



## Polyurethanes from hydrolysable tannins obtained without using isocyanates



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### ABSTRACT

Hydrolysable chestnut tannins, which contain several hydroxyl groups, were reacted with dimethyl carbonate, and then with hexamethylenediamine. The dried product was analyzed in MALDI-TOF, <sup>13</sup>C NMR and FTIR spectrometry. The spectra revealed the presence of urethane functions and their yield was relatively high. This synthesis of polyurethanes is interesting because it does not depend on using isocyanates as reactants while instead utilizing a natural material, hydrolysable chestnut tannin, as their major constituent.

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### 1. Introduction

Vegetable tannins have been used to tan leather either alone or accompanying other tanning agents for several thousand years. They are natural products obtained from plants and are very diffuse in the whole plant kingdom. The term natural vegetable tannins is used loosely to define two broad classes of chemical compounds of mainly phenolic nature, namely condensed or polyflavonoid tannins and hydrolysable tannins.

Condensed tannin-based resins for wood adhesives, thus phenolic-type resins derived from natural renewable materials, have been developed and are in commercial use in the southern hemisphere since the 1970s (Pizzi and Scharfetter, 1978; Pizzi, 1983). More recently these resins have received considerably renewed interest due to both their environment friendly, non-oil derived origin, their lower increasing cost as well as for the developments engendered on a range of different industrial applications (Pizzi, 2006). Among these tannin-based rigid foams

have been the focus of considerable interest as possible substitutes for polyurethane foams (Meikleham and Pizzi, 1994; Tondi and Pizzi, 2009). However, the existing installed industrial equipment for polyurethane foams is not adapted, in general, for tannin-based rigid foams. This has limited at present their potential application to substitute synthetic, oil-derived phenolic foams for applications such as floral foams and fire-resistant insulating foams

Polyurethanes can and have already been prepared for a variety of potential applications from polyols from renewable materials, including materials such as tannin (Peng et al., 2013; Ge et al., 2003; Ge and Sakai, 1993, 1998) and lignin (Faruk and Sain, 2013; Hatakeyama and Hatakeyama, 2013; Liu et al., 2013; Wang et al., 2013). However, polymeric isocyanates need always to be used in industry to prepare polyurethanes even if in conjunction with biosourced polyols. This has already been the case with oxypropylated flavonoid tannins (García et al., 2013) as with many other natural-derived polyols.

Studies on alternate chemical routes to prepare non-isocyanate based polyurethanes do already exist, where oligomers terminated with five-membered cyclic carbonate groups are reacted with diamines to form polyhydroxyurethanes (Rokicki and Piotrowska, 2002). Researches for developing green and sustainable chemistry involved vegetable oil derived materials as renewable resources. The technological barrier to the synthesis of biobased cyclic carbonates could be overcome by the chemical transformation of

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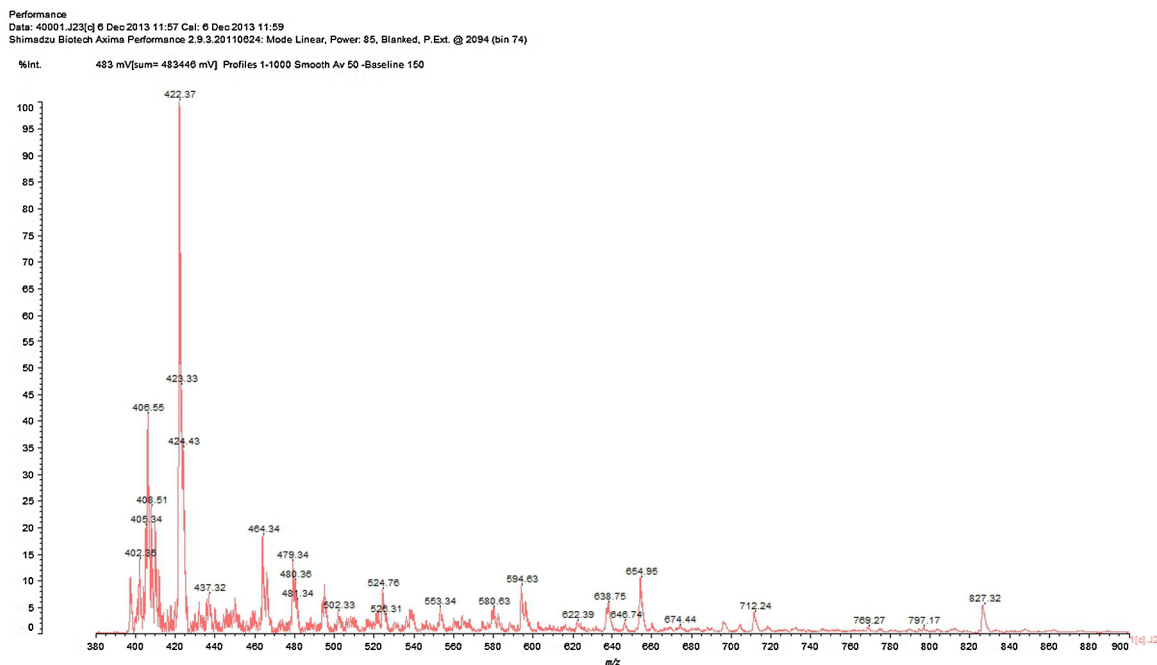


Fig. 1. MALDI-TOF Spectrum of the reaction products of carbonated hydrolysable chestnut tannin with hexamethylenediamine, 380 to 900 Da.

epoxidized vegetable oils or by the use of glycerine carbonate-based intermediates. Polyamines could also be produced from fatty diacids (Nohra et al., 2013).

Hydrolysable tannins, including chestnut, myrabolans, divi-divi, tara, algarobilla, valonea, oak and several other commercial tannin extracts are mixtures of simple phenols such as gallic acid and of esters of a sugar, mainly glucose, with gallic and digallic acids, such as monomeric and oligomeric pentagalloyl glucose from which the phenolic moieties are, however, easily separated. Thus, several studies (Pasch and Pizzi, 2002; Pizzi et al., 2009) have identified the main constituents of the main commercial

hydrolysable tannin such as chestnut tannin extract, as structures derived by either oligomerisation, or by hydrolysis of pentagalloyl glucose (Pizzi et al., 2009). The presence of gallic acid as the basic structure in hydrolysable tannins (Pasch and Pizzi, 2002; Pizzi et al., 2009; Radebe et al., 2013; Giovando et al., 2013) identifies them as an ideal raw material for the preparation of non-isocyanate-mediated polyurethanes, whatever their subsequent application. Besides this kind of process, the use of tannins in the manufacture of polyurethanes can provide interesting additional performances such as antioxidant characteristics (Noferi et al., 1997).

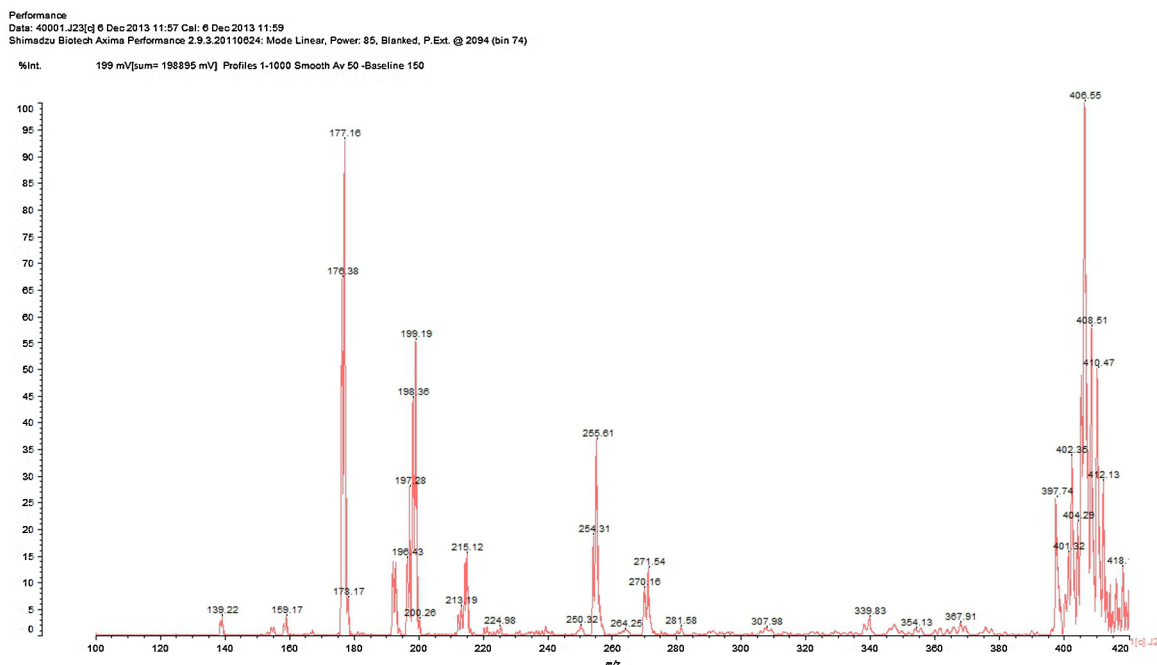


Fig. 2. MALDI-TOF Spectrum of the reaction products of carbonated hydrolysable chestnut tannin with hexamethylenediamine, 100 to 420 Da.

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