

Influence of Cardanol Oil on the Properties of Poly(lactic acid) Films Produced by Melt Extrusion

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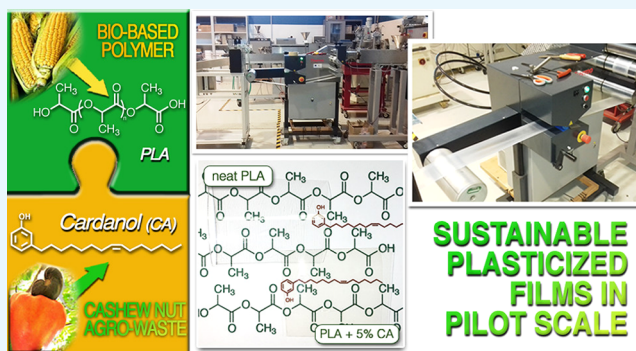
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ABSTRACT: Sustainable polymers from renewable resources are classified as biobased polymers. Poly(lactic acid) (PLA) is one of the most common biobased polymers applied in the biodegradable plastic industry as a feasible substitute of petrochemical-derived products. Cardanol oil (CA), a renewable resource and relatively low-cost side product of the cashew agro-industry, combined with neat PLA permitted the preparation of plasticized PLA/CA films by means of hot melt extrusion processes. Looking at packaging applications of the functional biobased PLA/CA films, chemical, mechanical, thermal, antioxidant, and barrier properties were studied. Thermal analysis revealed that the PLA glass-transition temperature decreased with the increasing content of CA, indicating that CA worked as a plasticizer for PLA. The presence of CA increased the oxygen transmission through the PLA/CA films; consequently, the permeability values were always appreciably higher for plasticized films. Nevertheless, the CA-plasticized PLA films showed good barrier properties similar to packaging materials commonly used in the food industry today. Release studies from PLA/CA films were carried out in four food simulants (physiological saline solution, ethanol, acetic acid, and isoctane) through spectrophotometric measurements and revealed the release effects only in simulants for fatty foods. Radical scavenging assays indicated the elevated antioxidant activity of CA-incorporated films compared to neat PLA.



INTRODUCTION

Poly(lactic acid) (PLA) is a biodegradable thermoplastic polyester derived from renewable sources such as corn. It can be considered an interesting biopolymer having physical, mechanical, and barrier properties similar to polystyrene and poly(ethylene terephthalate) (PET)^{1–3} as classes of polymeric materials of industrial relevance.

During the last decades among the biodegradable material studied, PLA has gained an increasing interest because of its biodegradation, which made it an interesting polymer for a large number of applications in food, packaging,⁴ and biomedical fields.^{5,6} For these reasons, PLA is approved by the US Food and Drug Administration (FDA) and considered “Generally Recognized As Safe” for its use as a food-contact polymer.⁷

Despite the possibility to process PLA by using technologies for the processing of common thermoplastic polymeric

materials, low deformation at break and high modulus have restrained applications of PLA to the rigid thermoformed packaging industry.

For this reason, the use of plasticizer additives is important to enhance the processability and flexibility of PLA-based films.^{8–13}

Cardanol (CA) is a peculiar mixture of naturally occurring phenolic compounds bearing a lipophilic alkyl chain of 15 carbon atoms in the meta position in comparison with the moderately polar hydroxyl group. The alkyl side chains may present different unsaturation numbers, varying from 0 up to 3 double bonds located in the positions 8, 11, and/or 14.^{14,15}

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Thanks to its molecular features, CA can be considered a promising source of green chemicals and materials.^{16–19}

The molecular structures of the CA components used as plasticizer/modifier of the PLA films produced in this work are shown in Figure 1.

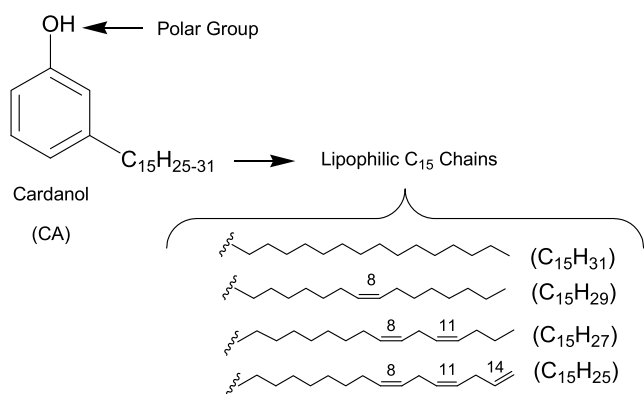


Figure 1. Chemical feature of the CA components.

Apart from current industrial uses, it has been demonstrated that the cashew nut-derived oils may exert antioxidant,²⁰ antifungal,²¹ antibacterial,^{22,23} and larvicidal activities.^{24,25}

In this work, we report the preparation and characterization of novel PLA/CA composites in view of their possible food packaging application. In particular, different amounts of CA oil were mixed with commercial PLA pellets and then processed to composite films PLA/CA by melt extrusion processes and characterized by chemical, mechanical, thermal, barrier, antioxidant, and release tests.

The release of CA from composite films was studied in four food simulants (physiological saline solution, 50% v/v ethanol, 3% w/v acetic acid, and isooctane) and showed interesting effects, regarding the different nature of the simulant environment.

EXPERIMENTAL SECTION

Materials. CA was kindly furnished by Oltremare S.r.l. (Bologna, Italy) and PLA Ingeo Biopolymer 2003D was provided in form of pellets by Nature Works LLC (Minnetonka, MN, USA). Acetonitrile (CH₃CN) and acetic acid for high-performance liquid chromatography (HPLC) were purchased from Sigma-Aldrich (Steinheim, Germany). Ultrapure (UP) water was produced by a Zeneer UP 900 Human Corporation system.

Characterization of CA Oil. Separation and quantification of CA components was performed by HPLC coupled with a diode array detector (DAD) and mass spectrometer (MS) on an Agilent Technologies (Waldbronn, Germany) modular model 1200 system, consisting of a vacuum degasser, a binary pump, an autosampler, a Thermostatted Column compartment, and DAD. Qualitative analyses were recorded after chromatographic separation using the same system equipped with a 6540 quadrupole time-of-flight mass analyzer with an electrospray ionization source. Analyses of the CA components were performed according to the procedure already reported in the literature.²⁶

Preparation of Neat PLA and PLA/CA Films. *PLA Film.* Film extrusion of neat PLA was performed in a HAAKE Rheomex 19/25 QC single-screw extruder with a PolyLab QC drive unit and a chill roll system. The material was previously

dried at 70 °C for 24 h. During the film extrusion, the temperatures in the feeding and die zones were set at 160 °C and the screw speed was set at 30 rpm. The lips of the sheet die and the speed of the chill roll system were settled to obtain an average thickness of the film of nearly 80 μm.

PLA/CA Films. PLA pellets were compounded with CA oil in different weight percentages (5, 10, and 15% w/w) by means of a batch mixer (HAAKE Rheomex QC 3000) at 160 °C with a rotor speed of 50 rpm for 20 min. The PLA/CA compound was then powdered by means of a rotation blades mill and then processed in a HAAKE Rheomex 19/25 QC single-screw extruder with a PolyLab QC drive unit and chill roll system to obtain the films. During the PLA/CA film, extrusion temperatures ranged from 140 to 170 °C, and the screw speed was 60 rpm. In analogy with the neat PLA film, processing an average thickness of the film of about 80 μm was obtained setting opportunely the lip of the sheet die and the speed of the chill roll system. PLA films incorporated with increasing amounts, 5, 10, 15% w/w, of CA were obtained and named as PLA/CA5, PLA/CA10, PLA/CA15, respectively.

Mechanical Test. For tensile tests, a total of five specimens were prepared for each composite type by cutting rectangular samples from extruded film in the longitudinal direction of extrusion. The test specimens were placed in a conditioning room at 24 °C and 50% relative humidity for 24 h. Specimens that measured 250 mm in the initial length and 25 mm in width with a thickness of about 0.07 mm were tested. Samples were then subjected to tensile testing according to ASTM D 882 using an MTS Alliance RT 50 tensile tester equipped with a 2 kN load cell and flat grip and the average of results considered. The experiments were conducted at the deformation rate of 1.5 mm/min.

Fourier Transform Infrared Spectroscopy. Fourier transform infrared spectroscopy (FT-IR) of the films was performed by a PerkinElmer FT-IR/NIR Frontier spectrometer. The measurements were acquired between 4000 and 550 cm⁻¹ with a resolution of 4 cm⁻¹ using the arithmetic average of four scans.

Scanning Electron Microscopy Measurements. The PLA and PLA/CA samples were analyzed by using a scanning electron microscope Zeiss Evo 40.

Calorimetric Characterization. Differential scanning calorimetry (DSC) measurements were carried out using a TA Instruments DSC Discovery under nitrogen flux of 50 mL min⁻¹. The samples of about 5 mg were cooled from 170 to 0 °C at 10 °C min⁻¹ and heated subsequently between 10 to 170 °C at 10 °C min⁻¹. The upper temperature of 170 °C was chosen to delete the previous thermal history of the samples.

Thermal Stability Evaluation. The thermogravimetric analysis (TGA) was performed using a Mettler-Toledo (Schwerzenbach, Switzerland) TGA/SDTA851e instrument. Samples weighting 10 mg were heated from 30 to 600 °C under nitrogen or synthetic air atmosphere (50 mL min⁻¹) at a scanning rate of 10 °C min⁻¹.

Oxygen Transmission Rate Measurements. Oxygen gas transmission rate (OTR) through neat PLA and PLA/CA films was determined according to ASTM standard D3985 using a Multiperm O₂ Extra Solution gas permeation instrument. Tests were performed at 23 °C, 101.325 kPa pressure and 50% RH. Samples were cut in circular shapes with a diameter of about 8 cm. The circular film measuring area was 50 cm² and the average thickness was 80 μm. Oxygen gas with a purity of >99.999% was used. Films were conditioned for at least 12 h in

the diffusion cell. The flow rate of dioxygen was monitored until a stationary state was reached. The average thickness of the samples was measured by a Mitutoyo Digimatic Micrometer model 293-832 (Illinois, USA). Five specimens were tested for each film type.

Release Studies. Release tests were performed at the ambient temperature recording the absorbance spectra of the neat PLA film and PLA/CA5 film, as a reference sample composite, by an Agilent Cary 5000 UV–vis–NIR spectrophotometer, operating in the wavelength range 200–800 nm, with an accuracy of ± 0.08 nm.

The release tests were carried out by total immersion of rectangular strip film pieces (24×32 mm), thickness of about $80 \mu\text{m}$, in 25 mL of food simulant contained in a closed glass tube kept under dim light. Migration tests were performed using four food simulants: (A) (0.90% w/v NaCl) representing aqueous foods ($\text{pH} > 4.5$); (B) (3% w/v acetic acid) representing acidic aqueous foods ($\text{pH} < 4.5$); (C) (50% v/v ethanol); and (D) (isooctane) for fatty foods. Test of the control PLA film were also run simultaneously to check for interferences. The films were periodically removed from the simulant, up to 28 days of contact, and the respective solutions analyzed through spectrophotometric measurements.

Antioxidant Activity of PLA Films. The 1,1 diphenylpicrylhydrazyl (DPPH) free-radical scavenging assay of PLA films was performed according to the methodology published²⁷ previously with some modifications. PLA films (0.1 g) were mixed with 3 mL of dimethyl sulfoxide (DMSO). The mixture was kept under magnetic stirring during 30 min at 25°C . After this, the resulting solution was allowed to rest for 10 min, and the obtained supernatant was used in the radical scavenging assay. An aliquot (10, 100, and $700 \mu\text{L}$) was added to 2.0 mL of 0.06 mmol L^{-1} DPPH in DMSO, and the sample volume was brought to 3.0 mL with DMSO. The mixture has stood in the dark for 30 min. Measurements were carried out in the spectrum range between 300 and 600 nm with a spectral resolution of 0.5 nm using a Cary 60 UV–Vis Spectrophotometer (Agilent) at a temperature of 25°C . Antioxidant activity was expressed in terms of IC_{50} values in mg mL^{-1} , using $\lambda = 521 \text{ nm}$ as the standard wavelength. DPPH activity was also calculated as previously published.²⁸

Radical scavenging activity (%) = $(1 - (A_{\text{sample}}/A_{\text{control}})) \times 100$; where A_{sample} and A_{control} are the absorbance of sample and control, respectively. The analyses were performed in duplicate.

RESULTS AND DISCUSSION

The CA used as additive in this work is itself a mixture of four compounds corresponding to the mono, di, tri-unsaturated components, and to the 3-*n*-pentadecylphenol, respectively, opportunely characterized by HPLC–DAD–MS analysis.²⁶

As shown in Figure 2, the presence of CA produced a light yellow color which is more evident in the case of the rolling film; however, the coloring is less evident in the unrolled film which still preserves its transparency.

The incorporation of CA into the PLA matrix was confirmed by FT-IR analyses, as shown in Figure 3. To identify and compare the bands related to CA chemical bonds, the CA spectrum is also displayed. Characteristics bands of PLA bond vibrations are strong absorptions bands at 1750 cm^{-1} , ascribed to the stretching vibrations of carbonyl groups, and at 1180 cm^{-1} , related to the C–O–C stretching mode, which are present in all film samples. The presence of CA can be

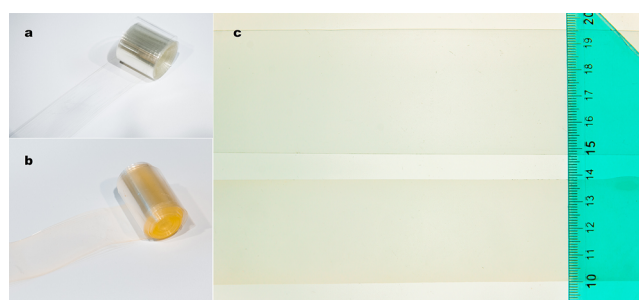


Figure 2. Picture of the neat PLA film (a), picture of the PLA/CA5 film (b), and comparison of the transparency of unrolled neat PLA with PLA/CA5 films (c).

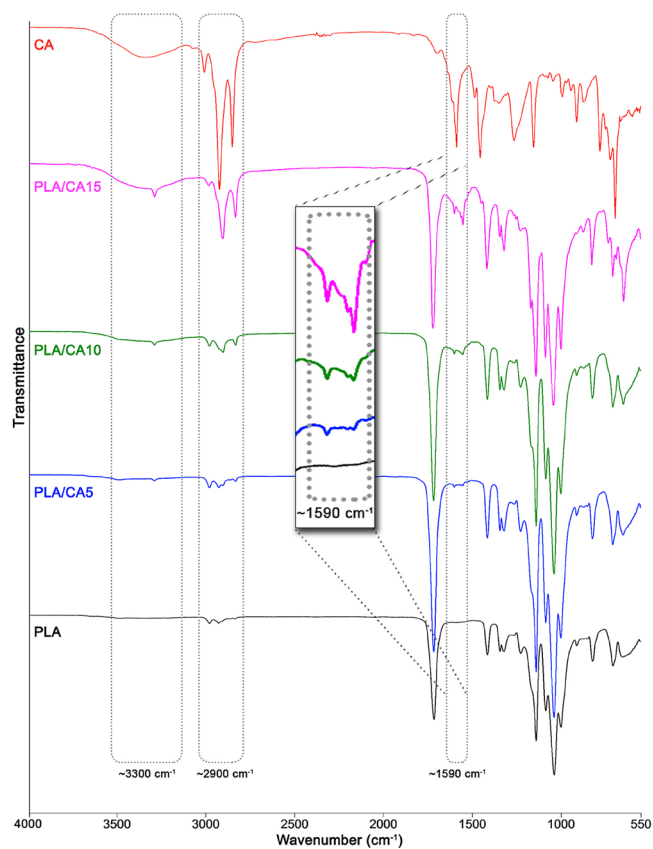


Figure 3. FT-IR spectra of CA, neat PLA film, and PLA films incorporated with CA.

confirmed by the appearance and increased intensity of the bands at 3300 , 2900 , and 1590 cm^{-1} , attributed to the asymmetric stretching of phenolic O–H bond and of alkyl C–H bonds and the stretching of the aromatic C=C bonds (as magnified in Figure 3), respectively, with the increasing of the CA content.

As shown in Figure 4, the UV–vis spectrum of the neat PLA film does not exhibit any significant absorption in the range of 260–380 nm. On the contrary, the spectrum of PLA/CA5 exhibits an absorption band centered at 274 nm typical of the CA moiety.

Scanning electron microscopy (SEM) analyses of neat PLA, PLA/CA5, and PLA/CA10 films show little domains presumably deriving from unmelted compound. However, 15% of plasticizer worsens the film extrusion resulting in a sticky film formation, with much more evidence of unmelted

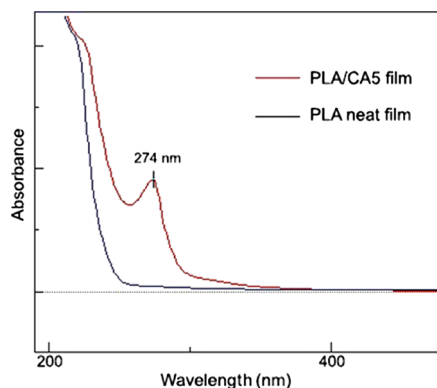


Figure 4. UV-vis spectra of neat PLA and PLA/CA5 film.

domains because of the lower extrusion temperature (140 °C) due to the increasing of fluidity related with the higher amount of CA (Figure 5d).

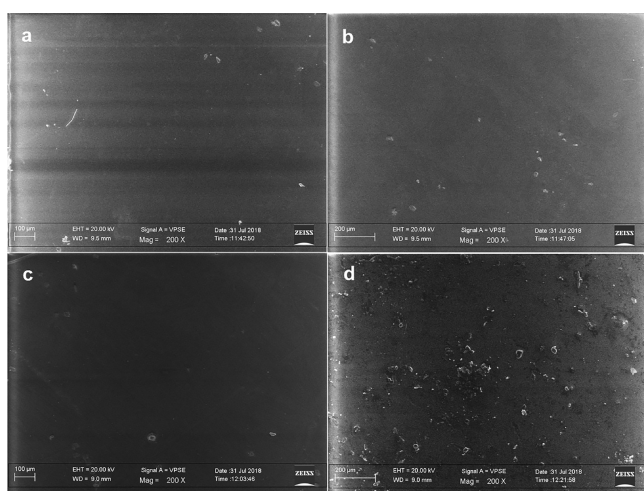


Figure 5. SEM images of (a) neat PLA, (b) PLA/CA5, (c) PLA/CA10, and (d) PLA/CA15.

Mechanical Characterization. The mechanical properties of PLA/CA film, prepared by extrusion process with different amounts of CA, were evaluated to assess its efficiency as biobased plasticizer for PLA films. Elastic modulus, tensile strength, and elongation at the break obtained by the tensile tests are reported in Table 1.

The results for the pristine PLA film and PLA/CA film show a significant change because of the amount of CA in the blend. In particular, neat PLA film shows the maximum tensile strength and elastic modulus with values of 73 MPa and 4.1 GPa, respectively. Tensile strength and elastic modulus decrease significantly when the content of CA grows, whereas

Table 1. Mechanical Parameters Extracted from the Stress–Strain Curves

sample	tensile strength (MPa)	std. dev.	elastic modulus (GPa)	std. dev.	elongation at break (%)	std. dev.
PLA	73	6	4.1	0.3	2.7	2
PLA/CAS	53	3	4.0	0.2	1.6	0.1
PLA/CA10	39	3	2.5	0.1	2.8	0.8
PLA/CA15	15.3	0.7	0.54	0.06	136.7	40

the elongation at break dramatically increases for PLA/CA15. This behavior is ascribable to the plasticizing effect of CA. Neat PLA shows a considerably low value of the elongation at break, nearly 3%, thus leading to a fragile behavior. The plasticizing effect becomes evident for films in which the amount of CA is at least 15%. In fact, the value of elongation at break equal to 136.7% is an indication of a very ductile behavior of the film. This is in agreement with the fact that the PLA film with 15% of CA has a glass transition temperature T_g of 22.8 °C, approximately 36 °C lower than the T_g of neat PLA, as shown in Table 2.

Unfortunately, the PLA/CA15 appears as a sticky film and therefore cannot be used for packaging applications. In light of these considerations, the mechanical properties of the films can be considered acceptable for our purpose when the amount of CA is of 5–10%.

Thermal Characterization. DSC thermogram of plasticized PLA at different CA contents is shown in Figure 6.

DSC curves of plasticized PLA (Figure 6) were characterized from glass transition, cold crystallization, and melting. Sometimes, the latter phenomenon was represented by a double peak ($T_{m1,m2}$) indicative of the melting of both α' and α crystalline phases.²⁹

The characteristic temperatures of glass transition, cold crystallization, and melting of plasticized PLA films are collected in Table 2. The glass transition temperature of the plasticized PLA decreased with the increasing content of CA, as evident from the data collected. Furthermore, the crystallization enthalpy of the plasticized PLA was found to be approximately twice that of the neat PLA, indicating that the amount of PLA involved in the crystal structures was doubled; furthermore, from Table 2, the melting enthalpy ΔH_m observed from these samples was close to their crystallization enthalpy ΔH_{cc} values. Moreover, the degree of crystallinity % X_c of plasticized PLA films dramatically increased with the addition of CA at contents of 5 wt %. No changes in crystallinity were registered in plasticized PLA films at higher CA content. As a matter of fact, we suppose that the polarity imparted by the –OH group bonded to the phenol moiety of the CA improves its affinity with molten PLA; on the other hand, the intercalation of the flexible lipophilic chains of CA in the polymeric network plays a significant role in the plasticization of PLA.

The degree of crystallinity (% X_c) was calculated according to eq 1

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

where ΔH_m was the melting enthalpy, ΔH_{cc} stands for the cold crystallization enthalpy, $\Delta H_{m(100\%)}$ indicates the melt enthalpy of theoretically 100% crystalline PLA (93 J g⁻¹),³⁰ and w indicates the weight fraction of PLA in plasticized compounds.

DSC thermogram of the CA sample is reported in Figure 7. The DSC curve of CA showed a large double endothermic peak between –65 and –40 °C (Figure 7) probably because of a melting process³¹ whose characteristics are collected in Table 2.

To evaluate the effect of the incorporation of CA on the thermal stability of the PLA matrix, TGA was performed in oxidative (synthetic air) and inert atmosphere (N₂). Figure 8 shows the TGA curves of neat PLA and incorporated with 5, 10, and 15 wt % of CA. From the thermogravimetric curves, it

Table 2. Thermal Properties of Neat and Plasticized PLA Samples^a

sample	ΔC_p (J g ⁻¹ K ⁻¹)	T_g (°C)	T_{onset} (°C)	T_{cc} (°C)	ΔH_{cc} (J g ⁻¹)	$T_{m1,m2}$ (°C)	ΔH_m (J g ⁻¹)	% X_c
PLA	0.559	58.7	56.8	128.9	-10.1	152.3	10.2	0.1
PLACA5	0.558	46.9	43.8	103.9	-24.5	143.0	28.4	4.4
PLACA10	0.642	36.9	31.9	92.7	-23.7	136.5	27.1	4.1
PLACA15	0.636	22.8	15.8	83.4	-22.2	129.1	25.3	3.9
CA						-56.6	-42.9	3.2

^a ΔC_p : specific heat discontinuity; T_g : midpoint glass transition; T_{onset} : onset glass transition; T_{cc} : cold crystallization peak temperature; ΔH_{cc} : cold crystallization enthalpy; $T_{m1,m2}$: melting peak temperatures; ΔH_m : melting enthalpy; and % X_c : degree of crystallinity.

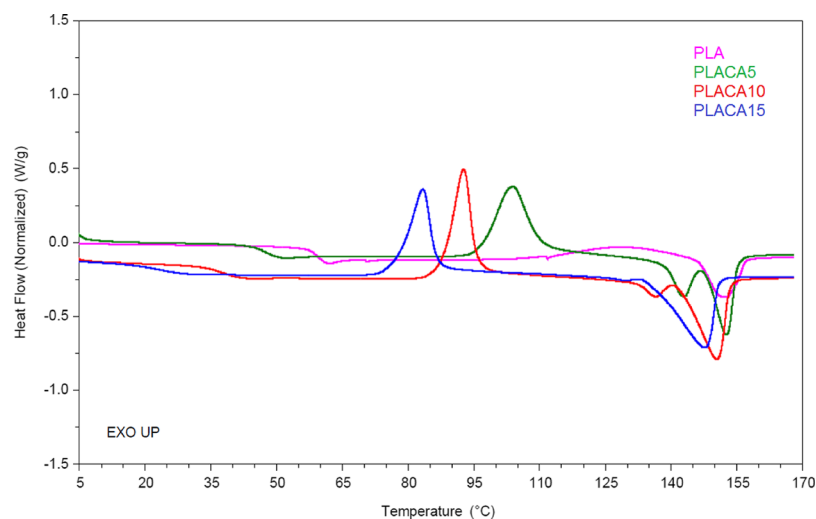


Figure 6. DSC curves of plasticized PLA samples at different CA contents.

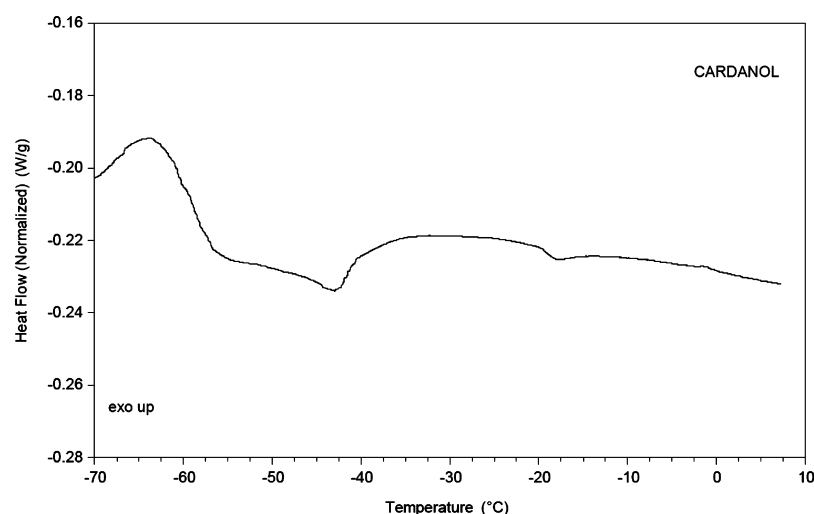


Figure 7. DSC trace of CA.

is observed that the increased amount of CA resulted in a more pronounced decrease of the thermal stability of PLA films, as summarized in Table 3.

Compared to PLA, CA has a lower temperature of degradation and, therefore, its chemical structure begins to decompose earlier than PLA, explaining the reduced thermal stability observed for the incorporated films, despite being reported as a natural occurring antioxidant.³²

A work published by Lomonaco and co-workers³³ reported that CA initiates to thermally decompose (T_{onset}) at 266 and 243 °C, under inert and oxidative atmospheres, respectively. Here, neat PLA films presented much higher thermal stabilities

than CA, with T_{onset} up to 342 °C, under inert atmosphere, and 334 °C, under oxidative atmosphere.

However, these observed reductions in thermal stabilities should be seen as obstacles neither for the proper incorporation of CA nor for its successful activity as a plasticizer, once PLA melting point is around 150 °C and its processing temperatures ranges from 140 to 170 °C, conditions considered mild when compared to those emulated in the thermogravimetric studies and completely safe for the processing of both matrix and plasticizer.

Oxygen Transmission Rate. Gas permeability is normally related to the quantitative evaluation of the barrier properties

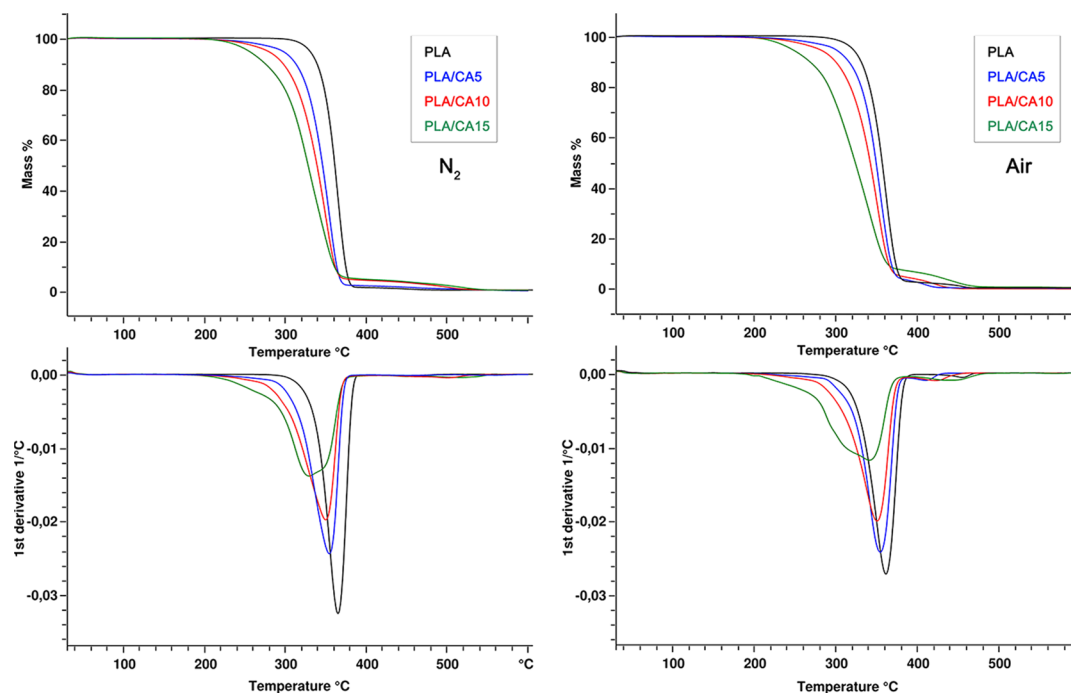


Figure 8. TGA curves for neat and CA-incorporated PLA films under inert and oxidative atmospheres.

Table 3. TGA Analysis of Neat and CA-Incorporated PLA Films

sample	inert (N ₂)			oxidative (synthetic air)		
	T _{onset} (°C)	T _{5%} (°C)	T _{max} (°C)	T _{onset} (°C)	T _{5%} (°C)	T _{max} (°C)
PLA	342	327	365	334	321	358
PLA/CA5	313	292	352	328	298	352
PLA/CA10	314	275	347	318	275	348
PLA/CA15	292	251	326	275	240	338

of a polymeric material. Oxygen permeability plays an important role in packaging application to control the shelf-life of foods, drinks, and goods. In polymers showing low-oxygen permeability coefficients, the oxidation is retarded and the shelf-life is extended. PLA is an attractive polymer for food packaging application, but it has moderate barrier properties if compared, for example, with PET which is commonly used in food packaging because of its excellent barrier properties against oxygen.³⁴ Therefore, it is of great importance that the addition of plasticizer does not significantly affect the barrier properties of the films.

Because barrier properties are strictly correlated with the free volume of the polymeric matrix, OTR of films plasticized with CA was investigated. Table 4 summarizes the permeability coefficient (P) values determined by the product of the OTR and the average thickness (80 μm) of neat and plasticized PLA with different CA concentrations.

Table 4. Barrier Properties against Oxygen as a Permeability Coefficient (P)

sample	P (cm ³ mm m ⁻² day ⁻¹ bar ⁻¹)
PLA	19.90 \pm 0.14
PLA/CA5	21.08 \pm 0.38
PLA/CA10	31.51 \pm 0.89
PLA/CA15	39.53 \pm 0.59

As expected, plasticized PLA films offer reduced barrier properties than the neat sample, evidenced by the increasing of P values according to the increasing contents of the plasticizer (CA) into the matrix. The values of permeability P are in agreement with the T_g values, as reported in Table 2. In fact, permeability increases with the decreasing of T_g , which is related to the greater free volume inside the PLA matrix because of plastification effects (Table 1), promoting a better permeation of oxygen.

Actually, only with higher amounts of CA incorporation, as in PLA/CA15, was observed a marked increase of P , which is still in the range of the oxygen permeability of plastic materials normally used in packaging applications.

Release Behavior. Plasticizers, being of rather low molecular weight, are potentially migrant from packaging materials into food or food simulant with which they are in contact. Simulants are less chemically complex than foods; for this reason, they are most commonly used to test the migration from food-contact materials.³⁵ Simulants proposed to mimic the migration from plastics into foods were introduced in the early-1980s (Directive 82/711/EEC): distilled water (simulant A) for aqueous food (pH > 4.5); acetic acid 3% in water (w/v) (simulant B) for acidic foods (pH \leq 4.5); ethanol 10% in water (v/v) (simulant C) for alcoholic foods, and olive oil (simulant D) for fatty foods. The old formulations of food simulants were recently modified by EU 10/2011 as follows: ethanol 10% (v/v) for aqueous food (simulant A); acetic acid 3% (w/v) for acidic food (simulant B); 20% (v/v) ethanol for alcoholic products (simulant C), 50% (v/v) ethanol (simulant D1) and vegetable oil (simulant D2) for fatty foods, and, last, Tenax (PPPO) for dry food (simulant E).³⁶

In this work, qualitative and preliminary studies of the release effect from PLA/CA films were conducted through spectrophotometric analysis by monitoring the absorbance of four food simulants (0.90% w/v NaCl, 3% w/v acetic acid, 50% v/v ethanol, and isooctane) in contact with the PLA/CA5 film as a reference sample. A solution of all simulants with neat PLA

film was monitored as blank samples to check the particle release or degradation from PLA film. No absorbance peaks were observed for all of the investigated simulants containing the neat PLA film. CA oil is insoluble in physiological saline solution and acetic acid 3% (w/v), and, as expected, in these two hydrophilic simulants no CA molecules have been detected from PLA/CAS film in any evaluated time intervals. On the contrary, CA oil is highly soluble in two investigated simulants for fatty foods: 50% (v/v) ethanolic aqueous solution and isooctane. The absorbance spectra of CA oil in ethanol solution show two main absorption peaks placed at about 272 and 278 nm, whereas in isooctane, one main absorbance peak is centered at 273 nm, as shown in Figure 9.

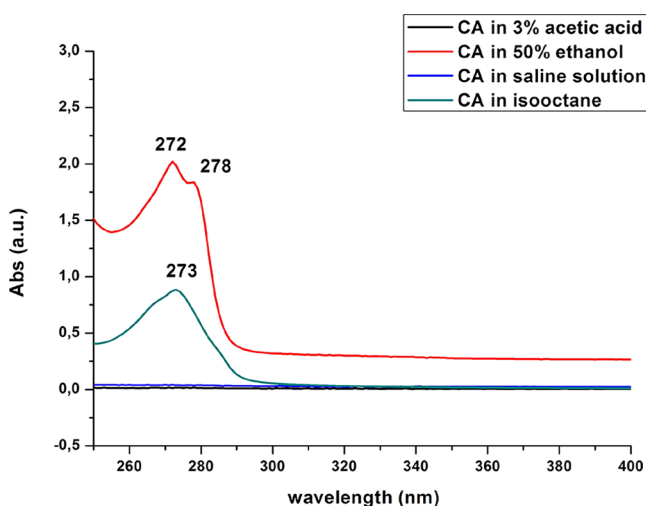


Figure 9. Absorbance spectra of CA oil in four food simulants.

Figure 10 shows an increase of the absorbance intensity at 272 and 278 nm relative to the release of CA in the ethanol

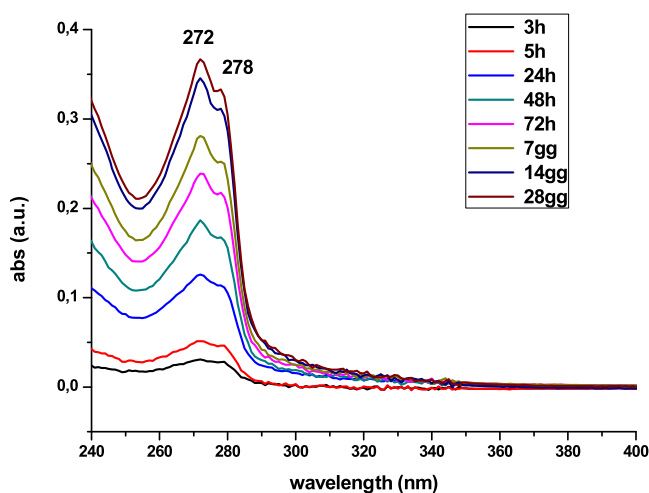


Figure 10. Absorbance spectra of ethanolic aqueous solution in contact with PLA/CAS film.

solution in contact with the PLA/CAS specimen with increasing the time of contact. A similar absorbance trend was also observed in isooctane simulant, in accordance with the CA solubility in this organic media.

Antioxidant Activity Assay. CA is widely known in scientific literature because of its elevated capacity to work as a

radical scavenger.^{12,20,21} To evaluate if along with the plasticizing effect, CA could also affect positively the stability of PLA films to radical oxidation, their antioxidant activities were measured by DPPH radical scavenging activity, and the results are presented in Figure 11 and summarized in Table 5.

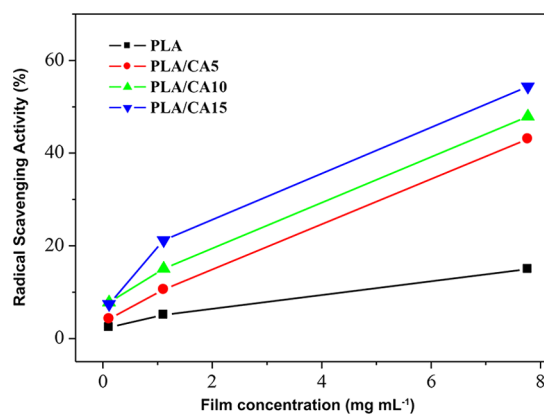


Figure 11. DPPH radical scavenging activity of PLA films.

Table 5. DPPH Radical Scavenging Capacity (IC_{50} and Inhibitions Values) of PLA Films

film	IC_{50} ($mg\ mL^{-1}$)	inhibition (%)
PLA	30.0	15
PLA/CAS	9.1	43
PLA/CA10	8.1	48
PLA/CA15	6.9	54

The PLA films incorporated with CA demonstrated good antioxidant activity, up to 54%, because of the strong antioxidant ability of CA to capture DPPH radicals. Even in the smallest concentration, PLA/CAS showed an inhibition activity of 43%, which is almost 3 times higher than that of neat PLA. Considering that the most used antioxidants (BHT and BHA) are petroleum-based, the use of a natural antioxidant for a biobased matrix, in this case, PLA, emphasizes the potential of CA to be used in films for food and packaging industry.

CONCLUSIONS

Potential active films derived from renewable resources were successfully developed by adding CA oil during melt extrusion process of the PLA polymer. CA acts as a plasticizer additive and can provide antioxidant properties improving the potential application of PLA films in food and biomedical packaging.

The UV-vis as well as the FT-IR results showed that CA was successfully incorporated into the PLA matrix. Tensile strength and elastic modulus of the PLA/CA films decreased significantly when the content of CA grows while the elongation at break increases. This behavior was ascribed to plasticizing effects of CA and was confirmed by DSC analyses. The exothermic peak of plasticized PLA (cooling run) was attributed to cold crystallization promoted by the biobased plasticizer. Cold crystallization was also indicative of an enhanced crystallization kinetic brought by the addition of CA.

Increased amounts of CA resulted in a reduction of PLA film thermal stabilities. Nevertheless, this reduction neither affected the proper incorporation of CA nor its successful activity as a plasticizer because the PLA melting point and processing

temperatures are much milder considering the thermal degradation temperatures. Effectively, PLA/CA15 was too sticky to be used for packaging purposes.

Plasticized PLA/CA films although displayed reduced barrier properties than that of neat PLA, it still presents good permeability values in the range of other plastic materials commonly used in packaging application. No release effect from PLA/CAS was observed up to 28 days for the film in contact with hydrophilic simulant environments, (A) (physiological saline solution) and (B) (3% w/v acetic acid), whereas in simulants for fatty foods, (C) (50% v/v ethanol) and (D) (isooctane), an increase of absorbance intensity was observed with the time of contact, indicating a controlled release of CA molecules in the studied time interval. These results, along with the strong antioxidant activity present by the incorporated films, emphasize the potential of this natural phenolic compound to be used in films for food and packaging industry.

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Notes

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