

## Assessment of non-ester monoterpenoids as biobased plasticizers for polylactide with improved ductile behaviour

R. Tejada-Oliveros, J. Gomez-Caturla<sup>\*</sup>, O. Fenollar, N. Montanes, J. Ivorra-Martinez, D. Garcia-Garcia

*Instituto de Tecnología de Materiales (ITM), Universitat Politècnica de València (UPV), Plaza Ferrándiz y Carbonell 1, 03801, Alcoy, Alicante, Spain*

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### ABSTRACT

Poly(lactide) (PLA) is a biodegradable aliphatic polyester derived from renewable resources. This material is characterized by high strength and stiffness; however, it has a high brittleness which makes it difficult to use in certain applications. In the present work, the plasticizing effect of different non-ester monoterpenoids, namely carvone, citral, citronellal and eucalyptol, on the mechanical, thermal, morphological, physical and chemical properties of PLA has been studied. In this case, different amounts (10 and 20 wt%) of each monoterpenoid were mixed with PLA in a twin-screw extruder and standardized samples were obtained by injection molding. The obtained results show how the addition of 20 wt% of the different monoterpenoids significantly improves the elongation at break of PLA, reaching values of 335.7 % for 20 wt% citral content, which represents an increase of about 4044 % with respect to pure PLA (8.1 %). In addition, a significant reduction in the tensile strength and Young's modulus of PLA has also been observed with the presence of monoterpenoids. The addition of monoterpenoids also leads to a decrease in the glass transition temperature and crystallization temperature of PLA due to the increased mobility of the polymeric chains caused by the plasticizing effect of the monoterpenoids, this decrease being more noticeable in the case of citral and citronellal, which are the monoterpenoids with the highest miscibility with PLA. Finally, it has been observed that the addition of monoterpenoids hardly affects the transparency of PLA, obtaining materials that may have a high potential in sectors such as food packaging. Therefore, it has been demonstrated that these non-ester monoterpenoids, especially citral, have a great potential to obtain environmentally friendly PLA formulations with improved toughness.

### 1. Introduction

During the last few years, the use of biopolymers as a sustainable alternative to the use of petrochemical-based plastics has increased. These biopolymers have a lower carbon footprint than commodity plastics and some of them may even have properties similar to those of the plastics most commonly used nowadays. Within the group of biopolymers, poly(lactide) (PLA) is currently the most commercially used polymer. According to European Bioplastics, it is estimated that during 2022, global PLA production was of 444,000 tons, representing 20.7 % of global biopolymer production, which was 2.22 million tons. In addition, it is estimated that by 2027 PLA production will reach 2.39 million tons, accounting for 37.9 % of global biopolymer production [1].

PLA is a bio-based, biodegradable, compostable and biocompatible aliphatic polyester derived from renewable resources such as corn, sugar cane or rice [2]. PLA can be synthesized by two routes, by

polycondensation of lactic acid or by ring-opening polymerization (ROP) of the lactide monomer [3,4]. This biopolymer is characterized by good mechanical properties, such as high stiffness and tensile strength, good transparency, good moisture resistance, good processability and if it is modified with the use of plasticizers it can possess barrier properties similar to polyethylene terephthalate (PET) [5–7]. This allows PLA to be used in a wide range of applications in different sectors, such as medicine, automotive, agriculture and textile industry [8,9]. However, PLA is very brittle at room temperature, with elongation at break of less than 10 %, partly due to its high glass transition temperature, which is around 60 °C [10]. The high brittleness of PLA limits its use in applications requiring a certain ductility, such as food packaging, where a high elongation is required [11].

In order to improve the ductility of PLA without affecting its biodegradability, different approaches have been proposed. One of them is the physical blending with other biodegradable ductile polymers such

<sup>\*</sup> Corresponding author.

E-mail address: [jaugoca@epsa.upv.es](mailto:jaugoca@epsa.upv.es) (J. Gomez-Caturla).

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as poly( $\epsilon$ -caprolactone) (PCL) [12,13], poly(butylene succinate) (PBS) [14], poly(butylene succinate-co-adipate) [15] or thermoplastic starch (TPS) [16,17]. However, the lack of total miscibility between polymers restricts the ability to improve the ductile properties of PLA. Another commonly used techniques to improve the ductile properties of PLA without affecting its environmental issues is plasticization with biobased compounds. Plasticizing is the most economical and simplest technique to improve the flexibility, processability and ductility of PLA. Plasticizers generally lead to an increase in the elongation at break of the polymer as a result of increased polymer chain mobility and a decrease in the glass transition temperature. There are a large number of studies in which biobased plasticizers such as citrates [18–20], tartrates [21], modified vegetable oils [22–24], oligomers of lactic acid [25,26], cinnamate esters [27], among others, have been successfully used to improve the ductile properties of PLA.

Terpenoids (isoprenoids) are organic compounds with great content of essential oils, present in many plants and flowers [28]. These compounds have a chemical structure consisting mainly of repeating isoprene units but, in contrast to terpenes, which are simple unsaturated hydrocarbons, they have oxygen-containing functional groups [29]. Functional groups present in terpenoids include alcohol (linalool, isopulegol, geraniol, citronellol or menthol), ketone (pulegone, piperitone, carvone and camphor), phenol (thymol and carvacrol), aldehyde (citral and citronellal) or ether groups (eucalyptol) [30–32]. Terpenoids are classified into different groups depending on the number of isoprene units in the molecule. One of the best known and most studied groups of terpenoids are monoterpenoids, whose structure consists of two isoprene units, with a total of 10 carbon atoms (C10) [29]. Monoterpenoids can be divided into three subgroups depending on their structure: aliphatic (citral, linalool, geraniol or lavandulol), monocyclic (thymol, menthol, eucalyptol or perylaldehyde) and bicyclic (camphor, borneo,  $\alpha$ - and  $\beta$ -pinene or thujone) [33]. These compounds are characterized by their strong aroma and odour as well as their antioxidant, antifungal, antibacterial, antiviral and antiparasitic properties [31, 33–35]. This makes monoterpenoids widely used as active ingredients in agricultural, pharmaceutical, cosmetic and food applications [36]. This fact, altogether with their structure as unsaturated molecules with reactive functional groups, gives monoterpenoids great potential to be used not only as functional compounds, but also as plasticizers in polymers. Currently there are few research studies in which non-ester monoterpenoids have been used as plasticizing agents for PLA. One of these studies was carried out by Celebi and Gunes [37], in which they studied the effect of the addition of different amounts of thymol and carvacrol (5, 10, 15 and 20 wt%) on the properties of PLA. The results obtained showed the effectiveness of terpenoids as a plasticizer as their incorporation into PLA resulted in a remarkable increase in the elongation at break of PLA from 2.9 % to 431.4 % and 417.4 % for PLA samples plasticized with 20 wt% carvacrol and thymol respectively. In addition, they also observed a decrease in the glass transition temperature and melting temperature of PLA with the presence of both monoterpenoids. However, the effectiveness of the use of ester-type terpenoids as plasticizers of aliphatic polyesters, such as PLA [38,39] or poly(3-hydroxybutyrate) (PHB) [40,41], has been shown to be effective.

The main objective of this work is to improve the ductility of PLA by using different non-ester monoterpenoids as potential biobased plasticizers, in order to obtain a more flexible PLA that can be used in different sectors, thus expanding its range of possibilities, and without affecting its sustainability. More specifically, in this study, the effect of the addition of different amounts (10 and 20 wt%) of carvone, citral, citronellal and eucalyptol on the mechanical, thermal, morphological, optical and chemical properties of PLA has been studied. In this context, plasticizers such as citral, citronellal and eucalyptol have hardly ever been combined with PLA as plasticizers in order to make more ductile polymer parts. Some studies have been made regarding the development of films, whereas there is no evidence of extrusion and injection moulded parts with this blends. Additionally, different amounts of plasticizer

are used, which amplifies the scope of the study and helps to better determine which amount of plasticizer is suitable for optimal effects in PLA.

## 2. Experimental

### 2.1. Materials

Poly(lactide (PLA) pellets grade Luminy® L130 ( $M_w = 242.31 \text{ g mol}^{-1}$  and a density of  $1.24 \text{ g cm}^{-3}$ ) were supplied by Total Corbion (Gorinchem, The Netherlands). All monoterpenoids used, R(-)-carvone (purity 98 %), citral (purity 95 %) citronellal (purity  $\geq 93.5 \%$ ), and eucalyptol (purity 99 %), were supplied from Sigma Aldrich (Madrid, Spain). The main characteristics and chemical structure of the monoterpenoids used as plasticizer for PLA are shown in Table 1.

### 2.2. Theoretical solubility parameters of PLA and monoterpenoids

The solubility parameter provides a theoretical estimation of the miscibility between a polymer and the different plasticizers used. In this case, the solubility parameter ( $\delta$ ) of PLA and the different non-ester monoterpenoids used as plasticizers have been obtained using the group contribution method proposed by Hoftyzer and Van Krevelen [42]. According to this method, the solubility parameter ( $\delta$ ) can be obtained as the sum of three components, which are related to the partial contribution to the total solubility parameter of the dispersion forces ( $\delta_d$ ), the polar forces ( $\delta_p$ ), and hydrogen bonding ( $\delta_h$ ) (Eq. (1)):

$$\delta^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \quad (1)$$

The equations proposed by Hoftyzer and Van Krevelen (Eqs (2)–(4)) were used to calculate the partial contributions of the solubility parameter:

$$\delta_d = \frac{\sum F_{di}}{V} \quad (2)$$

$$\delta_p = \frac{\sqrt{\sum F_{pi}^2}}{V} \quad (3)$$

$$\delta_h = \frac{\sqrt{\sum E_{hi}}}{V} \quad (4)$$

Where  $F_{di}$  is the contribution of the group to the dispersion forces,  $F_{pi}$  is the contribution of the group to the polar forces,  $E_{hi}$  is the contribution of the group to the hydrogen bond energy and  $V$  is the molar volume of the compound.

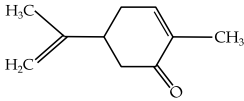
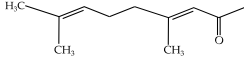
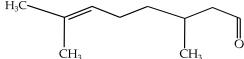
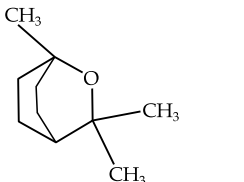
To obtain the theoretical miscibility between PLA and the different monoterpenoids, the solubility distance ( $R_a$ ) and the relative energy difference (RED) of all of them have been calculated using the following equations (Eq. 5-6):

$$R_a = \sqrt{4 \cdot (\delta_{d_{plast}} - \delta_{d_{PLA}})^2 + (\delta_{p_{plast}} - \delta_{p_{PLA}})^2 + (\delta_{h_{plast}} - \delta_{h_{PLA}})^2} \quad (5)$$

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

The  $R_a$  parameter represents the distance between the solubility coordinates of the plasticizer and the polymer, that is, how far apart the two compounds are in a 3D solubility space. Therefore, lower  $R_a$  values result in higher miscibility between them. The RED value is obtained by dividing the solubility distance ( $R_a$ ) by the interaction radius ( $R_0$ ), which determines the radius of the solubility sphere of a compound whose center is determined by the three solubility contributions. The RED parameter is indicative of the solubility between the two chemical compounds. If the RED value is 0, it indicates that the solubility parameters are the same and therefore the compounds are completely

**Table 1**  
Properties and structure of non-ester monoterpenoids used as plasticizers for PLA.

Monoterpenoid	Formula	Molecular weight (g mol <sup>-1</sup> )	Boiling point (°C)	Chemical Structure
Carvone	C <sub>10</sub> H <sub>14</sub> O	150.22	227–230	
Citral	C <sub>10</sub> H <sub>16</sub> O	152.23	229	
Citronellal	C <sub>10</sub> H <sub>18</sub> O	154.25	205–206	
Eucalyptol	C <sub>10</sub> H <sub>18</sub> O	154.25	176–177	

miscible. If the RED values are less than 1, both compounds will have high affinity and, therefore, a good miscibility, being higher as the value is closer to 0. If the value of RED is equal to 1, this indicates that both compounds are at the threshold of miscibility. Finally, RED values higher than 1 suggest poor miscibility between the compounds. In this case, for the RED parameter calculation between PLA and each of the monoterpenoids, the parameter  $R_0$  of PLA has been used which is 10.7 MPa<sup>1/2</sup> [43].

Table 2 shows the components of the solubility parameter and the solubility parameter calculated by the method proposed by Hoftyzer and Van Krevelen for PLA and the non-ester terpenoids, as well as the solubility distance ( $R_a$ ) and the RED parameter for each monoterpenoid with regard to PLA. As can be seen, the monoterpenoids used as plasticizers for PLA have a range of RED values between 0.65 and 0.90, these being less than 1, therefore a good miscibility between them and PLA could be expected. According to the obtained values, the terpenoid with the best miscibility with PLA is citral, followed by citronellal and carvone, while eucalyptol, with a higher RED value, 0.87, is theoretically the one with the lowest miscibility with the polymer. However, these results are theoretical, and the present work aims to corroborate them.

### 2.3. Sample processing

PLA pellets were dried in an air circulating oven for 12 h at 80 °C in order to remove moisture. Then, the PLA was first mixed manually in aluminum pots with 10 and 20 wt% of the different monoterpenoids. For the extrusion process, 30 g of each formulation were introduced in a 15-cc twin screw mini-extruder from Xplore Instruments BV (Sittard, The Netherlands). In this case, all formulations were mixed at 190 °C for 3 min at 180 rpm, as this extruder allows to recirculate the mixture internally in order to blend it well before extruding it. After this time, the material was discharged into the mold cavity placed in a microinjection

**Table 2**  
Theoretical solubility parameters, solubility distance ( $R_a$ ) and RED parameter of PLA and the different monoterpenoids used as plasticizers.

	$\delta_d$ (MJ/m <sup>3</sup> ) <sup>0.5</sup>	$\delta_p$ (MJ/m <sup>3</sup> ) <sup>0.5</sup>	$\delta_h$ (MJ/m <sup>3</sup> ) <sup>0.5</sup>	$\delta$ (MJ/m <sup>3</sup> ) <sup>0.5</sup>	$R_a$	RED
PLA	15.33	8.44	10.98	20.66	–	–
Carvone	15.91	4.92	3.58	17.03	8.28	0.77
Citral	16.48	4.69	5.14	17.89	7.31	0.68
Citronellal	16.02	4.43	4.99	17.35	7.34	0.69
Eucalyptol	14.23	2.39	4.23	15.04	9.33	0.87

machine from Xplore Instruments BV (Sittard, The Netherlands) in order to obtain standardized samples for further characterization. If more material was needed, another load of 30 g of the corresponding formulations was added, and the process repeated. Table 3 shows the composition of each formulation processed in this study.

### 2.4. Characterization techniques

#### 2.4.1. Mechanical properties

Tensile properties of the PLA and PLA plasticized with the different non-ester monoterpenoids were determined using an Ibertest ELIB 30 universal testing machine from S.A.E. Ibertest (Madrid, Spain) equipped with a 5 kN load cell according to ISO 527–2:2012. The tests were carried out at room temperature with an initial length of 50 mm and a crosshead speed of 20 mm min<sup>-1</sup>. At least five different specimens of each formulation were tested and the average values of the tensile strength, Young's modulus and elongation at break were calculated.

The impact absorbed energy of the samples was obtained following the guidelines of ISO 179:2010 using a Charpy test with a 6-J pendulum from Metrotec S.A. (San Sebastián, Spain). The absorbed energy of each formulation was calculated from the average of the energies obtained on 5 different notched specimens ("V" type at 45° and 0.25 mm notch radius). The notches were made using a HOYTOM BR.MT from HOYTOM (Bilbao, Spain) that allows to adjust the type of notch to be done in the sample. The sample is put in the machine and a saw-like device makes the notch in the position that the user has placed the sample in.

The shore D hardness of the different PLA formulations was determined following ISO 868:2003 with a durometer model 673-D from J. Bot S.A. (Barcelona, Spain). The hardness of each formulation was obtained from the average of 10 values taken at different points on various samples of each formulation.

#### 2.4.2. Differential scanning calorimetry (DSC)

Differential scanning calorimetry (DSC) tests of the different PLA formulations were carried out using a DSC Mettler-Toledo 821 calorimeter from Mettler-Toledo Inc. (Schwerzenbach, Switzerland) in nitrogen atmosphere with a flow rate 66 mL min<sup>-1</sup>. A triplicate analysis was performed on the different samples, which were subjected to a heating-cooling-heating cycle. The samples, weighing between 7 and 9 mg, were initially subjected to a heating cycle from 30 °C to 195 °C. Subsequently, they were cooled from 195 °C to –20 °C, and finally subjected to a second heating cycle from –20 °C to 220 °C, all of which were carried out at a constant rate of 10 °C min<sup>-1</sup>. During the second

**Table 3**

Composition and labelling of different formulations of PLA plasticized with different non-ester monoterpenoids.

Sample	Monoterpenoids content				
	PLA (wt.%)	Carvone (wt.%)	Citral (wt.%)	Citronellal (wt.%)	Eucalyptol (wt.%)
PLA	100	–	–	–	–
PLA/10CARVONE	90	10	–	–	–
PLA/20CARVONE	80	20	–	–	–
PLA/10CITRAL	90	–	10	–	–
PLA/20CITRAL	80	–	20	–	–
PLA/10CITRONELLAL	90	–	–	10	–
PLA/20CITRONELLAL	80	–	–	20	–
PLA/10EUCALYPTOL	90	–	–	–	10
PLA/20EUCALYPTOL	80	–	–	–	20

heating cycle, the glass transition temperature ( $T_g$ ), the cold crystallization peak temperature ( $T_{cc}$ ), the cold crystallization enthalpy ( $\Delta H_{cc}$ ), the melting peak temperature ( $T_m$ ) and the melting enthalpy ( $\Delta H_m$ ) of each formulation were obtained. Finally, the crystallinity ( $X_c$ ) of the PLA in each sample was determined using the following equation (Eq. 7):

$$X_c (\%) = \frac{\Delta H_m - \Delta H_{cc}}{\Delta H_m^0 \cdot (1 - w)} \times 100 \quad (7)$$

where  $\Delta H_m$  ( $J g^{-1}$ ) and  $\Delta H_{cc}$  ( $J g^{-1}$ ) represent the melting and cold crystallization enthalpies of PLA, respectively,  $\Delta H_m^0$  ( $J g^{-1}$ ) is the theoretical value of a fully crystalline PLA, that is,  $93.7 J g^{-1}$  [44], and  $1-w$  indicates the weight fraction of PLA in the analyzed sample.

#### 2.4.3. Thermogravimetric analysis (TGA)

Thermal degradation of PLA and different PLA formulations plasticized with different non-ester monoterpenoids were carried out by thermogravimetric analysis using a TG-DSC2 thermobalance from Mettler-Toledo (Columbus, OH, USA). During the analysis, samples with a weight between 5 and 7 mg were subjected to a heating cycle ranging from 30 °C to 600 °C with a heating rate of 10 °C  $min^{-1}$  under nitrogen atmosphere with a flow rate 66 mL  $min^{-1}$ . From the TGA curves of each sample, the onset degradation temperature ( $T_0$ ), defined as the temperature at which the sample loses 5 % of its mass, as well as the residual mass were obtained. Furthermore, the maximum degradation temperature ( $T_{max}$ ) for each sample was determined by analyzing the peak of the first derivative (DTG).

#### 2.4.4. Dynamic mechanical thermal analysis (DMTA)

Dynamic mechanical thermal analysis (DMTA) of the PLA and PLA plasticized with different non-ester monoterpenoids were performed on a Mettler-Toledo DMA1 (Columbus, OH, USA) using a single cantilever mode at a constant frequency of 1 Hz, with an amplitude of 10  $\mu m$ . Rectangular samples with a size of  $20 \times 6 \times 3 mm^3$  were subjected to a temperature sweep program from  $-50$  °C up to 100 °C at a constant heating rate of 2 °C  $min^{-1}$ . Parameters such as storage modulus ( $E'$ ) and dynamic damping factor ( $\tan \delta$ ) were determined as a function of increasing temperature. In addition, glass transition temperatures ( $T_g$ ) were obtained from the temperature of the maximum peaks of the  $\tan \delta$  curves.

#### 2.4.5. Field emission scanning electron microscopy (FESEM)

Plasticizing effect of non-ester monoterpenoids on PLA microstructure was analyzed using a ZEISS ULTRA 55 field emission scanning electron microscope (FESEM) from Oxford instruments (Abingdon, United Kingdom) operated at a voltage of 2 kV. Prior to testing, the fracture surface at room temperature of the impact samples of each formulation was coated with a thin layer of gold-palladium alloy under an argon atmosphere in an EMITECH sputter coating SC7620 model from Quorum Technologies, Ltd. (East Sussex, UK).

#### 2.4.6. Attenuated total reflection-fourier transform infrared spectroscopy (ATR-FTIR)

The chemical structure of PLA and PLA plasticized with the different non-ester monoterpenoids were analyzed using a Bruker S.A Vector 22 spectrometer (Madrid, Spain) equipped with a PIKE MIRacle™ single reflection diamond ATR accessory (Madison, Wisconsin, USA). The FTIR analysis of the samples was performed by 20 scans with a spectral resolution of 4  $cm^{-1}$  in the wavelength range of 4000 to 600  $cm^{-1}$ . Subsequently, the obtained spectra were adjusted to the baseline and normalized to a limiting ordinate of 1 absorbance unit.

#### 2.4.7. Static contact angle measurements

An optical goniometer model FM140 (110/220 V, 50/60 Hz) from KRÜSS GmbH (Hamburg, Germany) equipped with a video capture kit and analysis software (Drop Shape Analysis SW21; DSA1) was used to measure the static contact angle ( $\theta$ ) with water of PLA and PLA samples plasticized with different non-ester monoterpenoids. To obtain the contact angles, five drops of distilled water were deposited on the surface of the different samples with a microsyringe at room temperature. Ten measurements were taken from each drop 30 s after depositing it on the samples and an average value of the contact angle was obtained for all of them.

#### 2.4.8. Color properties

The color change in PLA due to the addition of the different non-ester monoterpenoids was studied in a Konica CM-3600d Colorflex-DIFF2 colorimeter from Hunter Associates Laboratory, Inc. (Virginia, USA) calibrated using a standard white tile. Color coordinates on the CIE  $L^*a^*b^*$  scale were obtained for each sample, where  $L^*$  represents the luminance, indicating the change between black ( $L^* = 100$ ) and white ( $L^* = 0$ ),  $a^*$  represents the coordinate from green ( $a^* < 0$ ) to red ( $a^* > 0$ ), and  $b^*$  represents the coordinate from blue ( $b^* < 0$ ) to yellow ( $b^* > 0$ ). At least five measurements were taken at random positions of different samples of each formulation and the average values were calculated. The yellowness index (YI) for each sample was calculated according to ASTM E313. The color difference between PLA and samples plasticized with the different non-ester monoterpenoids was calculated using the following equation (Eq. 8):

$$\Delta E = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2} \quad (8)$$

where  $\Delta L^*$ ,  $\Delta a^*$  and  $\Delta b^*$  are the differences between the corresponding color parameters of the plasticized samples and the color parameter values of the PLA ( $L^* = 37.8$ ,  $a^* = -0.18$ ,  $b^* = 1.07$ ).

## 3. Results and discussion

### 3.1. Mechanical properties of plasticized PLA with different non-ester monoterpenoids

Tensile mechanical properties are one of the main indicators of the plasticizing effect of a compound. Fig. 1 shows the tensile mechanical

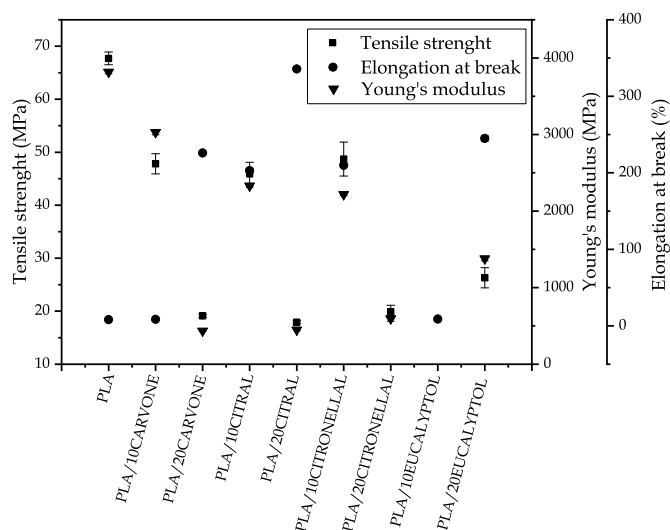


Fig. 1. Tensile test parameters obtained for PLA and PLA plasticized with different monoterpenoids.

properties of PLA and PLA plasticized with different non-ester monoterpenoids. As it can be seen, PLA has a tensile strength of 67.7 MPa, a Young's modulus of 3818 MPa and an elongation at break of only 8.1 %. These values show the stiffness and brittleness of neat PLA. The addition of the different non-ester monoterpenoids leads to a decrease in the resistant mechanical properties (tensile strength and Young's modulus) and an increase in the ductile mechanical properties (elongation at break) of PLA, this behaviour being more noticeable in the samples plasticized with 20 wt% of the different monoterpenoids. This increase in the elongation at break of plasticized samples is due to the increase in the free volume between the polymer chains and the decrease in the intensity of the secondary bonds between them due to the plasticizers, which leads to a higher mobility of the chains [45].

With regard to tensile strength, Fig. 1 shows that the highest decrease occurs by plasticization with 20 wt% citral, which is the non-ester monoterpenoid that is most miscible with PLA as previously indicated (see Table 2), giving a tensile strength of 17.9 MPa, which represents a reduction with respect to pure PLA of around 74 %. On the other hand, it can be observed that the addition of eucalyptol, which is the non-ester monoterpenoid with the highest RED value of the compounds used in this study, has the lowest effect on tensile strength, obtaining values similar to those of pure PLA for contents of 10 wt%. The Young's modulus has a similar behaviour to the tensile strength. As it can be seen in Fig. 1, the addition of the non-ester monoterpenoids leads to a considerable reduction in the stiffness of the material (indicated by a decrease in Young's modulus value), which is more noticeable after the addition of 20 wt% of the different terpenoids. In this case, the formulations with the lowest Young's modulus are those in which 20 wt% carvone and 20 wt% citral have been used, with 435 and 449 MPa respectively, which means a decrease in stiffness with respect to neat PLA of around 89 % for both formulations. As with the tensile strength, the sample plasticized with 10 wt% eucalyptol hardly affects the Young's modulus, obtaining a similar value to pure PLA, around 3615 MPa. On the other hand, it can be observed how the addition of non-ester monoterpenoids to PLA gives rise to a noticeable increase in the elongation at break of the material, especially in those formulations in which 20 wt% of the different compounds have been added. In this case, the highest elongation at break is observed in the samples plasticized with 20 wt% citral and citronellal, reaching an elongation of 335.7 % and 305.6 % respectively, which represents a percentage increase compared to PLA of 4044.4 % and 3672.8 %. These results show the effectiveness of these non-ester monoterpenoids as plasticizers for PLA. Similar behaviour was observed by Boonruang et al. [46] by plasticizing

PLA with different amounts of monoterpenoids such as thymol and carvone.

From the results obtained in the tensile tests, it can be seen that the used non-ester monoterpenoids that provide the greatest plasticizing effect to PLA are citral and citronellal, which are the compounds that present the highest theoretical miscibility with PLA, as it can be seen in Table 2. On the other hand, the plasticizing effect of eucalyptol is significantly lower than monoterpenoids with aldehyde functional groups, being this monoterpenoid the one with the lowest miscibility with PLA. Therefore, the results obtained show that the efficiency of monoterpenoids as plasticizers is related to their miscibility with the matrix, noting that the higher the miscibility, its plasticizing effect is greater [47]. This is due to the fact that the higher the miscibility, the dispersion of the plasticizer in the matrix is more homogeneous, creating additional free volume and thus facilitating the mobility of the polymer chains, which leads to an increase in ductility [48]. The results presented here are comparable to results of typical rubber-toughened PLA formulations and it even surpasses some of those materials. Gigante et al. [49] showed a maximum elongation at break of 276 % for PLA/PBAT blends, using 20 wt% of PBAT. In this study, a maximum elongation at break of 335 % was obtained for 20 wt% of citral, thus proving the efficiency of these natural based plasticizers in competition with the traditional PLA blends with other ductile polymers.

The plasticizing effect of the different non-ester monoterpenoids can also be observed in mechanical properties such as Shore D hardness and impact absorbed energy (Charpy). As it can be seen in Table 4, the addition of the terpenoids in PLA results in a reduction of the Shore D hardness, this decrease being greater in the formulations with 20 wt% of the different terpenoids. In this case, the lowest Shore D hardness is reached for the sample plasticized with carvone, obtaining a value of 37.8, which means a reduction of hardness with respect to PLA close to 50 %, while the use of eucalyptol hardly affects the hardness of PLA, which corroborates the low plasticizing effect of PLA due to its lower miscibility with the matrix. On the other hand, Table 4 shows how the addition of 10 wt% of the different non-ester monoterpenoids hardly modifies the toughness of PLA, obtaining very similar impact energy absorption values to PLA. However, all samples with plasticizer contents of 20 wt% did not break after the impact test due to the high ductility achieved by the plasticizing effect of the selected plasticizers. These results are in accordance with the mechanical tensile characterization carried out previously, which corroborates the high efficiency of non-ester monoterpenoids for PLA plasticization.

### 3.2. Thermal properties of plasticized PLA with different monoterpenoids

The effect of the different terpenoids on the thermal properties of PLA has been studied by DSC and TGA. Fig. 2 shows the calorimetric curves obtained from the second heating cycle of PLA and PLA plasticized with different non-ester monoterpenoids while Table 5 shows the main thermal parameters obtained from these curves. As can be seen in the table, pure PLA has a glass transition temperature ( $T_g$ ) of 61.6 °C, a

Table 4

Shore D hardness and impact absorbed energy of PLA and PLA plasticized with different monoterpenoids.

Sample	Shore D Hardness	Impact energy ( $\text{kJ m}^{-2}$ )
PLA	76.6 ± 1.3	7.2 ± 0.22
PLA/10CARVONE	63.3 ± 2.1	7.4 ± 0.20
PLA/20CARVONE	37.8 ± 2.1	NB <sup>a</sup>
PLA/10CITRAL	70.0 ± 1.9	7.7 ± 0.17
PLA/20CITRAL	43.5 ± 1.5	NB <sup>a</sup>
PLA/10CITRONELLAL	68.9 ± 1.4	7.2 ± 0.31
PLA/20CITRONELLAL	45.5 ± 1.9	NB <sup>a</sup>
PLA/10EUCALYPTOL	74.1 ± 1.3	7.3 ± 0.11
PLA/20EUCALYPTOL	66.2 ± 1.2	NB <sup>a</sup>

<sup>a</sup> NB = not break.

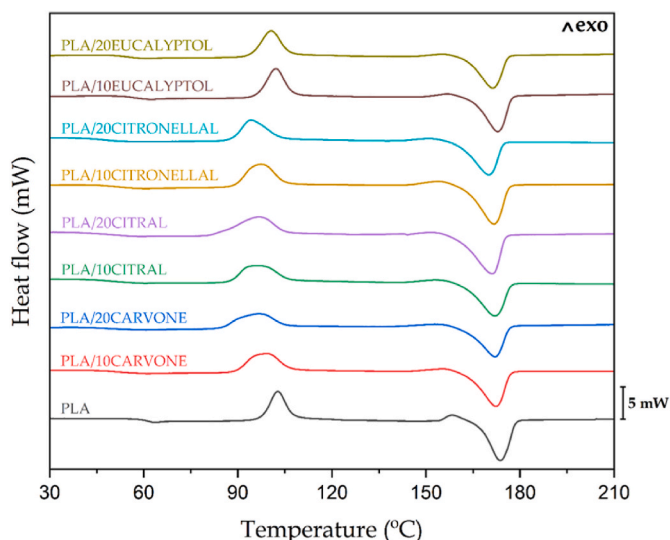


Fig. 2. Calorimetric curves of the second heating cycle of PLA and PLA plasticized with different non-ester monoterpenoids.

cold crystallization temperature ( $T_{cc}$ ) close to 103 °C and a melting temperature ( $T_m$ ) of 173.5 °C. The addition of terpenoids hardly affects the melting temperature of the material, obtaining for all formulations slightly lower values than those of pure PLA. However, it can be observed that  $T_g$  and  $T_{cc}$  decrease after incorporating the different plasticizers. This decrease in  $T_g$  and  $T_{cc}$  in plasticized samples is due to the different effects that they have on the internal structure of PLA. On the one hand, monoterpenoids increase the free volume between the polymer chains and give them a lubricating effect, resulting in a higher mobility of the polymer chains in the amorphous phase at lower temperatures. On the other hand, terpenoid-based plasticizers reduce the intensity of the secondary forces between the polymer chains, thus promoting their mobility [50]. In this case, it can be seen in Table 5 that the greatest decrease in  $T_g$  and  $T_{cc}$  with respect to pure PLA occurs in the samples plasticized with citral and citronellal. Specifically, it is observed that after the addition of these monoterpenoids, the  $T_g$  decreases by more than 10 °C and the  $T_{cc}$  by around 8 °C with respect to neat PLA. This higher decrease in temperatures is due to the higher miscibility of these compounds with PLA, which increases the mobility of the polymer chains. These results are in agreement with the higher plasticizing effect observed in the mechanical properties for these terpenoids. On the other hand, the monoterpenoid that has the least effect in the  $T_{cc}$  and  $T_m$  of PLA is eucalyptol, which is the plasticizer with the highest RED value and, therefore, the lowest miscibility with PLA.

With respect to the degree of crystallinity ( $X_c$ ), it can be seen in Table 5 that the addition of the different terpenoids hardly affects the crystallinity of PLA, obtaining crystallinity values similar to those of neat PLA in the plasticized samples. However, a slight increase in crystallinity can be seen in the sample plasticized with 20 wt% citral, in

which a crystallinity close to 16 % was obtained. This improvement in crystallinity is mainly due to the increased mobility of the polymer chains caused by the greater miscibility of this terpenoid with PLA. Gomez-Caturla et al. [38] observed a similar effect after incorporating 20 wt% of  $\alpha$ -terpinyl acetate into PLA, increasing from 5.2 % crystallinity of pure PLA to 17.3 % for the sample plasticized with the monoterpenoid. In this study, the real amount of plasticizer was lower than the nominal fraction of plasticizer used, therefore, it was the real amount that was used to calculate the crystallinity of the formulations (obtained by TGA).

The thermal stability of the samples studied in this work was obtained by thermogravimetric analysis (TGA). Fig. 3 shows the TGA curves and the first derivative of the TGA curves (DTG) of PLA and PLA plasticized with the different terpenoids. On the other hand, the main thermogravimetric parameters obtained from the curves, such as degradation onset temperature ( $T_0$ ), maximum degradation temperature ( $T_{max}$ ) and residual mass at 600 °C, are shown in Table 6. As can be seen in Fig. 3, the degradation of neat PLA takes place in a single stage, with a  $T_0$  of 354.3 and a  $T_{max}$  of 383.6 °C. After the addition of the terpenoids, the degradation of the samples is observed to occur in two stages, a first stage, between 150 and 250 °C, corresponding to the volatilization of terpenoids, and the second stage, between 350 and 450 °C, related to the degradation of the PLA polymeric chains. As it can be seen in Table 6, the addition of terpenoids in PLA results in a significant decrease in the degradation onset temperature ( $T_0$ ), being this reduction greater for formulations with a content of 20 wt% of the different plasticizers. This was expected due to the high volatility of terpenoids compared to PLA. This decrease in  $T_0$  in formulations plasticized with monoterpenoids is attributed to their low molecular weight and low boiling temperatures, which makes them highly volatile at low temperatures, causing their removal faster than polymeric chains [38]. In this case, the formulation with 20 wt% eucalyptol is the one with the lowest  $T_0$ , at around 172 °C, which means a decrease with respect to pure PLA at around 182 °C. This is due to the lower boiling point of eucalyptol compared to the other monoterpenoids. As shown in Table 1, eucalyptol has a boiling temperature of 176 °C while citral and carvone have the highest boiling points at around 230 °C, resulting in formulations plasticized with these monoterpenoids having higher degradation onset temperatures. In this case, processing of the PLA plasticized with 20 wt% eucalyptol leads to some plasticizer loss due to volatilization as TGA confirms. This loss of this terpenoid at the processing temperatures of the material together with its higher RED of 0.87 with regard to PLA may influence the lower plasticizing effect observed. Therefore, it is observed that the higher boiling temperature of the terpenoids leads to higher  $T_0$ . On the other hand, it is observed that the maximum degradation rate temperature ( $T_{max}$ ) of the formulations plasticized with the monoterpenoids are very similar to that of pure PLA, between 382 and 385 °C. Therefore, the addition of monoterpenoids does not influence on the thermal stability of PLA. This is probably due to the fact that at these temperatures the monoterpenoids have completely volatilized. This plasticizer loss is quite usual when monomeric plasticizers are used in PLA formulations. Llanes et al. [51] have reported this plasticizer loss during processing of

Table 5

Main thermal parameters of PLA and PLA plasticized with different non-ester monoterpenoids obtained by differential scanning calorimetry.

Sample	$T_g$ (°C)	$T_{cc}$ (°C)	$\Delta H_{cc}$ (J g <sup>-1</sup> )	$T_m$ (°C)	$\Delta H_m$ (J g <sup>-1</sup> )	$X_c$ (%) <sup>a</sup>
PLA	61.6 ± 1.6	102.8 ± 2.7	25.9 ± 2.1	173.5 ± 1.8	37.4 ± 1.9	12.4 ± 0.2
PLA/10CARVONE	51.3 ± 1.4	98.9 ± 2.0	25.1 ± 1.8	172.3 ± 1.4	35.2 ± 1.6	11.1 ± 0.2
PLA/20CARVONE	50.8 ± 1.3	95.9 ± 1.9	23.7 ± 0.6	171.9 ± 2.0	33.1 ± 1.5	11.4 ± 0.2
PLA/10CITRAL	48.4 ± 0.9	95.3 ± 2.2	27.3 ± 1.2	171.7 ± 2.1	36.6 ± 2.4	10.2 ± 0.3
PLA/20CITRAL	50.4 ± 1.1	96.9 ± 1.7	24.2 ± 1.5	170.8 ± 2.3	37.5 ± 1.9	16.2 ± 0.3
PLA/10CITRONELLAL	50.6 ± 0.9	97.2 ± 2.8	27.4 ± 2.0	171.3 ± 2.1	39.5 ± 2.6	13.3 ± 0.2
PLA/20CITRONELLAL	47.1 ± 1.2	94.2 ± 1.6	24.8 ± 1.3	169.8 ± 1.4	34.9 ± 1.1	12.3 ± 0.2
PLA/10EUCALYPTOL	56.5 ± 1.0	102.1 ± 2.0	27.8 ± 1.4	172.7 ± 2.0	36.4 ± 2.2	9.4 ± 0.3
PLA/20EUCALYPTOL	55.1 ± 1.7	100.6 ± 1.2	24.7 ± 1.6	171.0 ± 2.3	33.5 ± 1.8	10.6 ± 0.3

<sup>a</sup> Crystallinity was calculated according to the real plasticizer mass value obtained in TGA analysis.

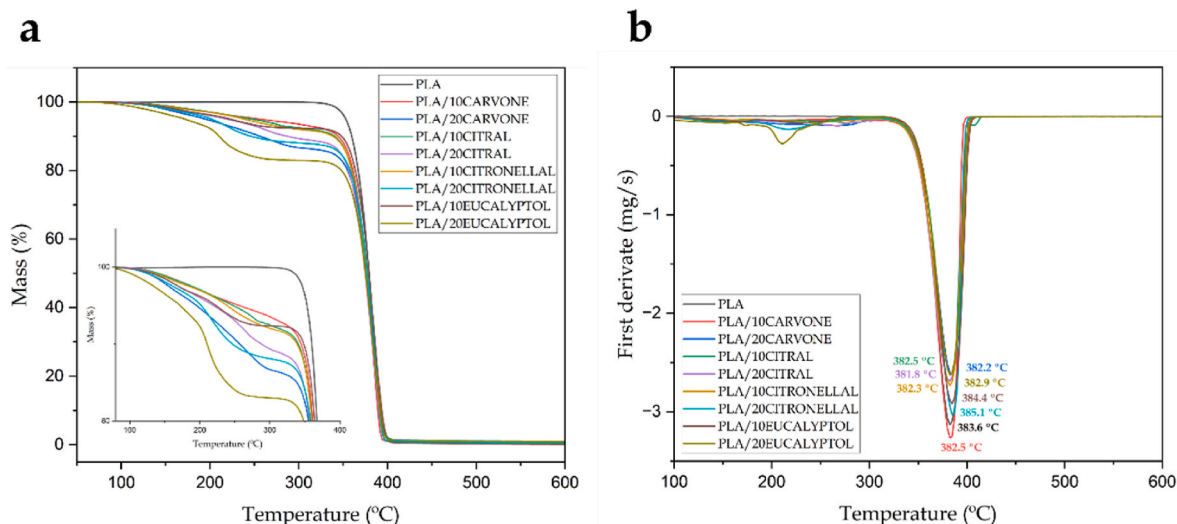


Fig. 3. Thermogravimetric curves (TGA) (a) and its first derivative (DTG) (b) of PLA and PLA plasticized with different non-ester monoterpenoids.

Table 6

Main thermal parameters of PLA and PLA plasticized with different monoterpenoids obtained by thermogravimetry.

Sample	$T_0$ (°C)	$T_{max}$ (°C)	Residual Mass (%)	Plasticizer real mass (wt.%) <sup>a</sup>
PLA	354.3 ± 3.3	383.6 ± 1.7	0.6 ± 0.1	–
PLA/10CARVONE	256.4 ± 2.3	382.5 ± 1.9	0.5 ± 0.1	9.4 ± 0.1
PLA/20CARVONE	195.6 ± 1.7	382.2 ± 1.6	0.6 ± 0.2	17.4 ± 0.2
PLA/10CITRAL	249.1 ± 1.8	382.5 ± 2.2	0.4 ± 0.1	9.3 ± 0.3
PLA/20CITRAL	221.2 ± 2.5	381.8 ± 2.3	0.4 ± 0.2	18.0 ± 0.5
PLA/10CITRONELLAL	240.0 ± 1.4	382.3 ± 1.9	0.3 ± 0.1	9.2 ± 0.4
PLA/20CITRONELLAL	202.6 ± 3.1	385.1 ± 1.9	0.5 ± 0.3	17.7 ± 0.2
PLA/10EUCALYPTOL	223.1 ± 1.4	384.4 ± 1.9	0.6 ± 0.3	9.2 ± 0.3
PLA/20EUCALYPTOL	172.4 ± 1.4	383.6 ± 1.9	0.7 ± 0.2	16.6 ± 0.7

<sup>a</sup> Real mass of the plasticizer in the formulations calculated at 290 °C.

PLA with dibutyl fumarate and dibutyl maleate isomers. They reported a 29 % plasticizer loss in plasticized formulations containing a nominal plasticizer content of 10.3 wt%, while this plasticizer loss was lower (of about 12 %) in samples plasticized with 14.3 wt% both fumarate and maleate. Even with this plasticizer loss attributable to volatilization during processing, the plasticization effects of the remaining molecules were remarkable, thus showing that good plasticization effects can be obtained with monomeric plasticizers even with some plasticizer loss. Arrieta et al. [52] have reported exceptional plasticization properties of a terpene, *i.e.* limonene on PLA, with an important plasticizer loss during processing thus corroborating the potential of these compounds as environmentally friendly plasticizers for PLA. Table 6 illustrates the plasticizer loss by reporting the real plasticizer amount in the formulation. As it can be seen, all plasticizers that had a nominal amount of 10 wt% present a real amount in the range 9.2–9.4 wt%, which implies a plasticizer loss of about 7 %. Whereas plasticizers with a nominal composition of 20 wt% present a real proportion between 16.6 and 18.0 wt%, which means a mass loss of about 13.5 %. It was observed that citral presented the lower mass loss, which corroborates its superior thermal stability. Finally, it is observed in Table 6 that the residual mass at 600 °C of all studied formulations is almost 0 %, which is indicative of

a total degradation of the components in the formulations.

### 3.3. Dynamic mechanical-thermal properties of plasticized PLA with different monoterpenoids

The dynamic mechanical-thermal properties of PLA and PLA samples plasticized with the different non-ester monoterpenoids have been obtained by DMTA. Fig. 4 shows the evolution of the storage modulus ( $E'$ ) and the dynamic damping factor ( $\tan \delta$ ) with respect to temperature. In addition, Table 7 shows the  $E'$  values of the formulations at different temperatures and the glass transition temperature ( $T_g$ ) of the formulations obtained from the maximum peak of the curves of  $\tan \delta$ . As it can be seen in Table 7, at low temperatures ( $-50$  °C) neat PLA presents a storage modulus of 2466 MPa, which remains almost constant up to 60 °C; above this temperature a dramatic decrease occurs in  $E'$ , which is associated with the glass transition temperature of PLA. Finally, at around 90 °C, a slight increase in the storage modulus is observed, this is ascribed to the cold crystallization of the samples at high temperatures, which induces an increase in the stiffness of the polymer chains. As observed in Fig. 4b, the glass transition peak seems to overlap with that induced by the cold crystallization resulting in a distorted (double) peak. This situation is not observed in almost all plasticized samples, since the decrease in  $T_g$  leads to a clear separation of these two phenomena, so that overlapping does not occur. After the addition of the plasticizers, it can be observed that at low temperatures ( $-50$  °C) the storage modulus of the samples decreases slightly with respect to PLA, although they still show high values, above 2000 MPa, except for the sample plasticized with 20 wt% eucalyptol, whose modulus at  $-50$  °C is 1636 MPa. This high modulus in the plasticized samples is due to the high stiffness of the polymer chains at this temperature. As the temperature increases, the storage modulus of the plasticized samples decreases, being this decrease more pronounced in the samples incorporating 20 wt% carvone, citral and citronellal, obtaining values of 369, 566 and 972 MPa respectively at 25 °C, which means a remarkable decrease in rigidity with respect to neat PLA, with a storage modulus of 2182 MPa at this temperature. This decrease in storage modulus with temperature is due to the increased mobility of the polymer chains in the amorphous regions due to the plasticizing effect of terpenoids, resulting in a higher free volume and a weakening of the interactions between polymer chains [27]. On the other hand, Fig. 4b and Table 7 show the glass transition temperatures of the different studied formulations (measured as the peak maximum of  $\tan \delta$ ). As can be seen, the addition of terpenoids leads to a clear decrease in the glass transition temperature of PLA, as observed by DSC. In this case, the lowest  $T_g$  is obtained for the sample

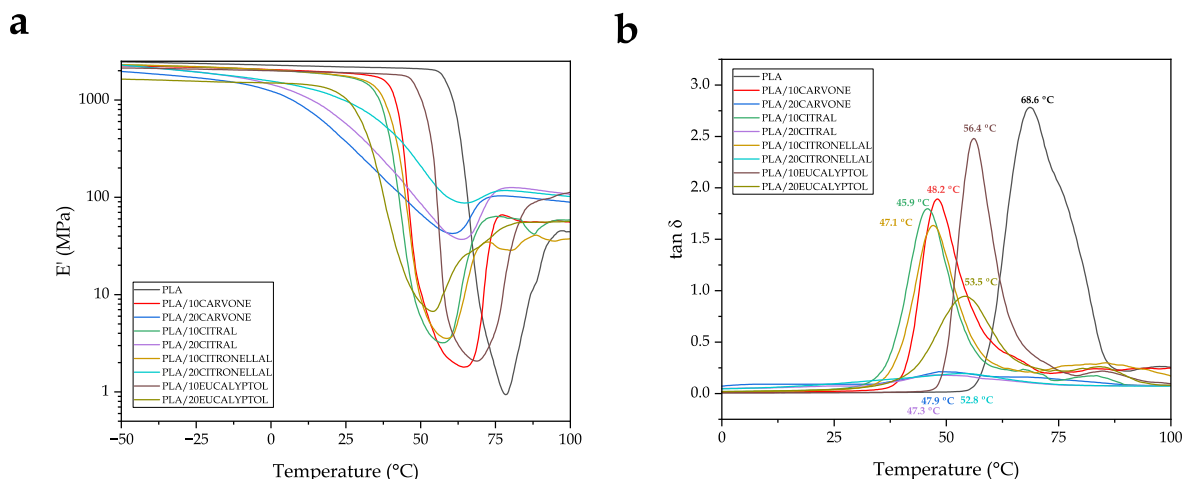


Fig. 4. Dynamic-mechanical-thermal curves of PLA and PLA plasticized with different monoterpenoids obtained by DMTA: a) storage modulus ( $E'$ ) and b) damping factor ( $\tan \delta$ ).

Table 7

Dynamic-mechanical-thermal properties of PLA and PLA plasticized with different non-ester monoterpenoids at different temperatures.

Sample	$E'$ (MPa) at -50 °C	$E'$ (MPa) at 25 °C	$E'$ (MPa) at 100 °C	$T_g$ (°C)
PLA	2466 ± 18	2182 ± 27	49.8 ± 2.5	68.6 ± 1.1
PLA/10CARVONE	2244 ± 29	1886 ± 16	55.7 ± 1.8	48.2 ± 0.8
PLA/20CARVONE	1963 ± 22	369 ± 28	88.6 ± 2.1	47.9 ± 1.3
PLA/10CITRAL	2296 ± 24	1730 ± 21	58.6 ± 2.7	45.9 ± 0.6
PLA/20CITRAL	2255 ± 18	566 ± 26	106.8 ± 3.1	47.3 ± 1.5
PLA/10CITRONELLAL	2303 ± 27	1763 ± 23	40.1 ± 0.9	47.1 ± 0.5
PLA/20CITRONELLAL	2281 ± 26	972 ± 17	101.6 ± 2.7	52.8 ± 1.8
PLA/10EUCALYPTOL	2133 ± 38	1906 ± 26	110.8 ± 3.2	56.4 ± 0.5
PLA/20EUCALYPTOL	1636 ± 23	1047 ± 30	56.6 ± 1.7	53.5 ± 1.7

plasticized with 10 wt% citral, where a  $T_g$  of 45.9 °C is obtained, which represents a decrease with respect to pure PLA of 22.7 °C. This is clear evidence of the plasticizing effect of the non-ester terpenoids used in this study, which has been corroborated by the mechanical properties obtained. Additionally, an increase in the width of the  $\tan \delta$  peak was observed in the samples with higher contents of plasticizer. This indicates a longer glass transition that allows the polymer to show great ductility in a wider temperature range than the pristine polymer. A very similar result was reported in previous studies for dibutyl itaconate [53].

### 3.4. Chemical structural properties of plasticized PLA with different monoterpenoids

The effect of the different monoterpenoids on the chemical structure of PLA was studied by FTIR-ATR. Fig. 5 shows the FTIR spectra of PLA and PLA plasticized with different amounts of the non-ester terpenoids. As can be seen, the typical IR absorbing bands of pure PLA can be observed in all plasticized samples. Among these absorption bands, those located at 868  $\text{cm}^{-1}$  and 754  $\text{cm}^{-1}$  are related to the  $\text{CH}_2$  group stretching vibrations. The band at 1043  $\text{cm}^{-1}$  is related to the symmetric stretching of the  $\text{C}-\text{CH}_3$  bond, and the band at 1081  $\text{cm}^{-1}$  is related to the  $\text{C}-\text{O}-\text{C}$  asymmetric stretching vibrations, while the band at 1180

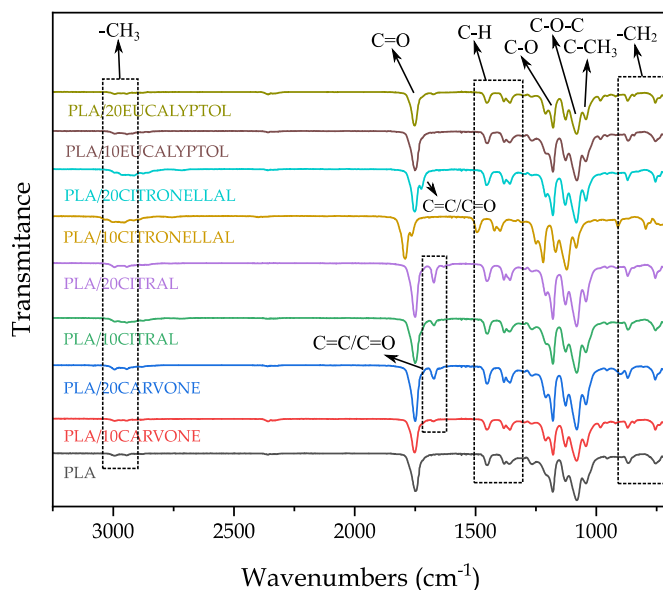


Fig. 5. FTIR spectra of PLA and PLA plasticized with different non-ester monoterpenoids.

$\text{cm}^{-1}$  is related to the  $\text{C}-\text{O}$  stretching vibrations of lactide units. A series of bands are also observed between 1300  $\text{cm}^{-1}$  and 1500  $\text{cm}^{-1}$ , which are attributed to symmetric and antisymmetric vibrations of the  $\text{C}-\text{H}$  bond in the methyl ( $\text{CH}_3$ ) groups. Another characteristic band can be seen at 1750  $\text{cm}^{-1}$  which is related to the  $\text{C}=\text{O}$  stretching. Finally, weak bands are observed at 2945  $\text{cm}^{-1}$  and 2995  $\text{cm}^{-1}$  attributed to asymmetric stretching vibrations of  $-\text{CH}_3$  groups [6,38]. The addition of the different monoterpenoids hardly affects the PLA spectrum, but some small changes are observed with some of them. As it can be seen in Fig. 5, the addition of citral and carvone leads to the appearance of a peak around 1672  $\text{cm}^{-1}$  which is related to the stretching vibration of the  $\text{C}=\text{O}$  group, which are in conjugation with  $\text{C}=\text{C}$  bonds, characteristics of these two plasticizers [54]. Furthermore, it can be observed that the intensity of the peaks related to the stretching vibration of  $-\text{CH}_2$  and  $-\text{CH}_3$  increases after the addition of these monoterpenoids [55]. This could mean that several molecules of plasticizer have reacted and bonded with PLA chains, increasing the concentration of methyl and  $\text{CH}_2$  groups in the chemical structure of the materials. These changes are more evident in the plasticized samples with 20 wt% of terpenoids. On



the other hand, in the sample plasticized with citronellal, a peak appears at around  $1724\text{ cm}^{-1}$  which is related to the stretching mode of  $\text{C}=\text{O}$  and a low intensity band at around  $2714\text{ cm}^{-1}$  related to aldehydic  $\text{C}-\text{H}$  stretching [56]. The peak at  $>1700\text{ cm}^{-1}$  could also be related to the  $\text{C}=\text{C}$  bonds in this plasticizer, which could be isolated or conjugated with  $\text{C}=\text{O}$  bonds [54]. All in all, the appearance of several peaks at  $\text{C}=\text{O}$  indicates the clear presence of the plasticizers in the formulation, which probably have bonded with the PLA chains.

### 3.5. Morphological properties of plasticized PLA with different non-ester monoterpenoids

The plasticizing effect of the selected terpenoids on PLA morphology was studied by FESEM. Fig. 6 shows the FESEM images of the fracture surfaces of pure PLA and PLA plasticized with different non-ester monoterpenoids. As can be seen, the unplasticized PLA sample (Fig. 6a) shows a flat and homogeneous surface, with no evidence of plastic deformation, which corresponds to a brittle fracture. After the addition of the terpenoid-based plasticizers, a remarkable change in the fracture surface can be observed, showing clear plasticization effects, except for the sample plasticized with 10 wt% eucalyptol (Fig. 6h), where a brittle fracture similar to that of neat PLA is observed, which corroborates the lack of plasticization for that amount of eucalyptol. This lack of plasticization is due to the lower miscibility between PLA and eucalyptol as noted by a high RED value. In the rest of the samples, a rough fracture can be seen, and in some of them small filaments of material can be observed, which is evidence of an increase in the ductility of the samples due to the plasticizing effect of terpenoids, as it was indicated by the increase in elongation at break in the mechanical properties section. This change in morphology can be seen most clearly in the samples plasticized with 20 wt% of citral and citronellal (Fig. 6e and g). In this case, the morphology of the samples agrees with what has

been observed in previous sections, which revealed that the addition of these terpenoids significantly improved the elongation at break of PLA. Moreover, the plasticizing effect observed by FESEM agrees with the solubility results obtained theoretically, as a higher plasticizing effect is observed for those monoterpenoids with lower RED parameters and contents of 20 wt%. Similar morphological changes have been observed by other authors after using biobased plasticizers, such as epoxidized oils [57,58], citrates [59], tartrates [21], and cinnamate esters [27] in PLA.

### 3.6. Contact angle of plasticized PLA with different monoterpenoids

Fig. 7 shows the water contact angle on the surface of PLA and PLA formulations plasticized with different monoterpenoids. This contact angle makes it possible to evaluate the effect of the different monoterpenoids on the hydrophobicity of PLA. As can be seen in Fig. 7a, PLA has a contact angle of  $68.9^\circ$ , being considered a hydrophobic material, since its contact angle with water is slightly higher than  $65^\circ$ , considered the threshold of hydrophobicity [60]. The incorporation of 10 wt% of the different terpenoids studied leads to an increase in the water contact angle, being this increase greater in the case of the sample plasticized with eucalyptol, with a contact angle of  $86.7^\circ$ . On the other hand, the addition of 20 wt% results in different behaviour depending on the monoterpenoid used. In the case of carvone and eucalyptol, the contact angle increases with respect to pure PLA, while the addition of 20 wt% citral and citronellal leads to a decrease in the hydrophobicity of the material, which is more pronounced in the case of citral, where a contact angle of  $55.5^\circ$  is obtained. Darie-Nita et al. [10] observed similar behaviour after incorporating different plasticizers, such as PLA oligomer, L-lactide, poly(ethylene glycol) and epoxidized soybean oil in PLA. This decrease may be due to the higher miscibility between these monoterpenoids and PLA and to the fact that these monoterpenoids,

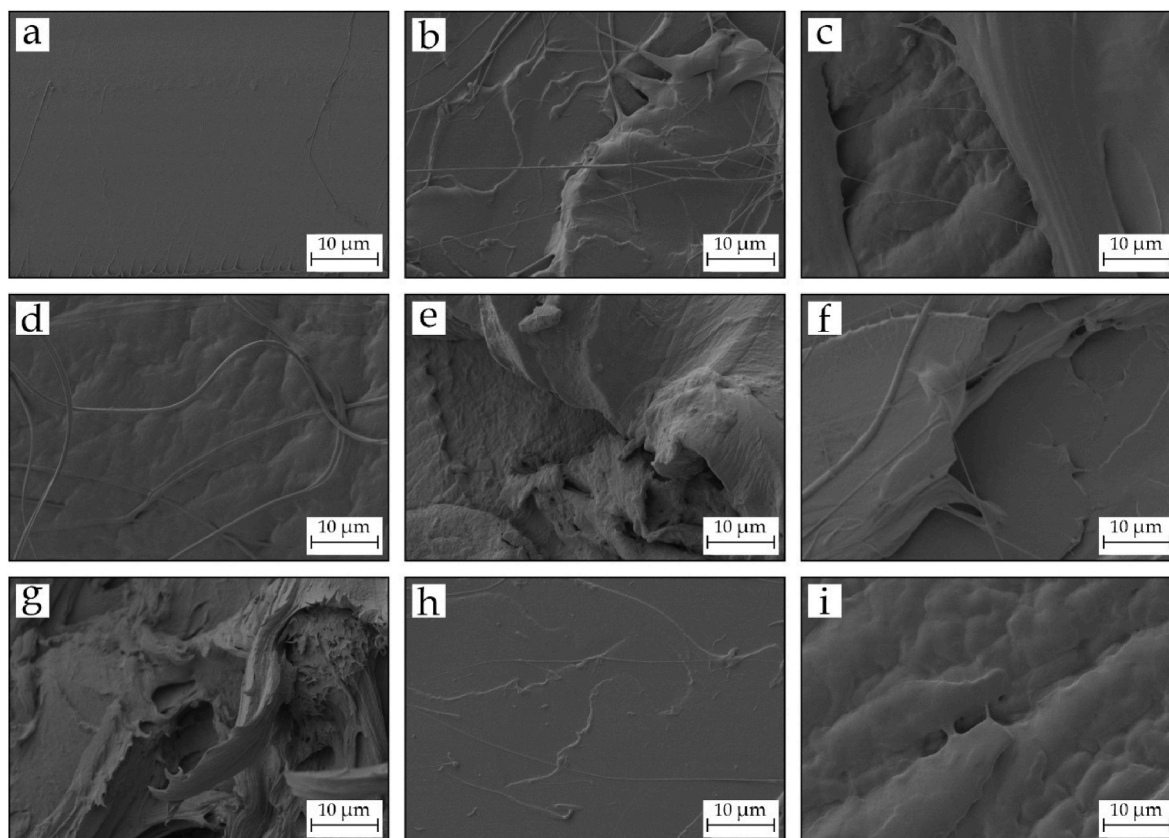


Fig. 6. FESEM micrographs at  $3000\times$  of PLA and PLA plasticized with different non-ester monoterpenoids: (a) PLA; (b) PLA/10CARVONE; (c) PLA/20CARVONE; (d) PLA/10CITRAL; (e) PLA/20CITRAL; (f) PLA/10CITRONELLAL; (g) PLA/20CITRONELLAL; (h) PLA/10EUCALYPTOL; (i) PLA/20EUCALYPTOL.

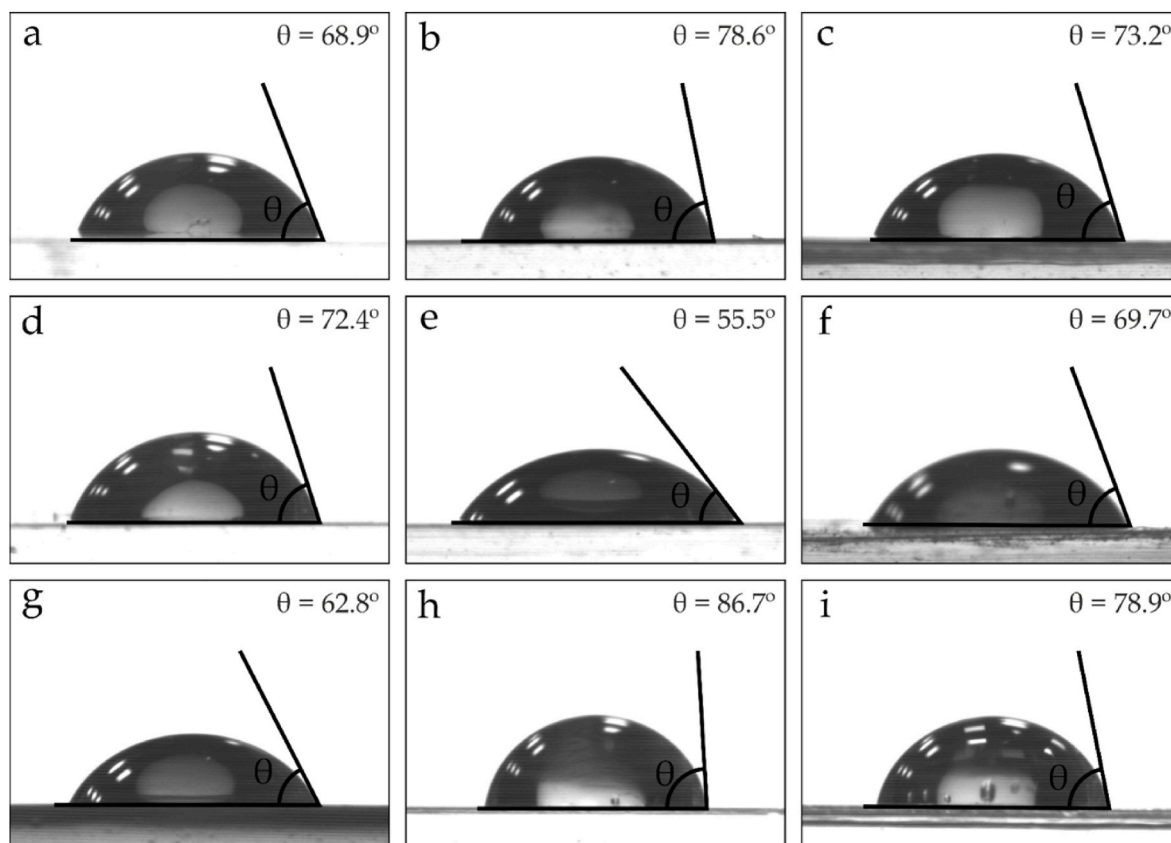


Fig. 7. Water contact angle on the surface of samples of PLA and PLA plasticized with different monoterpenoids: (a) PLA; (b) PLA/10CARVONE; (c) PLA/20CARVONE; (d) PLA/10CITRAL; (e) PLA/20CITRAL; (f) PLA/10CITRONELLAL; (g) PLA/20CITRONELLAL; (h) PLA/10EUCALYPTOL; (i) PLA/20EUCALYPTOL.

with the presence of aldehyde functional groups, introduce polar molecules (C=O) into PLA, which give rise to intermolecular interactions with water through hydrogen bonds, thus increasing the hydrophilicity of the samples [59].

### 3.7. Color properties of plasticized PLA with different monoterpenoids

The visual appearance of PLA and PLA samples plasticized with 10 and 20 wt% of the different non-ester monoterpenoids can be seen in Fig. 8. On the other hand, Table 8 gathers the color coordinates in CIE Lab space for each of the formulations developed as well as the

yellowness index and the total color difference ( $\Delta E$ ) of the plasticized samples with respect to PLA. One of the main properties of PLA is its transparency, which makes it interesting for use in certain applications such as food packaging [61]. Therefore, it is interesting to preserve this property after the addition of plasticizers. As can be seen in Fig. 8, the incorporation of the different terpenoids hardly affects the transparency of the samples. However, some changes in the color coordinates are noticeable after plasticizer addition. As can be seen in Table 8, after the addition of monoterpenoids, the luminance ( $L^*$ ) is hardly affected, obtaining values very similar to those of neat PLA, with slight variations. In this case, samples plasticized with citronellal have a slightly lower

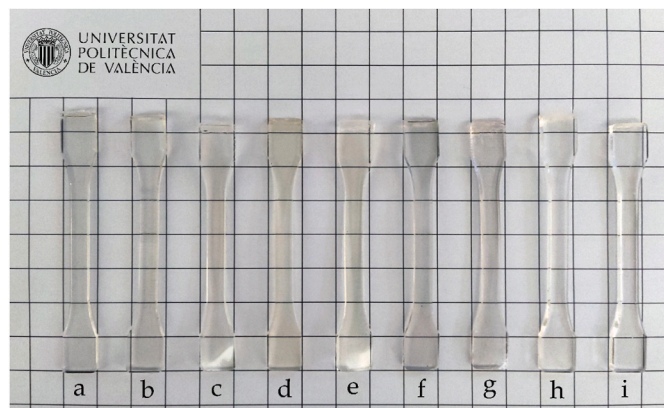


Fig. 8. Visual appearance of PLA and PLA plasticized with different monoterpenoids: (a) PLA; (b) PLA/10CARVONE; (c) PLA/20CARVONE; (d) PLA/10CITRAL; (e) PLA/20CITRAL; (f) PLA/10CITRONELLAL; (g) PLA/20CITRONELLAL; (h) PLA/10EUCALYPTOL; (i) PLA/20EUCALYPTOL.

Table 8

Luminance ( $L^*$ ), color coordinates ( $a^*b^*$ ), yellowness index (YI) and total color difference ( $\Delta E$ ) of PLA and PLA plasticized with different monoterpenoids.

Sample	$L^*$	$a^*$	$b^*$	YI	$\Delta L$
PLA	$37.8 \pm 0.02$	$-0.18 \pm 0.09$	$1.07 \pm 0.05$	$4.1 \pm 0.2$	–
PLA/10CARVONE	$37.3 \pm 0.05$	$-0.65 \pm 0.16$	$1.43 \pm 0.04$	$4.9 \pm 0.9$	0,77
PLA/20CARVONE	$37.4 \pm 0.16$	$-0.48 \pm 0.13$	$2.70 \pm 0.19$	$10.4 \pm 0.6$	1,70
PLA/10CITRAL	$41.1 \pm 0.04$	$-1.43 \pm 0.09$	$6.99 \pm 0.04$	$23.9 \pm 0.2$	6,89
PLA/20CITRAL	$37.2 \pm 0.03$	$-1.43 \pm 0.06$	$4.87 \pm 0.10$	$17.5 \pm 0.3$	4,05
PLA/10CITRONELLAL	$35.7 \pm 0.08$	$-0.15 \pm 0.10$	$1.41 \pm 0.13$	$5.8 \pm 0.6$	2,13
PLA/20CITRONELLAL	$35.8 \pm 0.08$	$0.35 \pm 0.10$	$1.49 \pm 0.13$	$6.9 \pm 0.2$	2,11
PLA/10EUCALYPTOL	$39.2 \pm 0.13$	$-0.42 \pm 0.25$	$1.09 \pm 0.14$	$3.8 \pm 0.5$	1,42
PLA/20EUCALYPTOL	$39.3 \pm 0.16$	$-0.34 \pm 0.11$	$0.85 \pm 0.17$	$3.0 \pm 0.7$	1,52

lightness than PLA, showing a darker shade in the samples, while samples plasticized with eucalyptol have a slightly higher lightness than PLA, resulting in a material with a higher brightness (Fig. 8). The  $a^*$  values of the plasticized samples are very similar to those of neat PLA, with a slight difference being observed in the samples plasticized with citral, where the  $a^*$  coordinate is slightly lower than that of PLA. However, the greatest difference is observed in the  $b^*$  values after incorporation of citral into PLA, leading to an increase in  $b^*$  values, which is indicative of the samples acquiring a more yellowish color. This is corroborated by the yellowness index (YI), which is used to determine the color change of a transparent sample to yellow [62]. In this case, it is also observed that the plasticized formulations with different percentages of citral are the ones with the highest YI values. This yellowish tone after the addition of citral is also clearly visible in Fig. 8. Moreover, as can be seen in Tables 8 and it is with citral that a greater color change occurs with respect to PLA, since with the rest of the monoterpenoids the color changes are almost negligible.

#### 4. Conclusions

In the present work, the potential of non-ester monoterpenoids as green plasticizers for PLA has been studied. Different amounts (10 wt% and 20 wt%) of carvone, citral, citronellal and eucalyptol have been incorporated into PLA, and their effects on the mechanical, thermal, chemical, physical, and morphological properties of the material have been studied. The addition of these non-ester monoterpenoids in PLA has resulted in a significant increase in elongation at break, especially for plasticizer contents of 20 wt%, due to an increase in chain mobility caused by the increase in free volume and the reduction of secondary interactions between the polymer chains. In this case, the greatest increase in ductility was obtained after the addition of 20 wt% citral and citronellal, which gave an elongation at break of 335.7 % and 305.6 % respectively, representing an increase of 4044.4 % and 3672.8 % compared to neat PLA (8.1 %). This plasticizing effect of the monoterpenoids was also reflected in a marked increase in the toughness of the samples plasticized with 20 % of the different monoterpenoids. Furthermore, with respect to the resistant mechanical strength properties, it could be observed that the addition of these non-ester monoterpenoids resulted in a reduction of the tensile strength and Young's modulus of PLA. Elongations at break similar or even superior to those of traditional rubber-toughened PLA formulations (such as PLA/PBAT blends). The thermal properties of PLA were also affected after the incorporation of the selected monoterpenoids. The thermal characterization by differential scanning calorimetry (DSC) showed how these compounds led to a noticeable decrease in the  $T_g$  and  $T_{cc}$  of PLA, being this reduction greater with those monoterpenoids that are more miscible with PLA, such as citral and citronellal, which reduced the  $T_g$  by around 10 °C and the  $T_{cc}$  by 8 °C with respect to neat PLA for both contents studied. The plasticizer mass loss due to volatility during processing was evaluated through TGA, which showed a mass loss between 7 and 13 %. Furthermore, it could be observed that the transparency and color of the PLA was hardly affected after the addition of these non-ester monoterpenoids. Among the terpenoids used in this study, the highest plasticizing effect on PLA has been achieved with citral and citronellal, which are the monoterpenoids with the lowest RED parameter and, therefore, the highest miscibility with PLA. On the other hand, it has been observed that eucalyptol, which has a RED parameter closer to 1, has the lowest plasticizing effect on PLA. Therefore, as it has been observed, non-ester monoterpenoids have a great potential as green plasticizers for PLA, which allow obtaining materials with high ductility and transparency without affecting the bio-based and biodegradable nature of the material. Moreover, this, together with the bioactivity of most of these non-ester monoterpenoids, makes these compounds of great interest for obtaining materials with applicability in sectors such as food packaging.

#### CRedit authorship contribution statement

**R. Tejada-Oliveros:** Investigation, Writing – original draft, Writing – review & editing. **J. Gomez-Caturla:** Investigation, Supervision, Visualization. **O. Fenollar:** Formal analysis, Visualization, Writing – original draft. **N. Montanes:** Project administration, Supervision, Validation, Writing – review & editing. **J. Ivorra-Martinez:** Methodology, Software. **D. Garcia-Garcia:** Conceptualization, Data curation, Supervision.

#### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### Data availability

Data will be made available on request.

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