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FURANIC COPOLYMERS WITH SYNTHETIC AND NATURAL PHENOLIC MATERIALS FOR WOOD ADHESIVES - A MALDI TOF STUDY

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ABSTRACT

The structure of traditional, linear phenol-formaldehyde (PF) resins and phenol-furfural (P-Furan) resins has been investigated by matrix-assisted laser desorption/ionization time of flight (MALDI-TOF) mass spectroscopy. The structure of a variety of oligomers has been obtained and the structures present in each of the two types of resins related to the reagent used either formaldehyde or furfural. The oligomers type and species distribution appeared rather different for each case. Comparison of a P-Furan resin with a Mimosa tannin-Furan resin showed some differences. This latter shows a greater proportion of self-condensed fuanic oligomers due to the manner in which it is prepared starting from furfuryl alcohol. Several different Tannin-Furan oligomers were also observed by MALDI TOF analysis.

Keywords: Oligomers distribution, phenol-furanic resins, tannin-furanic resins, wood adhesives.

INTRODUCTION

Synthetic phenol–furan resins are well known, at least in one field, namely as binders of sand for foundry core moulds. The increase interest in natural, renewable and environment friendly materials has recently brought the use of vegetable phenolic materials such as condensed flavonoid tannins derived from the bark of trees to become of interest for the application of phenolic-furanic coformulations as binders in wood particleboard, plywood and other wood-based panel applications (Abdullah and Pizzi 2013, Abdullah *et al.* 2013a,b). Their application has been mainly as wood adhesives (Navarrete *et al.* 2011) rather than as binders of sand for foundry core moulds. To better understand the mechanism and mixture of reaction products obtained the reaction of phenol used as a model compound, with formaldehyde and with furfural, has been studied by Matrix assisted laser desorption ionisation time of flight mass spectrometry. The work was then repeated for vegetable flavonoid tannins reacted with a furanic material and the products of these analysed in comparison to what observed for the model compounds.

This paper deals with the investigation of the structure of these resins by MALDI-TOF mass spectrometry.

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METHODOLOGY

Resins Manufacture

The manufacturing procedure and reagents proportions for the phenol-furan (P-Furan) resin have already been reported (Zhao *et al.* 1999). The procedure was as follows: To 62,7 g phenol were added 14,7 g water, 17,3 g methanol and 32,7 g furfural. 12,5 g of a 10% sulphuric acid solution in water was added and then the mixture was brought to reflux under continuous mechanical stirring and refluxed for 6.5 hours. The resin was, neutralized with a 30% NaOH warter solution and a final lot of 60 g methanol was added. The mixture was then cooled rapidly and stored. For the Tannin-Furanic resins commercial Mimosa (*Acacia mearnsii*, De Wildt) supplied by Silva Chimica (S.Michele-Mondovi, Italy) bark tannin extract was used to prepare the resin. The tannin solution was prepared by mixing 100 parts of mimosa tannin extract with 100 parts of water and its pH was adjusted to pH 10 with 33% of NaOH water solution. To the tannin solution were added 50 parts of furfuryl alcohol. And the mixture heated at 100 °C for 10 minutes.

***MALDI-TOF* Sample Preparation**

The freeze dried samples were dissolved in acetone (4 mg/mL). The sample solutions were mixed with an acetone solution (10 mg/mL acetone) of the matrix. As the matrix 2,5-dihydroxy benzoic acid was used. For the enhancement of ion formation either LiCl or NaCl were added to the matrix, namely LiCl for the phenol-furanic oligomers and NaCl for the tannin-furanic oligomers. The solutions of the sample and the matrix were mixed in equal amounts and 0.5 to 1 µL of the resulting solution were placed on the MALDI target. After evaporation of the solvent the MALDI target was introduced into the spectrometer.

MALDI-TOF-MS

The spectra were recorded on a AXIMA Performance MALDI instrument in the m/z range 80-1200 Da. Calibration of the equipment was done with red phosphorous for oligomers up to 2000 Da. The irradiation source was a pulsed nitrogen laser with at 337 nm with a laser pulse of 3 ns. The measurements were carried out using the following conditions: polarity-positive, flight path-linear, mass-high (20 kV acceleration voltage), 100-150 pulses per spectrum. The delayed extraction technique was used applying delay times of 200-800 ns.

RESULTS AND DISCUSSION

Table 1 reports the major peaks of the MALDI-TOF analysis of a P-Furan resin comparing it to that of a PF resin. The peak masses were calculated according to the expression $[M^+Li^+] = 7(Li) + 94$ (Phenol) + 172(P+Furfural). The absence of Furan-CH_2OH, Furan-CHOH, Furan-CH_2^+ and Furan- CH^+ groups is noticeable in the oligomers series in table 1. This is shown by the relative proportions of furanic moieties always being less than those of phenol. This could be due to several factors. First the furfural can react with itself. This reaction is not very favoured under alkaline reaction conditions, but although much slower it does nonetheless occur (Abdullah and Pizzi 2013). Furthermore, there is no trace in table 1 of any oligomers obtained exclusively by furfural polycondensation with itself, which is expected. Secondly, it could be that steric hindrance could limit the existence of these groups in phenol-furanic resins. This, however, is not likely to be the case. Finally, and the only acceptable explanation is that the bridges connecting phenols and furan rings are particularly stable: this is known to be the case. It means that the Furan-CH_2OH, Furan-CHOH, Furan-CH_2^+ and Furan- CH^+ species are absent simply either because the P-Furan resin cannot be cleaved by MALDI-TOF contrary to the case of P-formaldehyde resins where some of this type of cleavages might occur. The different reactivity of furfural and formaldehyde can also be at the origin of the absence of such species, so common as P-CH_2OH and P-CH_2^+ in PF resins (Table 1). Again, this supports that MALDI-TOF might lead to some misinterpretation of the results for resins presenting easily cleaved bonds, unless the reactions and their products are already known. This is of course not the case, and the type of p-furan resins formed are of the type as shown as follows (1134 Da):

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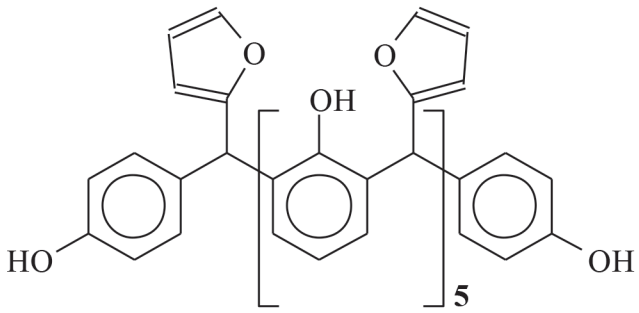
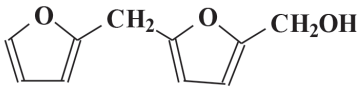


While in Table 1 the phenol-furanic oligomers are reported asbeing linear, it must be clearly pointed out that in the case of the phenol-furanic longer oligomers there is no reason why these could not be a mixture of linear and branched species, or even branched species alone.

Table 1. Comparison of oligomer species formed in phenol-formaldehyde and phenol-furan resins.

$M+Li^+$ (exp)	Oligomer type	
	Phenol-formaldehyde	Phenol-furanic
131	P CH_2OH	
207	P CH_2 P	
273		P F P
263	HOCH_2P CH_2 P (CH_2^+)$_2$	
313	P CH_2 P CH_2-P	
419	P CH_2 P CH_2 P CH_2 P	
435	P CH_2 P CH_2 P CH_2 P CH_2 OH	
445		P F P F P
450	HOCH_2P CH_2 P CH_2 P CH_2 P CH_2 OH	
525	P CH_2 P CH_2 P CH_2 P CH_2 P	
541	P CH_2 P CH_2 P CH_2 P CH_2 P CH_2^+	
556	P CH_2 P CH_2 P CH_2 P CH_2 P CH_2OH	
617		P F P F P F P
790		P F P F P F P F P
962		P F P F P F P F P F P
1134		P F P F P F P F P F P F P

As regards Tannin-furanic resins, the peaks at 104, 137, 177, 199, 215, 365, 397 and 551Da (Figure 1 and 2) indicate that self condensation of furfuryl alcohol has occurred, even at very alkaline pH. Thus structures of the following types are present (198 Da).



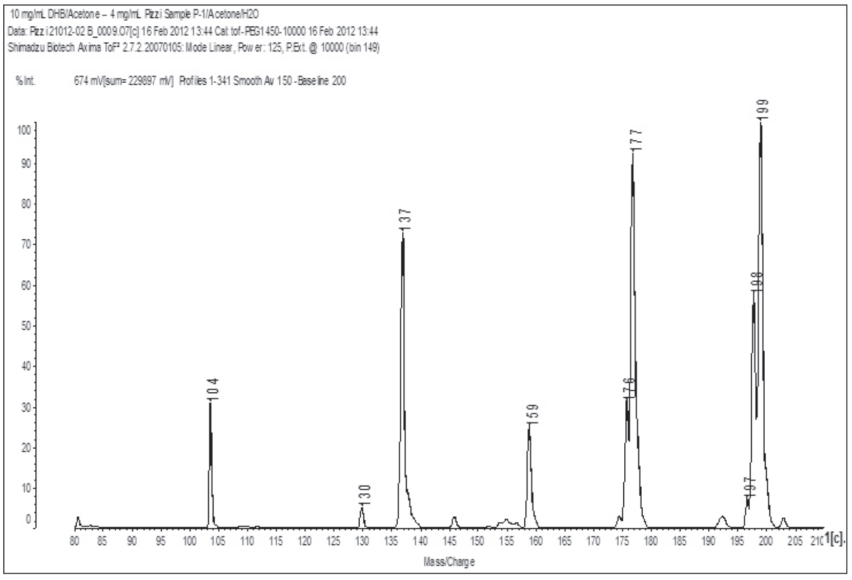


Figure 1. MALDI-TOF spectrum of reaction products of flavonoid mimosa bar tannin extract with furfuryl alcohol; 80Da to 210Da mass range.
Sample **mimosa tannin + furfuryl alcohol**; mass range: 80-210 Da.

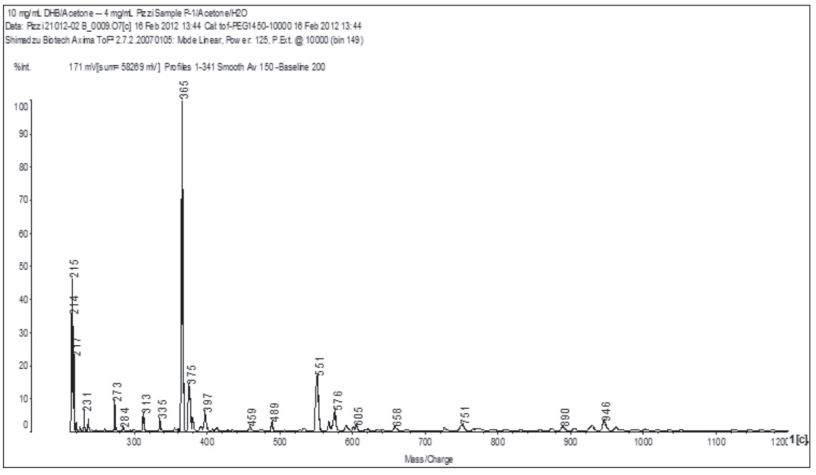


Figure 2. MALDI-TOF spectrum of reaction products of flavonoid mimosa bar tannin extract with furfuryl alcohol; 210Da to 1200Da mass range.
Sample **mimosa tannin + furfuryl alcohol** ; mass range: 210-1200 Da.

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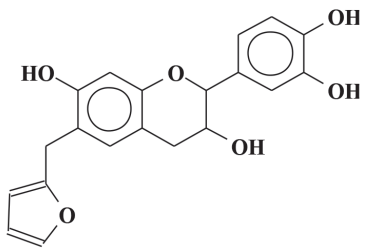
The peaks observed in Figures 1 and 2 belonging to the self condensation of furfuryl alcohol belongs to Fur-CH_2+ (104 Da), the 176/177 Da belongs to the Fur-CH_2-Fur specie, and the Fur-CH_2-Fur-CH_2OH (199 Da) but also to Fur-CH_2-O-CH_2-Fur. That this latter occurs is shown by the presence of the 215 Da peak generated by the rearrangement of the methylene ether bridge with emission of a molecule of formaldehyde that then recombines with the Fur-CH_2-Fur-CH_2OH (199 Da) giving the $HOCH_2$-Fur-CH_2-Fur-CH_2^+ peak at 215 Da. This rearrangement also account for the 137 Da peak, derived by the reaction of the split formaldehyde to form the $HOCH_2$-Fur-CH_2^+ species. The 365 Da peak also belongs to an oligomer formed by the furfuryl alcohol self condensation, Fur-CH_2-Fur-CH_2-Fur-CH_2-Fur-CH_2OH. The 397 Da peak also derives from the reaction of the 365 Da peak with the formaldehyde split from the 199 Da peak to form CH_2^+-Fur-CH_2-Fur-CH_2-Fur-CH_2-Fur-CH_2OH.

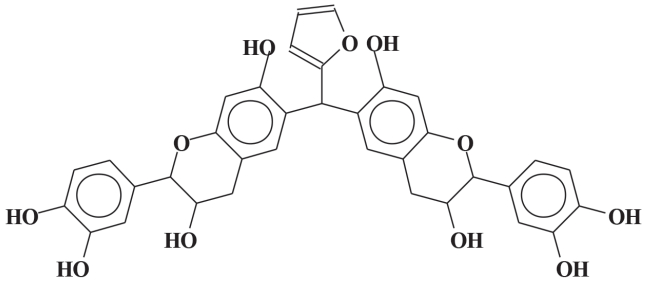
Equally the 551 Da peak represents the
CH_2^+-Fur-CH_2-Fur-CH_2-Fur-CH_2-Fur-CH_2-Fur-CH_2-Fur-CH_2OH oligomer.

The most common flavonoid repeating units present in extracted mimosa tannins are fisetinidin, robinetinidin, catechin and gallocatechin (Pasch *et al.* 2001). The peaks at 273Da representing a fisetinidin monomer (without Na^+, a common occurrence at low molecular weights for flavonoids MALDI) while the peak at 313 Da belongs to either a robinetinidi or a catechin, both of M.W. 290 + 1xNa^+. The peak at 375 Da can be explained by the presence of fisetinidin reacted with furfuryl alcohol



The oligomer represented by the 551 Da peak and the oligomer represented by the 658 Da peak is composed of two fisetinidin flavonoid units reacted with one furfuryl alcohol.

The peak at 946 Da was identified as a peak which consisted of two different types of flavonoid reacted with furfuryl alcohol.



The peak at 946 Da was identified as a peak which consisted of two different types of flavonoid reacted with furfuryl alcohol.

CONCLUSIONS

MALDI-TOF mass spectroscopy highlighted some of the main differences in comparative oligomers distribution of phenol-formaldehyde, P-Furan and Tannin-Furan resins for wood adhesives and other applications. In parallel to tannin-furan coreacted oligomers furan homopolymers are also formed in noticeable quantities due to the self condensation of furfuryl alcohol. This does not appear to be the case in P-Furan resins which are prepared in a different fashion. These latter are also different from PF resins.

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