



Effect of dibutyl itaconate on plasticization efficiency of a REX processed polylactide with peroxides

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ABSTRACT

This work reports the effect of a reactive extrusion (REX) process on polylactide (PLA) based formulations plasticized with dibutyl itaconate (DBI). As DBI contains a carbon-carbon double bond, it is suitable for reactive extrusion. REX was carried out in a co-rotating twin extruder with the addition of two different organic peroxides. The main aim of using REX during the blending of the DBI plasticizer with PLA is to improve the interaction between them so the obtained final properties of the formulations could be improved. Plasticization process allowed to improve the ductile properties of PLA, by using REX, an improvement on the tensile strength was obtained with a no remarkable change in ductility. The thermal characterization also revealed that the glass transition temperature T_g was reduced for all formulations including DBI. REX with DBI provided a slight increase in T_g and this effect was also evident in thermomechanical properties. Regarding the thermal degradation behaviour, the plasticizer reduced the onset degradation and the maximum degradation rate, while a slight improvement on thermal stability was observed by using REX with organic peroxides. Finally, plasticizer migration in water was observed in conventional extruded PLA/DBI formulations, while REX provided improved behaviour against migration.

1. Introduction

The dependency of petroleum has been growing over the years, one of the reasons of such situation is that petroleum is the raw material for the obtention of the most employed polymers. The new environmentally friendly protocols promoted by the governments are giving rise to new polymers obtained from natural resources with potential biodegradation characteristics, called biopolymers [1,2]. Currently, there are different kinds of biopolymers that can be obtained by various processes. It is worthy to highlight the increasing use of biopolymers obtained from natural resources, like polysaccharides (starch, pectin, cellulose, chitin, arabinosylans) or proteins (bean proteins, gluten, casein, zein, among others) [3–6]. Another promising group is that of bacterial polyesters or polyhydroxyalkanoates (PHA) which are obtained from bacterial fermentation [7,8]. Despite these biopolymers are increasingly used at industrial scale, polylactide (PLA), obtained by fermentation of starch-rich raw materials, is the most widely utilized biopolymer, with

important uses in 3D printing [9], medical applications [10], food packaging [11], automotive industry [12,13].

PLA offers balanced properties, with a good mechanical behaviour (tensile strength of 50–70 MPa) in combination with rather good barrier properties. This makes PLA very attractive for the food packaging industry. PLA is usually synthesized by ring opening polymerization (ROP) of lactide, which can be obtained by fermentation of starch-rich agricultural crops, such as corn, potato, and cassava [14–16]. Despite the interesting features that PLA offers, including biodegradation or disintegration in controlled composting conditions, its main drawback is its brittle behavior (low elongation at break of about 4%, or less). This limits its applications at temperatures below its glass transition temperature ($T_g \approx 55^\circ\text{C}$), due to low toughness and high brittleness. To overcome the problem, different strategies have been studied. Two of the most widely used approaches to overcome these problems are blending PLA with other flexible polymers, or plasticization [15,17,18]. By blending PLA with flexible polymers with low tensile modulus and

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high elongation at break, it is possible to improve the ductile properties of the obtained blends. A wide range of flexible polymers, such as poly- ϵ -caprolactone (PCL), polybutylene succinate (PBS), polybutylene adipate-co-terephthalate (PBAT), among others, have been proposed to obtain tough binary or ternary PLA based formulations [19,20]. The main problem of this solution is that there is typically poor or missing compatibility between PLA and the other flexible polymers. This leads to phase separation phenomenon and hence, the mechanical properties are consequently reduced. To overcome, or at least minimize, the effects of the low compatibility in PLA binary and ternary blends, different strategies have been also proposed. Gardella et al. [21] reported about a remarkable improvement on PLA elongation at break by blending with 30 wt% PCL and using a PLA-g-MA copolymer to enhance interface interactions between PLA-rich phase and the PCL-rich phase. The elongation at break increased from 7% (neat PLA) up to 53% in the above mentioned compatibilized formulation. Plasticization is another widely used technical approach to provide PLA with improved toughness and flexibility, and it is the preferred option in many industrial applications [22]. Plasticizers also contribute to get a better processability, with a clear increase in flexibility, workability or distensibility, as defined by the IUPAC [23,24]. The plasticizer reduces the short-range intermolecular forces between polymer chains. As a result, less energy is required to promote polymer chain motion, thus allowing the improvement of the ductile properties of the polymer [25].

A wide range of chemical compounds have been proposed as plasticizers for PLA. Some examples are the petroleum-based polyethylene oxide (PEO) [26], and polyethylene glycol (PEG) [27]. With the aim of providing more environmentally friendly PLA formulations, new bio-based plasticizers are continuously being proposed. Many of these bio-based or natural plasticizers can also provide interesting lower toxicity to PLA flexible formulations [25]. Citrate esters, such as acetyl tributyl citrate (ATBC), or triethyl citrate (TEC) are widely as biobased plasticizers for PLA and they are approved for food contact, enhancing their use in the packaging industry [28,29]. Another promising family of plasticizers for PLA are oligomers of lactic acid (OLA), which can be synthesized to tailor the desired properties in terms of reactivity and impact absorption properties [30]. Recently, epoxidized vegetable oils have been reported as suitable additives for enhancement of PLA plasticization, providing elongation at break values above 100% [31]. Remarkable plasticization properties on PLA have been also reported with glycerol and its esters, such as triacetin, tributyrin, trilaurin [23]. Another example is the plasticizer based on sugars or saccharide derivatives, that can be obtained from agricultural industry by products [32].

The best outcomes, in terms of plasticization efficiency, are obtained with low molecular weight molecules; nevertheless, their main disadvantage is that these low molecular weight compounds tend to migrate, with an associated stiffening effect over time [15]. In order to improve the long-term behaviour of plasticized polymers, reactive extrusion (REX) could represent an interesting and feasible technical solution, since it can contribute to a chemical anchoring (grafting) of the plasticizer molecules onto the polymer backbone, thus reducing at the same time their tendency to migrate. One of the challenges in polymer plasticization is to restrict plasticizer migration and obtain a balance between the decrease in tensile strength and the increase in elongation at break. Reactive extrusion (REX) has been successfully used to graft some plasticizer into the main backbone of a polymer. Hassouna et al. [27] showed the feasibility of grafting polyethylene glycol (PEG) on PLA by reactive extrusion with maleic anhydride and peroxides, thus leading to improved ductility. They also reported the feasibility of grafting other conventional plasticizers, such as citrate esters, into PLA backbone by using the same reactive extrusion process, thus leading to balanced ductile and resistant properties [33]. Interesting results have been obtained by Bruster et al. [34] by reactive extrusion of PLA with limonene and myrcene in the presence of organic peroxides as free radical initiators. In this case, presence of carbon-carbon double bonds in both

limonene and myrcene allowed covalent anchoring of plasticizer molecules on PLA chains with a subsequent increase in tensile strength.

Itaconic acid is currently mainly obtained at industrial scale by fungus fermentation, e.g. *Aspergillus terreus*, that metabolizes a carbon source and excretes itaconic acid [35,36]. Itaconic acid offers a very interesting chemical structure since, on the one hand, it contains two carboxylic groups that can be esterified with n-butanol (or other alcohols) to give dibutyl itaconate (DBI) and, on the other hand, it contains a carbon-carbon double bond with potential reactivity. Recently, Ivorra-Martinez et al. [37] have shown the exceptional plasticization properties of DBI on PLA by conventional extrusion process. In particular, an elongation at break of 322% can be obtained with 10 wt% DBI.

This work explores the potential of reactive extrusion (REX) of dibutyl itaconate (DBI) to provide PLA with improved toughness. The main objective of this work is to assess the suitability of REX with peroxides as a simple way to chemically anchor plasticizer molecules onto PLA backbone. The effect of two organic peroxides, i.e. dicumyl (DCP) peroxide and benzoyl peroxide (BPO) used during the reactive extrusion is addressed in this work. The main effects of REX with these two peroxides on mechanical, thermal, thermomechanical, morphological, migration, and disintegration behavior are studied.

2. Materials and methods

2.1. Materials

PURAPOL L130 PLA grade from Total Corbion (Gorinchem, The Netherlands) with a density of 1.24 g/cm³ and a melt flow index according to ISO 1133-A of 23 g/10 min (210 °C/2.16 kg), or 10 g/10 min (190 °C/2.16 kg), was used. The stereochemical purity of the L-isomer is $\geq 99\%$, and the residual monomer content is less than 0.3%. Dibutyl itaconate (CAS number 2155-60-4) was supplied by Sigma-Aldrich S.A. (Madrid, Spain). As reactive extrusion initiators, dicumyl peroxide with 98% purity from Sigma Aldrich (Madrid, Spain), and benzoyl peroxide (BPO), Luperox A75, from Sigma Aldrich (Lyon, France) were used as received. Fig. 1 gathers the schematic plot of the chemical structure of all materials.

2.2. Processing of plasticized PLA formulations by reactive extrusion (REX)

PLA was introduced in a hot air drier at 100 °C for 5 h to remove any residual moisture, avoiding the hydrolysis during the hot melt manufacturing process performed in a 15 cc twin-screw micro compounder from Xplore instruments BV (Sittard, The Netherlands). The appropriate materials considered for the preparation of the different formulations (see Table 1) were weighed in an analytical balance and further subjected to a thermal cycle at 90 rpm with a temperature profile of 170 °C–180 °C – 190 °C. The reactive extrusion process lasted 6 min

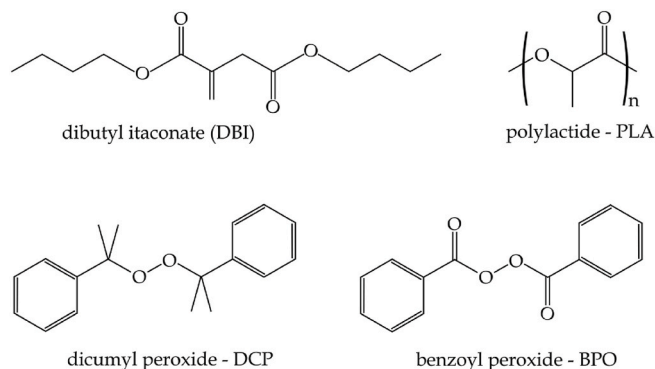


Fig. 1. Chemical structure of the employed materials for REX with PLA and DBI.

Table 1

Formulations for conventional and reactive extrusion (REX) of polylactide (PLA) plasticized with dibutyl itaconate (DBI) by using different organic peroxides.

Code	PLA (wt.%)	DBI (wt.%)	DCP (phr) ^a	BPO (phr) ^a
PLA	100	0	0	0
PLA-DCP	100	0	1	0
PLA-LU	100	0	0	1
PLA-10DBI	90	10	0	0
PLA-10DBI-DCP	90	10	0.5	0
PLA-10DBI-BPO	90	10	0	0.5
PLA-20DBI	80	20	0	0
PLA-20DBI-DCP	80	20	1	0
PLA-20DBI-BPO	80	20	0	1

^a Parts by weight of peroxide per one hundred weight parts of PLA/DBI formulation.

for all compositions. After the REX process, standard samples were obtained in a micro injection molding unit from Xplore instruments BV (Sittard, The Netherlands) at 190 °C and a mold temperature of 30 °C. An injection pressure of 8 bar was applied for 1 s to fill the mold, and a packing pressure of 6 bar was hold for an additional 1s.

2.3. Characterization

2.3.1. Mechanical properties

Tensile characterization of injection molded samples was performed by using a universal testing machine Instron 5967 (Norwood, USA) under ISO 527-2:2012. The testing machine was equipped with a 500 N load cell and the cross-head speed was set to 20 mm/min. The main tensile parameters, *i.e.* maximum tensile strength (σ_T), tensile modulus (E_T) and elongation at break (ϵ_b) were collected and calculated after the tests. Tensile toughness (U_T) was calculated by integrating the area under the tensile stress vs tensile strain curve as proposed in the following Equation (1):

$$U_T = \int_0^{\epsilon_b} \sigma \cdot d\epsilon \quad (1)$$

2.3.2. Fracture morphology characterization

As the obtained materials did not break under conventional Charpy impact test, samples were broken in tensile tests with aggressive conditions (300 mm/min crosshead speed), with the main aim of assessing the appearance of plastic deformation in plasticized PLA formulations, which was further characterized by field emission electron microscopy (FESEM, in a ZEISS ULTRA 55 FESEM from Oxford Instruments (Abingdon, UK). The working distance was set to 4 mm and the electron beam acceleration voltage was 2 kV. Prior to observation, the fracture surfaces were subjected to a sputtering process with gold-palladium alloy in a SC7620 sputter coater from Quorum Technologies Ltd. (East Sussex, UK).

2.3.3. Thermal properties

To assess the effect of REX on thermal properties of DBI plasticized PLA, differential scanning calorimetry (DSC) was considered. To do this, a Mettler-Toledo 821 calorimeter (Schwerzenbach, Switzerland) was employed. The degree of crystallinity (χ_c) was calculated by means of Equation (2), where w is the weight fraction of PLA in each formulation, ΔH_m^0 is the melt enthalpy of a theoretically fully crystalline PLA considered as 93 J/g [38], ΔH_m is the melting enthalpy and ΔH_{cc} is the cold crystallization enthalpy:

$$\chi_c (\%) = \frac{\Delta H_m - \Delta H_{cc}}{\Delta H_m^0 \cdot w} \cdot 100 \quad (2)$$

All formulations were subjected to a temperature program from 30 °C to 200 °C; after that, a cooling step down to -40 °C was scheduled to provide a controlled cooling rate and, finally, a second heating step up to

200 °C was programmed. All steps were carried out at a heating/cooling speed of 10 °C/min. To prevent thermal oxidation, a nitrogen atmosphere was used (66 mL/min). Some relevant thermal parameters, such as melt crystallization temperature (T_{mc}), enthalpy of melt crystallization (ΔH_{mc}), glass transition temperature (T_g), cold crystallization temperature (T_{cc}), enthalpy of cold crystallization (ΔH_{cc}), melting temperature (T_m) and melting enthalpy (ΔH_m) were collected from the second heating cycle. All DSC tests were run in triplicate and average thermal parameters were calculated.

With regard to the thermal degradation, thermogravimetry (TGA) was used to obtain the main degradation parameters, mainly the temperature required for a mass loss of 5% ($T_{5\%}$), the maximum degradation rate (T_{max}), and the char residue. TGA characterization was carried out in a TG-DSC2 thermobalance from Mettler-Toledo (Columbus, OH, USA). To this effect, a heating cycle from 30 °C to 700 °C at 10 °C/min under air atmosphere was used. All formulations were tested in triplicate to obtain reliable results. In addition, isothermal tests were performed in order to assess the plasticizer volatilization. To this effect a ramp from 30 °C to 190 °C at 50 °C/min under air atmosphere was used, and this temperature was maintained for 30 min.

2.3.4. Thermomechanical properties

Mechanical properties under dynamic conditions profile were measured by means of dynamic mechanical thermal analysis (DMTA) in a Mettler-Toledo DMA1 (Columbus, OH, USA) under a single cantilever mode. Injection molded samples with dimensions 20 × 5 × 2 mm³ were used, with a maximum deflection of 10 μm and an oscillation frequency of 1 Hz. The employed heating cycle was set from -100 °C up to 100 °C with a heating rate of 2 °C/min.

2.3.5. Disintegration in controlled compost soil

Samples were buried in compost to replicate the conditions proposed in ISO 20200 under a relative humidity of 55%, and a temperature of 58 °C. To this effect, hot pressed (at 170 °C) samples with dimensions 25 × 25 × 1 mm³ were used to follow up the disintegration process. Every week each sample was extracted, rinsed with water, dried with a paper and then, the weight loss was measured by means of Equation (3), where W_0 is the initial mass of the sample and W_f is the mass of the sample after the test:

$$\text{Weight loss (\%)} = \frac{W_0 - W_f}{W_0} \cdot 100 \quad (3)$$

2.3.6. Water uptake properties

Water absorption/plasticizer migration test was performed following the ISO 62:2008. Samples (80 × 10 × 4 mm³) were immersed in distilled water at room temperature for a period of 15 weeks. Each week, samples were extracted from the water and were dried with paper to measure the mass on an analytical balance AG245 from Mettler-Toledo (Schwerzenbach, Switzerland) with a precision of ±0.1 mg. Samples were immersed again in the water after the measurement. The weight change was calculated by Equation (4), where W_t is the weight of the sample after the extraction and W_0 is the initial weight of the sample:

$$\text{Weight change (\%)} = \frac{W_t - W_0}{W_0} \cdot 100 \quad (4)$$

3. Results and discussion

3.1. Mechanical properties of plasticized PLA with DBI by REX

The main results of tensile tests are summarized in Table 2, while Fig. 2 gathers the tensile stress (σ)-strain (ϵ) curves obtained during the same tests. First, we observed that REX of neat PLA with both peroxides produced slight differences in terms of mechanical properties, with only a slight increase in tensile strength and elongation at break. Li et al. [39] reported similar results by reactive extrusion of PLA with 0.5 phr DCP.

Table 2

Summary of mechanical properties obtained by tensile testing of neat PLA and plasticized PLA formulations with different DBI content processed by conventional and reactive extrusion.

Code	E_t (MPa)	σ_t (MPa)	ϵ_b (%)	UT (kJ/mm ³)
PLA	2995 ± 23	65.8 ± 1.0	3.1 ± 0.1	1.5 ± 0.1
PLA-DCP	2977 ± 31	71.8 ± 2.2	4.0 ± 0.2	2.1 ± 0.1
PLA-BPO	3022 ± 27	64.9 ± 1.2	3.2 ± 0.1	1.5 ± 0.1
PLA-10DBI	1346 ± 22	24.7 ± 0.4	248.8 ± 3.2	34.4 ± 0.4
PLA-10DBI-DCP	1162 ± 19	27.3 ± 0.6	276.1 ± 4.3	48.9 ± 0.8
PLA-10DBI-BPO	1420 ± 16	27.1 ± 0.2	279.1 ± 1.2	42.3 ± 0.8
PLA-20DBI	108 ± 6	20.6 ± 0.1	279.0 ± 7.9	37.7 ± 0.9
PLA-20DBI-DCP	79 ± 7	24.3 ± 0.3	274.2 ± 7.0	46.5 ± 1.0
PLA-20DBI-BPO	175 ± 4	25.2 ± 0.4	278.0 ± 4.0	39.3 ± 0.9

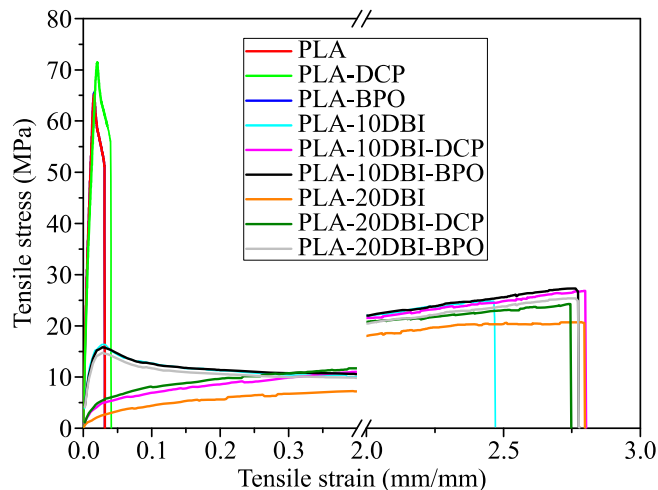


Fig. 2. Stress-strain curves for samples subjected to tensile test.

Free radicals obtained after the decomposition of the organic peroxides can promote hydrogen abstraction from the PLA backbone, leading to some overlapped phenomena, including branching and/or crosslinking, with the subsequent restriction on chain mobility, in accordance to the observed experimental results. Peng et al. [40] and Khajeheian et al. [41] reported about this branching and/or crosslinking phenomenon on PLA processed by reactive extrusion. We observed that conventional extrusion of PLA with DBI leads to a dramatic change in mechanical properties, thus showing exceptional plasticization efficiency. The brittle behaviour of neat PLA is related to its low elongation at break of around 3.1%, by plasticization with DBI, the elongation at break increases up to 248.8% for PLA-10DBI and 279.0% for PLA-20DBI, thus showing a remarkable increase in ductile properties and toughness. As can be seen in Table 2, the tensile toughness is improved from 1.5 kJ/mm³ (neat PLA) up to 34.4 kJ/mm³ and 37.7 kJ/mm³ for the plasticized PLA formulations containing 10 wt% and 20 wt% DBI, respectively. As tensile toughness is obtained by integrating the area under the tensile curve, the plasticized formulations with a clear improvement in elongation at break provide also improved toughness, as confirmed by literature works dealing with PLA formulations in presence of different plasticizers [42–44].

As expected, plasticization of PLA with DBI led to a decrease in tensile strength and tensile modulus. Neat PLA offers a tensile strength of 65.8 MPa, which is higher than most commodities polymers, as low- and high-density polyethylene, with tensile strength values ranging from 20 to 30 MPa [45]. As reported in Table 2, the plasticized formulations of PLA with DBI by conventional extrusion give interesting tensile strength values of 24.7 MPa (PLA-10DBI) and 20.6 MPa (PLA-20DBI), since these values fall into the typical range for most commodities. Regarding the tensile modulus, PLA is a stiff polymer with

a tensile modulus of 2995 MPa. In the case of plasticized PLA with DBI by conventional extrusion, the tensile modulus decreases to 1346 MPa and 108 MPa for a DBI content of 10 wt% and 20 wt%, respectively.

Reactive extrusion of PLA and DBI in presence of organic peroxides provides a new approach to PLA plasticization. The free radicals resulting from decomposition of the organic peroxides during REX promote hydrogen abstraction from the PLA backbone and breaking of the carbon-carbon double bond in DBI. In this way, activated DBI molecules can react with PLA chains to covalently bond DBI into PLA backbone. In addition to this, branching and/or crosslinking reactions could also occur, as well as DBI oligomerization [46–48]. Brüster et al. [34] suggested that REX of PLA with terpenes (with carbon-carbon double bonds), could lead to a crosslinked structure, but FTIR and NMR characterizations of the PLA/terpenes processed by REX did not show any relevant change in the chemical structure of the components. They also observed some oligomerization of terpenes. Finally, they conclude that the chemical changes produced during REX are very diluted and cannot be detected, even if an increase in tensile strength by using REX with terpenes was observed. In addition, as proposed by Brüster et al. [49], plasticizer molecules chemically bonded to the PLA backbone can act as starting points for plasticizer polyaddition. During the reactive extrusion, improvement of the interaction between polymer and plasticizer occurs. Because of this, the phase separation that promotes the migration is reduced. Moreover, the employment of a reactive extrusion can lead to an improvement of the mechanical strength of the plasticized formulations [34,50]. As the rheology of the plasticized polymers obtained by REX and their viscoelastic behaviour is related to all reactions occurring during REX (chain extension, branching, plasticization, crosslinking, plasticizer oligomerization, and so on), oscillatory rheometry has been used to qualitatively characterize these changes and assess their extent. In particular, the van Gurp-Palmen plots of the phase angle (δ) versus the complex modulus (G^*), give an idea of the branching degree obtained after REX [51–54].

In this regard, the formulations containing 10 wt% DBI, processed by REX, led to an increase in the tensile strength from 24.3 MPa (conventional extrusion) to values around 27.0 MPa (REX). This increase is also observed for the plasticized PLA formulation containing 20 wt% where an increase from 20.6 MPa (conventional extrusion) to values around 25 MPa was found. This means that at least an improvement of 10% in tensile strength is obtained by using REX instead of conventional extrusion. Yu et al. [55] also observed a similar effect when maleic anhydride was grafted onto PLA to improve the interaction with PEG plasticizer. The effects of peroxide type on tensile modulus are noteworthy. Despite DCP provides a decrease in tensile modulus in both plasticized formulations, BPO leads to improvement in elongation at break. As for the elongation at break, the values obtained in all cases for the plasticized PLA formulations processed by REX, are close to 280%. This means that REX provides not only an increase in terms of tensile strength, but also ductile properties are maintained. Hassouna et al. [27, 33] reported similar results in plasticized PLA formulations with chemically anchored plasticizer molecules (citrate of PEG) to PLA by reactive extrusion. As observed in Table 2, the tensile toughness is dramatically increased in both plasticized PLA formulations processed by conventional or reactive extrusion. It is worthy to note the positive effect of REX with both DCP and BPO peroxides on tensile toughness, which is a consequence of the observed tensile strength, while the elongation at break is maintained (or even improved).

3.2. Morphology of plasticized PLA formulations

The fracture surface of the different formulation is showed in Fig. 3. Unplasticized formulations (Fig. 3a–c) show the typical flat surfaces, with no plastic deformation marks, of a brittle polymer [56]. The addition of DBI plasticizer lead to an improvement in the ductile properties, as already observed in the mechanical characterization, and this effect can be also found in the fracture morphology. Fig. 3d and g show

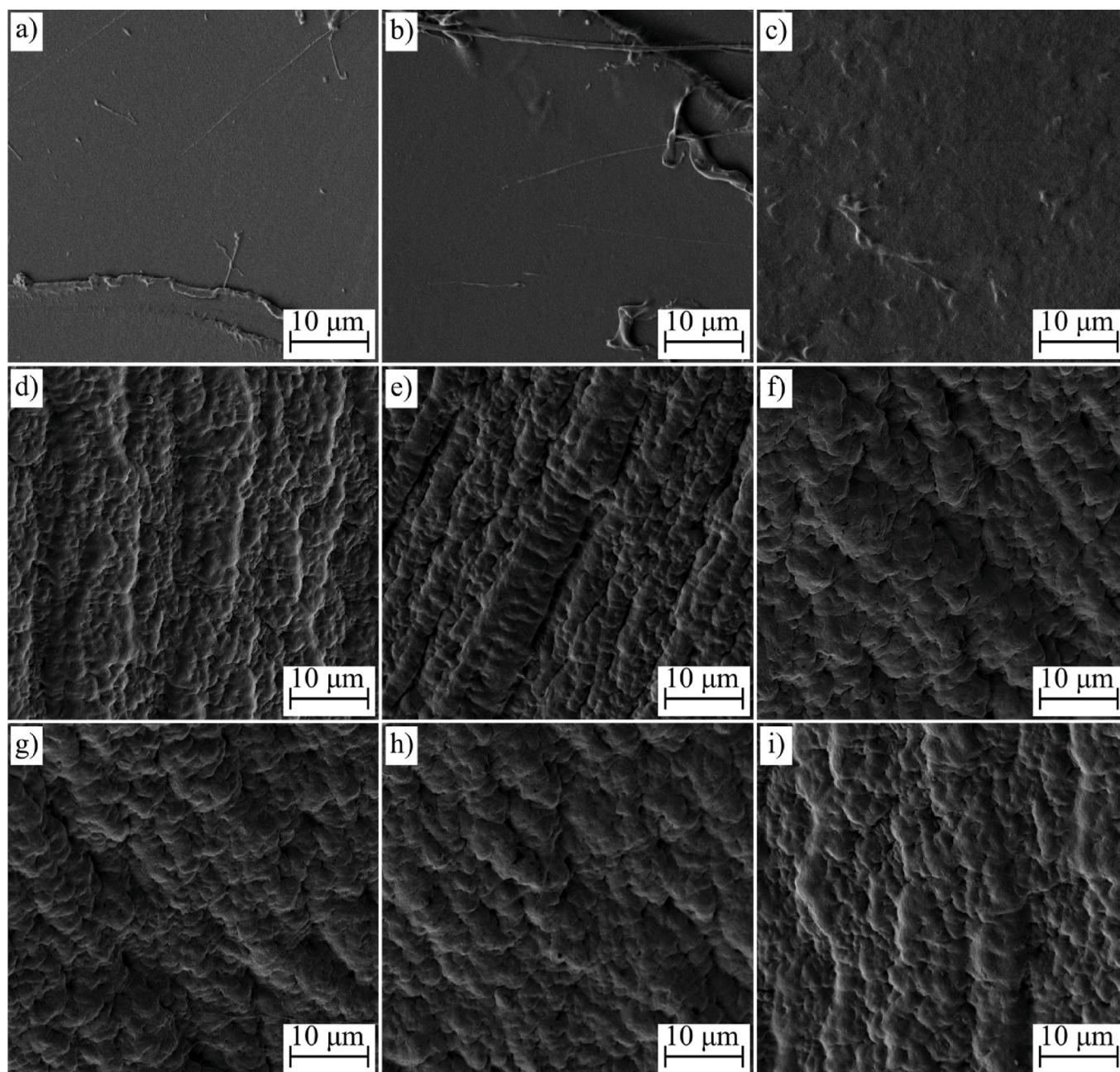


Fig. 3. Field emission scanning electron microscopy (FESEM) images taken at $1000\times$ (scale bar is $10\ \mu\text{m}$), corresponding to a) PLA; b) PLA-DCP; c) PLA-BPO; d) PLA-10DBI; e) PLA-10DIB-DCP; f) PLA-10DBI-BPO; g) PLA-20DBI; h) PLA-20DBI-DCP and i) PLA-20DBI-BPO.

the fracture of PLA-10DBI and PLA-20DBI; in both cases, a high roughness is observed as a consequence of the plastic deformation during the fracture process. Sungsanit et al. [57] observed a similar morphology change by the addition of polyethylene glycol (PEG) into PLA. The plasticized PLA formulations with DBI processed by REX with peroxides also show a ductile behavior, already observed by mechanical characterization and confirmed by the analysis of surface morphology. No evidence of plasticizer saturation can be detected by FESEM study. In some cases, an excess of plasticizer can lead to a phase separation, as observed by Yang et al. [58] in plasticized PLA formulations with isosorbide dioctoate and dioctyl terephthalate (DOTP). In that work, presence of spherical droplets in the surface of PLA formulations with 20 wt% DOTP, evidenced phase separation.

3.3. Thermal properties of plasticized PLA formulations

Fig. 4 gathers the DSC plots corresponding to first heating (Fig. 4a), cooling (Fig. 4b), and the second heating steps (Fig. 4c). The first effect to be noticed is the different crystallization behaviour of the samples during the cooling. As can be seen in Fig. 4b, while some formulations show an exothermic peak during the cooling stage, related to a crystallization process, other formulations do not show this behaviour. PLA has been widely reported in literature as a polymer with a low crystallization rate, as a polymer that mostly crystallizes during heating [59]. Gui et al. [60] reported that the low crystallization ability of PLA can be tuned by the introduction of additives such nucleating agents, allowing an exothermic peak to appear in the cooling cycle. Tiwary et al. [61] observed that peroxides like DCP can act as nucleating agents, promoting the melt crystallization peak during cooling. The low

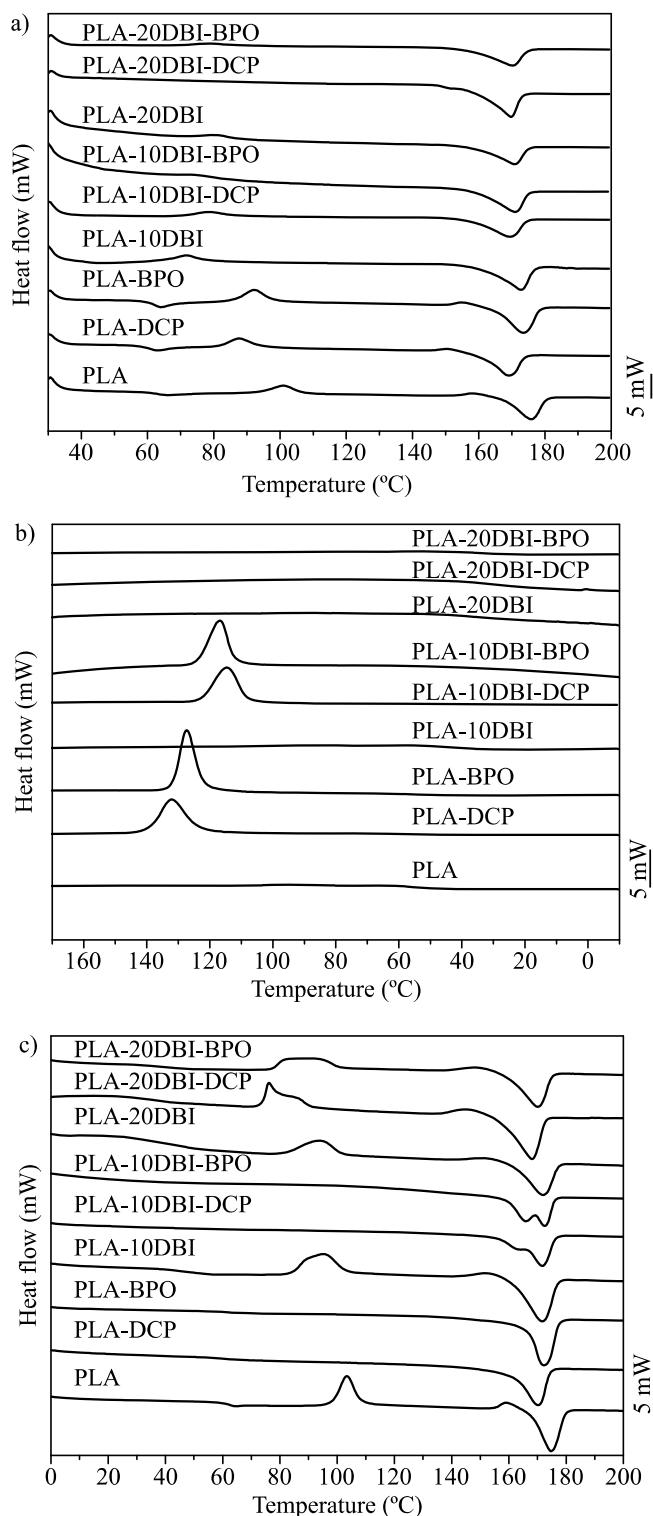


Fig. 4. DSC thermograms of neat PLA and plasticized PLA formulations with DBI processed by conventional and reactive extrusion processes, corresponding to a) first heating, and b) the cooling and c) second heating.

crystallization rate of neat PLA can be clearly seen in Fig. 4b, since no crystallization peak is observed during the cooling stage at a controlled cooling rate of $-10\text{ }^{\circ}\text{C}/\text{min}$. Nevertheless, the DSC thermograms corresponding to PLA-DCP and PLA-BPO show a crystallization peak located at around $130\text{ }^{\circ}\text{C}$ during the cooling stage; this peak is also observed for plasticized PLA formulations containing 10 wt% DBI processed by REX, but the maximum temperature peak is moved down to

lower temperatures. Li et al. [62] reported that plasticizer addition can enhance the crystallization ability of PLA by increasing the chain mobility; hence, the rearrangement to a packed structure can occur at lower temperatures. All other PLA-based formulations in this study do not show a crystallization peak during cooling, thus indicating the low ability of PLA to crystallize even with controlled cooling conditions. As expected, all formulations without melt crystallization during cooling (Fig. 4b) show the characteristic cold crystallization process (Fig. 4c) during the second heating cycle.

Tables 3 and 4 gathers the most relevant thermal parameters obtained during the DSC cycles. The effect of the plasticizer is also observed in both heating cycles, since for example in the second heating cycle the cold crystallization peak temperature of neat PLA (Fig. 4c), located at $103.3\text{ }^{\circ}\text{C}$ is moved down to $94.0\text{ }^{\circ}\text{C}$ in PLA-20DBI formulation. This decrease is attributable to the increased chain mobility that the plasticizer provides. This decrease is even more pronounced in PLA-20DBI-DCP formulation, processed by REX; in this case, the cold crystallization peak appears at $76.2\text{ }^{\circ}\text{C}$, due to a synergetic effect induced by the peroxides coupled with the plasticizer.

Another important effect provided by plasticizer addition into PLA is the decrease in the glass transition temperature (T_g). Ruellan et al. [63] reported this effect for a wide variety of plasticizers for PLA. In general, plasticizers increase the free volume; this, enhances chain motion and, subsequently, the T_g is reduced. Neat PLA has a T_g of about $60\text{ }^{\circ}\text{C}$. The reactive extrusion without plasticizer didn't affect the T_g , as can be seen in Table 4. As expected, the T_g of plasticized PLA formulations containing 10 wt% and 20 wt% DBI decreased to values of $45.2\text{ }^{\circ}\text{C}$ and $42.1\text{ }^{\circ}\text{C}$, respectively, thus showing the high plasticization efficiency that DBI provides to PLA. The T_g of the plasticized PLA formulation containing 20 wt% DBI, subjected to REX with peroxides, is slightly reduced down to values of $36.6\text{ }^{\circ}\text{C}$. Same behaviour has been reported by Hassouna et al. [27], in plasticized PLA by reactive extrusion with maleic anhydride and PEG. As expected, plasticization of PLA with PEG promoted a reduction in T_g . Nevertheless, when PEG was grafted onto PLA backbone by REX with maleinized PLA, an additional reduction in T_g was achieved. As they conclude, this effect is promoted by the presence of PLA-g-PEG chains that allow an extra increase of the free volume, with a positive effect on decreasing T_g . The reduction in the T_g temperature is observed in both heating cycles by the plasticizing effect provided by DBI.

Regarding the melting behaviour of the samples, a single peak is observed in most of the samples, except those containing 10 wt% DBI, processed by REX with DCP and BPO in the second heating cycle. As proposed by Viamonte-Aristazábal et al. [64], the presence of different melting peaks is due to the formation of different type of crystals, such as an orthorhombic α form (the most common) and trigonal β form, that melt at different temperatures. The melting temperature for neat PLA is $174.7\text{ }^{\circ}\text{C}$ (in the second heating cycle) and a small reduction of this value is observed in all formulations. Plasticization by conventional or reactive extrusion increases the ability of PLA to crystallize; as a result, a higher number of lamellae appear but they are thinner. This modification in the crystalline structure leads to a reduction in the melting temperature, as proposed by Hassouna et al. [33]. Small differences are observed between the first and the second heating step.

Finally, the degree of crystallinity of neat PLA was measured to be 22.5%; this value is increased by using REX with peroxides. The peroxides allowed the sample to form crystals during cooling, due to the nucleating effect induced, as observed in Fig. 4b [61]. As a result, the calculated degree of crystallinity is about 40%. The addition of plasticizers also has a similar effect on the degree of crystallinity, with a value of 26.9% for the PLA-20DBI; in this case, the increased chain motion facilitates the crystal formation [65]. As can be seen, REX with peroxides increases the degree of crystallinity of the samples compared with plasticized formulations processed by conventional extrusion. In this sense, Kfoury et al. [66] obtained similar results by using polyethylene glycol methyl ether acrylate as a PLA plasticizer by means of reactive

Table 3

Summary of the main thermal properties obtained by DSC in the first heating and cooling corresponding to neat PLA and plasticized PLA formulations with DBI processed by conventional and reactive extrusion processes.

Code	First heating						Cooling	
	T_g (°C)	T_{cc} (°C)	ΔH_{cc} (J/g)	T_m (°C)	ΔH_m (J/g)	$\chi_c\%$	T_{mc} (°C)	ΔH_{mc} (J/g)
PLA	63.2 ± 0.2	101.0 ± 0.3	14.3 ± 0.4	175.7 ± 0.2	46.8 ± 0.5	34.9 ± 0.4	–	–
PLA-DCP	60.8 ± 0.3	87.6 ± 0.4	9.4 ± 0.3	168.9 ± 0.2	47.2 ± 0.4	41.1 ± 0.7	132.2 ± 0.1	38.0 ± 1.1
PLA-BPO	62.2 ± 0.2	92.2 ± 0.4	9.0 ± 0.2	173.4 ± 0.2	47.0 ± 0.7	41.3 ± 0.8	127.3 ± 0.2	36.0 ± 0.9
PLA-10DBI	–	71.7 ± 0.5	6.0 ± 0.3	172.7 ± 0.3	38.1 ± 0.4	38.4 ± 0.7	–	–
PLA-10DBI-DCP	–	78.2 ± 0.4	7.2 ± 0.2	169.4 ± 0.3	45.0 ± 0.3	47.1 ± 0.8	114.6 ± 0.2	33.1 ± 0.9
PLA-10DBI-BPO	–	76.3 ± 0.3	10.0 ± 0.2	171.2 ± 0.4	48.8 ± 0.5	46.6 ± 0.9	123.5 ± 0.3	39.5 ± 1.0
PLA-20DBI	–	80.8 ± 0.2	3.2 ± 0.2	170.8 ± 0.4	35.1 ± 0.3	42.9 ± 0.8	–	–
PLA-20DBI-DCP	–	–	–	169.7 ± 0.3	38.8 ± 0.4	52.7 ± 0.7	–	–
PLA-20DBI-BPO	–	78.4 ± 0.3	2.6 ± 0.2	170.1 ± 0.3	34.7 ± 0.5	43.6 ± 0.6	–	–

Table 4

Summary of the main thermal properties obtained by DSC in the second heating corresponding to neat PLA and plasticized PLA formulations with DBI processed by conventional and reactive extrusion processes.

Code	Second heating					
	T_g (°C)	T_{cc} (°C)	ΔH_{cc} (J/g)	T_m (°C)	ΔH_m (J/g)	$\chi_c\%$
PLA	62.2 ± 0.3	103.3 ± 0.2	24.3 ± 0.5	174.7 ± 0.2	45.2 ± 0.8	22.5 ± 0.5
PLA-DCP	59.7 ± 0.4	–	–	170.2 ± 0.3	36.0 ± 0.7	39.1 ± 1.1
PLA-BPO	61.2 ± 0.3	–	–	172.2 ± 0.1	41.1 ± 0.7	44.6 ± 1.2
PLA-10DBI	45.2 ± 0.4	94.9 ± 0.2	24.3 ± 0.4	171.6 ± 0.2	45.2 ± 0.6	25.0 ± 0.6
PLA-10DBI-DCP	–	–	–	164.2 ± 0.2	32.1 ± 0.7	38.5 ± 1.0
PLA-10DBI-BPO	–	–	–	171.6 ± 0.3	32.9 ± 0.6	39.5 ± 1.3
PLA-20DBI	42.1 ± 0.2	94.0 ± 0.3	19.8 ± 0.3	171.8 ± 0.3	39.8 ± 0.8	26.9 ± 0.7
PLA-20DBI-DCP	36.6 ± 0.3	76.2 ± 0.3	19.6 ± 0.4	168.1 ± 0.3	46.6 ± 0.9	36.7 ± 0.9
PLA-20DBI-BPO	40.1 ± 0.3	84.9 ± 0.4	21.4 ± 0.4	169.9 ± 0.3	42.1 ± 0.7	28.1 ± 0.8

extrusion and physical blending. They reported an increase in the degree of crystallinity on plasticized formulations subjected to REX, in comparison to those obtained by physical blending or conventional extrusion. As they propose, this effect emerges by the higher free volume that appear after the reactive extrusion, due to a higher number of chain-ends that also can explain the T_g reduction. Another effect to highlight is that during the first heating, samples were taken from the test samples manufactured by injection molding. During the manufacturing process, polymer is forced to flow inside of the mold, with this effect nuclei formation is enhanced and consequently an increase in the degree of crystallinity is observed compared with the second heating cycle [67]. But in general terms the same trends with the addition of plasticizer and the performed reactive extrusion are observed.

Results of thermogravimetric (TGA) characterization of PLA and plasticized PLA formulations with DBI by conventional and reactive extrusion are shown in Fig. 5, while the main parameters are summarized in Table 5. PLA degradation process is characterized by a single step, with an initial degradation temperature ($T_{5\%}$) of 327.7 °C, and a maximum degradation rate (T_{max}) at 373.7 °C. Lizundia et al. reported similar temperatures and a single step degradation for neat PLA [68].

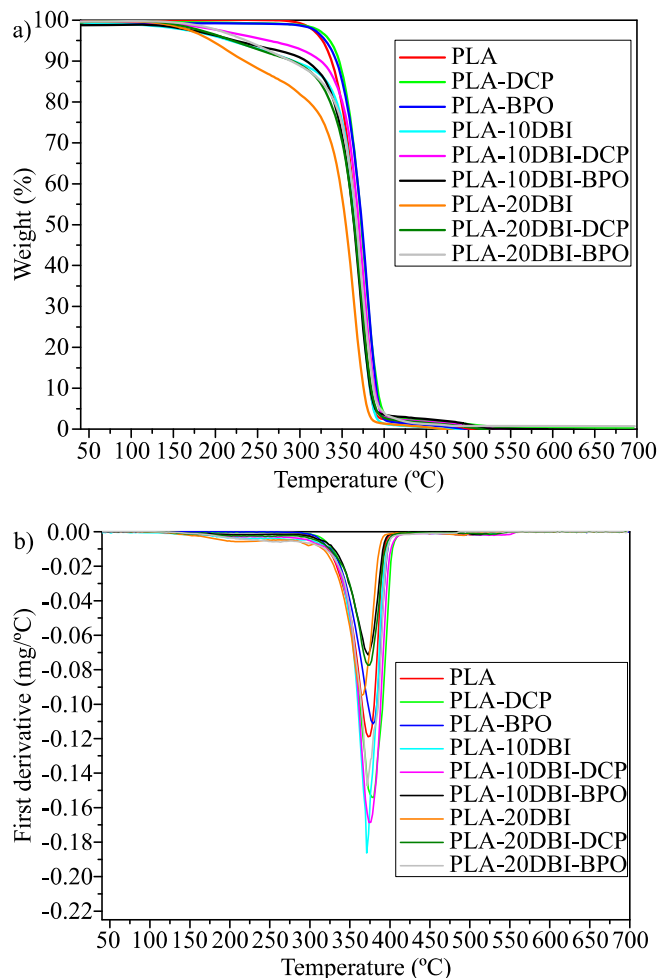


Fig. 5. Thermogravimetric curves of neat PLA and plasticized PLA formulations with DBI processed by conventional and reactive extrusion. a) sample weight vs temperature; b) first derivative (DTG) of the mass loss vs temperature.

REX of neat PLA with DCP improved the thermal stability by shifting the $T_{5\%}$ up to 336.1 °C, and the T_{max} up to 378.1 °C. Similar results were obtained by REX of PLA with BPO as free radical initiator during REX. As mentioned above, REX of PLA with peroxide leads to some possible phenomena, such as branching, chain extension or crosslinking, all these, having a positive effect on the thermal stability [69].

The addition of plasticizers into a polymer typically leads to a decrease in thermal stability, since most plasticizers are more volatile than polymers. DBI molecules have low molecular weight compared to that of PLA. DBI weight loss starts ($T_{5\%}$) at 164.9 °C and the maximum degradation rate is located at 227.3 °C, which means that it is expected

Table 5

Summary of thermal degradation properties obtained by TGA tests, corresponding to neat PLA and plasticized PLA formulations with DBI processed by conventional and reactive extrusion.

Code	$T_{5\%}$ (°C)	T_{max} (°C)	Residue (%)
PLA	327.2 ± 0.5	373.7 ± 0.5	0.2 ± 0.1
PLA-DCP	336.1 ± 0.4	378.1 ± 0.4	0.4 ± 0.1
PLA-BPO	335.2 ± 0.5	376.5 ± 0.3	0.5 ± 0.1
PLA-10DBI	217.9 ± 0.3	371.2 ± 0.4	0.2 ± 0.1
PLA-10DBI-DCP	224.3 ± 0.3	374.4 ± 0.4	0.3 ± 0.1
PLA-10DBI-BPO	224.0 ± 0.4	373.0 ± 0.4	0.3 ± 0.1
PLA-20DBI	195.3 ± 0.3	365.7 ± 0.3	0.2 ± 0.1
PLA-20DBI-DCP	220.6 ± 0.5	373.4 ± 0.3	0.3 ± 0.1
PLA-20DBI-BPO	237.5 ± 0.5	371.9 ± 0.4	0.3 ± 0.1

that plasticizer would be lost during the manufacturing of the samples [37]. Due to the low thermal stability of the plasticizer compared with PLA, the plasticized formulations offer lower thermal stability. As a result, the degradation process of the plasticized formulation takes place in two steps; a first degradation process, where the plasticizer volatilizes, and a second stage where the PLA chains decompose. In this regard, the formulation with the lowest thermal stability is the one with the highest amount of DBI (PLA-20DBI) with a $T_{5\%}$ of 195.3 °C, and a T_{max} of 365.7 °C. As one can see, the main difference of the TGA thermograms of plasticized PLA formulations compared with PLA, emerge in the initial temperature degradation, due to the presence of a first degradation step related to DBI volatilization.

Reactive extrusion (REX) could be an interesting technical approach to overcome this decrease in thermal stability provided by monomeric plasticizers. In this sense, it can clearly be seen that the plasticized PLA formulations subjected to REX with DCP or BPO show a noticeable increase in the $T_{5\%}$, compared to formulations processed by conventional extrusion. The most surprising result is obtained for the plasticized formulation containing 20 wt% DBI, where $T_{5\%}$ increases from 195.3 °C (PLA-20DBI), up to 220.6 °C (PLA-20DBI-DCP), and 237.5 °C (PLA-20DBI-BPO), thus showing a clear advantage of REX compared to conventional extrusion. As it has been indicated previously, REX of PLA with DBI in the presence of organic peroxides leads to a different overlapped phenomenon, including plasticization, chemical anchoring of DBI on PLA backbone, branching, crosslinking, or even, DBI oligomerization. All these phenomena reduce the volatility of DBI and play a key role effect on thermal stabilization. Marsilla et al. [70], reported an improvement in the thermal stability of poly(lactic acid) formulations with the use of itaconic anhydride processed by REX with DCP. They concluded that this improvement is related to the increased crystallinity of the samples, variations in the molecular mass or crosslinking changes achieved during the reactive extrusion.

In addition, to confirm the improvement of the reactive extrusion in terms of thermal stability of the plasticizer, some tests are performed under isothermal conditions. In this case, Fig. 6 shows some of the test. PLA shows a low weight reduction at 190 °C, as the heating of the sample is performed with a high heating rate during the test some moisture present in the sample evaporates leading to this small weight reduction. But with the addition of the plasticizer an increase in weight loss appeared due to its volatility below the boiling point of DBI. In this case, for the extrusion time employed (6 min) around 2.3% of the plasticizer is lost in the process. With the addition of the peroxides, this effect is reduced up to 1.2%, as proposed above with REX is possible to improve the interaction between PLA and DBI that helps to reduce volatility.

3.4. Thermomechanical properties of plasticized PLA formulations

The dynamic-mechanic behaviour of the plasticized samples was observed by means of DMTA. The obtained DMTA curves are gathered in Fig. 7, while Table 6 summarizes the main parameters obtained by

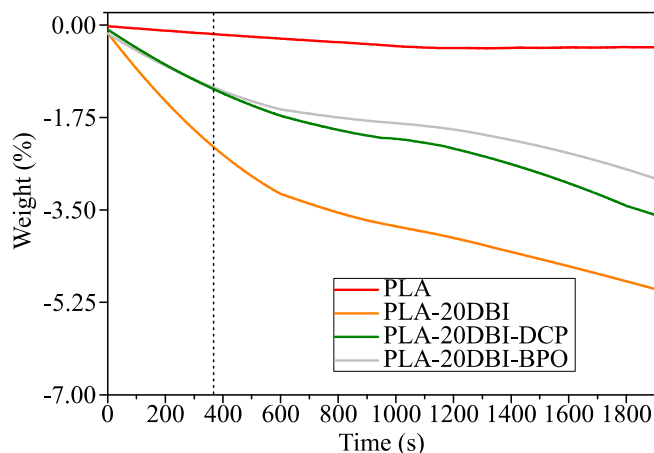


Fig. 6. Isothermal thermogravimetric curves of neat PLA and plasticized PLA formulations with DBI processed by conventional and reactive extrusion.

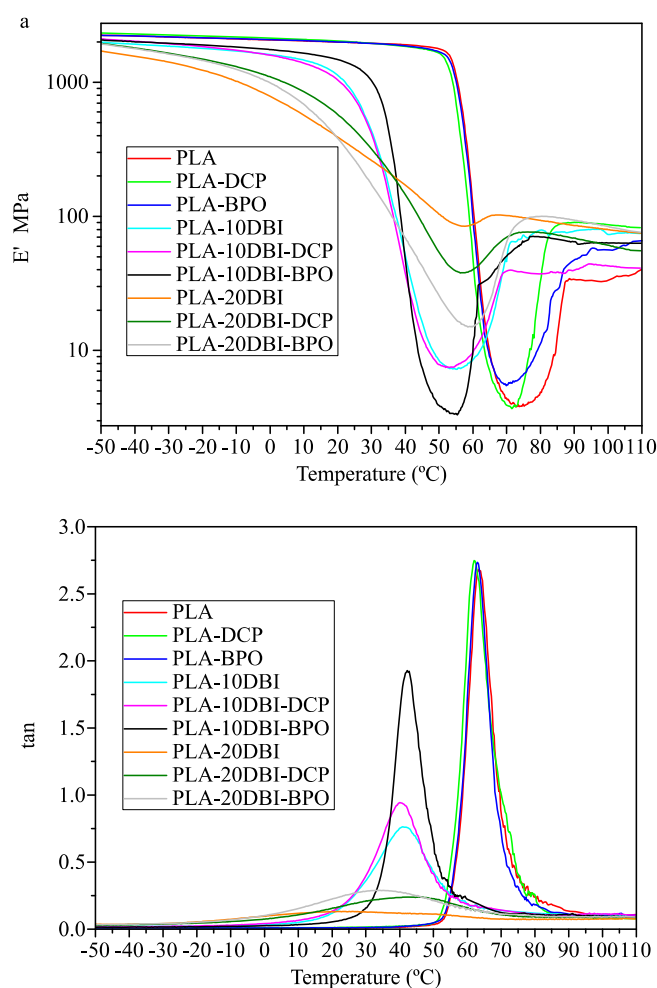


Fig. 7. Dynamic-mechanical thermal analysis (DMTA) curves of neat PLA and plasticized PLA formulations with DBI processed by conventional and reactive extrusion. a) storage modulus (E') vs temperature; b) dynamic damping factor ($\tan \delta$) vs temperature.

DMTA analysis. The evolution of the storage modulus (E') as a function of temperature is shown in Fig. 7a. A typical DMTA curve for PLA starts at low temperatures, with a glassy state region up to temperatures close to T_g . Close to this temperature, E' decreases by three orders of

Table 6

Summary of DMTA properties of neat PLA and plasticized PLA formulations with DBI processed by conventional and reactive extrusion: glass transition temperature (T_g), dynamic damping factor ($\tan \delta$) and storage modulus (E') at different temperatures.

Code	T_g (°C)	$\tan \delta$ peak height	$\tan \delta$ peak FWHM ^a (°C)	E' at -20 °C (MPa)	E' at 25 °C (MPa)	E' at 100 °C (MPa)
PLA	63.7 ± 1.2	2.68 ± 0.05	8.7 ± 0.4	2137 ± 20	1997 ± 19	42 ± 5
PLA-DCP	62.2 ± 1.0	2.73 ± 0.03	9.9 ± 0.4	2216 ± 27	1995 ± 17	84 ± 6
PLA-BPO	63.1 ± 1.3	2.73 ± 0.06	8.1 ± 0.5	2139 ± 29	1990 ± 16	62 ± 8
PLA-10DBI	41.4 ± 0.8	0.75 ± 0.04	20.5 ± 0.8	1782 ± 21	805 ± 9	74 ± 4
PLA-10DBI-DCP	40.6 ± 0.9	0.94 ± 0.04	17.4 ± 0.9	1841 ± 18	760 ± 9	40 ± 5
PLA-10DBI-BPO	42.4 ± 1.1	1.92 ± 0.03	20.5 ± 0.9	1901 ± 23	1322 ± 14	63 ± 7
PLA-20DBI	29.3 ± 1.2	0.13 ± 0.02	84.3 ± 1.5	1228 ± 16	320 ± 6	78 ± 5
PLA-20DBI-DCP	45.5 ± 0.8	0.23 ± 0.03	54.3 ± 1.3	1480 ± 18	442 ± 8	56 ± 4
PLA-20DBI-BPO	34.2 ± 0.7	0.29 ± 0.02	52.7 ± 1.4	1451 ± 15	252 ± 6	77 ± 5

^a FWHM: full-width at half-maximum from the $\tan \delta$ peak.

magnitude, leading to a glass transition region that is followed by a first rubbery plateau, in which the minimum E' values are measured. After that, the cold crystallization allows an increase of E' , due to the rearrangement of PLA chains to a packed structure, which gives increased resistance. Once the cold crystallization comes to an end, the E' stabilizes, and second rubbery plateau is observed. Finally, if the temperature increases, close to the melting process, E' tends to null values [71]. As seen in Fig. 7a, neat PLA shows an almost invariable E' value in the glassy state region, up to temperatures close to 60 °C. Above 60 °C, a clear decrease in E' can be clearly detected (glass transition region), thus changing from a glassy to a rubbery state [72]. Despite the different criteria to assess the T_g by DMTA, the most widely used criterion is the peak maximum of the dynamic damping factor, $\tan \delta$ (Fig. 7b). This effect emerges as an α -relaxation process and appears at temperatures around 66 °C, as reported by Olmedo-Martinez et al. [73]. At 80 °C, a recovery of the E' to higher values can be observed, which is attributable to the cold crystallization process taking place above this temperature, as observed by DSC. This effect was also observed by Feng et al. for neat PLA [74]. It is worthy to note that neat PLA and all PLA formulations plasticized with DBI processed by conventional and reactive extrusion show this cold crystallization phenomenon. This is due to the fact that samples were manufactured by injection molding: during this process, a fast-cooling rate is applied to the samples, thus limiting the crystallization ability of the samples [75].

Plasticization of PLA with DBI leads to a decrease in the E' at low temperatures, as expected, since plasticization gives a reduction of stiffness. This effect was also reported by Jia et al. [76], in PLA formulations plasticized with PEG. At room temperature, the effect of the plasticizer is a clear decrease of the stiffness, due to increased chain mobility. Nevertheless, with the increase of the temperature, the plasticized PLA formulations are ready to be packed, thus giving a higher degree of crystallinity, as observed in DSC. As a result, the plasticized PLA formulations exhibit a higher stiffness at 100 °C.

Another noticeable change that can be observed by DMTA is the decrease in the peak maximum of the dynamic damping factor, $\tan \delta$. As mentioned above, this peak is related to an α -relaxation attributable to the T_g of the material. As previously observed by DSC, the amount of DBI considered in each formulation allowed to progressively reduce the T_g of PLA. This trend is also observed by DMTA. Another effect of the plasticizer on the $\tan \delta$ peak is the change in its width and height. While neat PLA offers a sharp peak with a high $\tan \delta$ peak value, the addition of DBI leads to broader peaks with lower $\tan \delta$ values, as can be seen by the full-width at half-maximum (FWHM) values of the corresponding peaks reported in Table 6. This phenomenon allowed the samples to acquire a ductile behaviour at temperatures that are slightly below than T_g , since the change from a glassy to a rubbery state occurs in a wider temperature range. This effect was also observed by Llanes et al. [77], in PLA formulations plasticized with dibutyl fumarate.

Neat PLA subjected to REX with peroxides shows no significant differences with regard to PLA processed by conventional extrusion. For REX samples without plasticizer, the differences were not highly

noticeable, since the higher difference arises by its higher ability to crystallize, as already observed in DSC. DMTA allows identifying an interesting effect of REX on plasticized PLA formulations. The plasticized PLA formulation containing 20 wt% DBI, processed by conventional extrusion, shows a T_g of 29.3 °C, while this is increased to values of 45.5 °C, and 34.2 °C by REX with DCP, and BPO, respectively. Brüster et al. [34], observed similar phenomenon on plasticized PLA with myrcene. While the T_g of the PLA containing 20 wt% myrcene led to a T_g of 54.3 °C, REX provided a slight increase in T_g up to values of 57.1 °C. This effect was also highlighted by the Kfoury et al. [50], by using 2, 5-bis(tert-butylperoxy)-2,5-dimethylhexane to carry out reactive extrusion of PLA with different plasticizers derived from PEG. As they propose, the increase of the height of $\tan \delta$ peak was promoted by the grafting of the plasticizer to PLA backbone.

3.5. Disintegration of plasticized PLA formulations with DBI

All the developed formulations were subjected to a disintegration test following ISO 20200:2015 and the obtained results are summarized in Fig. 8 in terms of weight loss. Fig. 9 gathers some images showing the appearance of the samples during the test. PLA is known by its ability to biodegrade or disintegrate under composting conditions. During composting, the presence of water initiates a random chain scission process, due to the ester groups that are very sensitive to hydrolysis. Hydrolysis promotes the cleavages of the ester group, and as a result the carboxylic end groups contribute to self-catalyzing the hydrolysis process. The effect of the microorganism also plays an important role, since the chains up to 10 kDa can be metabolized, leading to an enzymatic degradation yielding H₂O, CO₂, and humus [78]. In Fig. 8, the two degradation stages

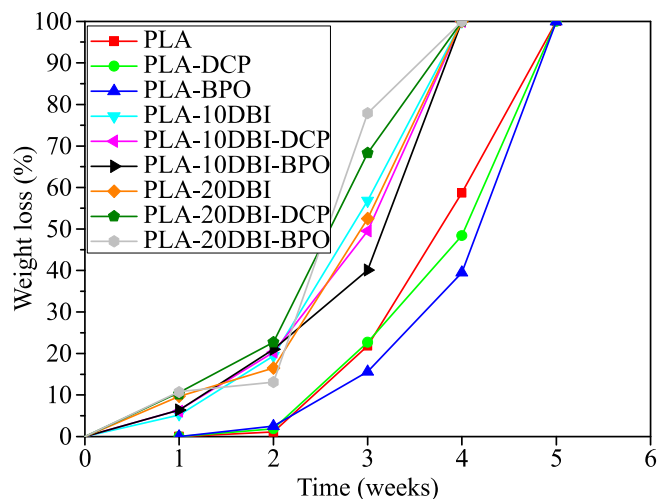


Fig. 8. Weight loss as a function of time (weeks) during the disintegration test of neat PLA and plasticized PLA formulations with DBI processed by conventional and reactive extrusion.

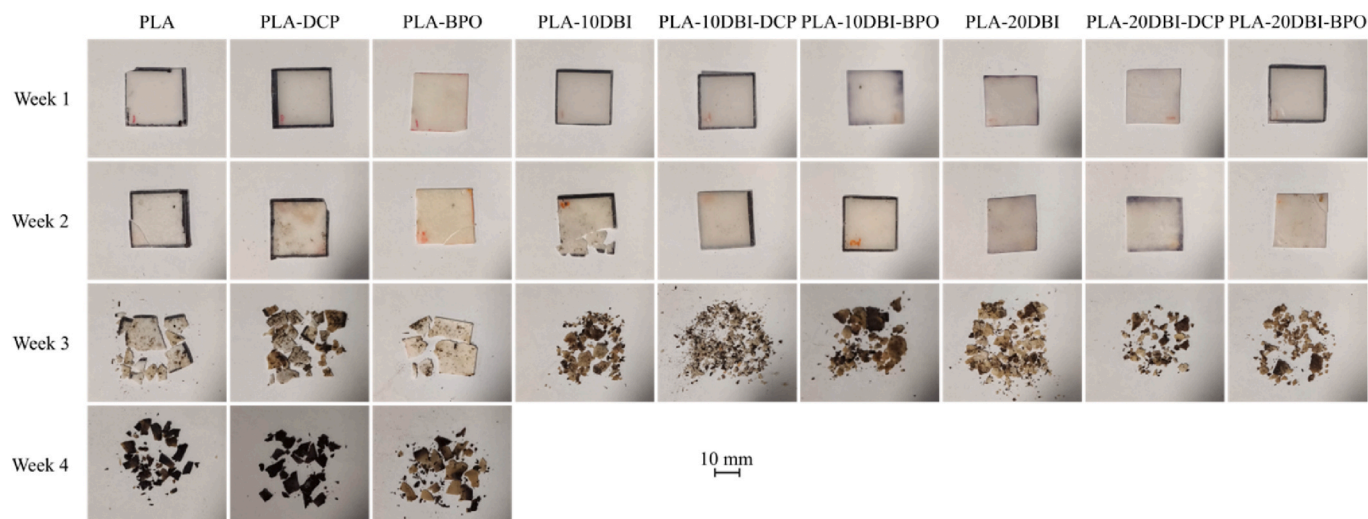


Fig. 9. Visual aspect during disintegration test as a function of elapsed time in weeks for neat PLA and plasticized PLA formulations processed by conventional and reactive extrusion.

can be observed; during the first two weeks the weight loss is not noticeable, after two weeks of composting the weight reduction is more pronounced.

The obtained results show that PLA can be completely disintegrated in less than 5 weeks under simulated compost conditions. The disintegration time can be reduced by plasticization with DBI, as the plasticized formulations took less than 4 weeks to be fully disintegrated. The plasticizer modification of the internal structure of the samples allow to increase the water diffusion rate, allowing water to enter inside the sample and promoting the hydrolytic degradation of the sample [79]. Despite the effects of REX are very interesting in terms on mechanical properties, increase in T_g and improved thermal stability, REX has low effect on disintegration rate. Some authors propose that the lower degrees of crystallinity of the samples enhance the disintegration of the samples. Highly crystalline regions of packed the polymer chains made the scission of the chains more difficult than in the amorphous regions, as proposed by Sedničková et al. [80]. In this regard, the unplasticized formulations with the peroxides show a lower weight loss at week 4 than the neat PLA, since degree of crystallinity calculated by DSC is higher in these samples.

3.6. Water uptake-plasticizer migration properties of plasticized PLA formulations with DBI

Fig. 10 gathers the sample's weight change during immersion in distilled water for 15 weeks. In general terms, two different behaviors can be observed: on the one hand, the water molecules can enter the polymer structure thus leading to a weight gain, while on the other hand, plasticizer migration to the water could also occur, with the subsequent weight loss. Both processes are overlapped and the amount of plasticizer and the use of conventional vs reactive extrusion play a key role in which phenomenon is predominant. The typical behaviour during this test is an increase in weight due to the water absorption of the samples. Despite PLA has a mainly hydrophobic behaviour, an increase of weight up to 0.7% is observed after 8 weeks. The water uptake rate under the immersion (distilled water at 25 °C) is low. To increase the water uptake rate, it is necessary to increase the temperature, as it happens in composting conditions at temperatures close to 60 °C [78].

Plasticized PLA formulations containing 10 wt% DBI, processed by either conventional or reactive extrusion, showed a similar behaviour during all the test, despite the higher degree of crystallinity as observed in DSC. Porfyrís et al. analyzed the water uptake for semi-crystalline and amorphous PLA grades, showing that the amorphous grade tends to

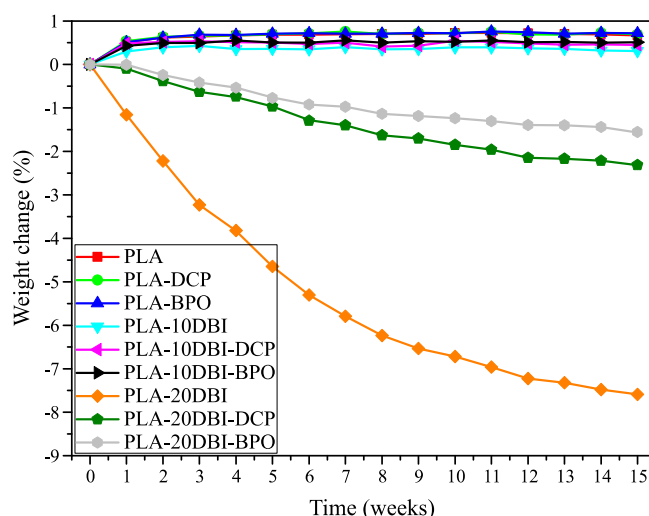


Fig. 10. Water uptake as a function of elapsed time in weeks during the water uptake test.

absorb more water than the semicrystalline, since the water uptake mainly occurs in the amorphous regions [81]. The introduction of 10 wt % DBI led to a reduction of the water uptake capacity. Values of 0.4% and near 0.5% for those with peroxides were obtained after week 3, after that some weight loss was observed. It is important to bear in mind that both weigh gain (water uptake), and weight loss (plasticizer migration), overlap, so that, even if plasticized PLA formulations show a decrease in the water uptake, it is more correct to say that the overall result coming from both mechanisms is a decrease in the weight gain compared to PLA. As reported by DSC, the plasticizer increased the degree of crystallinity, so the extent of amorphous region able to absorb water is reduced. In addition, Arrieta et al. reported that limonene in PLA increased the hydrophobic behaviour of the sample, limiting the affinity with water, thus the water uptake is reduced [82].

A clear different behaviour of the samples is observed for the samples with 20 wt% DBI, with a clear weight loss, suggesting that plasticizer migration is more intense than water uptake mechanism. The weight loss of these formulations appears from the first week, so the loss is related with a DBI migration to water. Due to the high amount of plasticizer contained in the PLA matrix, the plasticizer can migrate to water. For the PLA-20DBI sample, the weight loss at week 15 is 7.6% and the trend

followed by the sample suggests that higher weight can be lost with a longer immersion time. For samples containing 20 wt% DBI subjected to REX with both peroxides, this phenomenon is less pronounced, which is a positive effect, since limited plasticizer migration suggests that plasticizer has been chemically anchored to the PLA backbone. Similar behaviour was reported by Sirisinha et al. [83], by following the hydrolytic degradation of PLA in a sodium phosphate buffer at 70 °C. Under these conditions, PLA lost around 55 wt% after 30 days, but the plasticized PLA formulations with PEG showed a weight loss of 65% for the same period. In addition, they reported the positive effect of a copolymerization by reactive extrusion, that allowed to reduce the weight loss during the hydrolytic degradation.

4. Conclusions

We have demonstrated that reactive extrusion (REX) process of polylactide (PLA) is a process suitable to tune the overall performance of plasticized formulations. This ester of itaconic acid named dibutyl itaconate (DBI) contains a carbon-carbon double bond suitable for reactive extrusion by introduction of peroxides as dicumyl peroxide (DCP) and benzoyl peroxide (BPO), that act as radical initiators. Mechanical properties are improved in terms of tensile strength, while ductile properties are maintained. The plasticizer efficiency is showed by the T_g reduction from 62.2 °C (neat PLA) to values below 40 °C, the REX only promote a small increase of this parameter as showed in DSC and DMTA. Thermal degradation behavior of the plasticized samples is improved by REX with an increase of the initial degradation temperature. During the immersion of the samples in water, weight loss was observed in formulations with 20 wt% DBI, due to plasticizer migration, even if the improved interaction with DBI chains reduced this trend.

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Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Juan Ivorra-Martinez reports financial support was provided by Spain Ministry of Science and Innovation. Jaume Gomez-Caturla reports financial support was provided by Spain Ministry of Science and Innovation. Nestor Montanes reports financial support was provided by Spain Ministry of Science and Innovation. Nestor Montanes reports financial support was provided by Government of Valencia. Luis Quiles-Carrillo reports financial support was provided by Polytechnic University of Valencia.

Data availability

Data will be made available on request.

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