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Hydrophobisation of tannin-based foams by covalent grafting of silanes

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ABSTRACT

Thermally insulating foams based on Mimosa bark extracts (*Acacia Meansii*) were hydrophobised with the aim of decreasing their sensitivity to moisture. Two different formulations leading to rigid foams presenting similar porosity were prepared, and were covalently grafted with three kinds of organosilanes. Non-treated and hydrophobised samples were all thoroughly characterised by FTIR spectroscopy, contact angle measurements and corresponding surface energy calculations, water sorption and thermal conductivity studies. Hydrophobisation produced a significant repellence towards liquid water but did not prevent water vapour sorption. Water uptake, however, was limited compared to the non-treated materials. As a result, the increase of thermal conductivity at high relative humidity was lower after hydrophobisation.

1. Introduction

The dependence on temperature and moisture content of heat transfer in thermally insulating porous materials was repeatedly confirmed by many investigators during the past years (Abdou and Budaiwi, 2013; Jerman and Černý, 2012; Lacoste et al., 2014; Yu et al., 2015). Thermal properties such as thermal conductivity, specific heat and thermal diffusivity were found to increase with temperature, but within a limited range related to the characteristic climatic conditions in which the materials have to be used. In other words, the observed changes of thermal properties were not dramatic as far as only temperature was involved. On the contrary, the dependence on moisture content – itself related to relative humidity – was far more important, leading to much less insulating materials at higher moisture content. Such impact varies with composition, porosity and internal structure of the material. From this point of view, tannin-based foams are really concerned by this question, due to their promising insulation properties (Basso et al., 2011; Szczurek et al., 2014; Tondi and Pizzi, 2009).

The chemical modification of materials for turning their hydrophilic character into a more hydrophobic one, i.e., for lowering their affinity for humidity, is nowadays of particular interest. Tannin foams originally have a really high hydrophilic character due to the presence of a huge amount of hydroxyl (–OH) groups (Pasch et al., 2001), which can bind very easily to water molecules. These materials were also shown to be able to absorb several times their own weight of liquid water when soaked inside (Tondi et al., 2009). For limiting this problem, hydrophobisation of tannin foams has been considered in two recent papers. In the first one (Tondi and Petutschnigg, 2015a), tannin foams were heat-treated by infrared with various incident powers for decreasing the surface content of hydroxyl groups. In the second one (Rangel et al., 2016), tannins were grafted with fatty chains, and then the as-modified materials were used to prepare foams. In both cases, although clear trends were observed, the effect was limited. It was therefore wondered whether grafting organosilanes, some of them based on perfluoroalkyl chains far more hydrophobic than fatty chains, and taking the place of hydroxyl groups if used in excess, would be a more efficient solution.

It is indeed well known that organosilanes can be covalently grafted on various surfaces for giving them hydrophobic character (Abidi et al., 2007; Akamatsu et al., 2001; Cohen et al., 1992; Cosnier et al., 2005; Fadeev and Yaroshenko, 1996; Krajewski et al., 2004; Picard et al., 2001; Takei et al., 1997). Grafting is generally performed by reaction between –OH surface groups and alkoxy groups of organosilane compounds as presented in Fig. 1 (Castro

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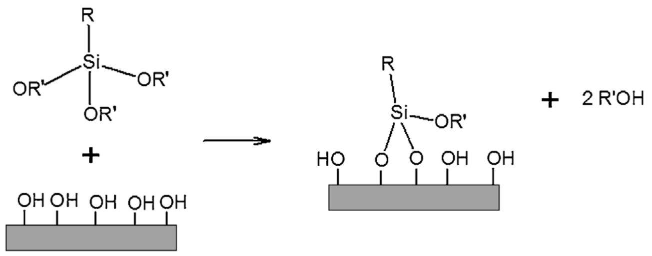

Fig. 1. Schematic representation of the grafting process of organosilane compounds on a material surface bearing hydroxyl groups.

et al., 1996; Picard et al., 2001; Schondelmaier et al., 2002). Successive reactions, for instance second silylation with the first layer or condensation involving two neighbouring groups from different grafted molecules may also occur as reported elsewhere (Cohen et al., 1992; Cosnier et al., 2005; Derouet et al., 1998), leading to a layer of organosilane compound at the surface of the materials and making the latter hydrophobic, or at least much less hydrophilic. As the surface chemistry of tannin-based materials is mainly based on −OH groups, the same kind of hydrophobisation process is therefore expected.

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 organic foam samples were synthesised for this study from two different formulations. Grafting of the foam was performed by use of different organosilanes RSi (OR')$_3$, R being $C_8F_{17}C_2H_4$ or C_2H_3 and R' being CH_3 or C_2H_5 with the purpose of investigating the influence of functional (R) and alkoxy (R') groups on the hydrophobisation efficiency. These reagents were chosen because formerly shown to provide hydrophobic character to various surfaces (Abidi et al., 2007; Cosnier et al., 2005; Krajewski et al., 2004; Kujawa et al., 2014; Picard et al., 2001).

2. Experimental

2.1. Materials

2.1.1. Foams preparation

Two formulations based on commercial Mimosa tannin, kindly supplied by SilvaChimica (San Michele Mondovi, Italy) and commercialised under the name "Fintan OP", were tested. The industrial extraction process of this kind of tannins has been explained in detail elsewhere (Braghiroli et al., 2014). Briefly, fresh Mimosa bark (*Acacia Mearnsii*) was subjected to leaching in a sodium bisulphite aqueous solution at 70 °C. The resultant solutions were concentrated and then spray-dried to yield a light-brown powder containing 80–82 wt.% of phenolic flavonoid materials, 4–6 wt.% of water, 1 wt.% of amino acids and other components such as monomeric and oligomeric carbohydrates consisting of broken pieces of hemicellulose.

"Standard-PEG" tannin-based foams (here simply called "Standard") were obtained by physical foaming according to the method described elsewhere (Basso et al., 2013), and tannin-based "meringues" (here referred to as "Meringue") were prepared by polymerisation and hardening of a liquid, tannin-based, foam as described in another paper (Szczurek et al., 2014). Briefly, Standard foams were obtained by expansion due to a gas produced in situ in the resin undergoing polymerisation, whereas Meringue foams were obtained by frothing of a tannin-based resin. After hardening, foams were dried at room temperature during one week. The corresponding formulations are given in Table 1.

Table 1
Mimosa tannin-based foams formulations. All amounts are expressed in grams.

Ingredients	Standard-PEG foam	Meringue foam
Tannin	30	20
Water	6	30
PEG400[a]	8	–
Furfuryl alcohol	10.5	–
Formaldehyde (37%)	7.4	–
Hexamine[b]	–	1.42
Surfactant[c]	–	3
pTSA[d]	11 (65% aqueous solution)	1.12 (pure)
Diethylether	4	–

[a] Polyethylene glycol of molecular mass 380–420 g mol^{-1}.
[b] Hexamethylenetetramine (also known as 1,3,5,7-tetraazaadamantane).
[c] Tween® 80 (also known as Polyoxyethylenesorbitan (20) sorbitan monooleate or Polysorbate 80).
[d] Para-Toluenesulfonic acid (also known as 4-methylbenzenesulfonic acid).

2.1.2. Hydrophobisation process

Foam grafting was performed with the three different reagents listed in Table 2, all used as received without further purification. In a typical experiment, 2 g (i.e., approximately 30 cm^3) of foam sample was soaked inside the organosilane solution (approximately 100 cm^3) for 3 h (see below for details), during which grafting reactions were assumed to occur according to the scheme shown in Fig. 1. All reagents were added in large excess with respect to the hydroxyl groups supposed to be present in the tannin foam. This excess amount was calculated based on the assumption that all hydroxyl groups formerly existing in the flavonoid unit remained and were still available in the final foam. As the amount of tannin per gram of final foam is known, and as Mimosa tannin is predominantly composed of prorobinetinidin (Pasch et al., 2001) which contains five −OH groups, the number of hydroxyls per gram of foam could be estimated. Then, it has been considered that each grafting molecule was able to react with only one −OH group, even if organosilanes have three other active sites. Finally, the corresponding theoretical amount of hydrophobised agent was multiplied by a factor 2. The main reason for using excess amounts is the requirement of getting a surface fully saturated with hydrophobic chains, taking into account the fact that, given the expected heterogeneous distribution of hydroxyl groups in the foam, the probability of finding three nearest −OH neighbours able to react with one single organosilane molecule is probably low. As an additional precaution, all reagents listed in Table 2 were fresh, i.e., directly obtained from the supplier and never used before. Once open for the first time just before doing the experiments, all reagents were carefully kept in a desiccator for limiting their sensitivity to moisture.

The impregnation procedure was defined according to the reagent employed:

- C8Me was dissolved in dry methanol, and the reaction took place in a beaker under stirring at 400 rpm formerly installed in a vacuum bell jar at room temperature.
- C8Et was dissolved in dry ethanol at room temperature, and the reaction was performed as above.
- VTM was dissolved in pure toluene, and the reaction was performed under reflux at 110 °C in a round-bottom flask equipped with a condenser as explained elsewhere (Cosnier et al., 2005).

After 3 h, the hydrophobised Standard-type and Meringue-type samples were dried for 2 h in a vacuum oven at 60 °C, and were labelled SC8Me, SC8Et, SVTM, MC8Me, MC8Et and MVTM depending on the chemical used: C8Me, C8Et and VTM, respectively.