Polyphenolic resins prepared with maritime pine bark tannin and bulky-aldehydes

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ARTICLE INFO

ABSTRACT

Tannin-based resins were prepared by acid-catalized polycondensation of maritime pine (*Pinus pinaster* Ait.) bark condensed tannin (CTs) and several aldehydes (A) in different molar ratio (CTs:A, 1.0:0.5; 1.0:1.0; 1.0:1.5) to assess the impact of the aldehyde chain structure on the novolac properties. The resin systems were characterized in term of reactivity, structural, morphological and thermal properties. Systematic relationships between aldehyde chain length and C-stage resin properties were established. When alkyl aldehydes with increasing chain lengths were used, reactivity with CTs decreased while C-stage resins exhibited systematic increases in bulk density, T_g and thermal stability. For the di-aldehydes and αβ-unsaturated aldehyde series, opposite trends were observed. This study on tannin-based novolacs demonstrates the potential to tailor aldehyde/tannin reactivity and C-stage resin properties in a systematic manner as a function of aldehyde chain length, functionality and unsaturation degree.

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1. Introduction

The environmental issues associated with a petroleum-based economy is urging material scientists to substitute oil-based materials with renewable sourced compounds (Gardziella et al., 2000). Lignocellulosic biomass contains up to 30–40% polyphenols in the form of lignin and tannin (Zhu et al., 2011), providing wide opportunities for substituting phenol and phenol-based polymers with bio-based polyphenols. For condensed tannins (CTs) such opportunities were first explored by Pizzi's group in the late 1970s, 1980s and 1990s with the synthesis of tannin-based phenolic resins (Pizzi,

1980, 1982; Valenzuela et al., 2012) from mimosa, quebracho and pine tannins. In particular, tannins from common softwood species in Europe such as maritime pine (*Pinus pinaster* (Ait.)) and radiata pine (*Pinus radiata* (Don.)) can be easily extracted with hot water from the abundant bark byproduct already available within the forest products industry. These highly reactive oligomers are interesting candidates to substitute for phenol in the preparation of phenolic resins.
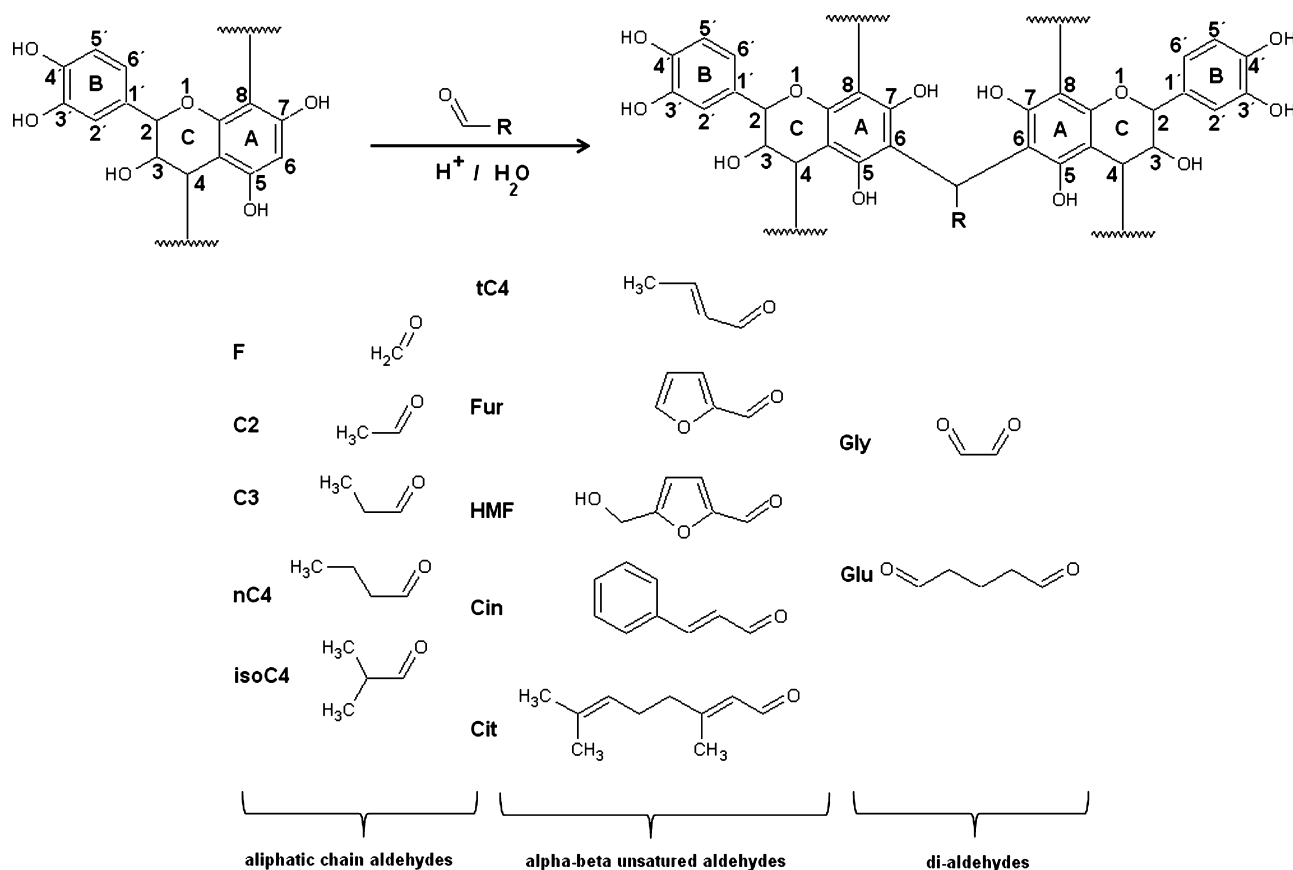
Novolac resins, the acid-catalyzed polycondensation product of phenol and formaldehyde (F) in molar excess of phenol, display rather linear topology as a result of phenol hydroxymethylation followed by condensation of hydroxymethylphenols into methylene or oxymethylene bridges. The latter linkage, less common in novolacs is prone to thermal decomposition and therefore releases F, now classified as carcinogenic, during the product lifetime (Binetti et al., 2006). In the CTs, multiple reaction sites are available for hydroxymethylation (aldehyde reaction), although it is believed to mainly occur on the C6 or C8 sites of the A-ring C_{15} flavonoid unit, leading mainly to C6 → C6 and C6 → C8, but also C8 → C8, methylene bridges (Fig. 1). Such polymer systems are therefore less likely to emit toxic F, as already demonstrated (Zhang et al., 2007) although alternative to the toxic F are highly desirable.

Following this bakelite-like chemistry, tannin-based phenolic resins have been succesfully prepared for several decades whereby

Fig. 1. Squematic acid-catalized polycondensation reaction of *P. pinaster* bark tannin with aldehydes. *Note*: Methylene bridge as full linkage between C15 flavonid unit was considered.

typically tannin can replace even totally phenol without impairing resin properties (Pizzi, 1980, 1994; Wang et al., 2009). Recently aldehydes, other than the F have been explored for the synthesis of phenolic polymers (Pizzi, 1983, Dongre et al., 1985; Opresnik et al., 1988; Wang et al., 2010). Glutaraldehyde (Glu) and glyoxal (Gly) have been established as ingredients for the preparation of phenolic foams with pine tannin (Lacoste et al., 2013) and for wood adhesives (Ballerini et al., 2005). Aside the health concerns associated with F, the search for alternative aldehydes for polymer formation with pine bark tannin is further justified by the extreme reactivity of the latter with F. Previous kinetic studies for the reaction of short-chain aliphatic aldehydes and furfural (Fur) with tannin corroborate the potential to tailor kinetics of network formation (Rossouw et al., 1980).

In this work we explore the potential of aldehydes (including natural) for acid-based polymerization with pine tannin for the synthesis of bio-based novolac resins. The impact of aldehyde structural features including chain length, functionality, degree of insaturation and conjugation on polycondensation with CTs is assessed systematically on polymer network formation and resulting thermal and physicochemical properties. Structure/property relationships are established for these bio-based resins.

2. Materials and methods

2.1. Chemicals

Commercial maritime pine (*P. pinaster*) bark tannin, supplied by DRT (Dérivés Résiniques et Terpéniques) from Dax, France, was used.

P. pinaster bark tannin was stored under dried conditions over silica gel in a vacuum desiccator before use.

Twelve aldehydes were considered for polycondensation with tannin (Table 1), pertaining to short-chain-, αβunsatured chain- and di-aldehyde groups. All aldehydes were stored in a refrigerator (5 °C) to prevent volatilization and oxidation prior to use.

2.2. Gel time estimation (aldehyde reactivity)

Gel time was used as a rough estimate of tannin reactivity toward aldehydes (Fig. 1) following standard method (BS 27(82835a), 1980) over the pH range of 0.5–10.0. Briefly, *P. pinaster* tannin aqueous solutions ($0.32 \, \text{mol L}^{-1}$, 45% (w/v)) were placed into a glass test tube and aldehydes aqueous solutions were added to establish T:A molar ratios of 1:0.5, 1.0:1.0, 1.0:1.5, 1.0:2.0. A weigth average molecular weight of $1250 \, \text{gmol}^{-1}$ was used to stablish the T:A ratio, considering as a fully catechin-based tannin (García et al., 2013, 2014). Standardized solutions of HCl (5% (v/v)) or NaOH (10% (w/v)) were added to adjust the pH value from 0.5 to 10 with intervals of 0.5 units using a calibrated pHmeter (Sartorius, PB-11, Germany). Gel time was also assessed at the natural pH of the tannins (3.5 ± 0.2) without catalyst.

A wire spring was placed in the test tube and the sample extract solution was gently mixed at room temperature (~23 °C) for ten seconds. The test tube was then placed in a boiling water bath (boiling point: 98 °C). The wire spring was gently moved up and down in the tube, and the gel time was recorded when the spring could no longer move freely in the test tube (Pizzi and Stephanou, 1993). The pH dependency of gel time was calculated from the initial slope of gel time vs. pH (0.5–3.5) and used as indicator of aldehyde reactivity in s (pH^{-1}) as per a method proposed by Pizzi (1994).