abdullah, M. Z. Abdullah, M. A. Joseph, *Int. Commun. Heat Mass Transfer* **2010**, *37*, 131.
- [49] H. M. Yoo, S.-Y. Jeong, S.-W. Choi, *e-Polymers* **2021**, *21*, 702.
- [50] B. Wang, J. Chen, H. Peng, J. Gai, J. Kang, Y. Cao, *J. Macromol. Sci., Part B* **2016**, *55*, 894.
- [51] Y. Sun, Z. Liu, L. Zhang, X. Wang, L. Li, *Int. J. Biol. Macromol.* **2020**, *143*, 334.
- [52] E. T. Bird, A. E. Bowden, M. K. Seeley, D. T. Fullwood, *Mater. Des.* **2018**, *137*, 414.
- [53] S. E. Salih, A. F. Hamood, A. H. Abd Alsalam, *Mod. Appl. Sci.* **2013**, *7*, 33.
- [54] G. Wypych, *Handbook of Plasticizers*, ChemTec Publishing, Toronto **2004**.
- [55] M. Bocqué, C. Voirin, V. Lapinte, S. Caillol, J.-J. Robin, *J. Polym. Sci., Part A: Polym. Chem.* **2016**, *54*, 11.
- [56] C. Bueno-Ferrer, E. Hablot, M. D. C. Garrigós, S. Bocchini, L. Averous, A. Jiménez, *Polym. Degrad. Stab.* **2012**, *97*, 1964.
- [57] A. K. Mohapatra, S. Mohanty, S. K. Nayak, *J. Thermoplast. Compos. Mater.* **2016**, *29*, 443.
- [58] V. Mittal, T. Akhtar, N. Matsko, *Macromol. Mater. Eng.* **2015**, *300*, 423.
- [59] L. Mascia, Y. Kouparitsas, D. Nocita, X. Bao, *Polymers* **2020**, *12*, 769.
- [60] J. M. Ferri, M. D. Samper, D. García-Sanoguera, M. J. Reig, O. Fenollar, R. Balart, *J. Mater. Sci.* **2016**, *51*, 5356.
- [61] W. Xuan, M. Hakkarainen, K. Odellius, *ACS Sustainable Chem. Eng.* **2019**, *7*, 12552.
- [62] A. Orue, A. Eceiza, A. Arbelaz, *Ind. Crops Prod.* **2018**, *112*, 170.
- [63] A. A. Singh, S. Sharma, M. Srivastava, A. Majumdar, *Int. J. Biol. Macromol.* **2020**, *153*, 1165.
- [64] H. Tian, D. Liu, Y. Yao, S. Ma, X. Zhang, A. Xiang, *J. Food Sci.* **2017**, *82*, 2926.
- [65] C. Unterweger, O. Brüggemann, C. Fürst, *Polym. Compos.* **2014**, *35*, 227.
- [66] B. W. Chieng, N. A. Ibrahim, Y. Y. Then, Y. Y. Loo, *Polym. Eng. Sci.* **2016**, *56*, 1169.
- [67] M. Bouti, R. Irinislimane, N. Belhaneche-Bensemra, *J. Polym. Environ.* **2022**, *30*, 232.
- [68] L. Lin, C. Deng, G.-P. Lin, Y.-Z. Wang, *Ind. Eng. Chem. Res.* **2015**, *54*, 5643.
- [69] F.-J. Li, S.-D. Zhang, J.-Z. Liang, J.-Z. Wang, *Polym. Adv. Technol.* **2015**, *26*, 465.
- [70] O. Fenollar, D. Garcia-Sanoguera, L. Sanchez-Nacher, J. Lopez, R. Balart, *J. Mater. Sci.* **2010**, *45*, 4406.
- [71] S. A. N. A. Zuber, A. Rusli, H. Ismail, in 6th Int. Conf. on Recent Advances in Materials, Minerals and Environment, RAMM 2018 (Eds: S. Sreekantan, Z. Lockman), Elsevier, New York **2019**, pp. 560–567.
- [72] S. Rojas-Lema, J. Ivorra-Martinez, J. Gomez-Caturla, R. Balart, D. Garcia-Garcia, *J. Appl. Res. Technol. Eng.* **2021**, *2*, 71.
- [73] H. Celebi, E. Gunes, *J. Appl. Polym. Sci.* **2018**, *135*, 45895.
- [74] M. L. Iglesias Montes, V. P. Cyras, L. B. Manfredi, V. Pettarín, L. A. Fasce, *Polym. Test.* **2020**, *84*, 106375.
- [75] M. Altenhofen Da Silva, M. G. Adeodato Vieira, A. C. Gomes Maçumoto, M. M. Beppu, *Polym. Test.* **2011**, *30*, 478.
- [76] R. G. M. Van Der Sman, *J. Phys. Chem. B* **2013**, *117*, 16303.
- [77] S. Gumus, G. Ozkoc, A. Aytac, *J. Appl. Polym. Sci.* **2012**, *123*, 2837.
- [78] C. Mangeon, L. Michely, A. Rios De Anda, F. Thevenieau, E. Renard, V. Langlois, *ACS Sustainable Chem. Eng.* **2018**, *6*, 16160.
- [79] I. Harte, C. Birkinshaw, E. Jones, J. Kennedy, E. Debarra, *J. Appl. Polym. Sci.* **2013**, *127*, 1997.
- [80] J. Muller, C. González-Martínez, A. Chiralt, *Eur. Polym. J.* **2017**, *95*, 56.
- [81] K.-M. Choi, M.-C. Choi, D.-H. Han, T.-S. Park, C.-S. Ha, *Eur. Polym. J.* **2013**, *49*, 2356.
- [82] J. M. Ferri, D. Garcia-Garcia, N. Montanes, O. Fenollar, R. Balart, *Polym. Int.* **2017**, *66*, 882.
- [83] F. Hassouna, J.-M. Raquez, F. Addiego, P. Dubois, V. Toniazzo, D. Ruch, *Eur. Polym. J.* **2011**, *47*, 2134.
- [84] J.-V. Richard, C. Delaite, G. Riess, A.-S. Schuller, *Thermochim. Acta* **2016**, *623*, 136.
- [85] M. P. Arrieta, M. D. Samper, J. López, A. Jiménez, *J. Polym. Environ.* **2014**, *22*, 460.
- [86] V. Sessini, M. Palenzuela, J. Damián, M. E. G. Mosquera, *Polymers* **2020**, *12*, 210.
- [87] D. Battagazzore, S. Bocchini, J. Alongi, A. Frache, *RSC Adv.* **2014**, *4*, 54703.
- [88] J. P. De Araújo, R. C. Silva, J. C. C. Lima, P. Agrawal, T. J. A. De Melo, *Macromol. Symp.* **2016**, *367*, 82.
- [89] M. Cristea, D. Ionita, M. M. Iftime, *Materials* **2020**, *13*, 5302.
- [90] M. A. Shirai, C. M. O. Müller, M. V. E. Grossmann, F. Yamashita, *J. Polym. Environ.* **2015**, *23*, 54.
- [91] A. Agüero, M. C. Morcillo, L. Quiles-Carrillo, R. Balart, T. Boronat, D. Lascano, S. Torres-Giner, O. Fenollar, *Polymers* **2019**, *11*, 1908.
- [92] J. F. Balart, D. García-Sanoguera, R. Balart, T. Boronat, L. Sánchez-Nacher, *Polym. Compos.* **2018**, *39*, 848.
- [93] R. Nasrin, S. Biswas, T. U. Rashid, S. Afrin, R. A. Jahan, P. Haque, M. M. Rahman, *Bioact. Mater.* **2017**, *2*, 199.
- [94] F. X. Espinach, S. Boufi, M. Delgado-Aguilar, F. Julián, P. Mutjé, J. A. Méndez, *Composites, Part B* **2018**, *134*, 169.
- [95] M. Rosato, D. Rosato, *Injection Molding Handbook*, Springer, Berlin, Heidelberg **2000**.
- [96] R. R. Panchal, D. O. Kazmer, *J. Manuf. Sci. Eng.* **2010**, *132*, 064503.
- [97] X. Sun, P. Tibbenham, D. Zeng, X. Su, S. Huang, H.-T. Kang, *Int. J. Adv. Manuf. Technol.* **2019**, *103*, 4095.