Bark polyflavonoids from *Pinus radiata* as functional building-blocks for polylactic acid (PLA)-based green composites

D. E. García^{1,2,3*}, J. C. Carrasco⁴, J. P. Salazar⁵, M. A. Pérez⁶, R. A. Cancino⁵, S. Riquelme^{5,7}

¹Laboratorio de Fitoquímica, Departamento de Química Ambiental, Facultad de Ciencias, Universidad Católica de la Santísima Concepción (UCSC), Concepción, Biobío, Chile

²Centro de Investigación en Biodiversidad y Ambientes Sustentables (CIBAS), UCSC, Concepción, Biobío, Chile

³Investigador Asociado Área de Productos Químicos, Unidad de Desarrollo Tecnológico (UDT), Universidad de Concepción, Concepción, Biobío, Chile

⁴Área de Biomateriales, UDT, Universidad de Concepción, Concepción, Biobío, Chile

⁵Área de Productos Químicos, UDT, Universidad de Concepción, Concepción, Biobío, Chile

⁶Departamento de Polímeros, Facultad de Ciencias Químicas, Universidad de Concepción, Concepción, Chile

⁷Programa de Doctorado en Ciencias y Tecnologías Analíticas, Universidad de Concepción, Concepción, Biobío, Chile

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Abstract. Polylactic acid (PLA) was melt-blended with *Pinus radiata* unmodified and modified (hydroxypropyld) bark polyflavonoids in order to use such polyphenolic building-blocks as functional additives for envisaged applications. Rheological, morphological, molecular, thermal, and flexural properties were studied. Polyflavonoids improved blend processability in terms of short-time mixing. Furthermore, hydroxypropylated polyflavonoids improve miscibility in binary and ternary blends. Blend-composition affects crystallization-, melting-, and glass transition-temperature of PLA, as well as thermal resistance, and flexural properties of the blends. Polyflavonoids induced PLA-crystallization, and polymer-chain decomposition. Modified and unmodified bark polyflavonoids from radiata pine can be used successfully in PLA-based green composites beyond the food-packaging applications. The high compatibility between PLA and hydroxypropyld polyflavonoids highlights the potential of such phenolic derivatives for PLA-based material design.

Keywords: polymer composites, hydroxypropyl polyflavonoid, radiata pine, polymer processability

1. Introduction

The most important polymers in bioplastic engineering are aliphatic polyesters such as polylactic acid (PLA) [1]. Blending of PLA with other polymers such as polypropylene, natural rubbers, polyglycols (PEG), polyvinyl acetate, polyolefins, polymethyl methacrylate, and polycarbonate is an useful route towards modifying properties [2]. In addition, oligomers/polymers from lignocellulosic resources have been used as additives in order to reduce cost [3–5]. In fact, many

advantages are recognized in binary and ternary blends regarding well dispersion into the PLA-matrix, and the nucleating effect of certain biopolymers which induced dramatic changes on mechanical properties [6].

Moreover, lignin and condensed tannin (polyflavonoids) have been successfully blended with PLA [7]. However, there are few reports which describe the effect of polyflavonoids on the PLA physicochemical properties. Polyphenols properties such as an-

*Corresponding author, e-mail: d.garcia@udt.cl

tioxidant capacity, strong UV-absorption, and remarkable biological activity (antibacterial/antifungal) enables utilizing polyflavonoids as functional building-blocks for PLA-based composites. Such selected properties might be considered in order to design functional materials based on key polyphenols properties such as O₂-active barrier for food packaging, UV-filter for selected outdoor applications, antimicrobial surfaces for food industry, as well as functional films and plastic devices for agriculture.

On the other hand, polyflavonoids are highly abundant in bark that is expected to play an important role in bioplastics engineering, and thermosetting systems [8, 9]. However, limited solubility in organic solvents and molten thermoplastics, and low thermal resistance of polyflavonoids are well-known drawbacks for polymer formulation, that is why chemical modification with alkylene oxides enabling less polar derivatives highly desirable for biomaterial design [10]. Hydroxypropyl polyflavonoids (HPT, Figure 1) from pine bark is easily synthesized at room temperature with propylene oxide, and the versatility as macro building-blocks has been demonstrated in several chemistries [11].

This work reports the preparation and characterization of several PLA-based blends using bark polyflavonoids (with and without chemical modification) as the main functional additive. Rheological, morphological, molecular, thermal, and flexural analyses were performed. The new types of PLA-based coloured materials are expected to play an important role beyond the traditional food-packaging applications of PLA.

2. Materials and methods

2.1. Chemicals

2.1.1. Polylactic acid (PLA)

Partially crystalline PLA (Polylactic acid) of Natureworks Ingeo™ Biopolymer 3251 grade supplied by NatureWorks® Co. LLC, USA, was the thermoplastic used in this study: average M_w 90 000–150 000 Dalton, polydispersity (D) 1.6, melting temperature (T_m) 170 °C, glass transition temperature (T_g) 61 °C, and L-lactide content of 98%.

2.1.2. Polyflavonoid

Non-water soluble radiata pine bark polyflavonoids (PRI) extracted with methanol/water solution (1:20, w/v) at 120 °C was used [12]. Briefly, PRI are represented by a broad mixture of polyphenols (D : 1.5–2.8) mostly 4→8 linked [13, 14].

2.1.3. Hydroxypropyl polyflavonoid (PRI-3)

PRI-3 was synthesized by open-ring reaction (S_N2) using propylene oxide (PO) in alkali media (pH: 12) at room temperature (20–22 °C) as described by García *et al.* [8]. The parameters of the derivatization were described in detail elsewhere [9].

Briefly, PRI (100 g, ca. 80 mmol) was dissolved in 500 mL aq. 2 molL⁻¹ NaOH, adjusted to pH 12 and stoichiometric PO-charge added. The reaction was carried out for 24 h with stirring. Before that, HCl (40% v/v) was added to adjust the pH to 2, producing a precipitate that was centrifuged. The supernatant was collected by decantation and the precipitate was washed five times with distilled water and freeze-

Figure 1. Chemical structure of hydroxypropyl polyflavonoid (C₁₅ unit fully modified by hydroxypropylation)

dried. Reaction yields ranged from 82–90 wt% and the substitution degree (DS) was determined by $^1\text{H-NMR}$ (DS: 3.0 ± 0.2).

2.1.4. Plasticizer

CARBOWAXTM (polyethylene glycol- M_w 400 $\text{g}\cdot\text{mol}^{-1}$) supplied by Dow Chemical Company (Chile) was used as a conventional plasticizer. Technical specifications are described as follow: density: $1.13 \text{ g}\cdot\text{cm}^{-3}$, viscosity (100 °C): $7.3 \text{ mPa}\cdot\text{s}$, average number of repeating oxyethylene units (n): 8.7.

2.2. Blends formulation

Blends based on PLA were prepared at 170 °C for 15 min in a torque rheometer (Brabender 50 EHT, Germany). Binary blends were prepared in order to understand the effect of components on physicochemical properties (Table 1). Ternary blends were formulated with modified and unmodified polyflavonoids (10, 20, 30 wt%), as well as PEG.

2.3. Preparation of the blends

Solid components (PLA, PRI, and PRI-3) were pre-treated by oven-drying at 60 °C for 72 h to eliminate possible absorbed water on the surface of the particles. In a specific order components were added in a rheometer. PLA and polyflavonoids were mixed for 2 min in a mixer (mini SWJB Lab mixing equipment, China), and loaded into the chamber (time mixing, t_{mix} : 0). In ternary blends, PEG was loaded after

the PLA-melting (t_{mix} : 1.5 min). Three blends of each formulation were prepared.

2.3.1. Cold-blend processing

Blends were ground in an electric mill (IKA, Basic MF10, China) and 30 g charges were compression moulded on a LabTech LP20-B press (T : 175 °C, t : 5 min, p : 32 bar). Laminates of 100 mm^2 (thickness: 1.5 mm) were used for the flexural, and microscopy testing.

2.4. Physicochemical properties

2.4.1. Rheology

Rheology measurements were carried out in a torque rheometer with roller blades. The rotor speed was 50 rpm, and the free volume of the chamber was 20% of the total volume.

2.4.2. Confocal microscopy (particle size distribution)

Particle morphology of the blends was assessed by confocal fluorescence microscopy.

The fluorescence emission pattern of polyflavonoids (powder), and blends (laminate) were assessed by a systematic analysis. Dry samples were irradiated (Laser I: $\lambda_{405 \text{ nm}}$, Laser II: $\lambda_{488 \text{ nm}}$, and Laser III: $\lambda_{561 \text{ nm}}$), and fluorescence emission recovered. A Zeiss LSM 780 confocal microscope with several diode laser and a Coherent Chameleon laser (Ti:sapphire) for one-photon, was used in the experiments. Samples were

Table 1. Composition of PLA-based blends prepared at 170 °C

Blend	Component [wt%]				Code
	PLA	PRI	PRI-3	PEG	
PLA/PRI	80	20	0	0	PLA ₈₀ /PRI ₂₀
	70	30	0	0	PLA ₇₀ /PRI ₃₀
	60	40	0	0	PLA ₆₀ /PRI ₄₀
PLA/PRI-3	80	0	20	0	PLA ₈₀ /PRI-3 ₂₀
	70	0	30	0	PLA ₇₀ /PRI-3 ₃₀
	60	0	40	0	PLA ₆₀ /PRI-3 ₄₀
PLA/PEG	80	0	0	20	PLA ₈₀ /PEG ₂₀
	70	0	0	30	PLA ₇₀ /PEG ₃₀
	60	0	0	40	PLA ₆₀ /PEG ₄₀
PLA/PRI/PEG	60	10	0	30	PLA ₆₀ /PRI ₁₀ /PEG ₃₀
	60	20	0	20	PLA ₆₀ /PRI ₂₀ /PEG ₂₀
	60	30	0	10	PLA ₆₀ /PRI ₃₀ /PEG ₁₀
PLA/PRI-3/PEG	60	0	10	30	PLA ₆₀ /PRI-3 ₁₀ /PEG ₃₀
	60	0	20	20	PLA ₆₀ /PRI-3 ₂₀ /PEG ₂₀
	60	0	30	10	PLA ₆₀ /PRI-3 ₃₀ /PEG ₁₀

PLA: poly-lactic acid, PRI: unmodified radiata pine polyflavonoid, PRI-3: hydroxypropyl radiata pine polyflavonoid (DS: 3), PEG: polyethylene glycol

observed with a C-Apochromat objective lens (63 $\times$, numerical aperture 1.2) in the opposite side of the cover slip. The images were obtained by the average of two scans. In all experiments, at least three sites of the blend were studied, and no appreciable variation was observed in the fluorescence properties among or within-sample. Considering the numerical aperture and the wavelength of excitation, the spatial resolution was approximately 200 nm. The optical zoom was 63 $\times$. A further digital zoom was used. The percentages of the lasers nominal powers were 1.2% ($\sim 20 \mu\text{W}$) for a 20 $\times$ objective.

Image-analysis of the maximum intensity projection was used in order to estimate the polyflavonoid particle size distribution as a referential parameter of component miscibility. IMARIS software (version 7.5.2, module Pro program) allowed estimating various types of numerical values based on the three-dimensional structures in confocal images.

Volume calculation of polyflavonoid particles was carried out using an automatic segmentation tool (Spots). The following parameters were considered: (1) different sizes, (2) estimated diameter, (3) quality above automatic threshold, (4) region growing -absolute intensity threshold with 7000 (for red channel) and 7500 (for green channel)-, and (5) diameter from volume. The segmented particles volume values of each image were plotted in a normalized histogram (in logarithmic scale). A range of relationship between volume, and volume sum of particles corresponding to this range was performed. Three replicates were averaged in order to define particle size distribution trends.

2.4.3. Molecular weight (M_w) distribution

Molecular weight distribution of the PLA after processing was acquired by size exclusion chromatography (SEC). Neat-PLA, processed-PLA and powdered blends (1 g) were dissolved in 70 mL of chloroform at room temperature (20–22 °C) during 7 days under stirring. The resulting suspension was centrifuged for 5 min at 4000 rpm, and an aliquot (50 μL) was analyzed using isocratic chloroform-eluted at 22 °C. Instrument (GPC Shimadzu, Japan) was equipped with DAD, and RID detectors. Polystyrene-divinylbenzene standards (Phenogel[®]) were used for calibration.

2.4.4. Thermal properties

Differential scanning calorimetry (DSC)

DSC analysis was performed on a NETZSCH DSC instrument (204 F1 Phoenix, Germany). Samples (7 $\pm$ 3 mg) were sealed in high pressure steel pans; at a cooling rate of 10 °C $\cdot$ min⁻¹, and heated from 50 to 160 °C at 20 °C $\cdot$ min⁻¹ heating rate under N₂ atmosphere, flow rate 20 mL $\cdot$ min⁻¹. The sample was then cooled back to 50 °C at 10 °C $\cdot$ min⁻¹, and heated again from 50 to 250 °C at 20 °C $\cdot$ min⁻¹. The glass transition temperature (T_g) of the blends was taken as the mid-point in the C_p step on the 2nd run associated at the second order thermal transition.

Thermal stability

Thermal stability was carried out using thermogravimetric analysis (TGA) performed on a NETZSCH TGA instrument (TG 209 F3 Tarsus, Germany). Samples of 6 $\pm$ 2 mg was heated at 10 °C $\cdot$ min⁻¹ from 25 to 600 °C under N₂ atmosphere, flow rate 20 mL $\cdot$ min⁻¹. The degradation temperature (T_d) was determined from the temperature peak obtained in the 1st derivative curve. The $T_{5\%}$ (5% of mass loss) was determined based on the TGA thermogram.

2.5. Flexural testing

Pressed laminated samples were cut with a die (gage length 60 mm, width 1.5 $\pm$ 0.2 mm) and kept in a climate chamber oven overnight (T : 23 $\pm$ 1 °C, p : 1.0 atm, relative humidity: 50 $\pm$ 3%), and the Young's modulus (E) were determined [15]. Universal tensile testing machine (SmarTens 005, KARG Industrietechnik, Germany) was used employing a crosshead speed of 10 mm $\cdot$ min⁻¹. Eight laminate samples for each treatment were used for the flexural test analysis.

3. Results and Discussion

3.1. Evaluation of processability by torque rheometer

Selected torque-rheometer plots as a function of time at 50 rpm is provided (Figure 2).

Modified (PRI-3), and unmodified polyflavonoids (PRI) reduced the PLA-softening point. The decreasing of the torque on PRI-based blends associated to the PLA-softening point was clear, and it can be observed around 1.5 min. Modified polyflavonoid favors the earliest PLA-softening point (t_{mix} : 0.8 min) re-

Figure 2. Rheological behaviour of neat PLA, and selected PLA-based blends prepared at mixture temperature of 170 °C (t_{mix} : 15 min)

regardless blend-composition. The dramatic influence of polyflavonoids on the PLA behavior is unexpected. However, the structure of polyphenol in terms of aromatic-content might be affecting the heat-transfer process during the mixing. In addition, the low heat-capacity of aromatic compounds in binary and ternary thermodynamical systems is a well-known issue [16]. However, the apparent low heat-capacity of polyflavonoids is not enough reason for the remarkable shifting of the PLA-softening point. Chemical interaction between PLA-chain and modified polyflavonoids grafting moieties apparently affects PLA-thermal behavior. In fact, it is important to bring the homogenization times to a minimum. However, modified polyflavonoid reduced the mixing-time significantly at

the expense of the higher torque values (torque: 40–80 Nm). In contrast, unmodified polyflavonoids reduced slightly the torque in comparison to the neat PLA (Figure 3).

Blends prepared with modified polyflavonoid (PRI-3) induced the higher torque values. The high aliphatic OH-content of polyflavonoid derivatives in comparison to the lower ones of neat polyflavonoids apparently increases the viscosity during the melting, and in consequence the resistance to the rheometer blades. The differences in torque values can be explained considering that the viscoelastic properties of polyflavonoids dramatically change upon hydroxypropylation [9–11]. It is well-known that the aliphatic –OH functionalities enhance hydrogen-bridge interaction between polymer chains. In addition, strong association between linear aliphatic PLA's chain, and the hydroxypropyl grafting from the derivatives during blending might be also considered.

On the other hand, low interaction between neat polyflavonoids and PLA-chains can be explained in terms of the high differences in polarity of the two biopolymers [10, 17]. However, molecular association between PLA and polyflavonoids in the molten-state has not been documented before.

3.2. Molecular weight distribution

A dramatic effect of the blend-composition, and the processing strategy on the PLA- M_w was observed (Figure 4).

Figure 3. Maximal torque associated to the PLA-melting in function of the polyflavonoid-content for PLA-based blends prepared at 170 °C (t_{mix} : 15 min). (a) binary blends (PLA/PRI, and PLA/PRI-3). (b) ternary blends (PLA/PRI/PEG, and PLA/PRI-3/PEG). $N = 3$. Note: data illustrate the torque variation during the first two minutes of mixing.

Figure 4. Selected GPC-traces of PLA from PLA-based blends illustrating changes of the molecular weight distribution. Thermal treatment: 170 °C, 15 min.

PEG as a blend-components affected slightly the M_{wPLA} . However, degradation of PLA in polyflavonoid-based binary blends was the highest regardless the polyflavonoid-type. The degradation mechanisms of PLA-based materials have been well-described [1, 17, 18]. In fact, several components on blends have been recognized as degradation promoters of PLA-degradation [22–26]. M_{wPLA} decreased in ca 40 000 g·mol⁻¹ suggesting random cleavages on the polymer chains apparently by the effect of the polyflavonoid acidity (natural pH: 3.0–4.5). However, 15 minutes of PLA-processing on the rheometer (T : 170 °C) also affects the M_{wPLA} from $15.4 \cdot 10^4$ to $13.8 \cdot 10^4$ g·mol⁻¹.

Unmodified polyflavonoids had the biggest influence in PLA-degradation (Figure 5a). The results highlight the influence of polyphenols as the main source of PLA-degradation.

On the other hand, increased D as (dispersity) a function of the polyflavonoid-content can be interpreted as a greater diversity of degraded polymer-chains during the blending [11].

It is worth noticing that the modified polyflavonoids (PRI-3) had a minor effect on polydispersity even at the highest derivatives-charge (Figure 5b). Apparently the replacement of the acidic hydroxyl groups (–OH, pK_a : 9–10) by the hydroxypropyl chain (–OH, pK_a : 13–16) decreases the detrimental effect of polyflavonoids on PLA-degradation during processing. The remarkable influence of polyflavonoids on the M_{wPLA} can be used as an advantage for PLA/polyflavonoid blend formulation, considering that the

Figure 5. Molecular weight features of PLA-based blends prepared at 170 °C (t_{mix} : 15 min). (a) Molecular weight distribution in function of the component-content, (b) dispersivity values (D) in function of the blend-type. $N = 3$.

biodegradability and disintegration of PLA, and PLA-based materials are strongly associated to the M_w of

the polymer-matrix, the crystallinity degree, and the chemical lability of selected functional groups [18]. That is why polyflavonoids can be used for tailoring PLA's molecular properties. In addition, polyflavonoids also might be advantageous as functional additives for several biopolymers such as starch, cellulose, and commercial biodegradable aliphatic copolymers (Ecoflex[®] and Ecovio[®]) [3, 24, 26].

3.3. Morphology

3.3.1. Confocal fluorescence microscopy (spectrum pattern)

Confocal fluorescence microscopy is an extremely useful tool enabling polyphenols quantification [19]. The strong fluorescence pattern of polyflavonoids can be used to estimate particle size and particle shape, considering the fact that polyflavonoid-derived composites have a typical dark appearance.

Considering that polyflavonoid blends are colored composites (image not-shown), the evaluation of fluorescence emission pattern was performed considering that PLA, and PEG are not-active fluorescent molecules. Such features were utilized in order to study the morphological features of PLA-based blends [11, 20].

The emission spectra of PRI and PRI-3 were assessed by the three types of lasers (λ_I : 405 nm, λ_{II} : 488 nm, λ_{III} : 561 nm). Chemical modification has a negligible influence on the emission pattern (Figure 6a). Results allowed concluding that fluorescence measurements are not affected significantly by hydroxypropylation. Apparently, the structural variations upon derivatization do not affect the energy emission pattern.

Based on such findings, fluorescence emission pattern of binary and ternary PLA-based blends was assessed by two lasers (λ_I and λ_{III}) covering the entire range of wavelength. As expected, marginal differences regarding emission pattern in function of blend-composition were observed (Figure 6b).

Regardless blend-composition, maximal fluorescence emission (λ_I) oscillated between 480 and 520 nm, while Laser III (λ : 561 nm) induces an emission pattern in a narrow range of wavelength (600–630 nm). That is why red light was used in order to assess the morphological features of the blends.

Figure 6. Fluorescence emission features of polyflavonoids, and polyflavonoids-based blends prepared at 170°C (t_{mix} : 15 min). (a) emission spectra of modified (PRI-3), and unmodified (PRI) polyflavonoids, (b) emission spectra of PLA-based blends, (1) PLA₇₀/PRI₃₀ (Laser λ_I : 405 nm), (2) PLA₇₀/PRI₃₀ (Laser λ_{II} : 561 nm), (3) PLA₆₀/PRI-3₂₀/PEG₂₀ (Laser λ_I : 405 nm), and (4) PLA₆₀/PRI-3₂₀/PEG₂₀ (Laser λ_{II} : 561 nm).

3.3.2. Particle size distribution (image-processing)

Maximal intensity projection of selected PLA-based blends is shown (Figure 7).

Image-processing revealed remarkable differences in morphology of polyflavonoid particles dispersed on the PLA-matrix (N). The methodology allowed a high count of particles. Particle volumes were determined on the basis of a selective channel (red, λ_{III} : 561 nm). PRI-3-based blends exhibited the smallest particles volume, which describes the better miscibility of polyflavonoid derivatives (Figure 8a), whereas the particle size of PRI, and PRI-3 were rather similar (see Figure 8b).

However, PRI particles volume was the biggest in ternary blends. Apparently, certain interaction between polyflavonoids and PEG affects significantly the con-

Figure 7. Maximum intensity projection of selected PLA-based blends prepared at 170 °C (t_{mix} : 15 min). (a) PLA₇₀/PRI₃₀, (b) PLA₇₀/PRI-3₃₀, (c) PLA₆₀/PRI₂₀/PEG₂₀, (d) PLA₆₀/PRI-3₂₀/PEG₂₀.

formational features during the blending. The result matches with the spherical particle morphology clearly visible on the maximum intensity projection image (see Figure 7c). In fact, it is well-known that PEG interacts strongly with polyflavonoids via hydrophobic domains [11, 21]. The H–H interaction enables an open-conformation of the polyflavonoid molecules, so increasing volume was apparently associated to molecular complexation during the melt-blending. Normalized histogram (Figure 8) shows that polyflavonoid chemical modification enhances the miscibility on the PLA-matrix regardless the blend-type. On the other hand, unmodified polyflavonoids show similar particle volume distribution to the referential PRI volume (see Figure 8b). Limited solubility of

polyphenols on the PLA-matrix can be explained considering the high difference in polarity between PRI, and PLA.

As described previously by image-processing, PEG affects dramatically the polyflavonoid particle volume.

The low polarity of PRI-3 is a key factor to understand the better compatibility features of modified polyflavonoids on the PLA-matrix. Maximum interaction between the hydroxypropyl moieties with the PLA-chain, and PEG during the mixing highlights that the chemical modification is a feasible strategy in using polyflavonoids in bioplastics.

In addition, it is worth to highlight that confocal microscopy (fluorescence emission) coupling to image-

Figure 8. Normalized polyflavonoids particle volume of PLA-based blends assessed by emission fluorescence microscopy. (a) Polyflavonoids particle volumen (reference), (b) polyflavonoids particle volumen in blends (binary blend: PLA_{70%}, ternary blends: PLA_{60%}/PEG_{10%}). Note: polyflavonoid particles volume is expressed in logarithmic scale.

processing is a useful technique in estimating the morphological parameters of PLA biopolymer blended with natural polyflavonoids.

3.4. Thermal properties

3.4.1. DSC analysis

Selected thermograms illustrate the T_g , and T_m of the neat PLA, and PLA-based blends (Figure 9). It is evident that neat PLA has a T_g of 60 °C, and T_m of 170 °C. In binary blends polyflavonoids did not significantly influence the T_{gPLA} value. However, such polyphenols induce the PLA-crystallization (T_c : 100 °C) to a high extent. The nucleating effect of polyflavonoids in PLA-based blends has been not well-clarified in previous works. Differences in polarity, hydroxyl-content, and conformational features are factors apparently affecting the PLA-crystallization behavior induced by polyflavonoids.

On the other hand, PEG induces a reduction of T_{gPLA} (55.6 °C), as well as the T_{cPLA} . The synergetic effect of PEG on the PLA-thermal properties has been pre-

viously reported, as well as on the crystallization behavior [22–26]. The remarkable effect on thermal properties can be explained considering that PEG favors the breaking of intermolecular hydrogen bridges of PLA during processing, prone to an early melting, and a significant T_g reduction.

In addition, Figure 9b, 9c shows in detail the thermal behavior of all tested blends according to the component-loading. Polyflavonoid induces a significant T_{mPLA} and T_{cPLA} reduction in ternary blends. However, the variation of T_g , T_c , and T_m in binary blends was negligible. In contrast, PEG significantly affects the T_{gPLA} , T_{mPLA} and T_{cPLA} values.

It is worth noticing that the depression of the T_{gPLA} , and T_{cPLA} was remarkable in PRI-3-based blends. The results describe the advantageous effect of the chemical modification on the miscibility features.

Apparently, polyflavonoids act as an effective nucleating agent in PLA-based blends. The PLA-crystallization during the blend-cooling has an important impact on the mechanical properties. Several salts

Figure 9. Thermal behavior (DSC) of PLA-based blends prepared at 170 °C (t_{mix} : 15 min) considering the second heating. (a) Selected DSC-traces, (b) transitional temperatures in function of polyflavonoid-content (binary blends), (c) transitional temperatures in function of polyflavonoid-content (ternary blends). $N = 3$.

(talcs), organic compounds (amines), fibers, nanotubes, and commercial nucleating (3801X, and LAK) have been reported as nucleating agent in PLA-based blends [23, 24]. However, to our knowledge it is the first time that polyphenols from pine bark are reported as nucleating agents in PLA-matrix in a wide range of composition.

The synergic effect between PEG and polyflavonoids on the PLA thermal behavior (T_g , T_c , T_m) has been also reported in several systems [25, 26]. The similarities regarding functional groups of PEG and PLA apparently favor the mobility of the chain and breaks the intermolecular hydrogen bonds which reduce transitional temperatures.

Since the T_g value is an excellent indicator of chain mobility, plasticizing efficiency has therefore been evaluated by measuring the T_g shifting as a function of plasticizer concentration. All the binary blends show only one T_g in the DSC-thermogram indicating an apparent good miscibility between PLA, PRI-3, and PEG. The decrease of T_g highlights the effect of the plasticizer in PLA compositions with increasing molecular mobility. The plasticizing effect is confirmed by the modification of T_g which is significantly decreased by comparison to the neat PLA matrix (T_g : ~60 °C).

3.4.2. TGA analysis

The selected thermograms showed that a significant change to the degradation temperatures according to the blend-composition was observed (Figure 10). The T_d values were above 300 °C. However, a remarkable effect of components on the $T_{5\%}$, and T_d of ternary blends was noticed.

Thermal behavior of binary and ternary-blends reveals a significant effect of the polyflavonoids-content (Figure 10).

Neat polymers (PLA, PEG), exhibited a single decomposition peak, indicating that they degraded mainly in one step (data not-shown). Polyflavonoid-content affects the $T_{5\%}$, and T_d significantly. The results can be explained considering that polyphenols are thermally unstable building-blocks, prone to yield carbonaceous residues as a consequence of pyrolytic processes [9, 11].

PRI-3-based ternary blends show the lowest T_d . The result is unexpected considering the high thermal stability of PRI-3 in comparison to unmodified bark polyflavonoids described in previous reports [11]. However, polyflavonoid's DS cannot be considered as the unique factor affecting thermal decomposition of the blends. The substitution pattern on the C₁₅ polyflavonoid unit (see Figure 1) seems to be a key factor

Figure 10. Thermal behavior (TGA) of PLA-based blends prepared at 170 °C (t_{mix} : 15 min). (a) Selected TGA-traces, (b) decomposition temperatures in function of polyflavonoid-content (binary blends), (c) decomposition temperatures in function of polyflavonoid-content (ternary blends). $N = 3$.

for polyphenols degradation [8, 9]. The low M_w distribution of the water-insoluble tannin fraction (PRI), as well as the lipophilic character of such polyflavonoids as a consequence of concomitants apparently affects the thermal stability of the blends in a differentiated manner.

On the other hand, all PLA-blends showed significant residues at 600 °C (<20%). Residual weight increased with increasing polyflavonoid-content, excepting in PLA-based ternary blends (Figure 11). The results point out that the polyflavonoid-based pyrolytic residues are significant products during the blend decomposition. However, a strong interaction between PEG, and polyflavonoids on the residual

weight was evidenced. Apparently, polyphenol-PEG complexation favored the volatilization rate at high temperatures (>400 °C).

3.5. Flexural testing

PLA-based blends exhibited a typical stress-strain curve which describes that the samples breaks before yielding (Figure 12). Curve morphology was affected by the blend-composition.

The flexural behaviour of the neat PLA showed characteristics of glassy polymers with low deformation at break. In contrast, PLA-based blends showed a different behaviour (Table 2).

In general, PLA/PRI blends show poor performance in term of Young's modulus (E). In contrast, the highest PRI-3-charge the highest E -values. The behavior can be explained by incompatibility between the neat polyflavonoids, and the PLA polymer due to the difference in polarity, and molecular features.

In addition, the E -modulus value dropped dramatically from 88 to 22 MPa with incorporation of PRI (10 wt%); indicating incompatibility. In contrast, E -modulus was improved in 15 MPa when PRI-3 was loaded from 10 to 30 wt%. This can be explained by the role of hydroxypropyl-chain which apparently acts as a compatibilizer moiety in binary-, and ternary-blends.

Figure 11. Residual weight at 600 °C of binary-, and ternary-blends prepared at 170 °C (t_{mix} : 15 min). $N = 3$.

Figure 12. Mechanical performance of PLA-based blends prepared at 170 °C (t_{mix} : 15 min). (a) Selected stress-strain curves, (b) E -modulus in function of the polyflavonoid content. $N = 8$.

Table 2. Mechanical performance of PLA-based blends prepared at 170 °C for 15 min

Blend	F_m [N]	σ_{fM} [MPa]	ε_{fM} [%]
PLA	37.5±5	2.70±1.0	16.6±5.0
PLA ₈₀ /PRI ₂₀	18.1±3	0.30±0.01	6.1±0.1
PLA ₇₀ /PRI ₃₀	12.4±2	0.15±0.01	4.5±0.3
PLA ₆₀ /PRI ₄₀	7.2±1	0.11±0.01	2.12±0.1
PLA ₈₀ /PRI-3 ₂₀	13.6±5	1.82±0.21	4.13±0.5
PLA ₇₀ /PRI-3 ₃₀	10.0±2	1.88±0.30	4.23±0.4
PLA ₆₀ /PRI-3 ₄₀	2.0±1	1.62±0.41	1.12±0.1
PLA ₆₀ /PRI ₁₀ /PEG ₃₀	11.3±2	0.46±0.33	14.7±0.9
PLA ₆₀ /PRI ₂₀ /PEG ₂₀	10.6±2	0.19±0.02	12.8±0.9
PLA ₆₀ /PRI ₃₀ /PEG ₁₀	9.6±1	0.09±0.01	11.6±0.7
PLA ₆₀ /PRI-3 ₁₀ /PEG ₃₀	8.0±1	0.21±0.02	12.4±0.9
PLA ₆₀ /PRI-3 ₂₀ /PEG ₂₀	10.4±2	0.25±0.02	10.87±0.6
PLA ₆₀ /PRI-3 ₃₀ /PEG ₁₀	15.0±3	0.46±0.03	14.4±0.3

Average±standard deviation, F_m : maximum force, σ_{fM} : flexural strength, ε_{fM} : flexural strain. $N = 8$.

4. Conclusions

PLA-based blends have been successfully prepared with *P. radiata* bark polyflavonoids, by melt-blending at 170 °C during 15 min. This compounding strategy is easy and potentially commercially viable for PLA applications beyond the food-packaging.

Modification of radiata pine polyflavonoids is a valuable alternative in order to improve the performance of such building-blocks in binary-, and ternary-blends. Chemical structure of the polyflavonoid's grafting influences: (1) the blend processability, (2) the component miscibility, (3) the PLA's melting-, and crystallization-processes, (4) the thermal resistance, and (5) the flexural performance.

Rheological behavior of PLA-based blends is dramatically affected by the type-, and component-compo-

sition. Considering the torque-rheometer data modified, and unmodified radiata pine polyflavonoids improved the processability of PLA in term of a short-mixing.

The image-processing using confocal fluorescence microscopy was successfully utilized in order to estimate the particle volume as an indicator of polyflavonoid's miscibility. The modified polyphenols showed higher compatibility features as a consequence of the dramatic reduction of the particle volume.

Polyflavonoid induces PLA-crystallization in a high extent. The synergetic effect of PEG with polyflavonoids is related to the chemical similarity of the polymer chains enhanced upon grafting (hydroxypropyl-chain). The result is highly relevant in view of polyflavonoid-based composites preparation.

Modified polyphenol decreases slightly the thermal stability of the blends below 300 °C. Such drawback is negligible considering that the PLA-processing temperature is around 170 °C.

On the other hand, the tannin acidity affects the PLA molecular weight distribution which influences the flexural performance. Also the thermal processing of the neat PLA affects the M_w of the polymer.

The increasing of the E -modulus of the blends as effect of a good mixing of polyflavonoids derivatives on the PLA-matrix was achieved.

P. radiata bark polyflavonoids might be used for PLA-based blends formulations in view of novel envisaged applications. Polyflavonoid-based composites seem to play a key role in polymer engineering in a near future.

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