

# CHEMISTRY, MORPHOLOGY, MICROTOMOGRAPHY AND ACTIVATION OF NATURAL AND CARBONIZED TANNIN FOAMS FOR DIFFERENT APPLICATIONS

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## ABSTRACT

Tannin based rigid foams are natural network structures obtained by polycondensations of polyflavonoid tannins and furfuryl alcohol. These foams have a wide range of characteristics. Mimosa tannin bark extract, and quebracho tannin bark extracts were used as building blocks. Physical tests such as water absorption, compression resistance, direct flame behaviour and measure of foam cells dimensions were carried out for each foam sample. A  $^{13}\text{C}$ -NMR analysis contributed to the chemical characterisation of the foams. Tannin based rigid foams appear suitable for a wide range of applications.

Tannin-based rigid foams, prepared from 95% natural material, are suggested for replacing synthetic phenol - formaldehyde foams in various applications. For that purpose, a few physical properties were measured: resistance to fire and chemicals, absorption of various liquids, permeability, thermal conductivity and mechanical (compressive and tensile) strength. Modifying the composition through the use of boric and/or phosphoric acid allowed substantial increase of fire resistance. The materials were also found to present good resistance to strong acid and bases, and to solvents. High affinity for water, but limited one for organic liquids, was also evidenced. Finally, slightly anisotropic mechanical properties were measured. The materials present a brittle behaviour, whether tested in compression or traction; nevertheless, their strengths, as well as their thermal conductivities, are fully comparable with those of their phenolic counterparts. Such materials of vegetable origins can compete with synthetic ones for most traditional applications.

Carbonisation of polyflavonoid tannin-formaldehyde-furfuryl alcohol rigid foams were found by MALDI-TOF to yield a tridimensional network in which to polynuclear aromatic hydrocarbon chains of high molecular weight are also covalently linked some furan resin structures surviving carbonisation. Structure conservation on carbonizing extends to furanic structures derived by the self condensation of furfuryl alcohol which are integral part of the total network. Some complex, tridimensional structures derived by the rearrangement to polyaromatic hydrocarbons of polyflavonoid tannins, constituted of aromatic benzene and furane rings and some formaldehyde-derived methylene bridges appear to be formed.

New tannin-derived/furanic carbon foams with high surface areas were obtained by chemical activation.  $\text{ZnCl}_2$  and  $\text{H}_3\text{PO}_4$  were used as activating agents and the stability of the foams structures obtained was evaluated. In addition to conventional textural analysis, the activated foam samples were analysed by nuclear magnetic resonance (NMR) and temperature programmed desorption with mass spectrometry analysis (TPD-MS).  $^{13}\text{C}$ -NMR analysis has allowed to understand the chemical rearrangements occurring and  $^1\text{H}$ -NMR has allowed to study interactions of the foam with water. TPD-MS yielded information on the surface chemistry of the activated carbon. Chemical activation was found to be effective for both treatments: the surface area increasing from 36  $\text{m}^2/\text{g}$  up to 1875  $\text{m}^2/\text{g}$  and 1265  $\text{m}^2/\text{g}$  for foams synthesised respectively with zinc chloride and phosphoric acid. It has been demonstrated that the final carbon foams exhibit mainly micropores. Moreover, different surface chemistry were obtained depending on the chemical treatment used. Therefore, it was shown that carbon foams with high surface areas and tailored surface chemistry can be synthesised from this biomass based precursor.