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Hydrophobisation of tannin-based foams by covalent grafting of silanes

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1 Introduction

The dependence on moisture content of heat transfer in thermally insulating porous materials was repeatedly confirmed by many investigators [1]. This dependence – itself related to relative humidity – leads to much less insulating materials at higher moisture content. Such impact varies with composition, porosity and internal structure of the material. Tannin-based foams are really concerned by this question, due to their promising insulation properties[2] and their originally high hydrophilic character due to the presence of a huge amount of hydroxyl (–OH) groups, which can bind very easily to water molecules.

For limiting this problem, hydrophobisation of tannin foams for lowering their affinity for humidity is of particular interest. Covalent grafting of organosilanes, some of them based on perfluoroalkyl hydrophobic chains, which take the place of hydroxyl groups, might be an efficient solution since it has been successfully tested on various surfaces [3]–[6]. Grafting is generally performed by reaction between –OH surface groups and alkoxy groups of organosilane compounds as presented in Fig. 1 [6], [7] leading a layer of organosilane compound at the surface of the materials and making the latter hydrophobic, or at least much less hydrophilic.

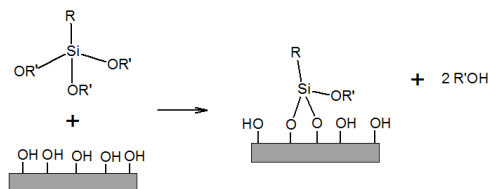


Figure 1: Schematic representation of the grafting process of organosilane compounds on a material surface bearing hydroxyl groups.

Thus, the aim of the present work was to prepare organosilane-grafted tannin-based foams and to quantify the efficiency of such hydrophobisation treatment by different techniques. Two different organic foam samples (here called “S” and “M”) were synthesised for this study. Grafting of the foam was performed by use of three different organosilanes $\text{RSi}(\text{OR}')_3$, R being $\text{C}_8\text{F}_{17}\text{C}_2\text{H}_4$ (called C8Me if R' is CH_3 and C8Et if R' is C_2H_5) or C_2H_5 (called VTM if R' is CH_3).

2 Methods

The effectiveness of the hydrophobisation process was evaluated by investigating the following characteristics and properties before and after treatment: contact angle and surface energy, water vapour sorption, and thermal conductivity.

3 Results and discussion

The expected improved hydrophobic character of the treated materials was first tested by measuring the contact angles of various test liquids. Such a way allows getting information about the wettability of raw and grafted tannin-based foams and determining their surface free energy. For example, Fig. 2A shows that the

raw tannin-based type S foam, presenting low contact angle due to their highly hydrophilic character, was successfully hydrophobised. After treatment, the material indeed showed considerably higher water contact angle and a corresponding decrease of surface energy, mainly due to the vanishing of the polar part.

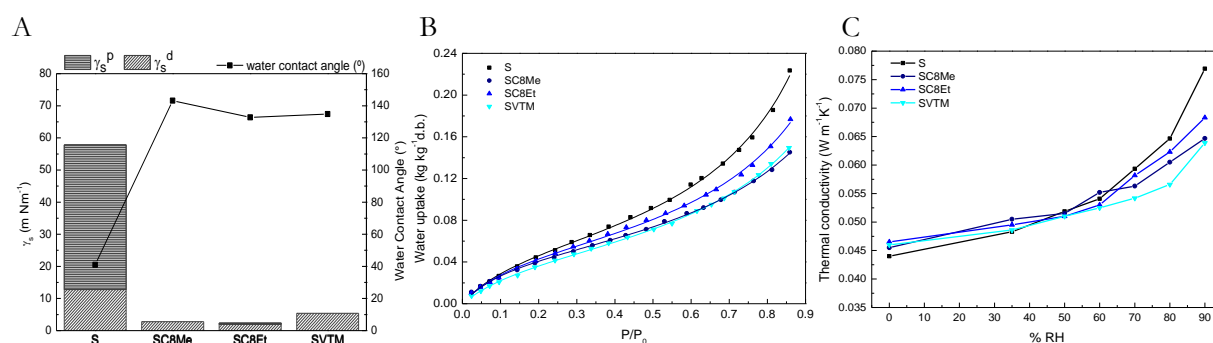


Figure 2: A) Surface energy -dispersive and polar parts- and corresponding water contact angles, B) sorption isotherms of water on dry basis (d.b.) and C) thermal conductivity as a function of relative humidity, for raw and treated S foams.

Despite treated foams presented dramatically enhanced water repellence, checking their behaviour towards moisture sorption, proceeding through gas phase, was necessary because water vapour may not behave as liquid water. The sorption isotherms, see Fig. 2B, show that the water uptake on the samples decreased after treatment, but much less than expected and a significant amount of water still was sorbed.

The results may be explained by the fact that the agent grafted on the foam produced a hydrophobic layer on the extreme surface, providing the observed macroscopic water repellent character, but could not prevent the deep penetration of small water molecules at the microscopic level. Moreover, the tannin foams are able to swell or shrink depending on the relative humidity [8] which suggest the diffusion of water molecule inside the bulk, acting as a plasticiser and making the foam most probably permeable to water. This phenomenon has also been observed in several lignocellulosic materials [9].

As a consequence, the thermal conductivity, see Fig. 2C, still increased with relative humidity, but less than for non-treated foams, and especially near the saturation where liquid water may condense. Thus, the most efficient hydrophobisation treatment was able to limit the increase of thermal conductivity at the half of what was measured for the non-treated foam.

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