



Isocyanate free condensed tannin-based polyurethanes



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ABSTRACT

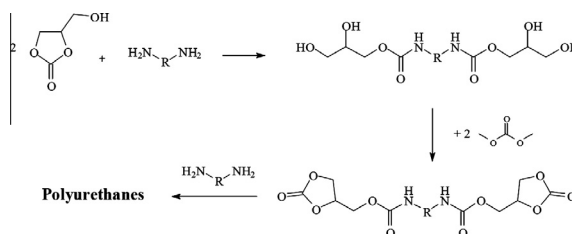
Condensed flavonoid tannins from Maritime Pine (*Pinus pinaster*), Mimosa (*Acacia mearnsii*), and Radiata Pine barks, and Quebracho (*Schinopsis lorentzii* and *balansae*) wood, were first reacted with dimethyl carbonate. Then hexamethylenediamine was added to these mixtures to form urethane linkages. The resulting materials were analyzed by Fourier transform infrared (FTIR) spectroscopy, matrix assisted laser desorption ionization time of flight (MALDI-TOF) mass spectrometry, gel permeation chromatography (GPC), and thermogravimetric analysis (TGA). Finally the resulting analysis indicated that the products obtained are polyurethanes. Initial wood coating applications tests were carried out under conditions of higher temperature and some pressure, and the contact angle of the surface coatings so prepared was measured.

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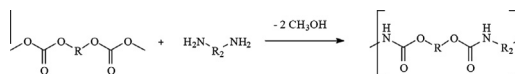
1. Introduction

Polyurethanes can be prepared for a variety of applications from polyols from many renewable materials, such as tannin [1–6] and lignin [7–10]. These biosourced polyols are reacted with polymeric isocyanates to prepare polyurethanes. This has already been the case with oxypropylated flavonoid tannins [11] as well as with many other natural-derived polyols. Alternate chemical routes to prepare non-isocyanate based polyurethanes, hydroxypolyurethanes, do already exist [12], which are obtained, not by the conventional reaction of polyols on diisocyanates, but by polyaddition of diamines on cyclic polycarbonates [13], such as

derivatives of glycerol carbonate and polyethylene glycol dicarbonate [14,15]:



They can also be prepared by polycondensation of diamines with carbonated molecules [16]:



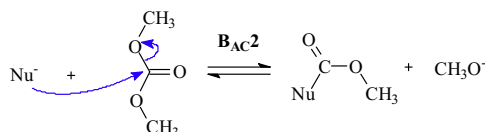
In this way, dimethyl carbonate is a good reagent and solvent that can be used for the first step of carbonation.

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Indeed, it is classified as a flammable liquid with an odor similar to methanol, which has not irritating or mutagenic effects, either by contact or inhalation (indexing from Merck). Therefore, it can be safely handled without special precautions required for harmful and mutagenic methyl halides and poisonous phosgene used for the synthesis of polycarbonates.

Carboxymethylation of hydroxyl groups by dimethyl carbonate group is generally observed at temperatures around 90 °C, which is close to the boiling point of dimethyl carbonate, by bimolecular nucleophilic substitution, acyl-cleaving, in basic catalysis ($B_{AC}2$) [17]:



With phenol, the transesterification of dimethyl carbonate is generally carried out in a liquid phase using homogeneous catalysts such as organic Sn, Ti, Al, Fe compounds and so on [18–20], which let think that carbonation of hydroxyl groups of phenolic structures of tannins is possible.

Recent such polyurethanes involved vegetal oil derived materials as renewable resources [21,22]. However, the environmental balance of vegetable oils for use in resins has been shown to be unfavourable, while tannin derived resins have been shown to present a favourable environmental balance (CTBA, Project BEMA, 2012, Mont de Marsan, Aquitaine France). More recently, a study on preparing polyurethanes without isocyanates based on hydrolysable tannins (*Castanea sativa*) was done [23]. These tannins, mostly composed of gallic acids and their derivatives, were prepared using dimethyl carbonate and hexamethylenediamine. In this paper, the same procedure to form polyurethane linkages is applied to flavonoid tannins which present however a greater number of hydroxyl groups. They are first analyzed by FTIR and MALDI-TOF spectrometry to determine the presence of urethane structure, the distribution of the oligomers formed and their level of condensation. Then by GPC to further evaluate their level of polymerization at the higher molecular weights, and finally by TGA to study the physical degradation of the polymers obtained. To complete this study, coating applications tests were carried out on Medium Density Fiberboards (MDF) pieces under conditions of higher temperature and some pressure, and the contact angle of the surface coatings so prepared was measured.

This present work is a first approach to demonstrate that the use of tannins instead of polyols can be implemented from reaction with dimethyl carbonate and a diamine. On the other hand, the different tannins extracts presented – Mimosa, Quebracho, Radiata and Maritime Pines, are not produced in the same amounts in the world. The present production of flavonoid type tannins is about 250 thousand tons/year, but the bark of trees rich in flavonoids, raisin skins waste from wine production and other sources indicate a possible potential of tannin extracts in millions of tons.

2. Experimental

2.1. Equipment

Purified Maritime Pine (*Pinus pinaster*) bark extract, where the majority of the carbohydrates of the extract were eliminated in a second organic solvent extraction, were provided by DRT (Dax, France). Quebracho (*Schinopsis lorentzii* and *balansae*) wood, Mimosa (*Acacia mearnsii* formerly *mollissima* de Wildt) bark, and Radiata Pine (*Pinus Radiata*) bark extracts were provided by Silva Chimica (S.Michele Mondovi', Italy).

Maritime and Radiata Pines tannins both present a majority of procyanidin and prodelphinidin flavonoid structures; whereas Quebracho tannin's major components are profisetinidin, and Mimosa tannin's prorobinetinidin (Fig. 1).

Dimethyl carbonate 99% was purchased at Acros organics (Geel, Belgium), and hexamethylenediamine tech. 70% at Aldrich Chemical Company Inc. (Milwaukee, USA).

2.2. Procedure

Tannins from four tree species were considered and reactions were conducted at ambient temperature. Dimethyl carbonate was used there both as a solvent (to obtain fluid material with tannins extract, between 45 and 50% w/w of powder) and a reactant. Then, twenty-one grams were added to ten grams of tannin extracts powders and mixed under mechanical stirring for two hours. Afterward, seven grams of hexamethylenediamine were added to the mixtures, in order to have a stoichiometry higher than tannin flavonoid units.

This addition generates a fast exothermic hardening of some substances in Mimosa and Quebracho solutions, so as the solutions became clear liquids with dark solids remaining in. On the contrary, Pines tannins in dimethyl carbonate reacted more slowly with the diamine until forming a kind of paste with a slight exotherm. Each reaction mixture so obtained was separated into two parts. One was left to harden at ambient temperature (between 20 and 25 °C) for at least 24 h, while the other was placed in an oven at 103 °C for 24 h. An additional mixture of dimethyl carbonate and hexamethylenediamine alone was prepared under the same conditions as a reference for MALDI-TOF analysis.

The material was tested for a coating application on the surface of Medium Density Fiberboards (MDF). The fresh pastes were first spread over the surfaces with a spatula, around 3–4 kg/m², for the materials were not adherent. Then the pine tannin based resins on the sample surfaces were covered with a silicone sheets and the MDF and placed on a hot platen at 170 °C, the silicone sheet at the bottom, with 3 kg of weight over them to apply pressure, and let for one hour before cooling the platen temperature. For Mimosa and Quebracho samples, because the materials were already rather hard but still ductile, the pressure needed to be higher, that is why they were covered with silicone sheets and placed into a press heated at 170 °C,

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