



# Hydroxypropyl tannin from *Pinus pinaster* bark as polyol source in urethane chemistry

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## ABSTRACT

Novel thermosetting polyphenol-based polyurethane (PU) films were prepared using condensed tannin (CTs) and hydroxypropyl tannin derivatives (HPTs) from *Pinus pinaster* bark and diisocyanates. Four HPTs with a degree of substitution (DS) rising stepwise from 1 to 4 were crosslinked with either an aromatic (polymeric methylene diphenyl diisocyanate (pMDI)) or an aliphatic isocyanate (hexamethylene diisocyanate (HDI)). Chemical structure, moisture sorption, thermal, and morphological properties of the films were studied. Properties varies with NCO:OH ratio (0.5–4.0), DS, diisocyanate type, and cross-link density (CD). Partial tannin hydroxypropylation (DS 2, 3) based/films showed a flexible-type character in term of Young's modulus, elongation and tensile strain. Significant relationships were established between CD and physicochemical properties. HPTs constitute suitable macro building-block polyols for urethane chemistry.

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## 1. Introduction

Polyurethanes (PUs) are popular materials due to their properties that can be readily tailored by component variation [1]. PU covers a wide range of products with different stiffness, hardness, and density, allowing the tailoring of products like rigid or elastic low-density foams and plastics with varying elasticity.

PU chemistry is based on the combination of polyols (i.e. polyethylene/propylene glycol) with isocyanates and additives. Aliphatic petroleum-based polyols are commonly used as the elastic segment. However, renewable

resources, like natural oils (e.g. cardanol), lignocellulosic residues, polyphenols, and starch have also been successfully utilized as substitutes for these petroleum-based polyols [2–4]. These materials have numerous advantages like low toxicity and inherent biodegradability [5–7].

However, the utilization of condensed tannins (CTs) and lignin as a partial substitution of common polyols in PU foams has been demonstrated to result in a loss of elasticity and gain in modulus [8–11].

Studies on the interaction of model compounds ((+) catechin) or CTs (*Mimosa mearnsii*), with monofunctional phenyl isocyanate or bifunctional toluene diisocyanate revealed preferential reactivity of the B-ring of tannin [12]. Based on this polycondensation reaction, CTs-based rigid foams were prepared. However, CTs used as polyol source exhibited low solubilization in the mixture before the foaming process. This limitation was overcome using

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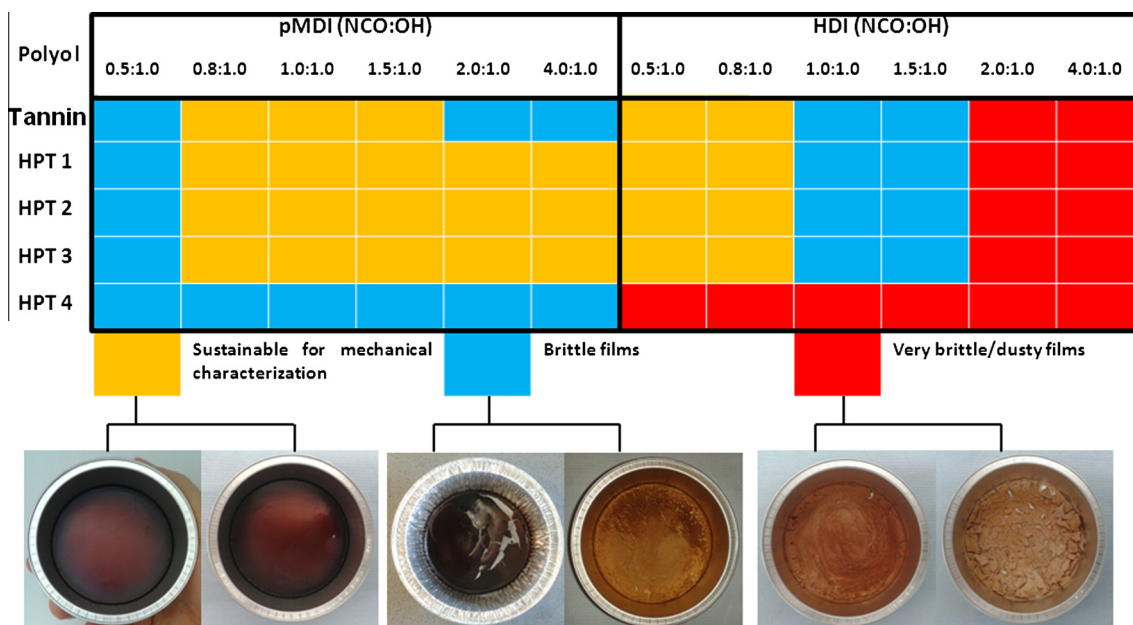


Fig. 1. Phase diagram of CT/HPT-PU according to the appearance of the cast film after curing at 105 °C for 3 h.

drastic condition in terms of temperature and liquefaction time ( $T$ : 80 °C,  $t$ : 5.5 h).

In contrast to these disadvantages, hydroxypropylated tannins from *Pinus pinaster* (Ait.) bark (HPTs) are derivatives with excellent potential to be used as macromeric building-blocks in biopolymer engineering [13]. These modified oligomers, which are obtained by a simple derivatization reaction with propylene oxide at room temperature, allow to tailor both thermal and solubility (in organic solvents) properties by choosing the degree of the chemical modification (DS) [14].

In this study, CT-PU and HPT-PU films were prepared. Degree of modification, diisocyanate type, and NCO:OH molar ratio were varied systematically to establish structure–property relationships.

## 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. Pine tannin contains flavonoid-3-ol ( $C_{15}$ ) units with high relative abundance of low  $M_w$  oligomers [13,15].

Two isocyanate types were used (polymeric methylene diphenyl diisocyanate (pMDI) and hexamethylene diisocyanate (HDI)). pMDI was stored in a freezer at  $-20$  °C to prevent oligomerization and volatilization. Gel Permeation Chromatography (GPC) analysis of commercial pMDI revealed a mixture of monomers (10%, -mMDI-), dimers (70%, -dMDI- uretidione), and trimers (20%; -tMDI-, isocyanurate). All chemicals were supplied by Sigma Aldrich, Seelze, Germany.

### 2.2. HPT synthesis

Four HPTs (DS: 1, 2, 3, 4) were synthesized for the polymer film casting. The parameters of the derivatization reaction were described in detail previously [13–15].

Briefly, tannin (100 g, ca. 80 mmol) was dissolved in 500 mL aq. 2 N NaOH and the pH was adjusted to 12. Each 125 mL aliquot was combined with a different molar equivalent of PO, leading to PO/ $C_{15}$  ratios from 1.0, 2.0, 3.0 and 4.0. The reaction was carried out for 24 h while stirring at room temperature ( $\sim 22$  °C). The mixture was subsequently heated to 60 °C for 30 min to remove any trace of unreacted PO before it was allowed to cool down. Adjusting the pH to 2 using conc. HCl (40% v/v) produced a precipitate that was centrifuged. The supernatant was collected by decantation and the precipitate was washed five times with distilled water and freeze-dried. Reaction yields ranged from 82 to 90 wt%.

### 2.3. Chemical analysis

The OH-content was determined by the combination of the Folin–Ciocalteu spectrophotometric method [16] and  $^1\text{H}$  NMR measurements [13].

### 2.4. Film preparation

The polymer film casting was performed according to a modified cast film method [17]. HPT-PU films were prepared with combinations of the two diisocyanates (pMDI or HDI) and the four HPTs (DS 1–4) at different NCO:OH ratios (0.5, 0.8, 1.0, 2.0, 4.0). CTs, HPTs, and the catalyst (1,4-diazabicyclo[2.2.2]octane, TEDA) were conditioned over silica gel under vacuum prior to use.

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