



## Synthesis of maleilated polyflavonoids and lignin as functional bio-based building-blocks



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### ARTICLE INFO

#### Keywords:

Polyflavonoids  
Lignin  
Radiata pine  
Chemical modification  
Maleic anhydride

### ABSTRACT

Polyflavonoids and lignin from *Pinus radiata* (D. Don.) biomass were esterified with maleic anhydride by several synthesis pathways (22 °C, 24 h). Influence of the solvent (dimethylformamide (DMF), DMF/H<sub>2</sub>O, acetone, formamide)-, the catalyst-type (H<sub>2</sub>SO<sub>4</sub>, NaHCO<sub>3</sub>), and the NaHCO<sub>3</sub>-change (70 and 100 mmol) on the esterification yield, and the degree of substitution (DS) were estimated. The effect of the maleilation on structural features was assessed by spectroscopy (FT-IR, UV-vis, RMN), and molecular exclusion chromatography. FT-IR, and <sup>1</sup>H-NMR provide valuable insight regarding the esterification extent. The results show that esterification of high molecular weight polyphenols exhibited reasonable yields (80–95 wt.%). A significant influence of the solvent-, and the catalyst was observed. Synthesis in formamide, as well as by the highest charge of the alkaline catalyst, exhibited the best performance toward the polyphenol's modification. Maleilation efficiency was strongly influenced by the polyphenol-type. Non-water soluble polyflavonoid derivatives exhibited the highest DS/monomer unit regardless the synthesis conditions. Carboxylated polyphenols from radiata pine may be used as functional co-polymer for new kinds of material applications.

### 1. Introduction

Polyphenols are widely distributed secondary metabolites with chemoprotective functions in nature. The high abundance of polyphenols in woody plants, as well as the remarkable biological activity highlight the interest for developing functional phenolic building-blocks in several science fields (García et al., 2016).

Polyphenols comprise low, and high-molecular weight (*M<sub>w</sub>*) molecules. Among polyphenolic compounds polyflavonoids (condensed tannins), hydrolysable tannins (gallic/ellagic acid derivatives), and lignin are high-*M<sub>w</sub>* polymers with recognized impact in bio-based material design.

Despite the relevance of polyflavonoids and lignin as natural building-blocks, the use of polyphenols in polymer formulation has been a challenge. Disadvantages such as low solubility in organic solvents, thermal instability, and the lack of reactive functionalities beyond hydroxyl groups (–OH) limited the use of polyphenols as functional co-polymers in materials science, environmental chemistry, agriculture, and biomedicine.

On the other hand, mechanical properties of several biobased materials deteriorate with polyphenols additives because the low compatibility/miscibility of such polar molecules in a nonpolar polymer matrix (Chen et al., 2014). Nevertheless, dimensional stability, as well as enhanced biological degradation of those composites, has been

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attributed to polyphenolic functionalities (García, 2014; Anwer et al., 2015).

Considering the physicochemical constrains, chemical modification of polyphenols is a viable strategy in order to tailor properties and diversify applications (Grigsby et al., 2013; García, 2014). For instance, esterification of polyflavonoids, and lignin with five-member unsaturated cyclic anhydrides provides several advantages: (1) the esterification is free of side-chain products, (2) cyclic anhydrides are more reactive than linear-chain counterparts, and (3) the unsaturated carboxylic chain is a desirable functionality for several kinds of polymerization pathways.

The  $\alpha$ - $\beta$  unsaturated carboxylic-chain from derivatives is considered to be a biologically active moiety. In addition, the grafting improves the miscibility with thermoplastics (FONDECYT, 2015).

Among commercial cyclic anhydrides, maleic anhydride (MAH) is a high-tonnage industrial chemical widely used for polymer manufacturing. In fact, several OH-containing compounds such polymers, heterocycles, cellulose, lignin, as well as wood chips, and silk were successfully esterified with maleic anhydride (Chen et al., 2014, 2003; Evtushenko et al., 2000; Wibowo et al., 2006; Abdul et al., 2011). The high reactivity of maleic-based derivatives highlights maleilation (esterification) as a viable pathway for a successful use of polyphenols into the industry of plastics (Toriz et al., 2004). However, nowadays applications of polyflavonoids in the industrial biobased materials framework are almost restricted to adhesive formulation (García, 2014; Berg et al., 2009).

On the other hand, the development of novel polyphenol-based materials is an important task worldwide. In general, biomass from pine (*Pinus pinaster*, and *Pinus radiata*), eucalyptus (*Eucalyptus globulus*, and *Eucalyptus nitens*), and Acacia (*Acacia mersii*) plantations provides several extractable compounds fairly undervalued. In order to valorize such polyphenolic fractions, polycarboxylic derivatives from pine biomass (bark and wood) might play an important role in several applications.

The aim of this work was to explore chemical modification of polyflavonoids and lignin from radiata pine. The derivatives were prepared by several synthesis runs, and the esterified products characterized by spectroscopic, and physicochemical methods.

The most feasible pathways in terms of solvent and catalyst are proposed based on the esterification efficiency.

## 2. Materials and methods

### 2.1. Polyphenolic feedstocks

#### 2.1.1. Polyflavonoids

Water-soluble polyflavonoids (TS) and water-insoluble polyflavonoids (TI) from *P. radiata* bark were isolated under pilot-plant conditions.

The extraction of polyflavonoids (TS and TI) were performed in methanol/water solution (1/20, wt./v) at 120 °C in a conical-made stainless steel reactor (800 L).

After the extraction process the TI-fraction was collected by precipitation during the methanol evaporation at 80 °C.

The TI fraction (12 kg) was washed with distilled water (40 °C), and oven dried at 60 °C during 48 h.

The TS (25 kg) remained soluble in the liquor after the precipitation of the TI-fraction. TS-containing solution was spray-dried, and the powder kept on a dessicator until use.

Briefly, *P. radiata* bark polyflavonoids comprise a broader polydispersity (D: 1.5–2.8) of flavonol-based oligomers mostly 4→8 linked (García et al., 2016).

TS-fraction is described as follows: highly hygroscopic polyphenol, moisture content: (7–18 wt%), color: pale brown powder; pH(H<sub>2</sub>O): 4.5, glass transition temperature (T<sub>g</sub>): 125 °C, decomposition temperature (T<sub>d</sub>): 220 °C. Such polyphenols possess a well-known hydroxyl groups

ratio determined by García et al. (2016) (<sup>1</sup>H-NMR – OH<sub>total</sub>/C<sub>15</sub>(monomer unit): 4.6 ± 0.1; –OH<sub>aliphatic</sub>: 1.2 ± 0.1, –OH<sub>aromatic</sub>: 3.4 ± 0.2). In addition, the soluble polyflavonoid fraction exhibits low molecular weight compounds determined by UPLC-MS/MS by García et al. (2018) (62% wt. polyflavonoids (mainly monomers, dimers, and trimers), sugars content (6% wt.), glucosides (4% wt.), and concomitant polyphenols 9% wt. (stilbene, phenolic acids and flavanols).

In contrast, the TI-fraction shows a sticky appearance, moisture content: 2–9 wt%, color: dark-brown powder; pH(suspension in H<sub>2</sub>O): 6.5, glass transition temperature (T<sub>g</sub>): 60–75 °C, decomposition temperature (T<sub>d</sub>): 200–230 °C. The structural features of the TI-fraction assessed by <sup>1</sup>H-NMR is describe as follow: (–OH<sub>total</sub>/C<sub>15</sub> (monomer unit: 4.2 ± 0.1; –OH<sub>aliphatic</sub>: 1.8 ± 0.1, –OH<sub>aromatic</sub>: 2.4 ± 0.2), and C–H aliphatic/C–H aromatic ratio:0.8)). TI-fraction are mainly composed of oligomers/polymers of flavanol units (86%wt.) and traces of lipophilic compounds (4.5% terpenes, fatty acids, and high molecular weight lipophilic moieties).

#### 2.1.2. Lignin

Lignin (L) from *P. radiata* wood was extracted by the Acetosolv process in acid media under pilot-plant condition. The method comprises: (1) delignification, (2) separation of lignin and hemicellulose, (3) acetic acid removal from the pulp, and (4) solvents separation (Berg et al., 2014).

Delignification was performed in a conical-made stainless steel reactor (volume of 800 L, DIN 1.4571) operated up to 12 bar. The extraction system consisted of a continuous extrusion press with a compression ratio of 1/5 (Vetter brand, type Bv) and a 3000 l dilution tank with stirrer (Berg et al., 2014).

*P. radiata* lignin was extracted with acetic acid/water (87/13, v/v) at 160 °C. Isolation was carried out by water adding to the black liquor, which induces the lignin precipitation, and the hemicellulose solubilization.

Lignin (5 kg) obtained from the pilot-plant was exhaustively washed with distilled water in order to remove the acid traces, oven-dried, and stored in a freezer (5 °C) prior to use.

## 2.2. Chemicals

Maleic anhydride (> 99%), sodium bicarbonate (≥ 99.5%), sulfuric acid (95.0–98.0%), dimethyl-formamide (DMF) (99.8%), formamide (99%), and acetone (99.5%) were provided by Sigma-Aldrich, Germany. All chemicals were used without further purification.

### 2.3. Synthesis of modified polyphenols (polyflavonoids and lignin)

In order to study the effects of the catalyst- and solvent-type the three kinds of polyphenols (TS, TI, L) were used. In addition, the effect of the polyphenol:catalyst ratio was evaluated (Table 1).

Briefly, polyphenols (25 mmol) were dissolved in 100 ml of the

**Table 1**

Synthesis parameter for the esterification of polyflavonoids and lignin with maleic anhydride at room temperature (22 ± 2 °C).

Synthesis run	Solvent (100 mL)	Catalyst (mmol)
1	DMF	H <sub>2</sub> SO <sub>4</sub> (20)
2	DMF	NaHCO <sub>3</sub> (70)
3	DMF/H <sub>2</sub> O (95/5, v/v)	NaHCO <sub>3</sub> (70)
4	DMF	NaHCO <sub>3</sub> (100)
5	Formamide	–
6	DMF/H <sub>2</sub> O (95/5, v/v)	NaHCO <sub>3</sub> (100)
7	Acetone	–
8	DMF	–

Synthesis runs were performed using 25 mmol of polyphenol, and 600 mmol of MAH. MAH: maleic anhydride, DMF: dimethyl formamide.

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