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Characterization of PLA-limonene blends for food packaging applications

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Abstract

Polymers derived from renewable resources are now considered as promising alternatives to traditional petro-polymers as they mitigate current environmental concerns (raw renewable materials/biodegradability). d-limonene can be found in a variety of citrus, indeed is the main component of citrus oils and one of most important contributors to citrus flavor. The incorporation of limonene in PLA matrix was evaluated and quantified by Pyrolysis Gas Chromatography Mass Spectrometry (Py- GC/MS). Transparent films were obtained after the addition of the natural compound. Mechanical properties were evaluated by tensile tests. The effect of limonene on mechanical properties of PLA films was characterized by an increase in the elongation at break and a decrease in the elastic modulus. The fracture surface structure of films was evaluated by scanning electron microscopy (SEM), and homogeneous surfaces were observed in all cases. Barrier properties were reduced due to the increase of the chain mobility produced by the d-limonene.

Keywords: PLA; limonene; plasticizer; packaging.

1. Introduction

Polymers derived from renewable resources are now considered as promising alternatives to traditional petro-polymers as they mitigate current environmental concerns (raw renewable materials/biodegradability). It is widely accepted that the use of long-lasting polymers for short-term and disposable applications, such as packaging, is not entirely satisfactory [1]. As a result, the biopolymer industry is growing rapidly since biodegradables polymers made from

renewable resources have a less negative effect on the environment compared to the conventional petroleum based materials largely used in commodities [2].

Polylactide (PLA) is one of the most promising bio-based polyester for food packaging [1,2] because of its good mechanical, superior transparency, ease of processing and availability in the market [3]. In this sense, poly(lactic acid) (PLA) is one of the most attractive biopolymers with many short-term or disposable applications, such as disposable cutlery (plates, cups, lids and drinking straws), bags and film packaging [4, 5]. PLA is also widely used in rigid and flexible food packaging applications[6] since it has been approved by the US Food and Drug Administration (FDA) as a food contact substance [7, 8].. However, the use of PLA for food packaging is somewhat limited because of its poor ductility, thermal and oxygen barrier properties [3].

Recent studies have been conducted on the use of limonene as a new novel monomer to obtain polyterpenes [9]. d-limonene can be found in a variety of citrus, indeed is the main component of citrus oils and one of most important contributors to citrus flavor [10, 11]. Is the most abundant monocyclic monoterpene in nature and represents more than 90% of orange peel oil, being the most important residue in the citrus industry [12]. The limonene diffusion through packaging has been widely studied in different food contact materials such as polyethylene (PE)[13], low density polyethylene (LDPE)[14], high density polyethylene (HDPE), polystyrene (PS)[15] and PLA[15, 16]. Furthermore, the sorption of aroma compounds through packaging materials have been reported recently by Salazar et al., (2012)[17], who found a plasticization effect of PLA films by aroma compounds after the sorption studies.

For many practical food packaging applications, it is desirable to modify the polymer matrix and many modifications have been proposed to improve PLA's performance. It is widely known that PLA plasticization is required in order to improve ductility [18, 19]. Although the addition of plasticizer increases the PLA gas permeability, this could be detrimental for food packaging use [3] since polymer barrier properties are of fundamental importance for food packaging applications [20]. López-Rubio & Lagaron, (2009) reported that the addition of the β-carotene to PLA showed a significant plasticization of polymer matrix [21]. In addition, the control of light transmission through packaging is an important parameter to preserve and protect some food products until they reach the consumer. So, additives are require for transparent PLA films to block light transmission[22]. Furthermore, PLA modified with natural origin compounds has been proposed as active packaging [8, 23, 24]. In this way, Hwang et al., (2011) proposed PLA with added α-tocopherol and resveratrol

as promising active functional membranes [8]. Jamshidian et al., (2012) studied PLA with ascorbyl palmitate although they reported high loss of antioxidant during polymer preparation and negatives results on PLA transparency [24].

Polymer modifiers should be miscible with polymer matrix, so it becomes necessary to analyze the effects of the additives on the thermal stability of the modified PLA formulations. Thermal degradation is responsible for serious damage to many polymeric materials during processing and use under high temperature conditions [25] Therefore, it become necessary to study the incorporation of modifiers into polymer matrix with the effect dependig on the chemical nature of the molecules and their interaction.

The aim of this work is to evaluate the performance of PLA films when two concentrations (15wt% and 20wt%) of d-limonene were added to the PLA matrix to obtain sustainable films. The amount of limonene incorporated into PLA matrix was studied by thermogravimetric analysis (TGA) and also with pyrolysis coupled with gas chromatography and mass spectrometric detection (Py-GC/MS). In order to evaluate the applicability for flexible food packaging materials, optical, mechanical and oxygen barrier properties of PLA and PLA-limonene films were also assessed.

2. Experimental Procedures

2.1. Materials

Poly(lactic acid) pellets (PLA 4032D, M_n = 217000 Da, 2 wt% D-isomer) was supplied by NatureWorks LLC (USA). D-limonene (M_w= 136.24 g/mol) was provided by Acros Organic (USA). The chemical structures of PLA and limonene are provided in Fig. 1.

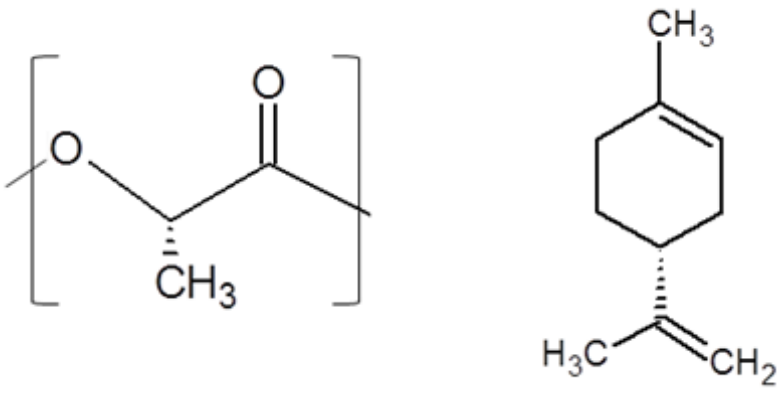

Figure 1. Chemical structures of PLA and limonene

2.2. Film preparation

The preparation of PLA with d-limonene was performed by adding limonene monomer to the PLA matrix. Since PLA is very hygroscopic, PLA pellets were previously dried in a vacuum oven at 60 ºC for 6 h. Blends were obtained by mixing PLA pellets and d-limonene in appropriate amounts, 15wt% or 20 wt% in a Haake Polylab mixer (Thermo Fischer Scientific Walham, USA). Samples were designated as PLA, PLA-Lim15 and PLA-Lim20. The melt mixing was performed at 180 ºC with 50 rpm rotor speed for 5 minutes for PLA pellets followed by 3 minutes after limonene addition. The blends were then molded into films at 170 ºC in a press (Mini C 3850, Caver, Inc. USA). The material was kept between the plates at atmospheric pressure for 5 minutes until melting and then submitted to the following pressure cycles, 3 MPa for 1 min, 5 MPa for 1 min, and 10 MPa for 3 min, with the aim of liberating the trapped air bubbles [19]. Film samples were then quenched at room temperature at atmospheric pressure.

2.3. FTIR analysis

Fourier transformed infrared spectroscopy (FTIR) measurements were carried out at ambient temperature in transmission mode by using a Perkin-Elmer Spectrum BX infrared spectrometer (Perkin–Elmer, Spain, S.L., Madrid Spain). Spectra were obtained in the 4000-600 cm^{-1} region, using 128 scans and 4 cm^{-1} resolution. A blank spectrum was obtained before each test to compensate for the humidity effect and the presence of carbon dioxide in the air by spectra subtraction.

2.4. Scanning Electron Microscopy (SEM)

Scanning electron microscopy (SEM) was used to observe the fracture surfaces morphology of the films samples generated from the tensile test in a Phenom SEM (FEI Company, Eindhoven, The Netherlands) using an acceleration voltage of 10 kV. Samples were covered with an Au layer in vacuum conditions prior to each measurement.

2.5. Thermogravimetric analysis

Thermogravimetric analysis (TGA) tests were carried out by using a TGA/SDTA 851 Mettler Toledo thermal analyzer (Schwarzenbach, Switzerland). Samples weighing around 5-10 mg were heated under dynamic mode. Measurements were performed at 10 ºCmin^{-1} from 30 to 600 ºC under nitrogen atmosphere (flow rate 50 mL min^{-1}) in order to prevent any thermoxidative degradation.

2.6. Py-GC/MS analysis

The amount of d-limonene incorporated into PLA films was measured by Py-GC/MS. Film samples were pyrolyzed with the use of a Pyroprobe 1000 instrument (CDS Analytical, Oxford, Pennsylvania, USA), which was coupled to a gas chromatograph (6890N, Agilent Technologies, Spain S.L., Madrid, Spain). The column used for the analysis was 30 m long HP-5 (0.25 mm thickness) using helium as carrier gas with a 50:1 split ratio. The GC oven was programmed at 40 ºC to 50 ºC by a stepped increase of 5 ºC min^{-1} and then the temperature was increased by 10 ºC min^{-1} to 300 ºC, where it was held for 5 min. For mass spectral detection Agilent 5973N mass selective detector was used. The transfer temperature from the GC to MS was set at 280 ºC. The mass selective detector was programmed to detect masses between 30 and 650 amu. Film samples were pyrolyzed at 1000 ºC for 0.5 s. The identification of PLA and PLA-limonene degraded products was confirmed by the characteristic fragmentation patterns observed in Py-GC/MS spectra or by comparison with literature mass spectra. The concentration of limonene incorporated into the film sample was determined from the peak area of the limonene component and by using the calibration curve from limonene standard solutions. The limit of detection (LOD), was calculated as three times the standard deviation which provided the signal-to-noise ratio in the lowest concentration standard, divided by slope of the calibration curve (LOD=3 SD/m). The slope (m) represents the sensitivity of the method. [26].

2.7. Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry (DSC) experiments were carried out in a TA Instrument Q100 calorimeter (New Castle, DE, USA). The heating and cooling rate for the runs was 10 ºCmin^{-1} in a nitrogen atmosphere, the typical sample weight was around 4 mg. Calibration was performed using an indium sample. The cycle program consisted in a first heating stage from -90 to 180ºC at a rate of 10ºC min^{-1}, followed by cooling to -90ºC and subsequent heating up to 200ºC at 10ºC min^{-1}. The glass transition temperature (T_g) was calculated from the first heating and was taken at the mid-point of heat capacity changes. The melting temperature (T_m) and cold crystallization temperature (T_{cc}) were obtained from the second heating, and degree of crystallinity (χ_c) was determined by using Equation 1, where ΔH_m is the enthalpy of fusion, ΔH_{cc} is the enthalpy of cool crystallization, ΔH_m^c is the heat of melting of purely crystalline PLA, taken as 93 J/g [27-31], and $1-m_f$ is the weight fraction of PLA in the sample

$$\chi_c = 100 \times \left[\frac{\Delta H_m - \Delta H_{cc}}{\Delta H_m^c}\right] \frac{1}{1-m_f} \qquad \text{Eq. 1}$$

2.8. Mechanical properties

Tensile tests were conducted at room temperature on an universal testing machine IBERTEST ELIB 30 (S.A.E. Iberstest, Madrid, Spain) according to the standard procedure UNE-EN ISO 527-3 [32]. Tests were performed on rectangular test pieces (10 mm x 100 mm), initial grip separation 50 mm, crosshead speed 5 mm min^{-1} equipped with a 5 kN cell.. Average percentage deformation at break (ε_B %), elastic modulus (*E*) and tensile strength (TS) were calculated from the resulting stress-strain curves as the average of five measurements from three films of each composition

2.9. Film color properties

Film color properties were evaluated measuring colour coordinates in the CIELAB colour space L* (lightness), a* (red-green) and b* (yellow-blue) were analyzed using a KONICA CM-3600d COLORFLEX-DIFF2, HunterLab, Hunter Associates Laboratory, Inc, (Reston, Virginia, USA). The instrument was calibrated with a white standard tile. Measurements were carried out in quintuplicate at random positions over the film surface. Average values for these five tests were calculated. Total color differences (ΔE), induced by limonene incorporation, with respect to the control PLA film was evaluated (Equation 2). The yellowness index (YI) was also measured.

$$\Delta E = \sqrt{\Delta a^2 + \Delta b^2 + \Delta L^2} \qquad \text{Eq. 2}$$

2.10. Oxygen permeability measurement

The oxygen transition rate (OTR) measurements were accomplished using an oxygen permeation analyzer from Systech Instruments-Model 8500 (Metrotec S.A, Spain) at a pressure of 2.5 atm. Measurements were conducted at room temperature. Films were clamped into the diffusion chamber and pure oxygen (99.9% purity) was then introduced into the upper half of the sample chamber while nitrogen was injected into the lower half of the chamber where there was an oxygen sensor. Measurements were done in triplicate and were expressed as oxygen transmission rate per film thickness (OTR.e). Thickness was measured at 25 ºC

using a Digimatic Micrometer Series 293 MDC-Lite (Mitutoyo, Japan) accurate to 0.001 mm from 10 readings taken at random positions over the 14 cm diameter circle films.

2.11. Wettability

Water contact angle measurements were performed at room temperature with an EasyDrop Standard goniometer FM140 (KRÜSS GmbH, Hamburg, Germany) equipped with a camera and analysis software (Drop Shape Analysis SW21; DSA1). The contact angle was measured by randomly putting 10 drops of distiller water (2 µl) on the surface film with a syringe. Five measurements were carried out for each sample an average values were calculated.

3. Results and Discussion

Fig. 2, shows the visual appearance of pure PLA films and PLA films with 15 wt% and 20 wt % of Limonene. The films have good transparenty even at high limonene concentrations; therefore limonene has not any effect on the transparency of the PLA.

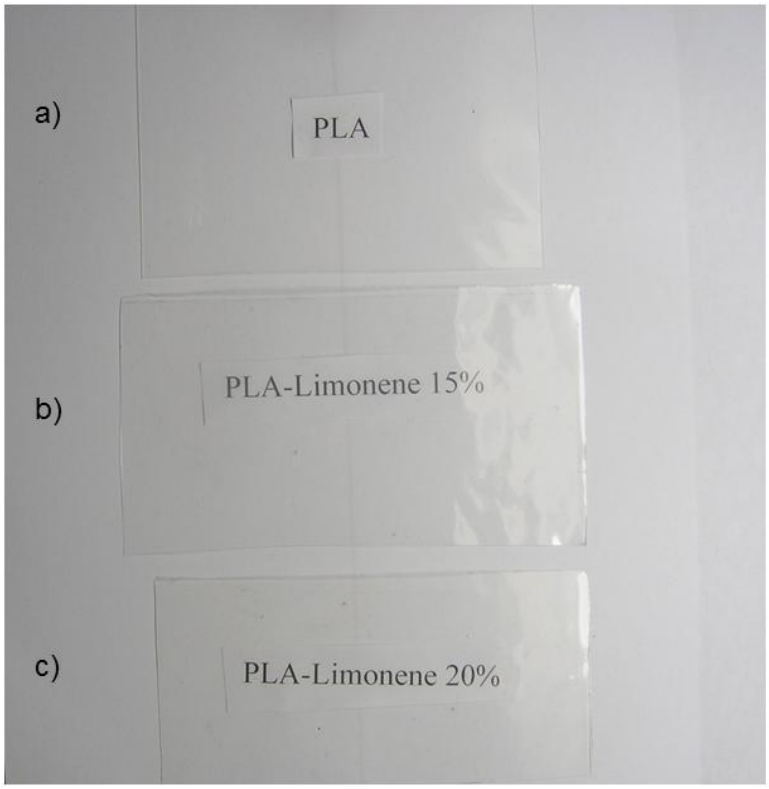

Figure 2. Visual appearance of films: a) PLA, b) PLA-Limo15 and c) PLA-Lim20

3.1. FTIR

FTIR spectra were recorded for PLA and PLA-Limonene films in order to investigate the chemical structure of the films and to study the characteristic peaks of the blend. The spectra are showed in Fig. 3, being arbitrarily offset for comparison. The spectrum region between 3000 cm^{-1} and 2860 cm^{-1} is characterized by –CH stretching bands [33]; this region shows a high absorption for PLA, with the intensities of these peaks decreasing with increase of limonene content. There is also a broad absorption due to the absorption of cyclohexene group at ≈ 3000 cm^{-1} where overlap –CH peaks (Fig. 3) [34]. In Fig. 3-b the most relevant spectrum bands are identified. The typical asymmetric stretching of carbonyl group (C=O) by lactide is present at 1760 cm^{-1} [35]. The 1450 cm^{-1} band is assigned to the CH_3 group [22]. The symmetric and asymmetric deformation band of -CH appeared at 1380 cm^{-1} and 1360 cm^{-1}, respectively. In the region between of 1000 cm^{-1} and 800 cm^{-1} the deformation vibration of =CH groups can be observed.

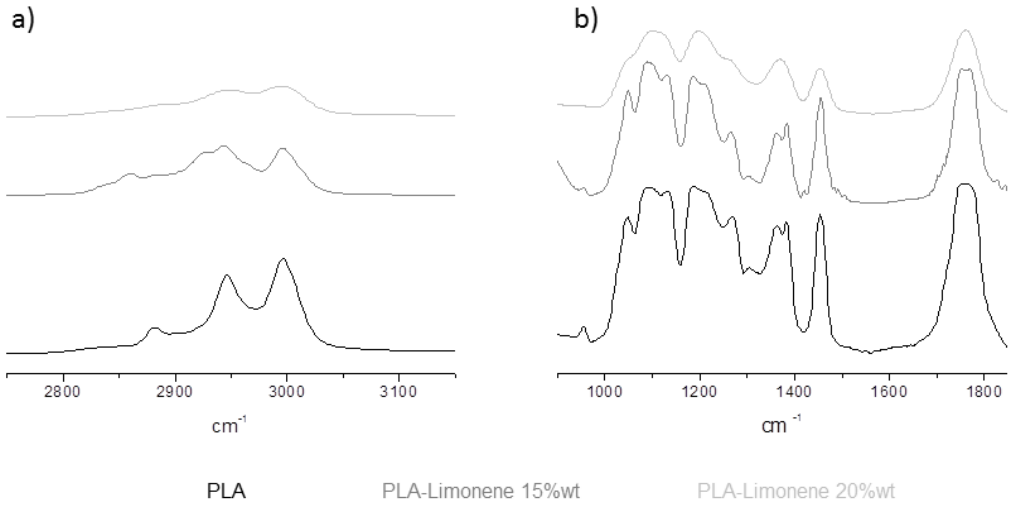

Figure 3. FTIR spectra of PLA and PLA limonene films

3.2. Thermogravimetric analysis

The effect of limonene on the thermal stability of PLA was studied by TGA. PLA decomposes in a single step process with an initial degradation temperature (T_0) of 322 ºC and maximum degradation rate temperature (T_{max}) centered at 370°C (Fig. 4). The addition of Limonene in the polymer matrix resulted in a two steps degradation processes, where the first degradation step, between 80-160 ºC, corresponds to the degradation of limonene, while the second step corresponds to the degradation of the PLA. From these results, it is possible to

estimate the remaining amount of limonene in the PLA matrix after processing, which is approximately 6.5 wt% and 8.5 wt% for the sample PLA-Lim15 and PLA-Lim20%, respectively. The T_0 and T_{max} of the studied samples are showed in Table 1. Fig. 4 also shows the derivative curves (DTG) and it could be observed that there is another step process overlapping PLA decomposition and may be also related to limonene. Similar behavior was observed by Martino et al. (2006) when PLA was plasticized with commercial adipates [36].

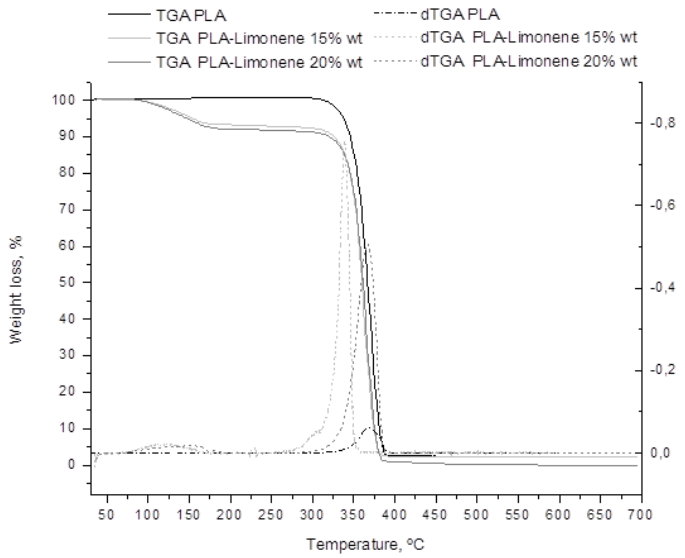

Figure 4. TGA and dTGA curves for PLA and PLA-Limonene films

3.3. Py-GC/MS

The quantification of the remaining amount of limonene after film processing was carried out by Py-GC/MS. This technique presents a high sensitivity and it could be useful to study smaller variations in materials' structures [5, 37, 38]. The optimization of Py-GC/MS conditions was based in the use of 0.5s and 1000ºC, since short pyrolysis time let to achieving good chromatographic resolution [38] and high temperature in order to elute the total amount of limonene in the sample in one pyrolysis. Therefore, these pyrolysis conditions allow limonene to be eluted in one and it could be quantified by using standard solutions. The peak at 7.5 min in the pyrogram corresponds to d-Limonene while the peak at 9.7 min corresponds to L-lactide (Fig. 5). There is another smaller peak at around 9.1 min that has been identified as mesolactide [38]. The limonene limit of detection (LOD) was 0.05 wt%. The results indicated that after processing there were remaining amounts of d-limonene of 8.9 wt% and 11.2 wt% in PLA-Lim15 and PLA-Lim20, respectively. Therefore, there is a loss of limonene during processing and the lost was more pronounced when the concentration of limonene was

increased. These results are in good agreement with Soto-Valdez et al., 2011 who reported that the amount of resveratrol lost during extrusion process of PLA-resveratrol films increased with higher resveratrol concentrations [39].

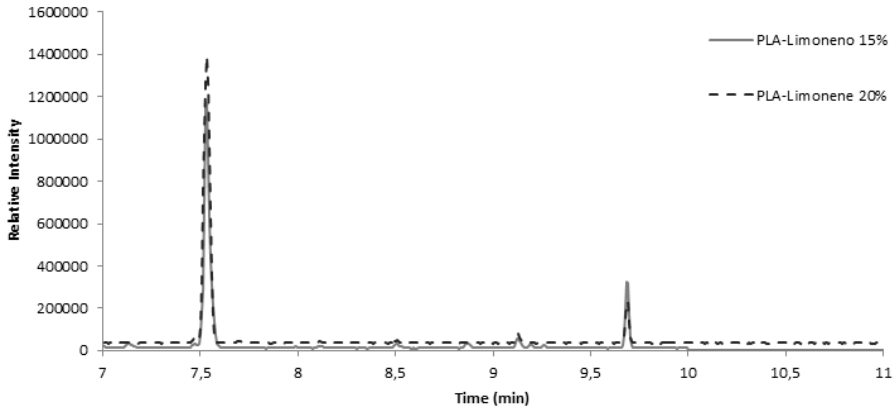

Figure 5. Pyrogram obtained for PLA-Limonene films at 1000ºC for 0.5s

3.4. DSC

DSC curves showed a single T_g for the additivated samples indicating the miscibility between limonene and PLA. In addition a significant reduction in T_g was observed (Table 1) accompanied by a decrease in the value of T_{cc} with the addition of d-limonene to the polymer matrix. These changes are due to the increase in the polymer chain mobility, indicating a plasticization effect. Moreover, degree of crystallinity (χ_c) of the blends decreased with increasing limonene content, due to enhanced polymer chain mobility [40] and the plasticization effect [39]. The low χ_c values obtained indicate that the all films are essentially amorphous. The lower amounts of crystals present when melt occurs in the sample containing limonene, produce a slight shifting of T_m to lower temperatures with respect to the neat PLA film.

Table 1. DSC and TGA results of PLA and PLA-Limonene films.

Parameter	PLA	PLA-Lim15	PLA-Lim20
$T_{0(\alpha=0,01)}$ (ºC)	322	109	105
T_{max} (ºC)	370	338	367
T_g (ºC)	60.3	30.2	33.8
T_{cc} (ºC)	99.8	75.1	72.7
T_m (ºC)	167.4	164.2	166.3
χ_c (%)	4.54	3.54	1.80

3.5. Mechanical properties

The plasticizer effect of limomene was also observed in the mechanical tests. The incorporation of limonene caused a reduction in elastic modulus and tensile stress values in accordance with χ_c decrease, and increased the elongation at break of the films (Fig. 6). Consequently, PLA-limonene films presented less brittleness than neat PLA. The most significant difference between the films with limonene and neat PLA film was the elongation at break, which was significantly lower for control PLA film. It is known that films for packaging require high flexibility to avoid breaking during processing and use [36]. The elongation increased from 1.5% (PLA) to 150% for PLA-lim15 and reached to a maximum of 165% for PLA-Lim20 film. These results display a significant improvement in the flexibility of PLA due of the plasticization effect achieved by limonene addition.

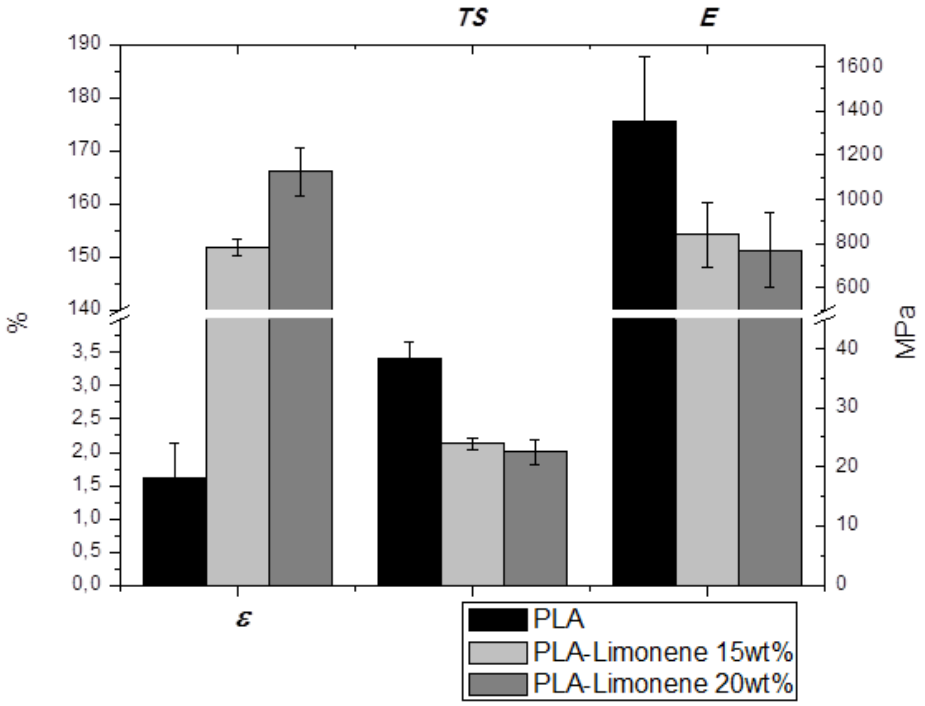

Figure 6. Elongation at break (ε, %), tensile stress (TS, MPa) and modulus (E, MPa) of PLA and PLA-Limonene films

3.6. SEM

Scanning electron microscopic (SEM) images were taken of the fractured surfaces after the tensile tests and are shown in Fig. 7. A smooth broken surface was observed for neat PLA film sample corresponding to brittle fracture nature of PLA (Fig. 7-a). PLA-Lim15 (Fig. 7-b) and PLA-Lim20 (Fig. 7-c) fracture surfaces show a great evidence of plastic

deformations with a uniform dispersion of limonene in the PLA matrix. Limonene addition significantly influences the morphological structural showing blended-PLA ductile behavior in accordance with their increased deformation at break.

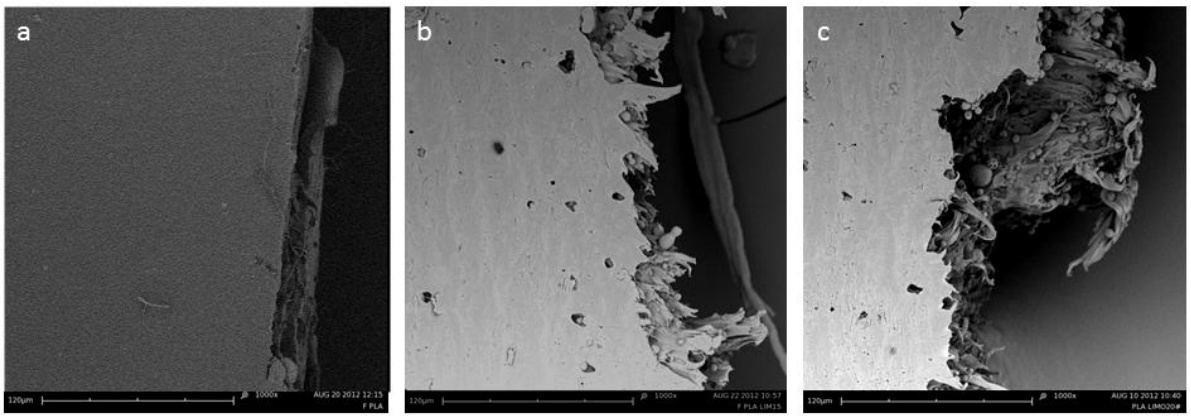

Figure 7. Fracture surface of a) neat PLA film, b) PLA-Lim15 film and c) PLA-Lim20 film

3.7. Film color properties

Table 2 shows the results obtained from the colorimeter analysis. When limonene is added to the film sample, a slight decrease in lightness values (L^*) was observed. However, PLA and also both PLA-limonene samples presented high L^* values showing their high brightness. Furthermore, no major differences were found for total color difference values. This result suggested high transparency for films containing limonene and the possibility to see through the film is one of the most important requirements for consumers [41]. Negative values obtained for a^* coordinate are indicative of a deviation towards green. However, these values are close to zero so it the green tone was not noticeable. Positive values obtained of b^* coordinate indicate a slight deviation towards yellow. Therefore, yellowness index was also determined. The YI is used to describes the change in color of a sample from clear toward yellow [22]. It was observed that the YI values increased with the limonene content increase. However, the highest YI value, achieved by PLA-Lim20, is a similar value that have been reported for other packaging plastic films such as PET [22].

Table 2. Color parameters from CIELab space, wettability and oxygen barrier properties of PLA, PLA-Lim15 and PLA-Lim20.

Parameter		PLA	PLA-Lim15	PLA-Lim20
Color	L*	94.08 ± 0.07	93.86 ± 0.10	93.32 ± 0.33
	a*	-1.03 ± 0.01	-0.99 ± 0.01	-1.31 ± 0.08
	b*	1.33 ± 0.05	1.27 ± 0.06	2.55 ± 0.47
	ΔE	-	0.24 ± 0.04	1.46 ± 0.50
	Y313 (65/10)	3.47 ± 0.07	3.49 ± 0.10	5.65 ± 0.85
Oxygen Barrier	OTR.*e* ($cm^3.mm.m^{-2}.d^{-1}$)	44.4 ± 0.9	84.0 ± 4.9	99.3 ± 2.6
Wettability	Θ^o	58.4 ± 3.7	75.3 ± 1.3	78.3 ± 2.1

3.8. Oxygen permeability measurement

The incorporation of limonene leads to an increase in the oxygen permeation (Table 2). This result is in accordance to T_g values. The increase in polymer chain mobility caused by limonene plasticization effect reduced the resistance of the PLA film to oxygen transmission, allowing the mobility of the oxygen molecules in the polymer matrix. Increases in OTR.e values with increasing amount of plasticizer in PLA matrix have been well reported in the literature [19, 42, 43]. Although, OTR.e values increased with limonene present it were still better than the levels obtained for commercial LDPE films in comparable conditions (OTR.e = $160 cm^3 \cdot mm \cdot m^{-2} \cdot d^{-1}$) [19].

3.9. Wettability

The hydrophilicity of films samples was investigated by water contact angle measurement. When limonene was added into the PLA matrix, the contact angle with water was increased from 58º to ≈75, showing a higher hydrophobic character of PLA-limonene blends. This behavior could be attributed to the limonene hydrophobic character. It has been reported that modifying the physicochemical properties of the material surface can control the water adsorption [41]. Therefore, PLA films containing limonene are also expected to have higher resistance to water adsorption than neat PLA film. PLA-limonene blends could be used in packaging formulations with reduced water adsorption requirements.

4. Conclusions

A complete characterization of PLA blended with d-limonene was carried out. PLA-limonene films maintained their transparency after the addition of the natural compound, but minor positive values of *b** coordinate indicated a slight deviation towards yellow. Py-

GC/MS analysis demonstrated that there was a remaining amount of limonene in the PLA matrix after processing. The results revealed that the addition of limonene into the PLA matrix decreases the glass transition temperature of the films. The T_{cc} and χ_c were also decreased while T_m was slightly reduced. Mechanical properties of the films were altered by the presence of limonene and good plasticization was observed. Barrier properties to oxygen were reduced due to the plasticization of the PLA matrix, but presented acceptable values for food packaging applications. Furthermore, d-limonene reduced the water adsorption of PLA matrix.

These results show potential feasibility of using d-limonene as a natural PLA plasticizer to obtain flexible films for food contact materials, and even to be tested as active compound in active packaging systems.

Acknowledgements

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