

EFFECTS OF DYNAMIC AGING (HYDROLYSIS AND CONDENSATION) BEHAVIOUR OF ORGANOFUNCTIONAL SILANES IN THE AQUEOUS SOLUTION ON THEIR PENETRABILITY INTO THE CELL WALLS OF WOOD

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The hydrolysis and condensation (aging) dynamics of aqueous solutions of (3-glycidyoxypropyl)trimethoxysilane (GPS), vinyltrimethoxysilane (VTS), and (3-aminopropyl)trimethoxysilane (APS) and their penetrability into the cell walls of European spruce (*Picea abies*) wood were studied to investigate the feasibility of using silanes as a cell wall modifying agent for wood and other lignocellulosic materials. The size distribution of silane particles in aqueous solution was determined using a dynamic light scattering apparatus and increased with the aging time, but at different rates depending on the silane monomer. With increasing aging time, the treated wood exhibited decreased cell wall bulking (swelling), and the water vapour sorption behaviour was less affected by treatments when compared with unmodified wood; SEM-EDX analysis revealed that there was a reduced amount of silane in the cell walls with increased aging time. These findings demonstrate the reduced accessibility of silane to cell walls following aging.

Keywords: Silane hydrolysis and condensation; Particle size distribution; Penetrability; Cell wall bulking; Equilibrium moisture content; SEM-EDX analysis

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INTRODUCTION

With the increased consciousness about environmental protection and concerns about the eventual exhaustion of petroleum and other non-renewable resources, bioresources such as agricultural and forest lignocellulosic materials are coming under increasing scrutiny for their potential as renewable and strategically accessible feedstocks (Park and Bronzino 2003). To more effectively utilize these bioresources as materials they are usually subjected to chemical and biological treatments such as mechano-chemical pulping for making paper (Sutermeister 2010), hydrophobation treatments of textile fabrics for improving resistance against water and wrinkles (Abhyankar et al. 1986), chemical modification of wood to dimensionally stabilize wood and improve its durability (Hill 2006), and plant fiber treatment for producing advanced bio-composites

(Samir et al. 2005). Most of these treatments of lignocellulosic materials involve a change in the structure and properties of the cell walls. Therefore, the accessibility of treating agents to the cell wall interior is a crucial prerequisite (Engström et al. 2006). The size of chemicals used must accordingly be smaller than the minute openings of very small pores in the cell wall polymeric network structure. The cell walls of lignocellulosic materials consist of semi-crystalline cellulose microfibrils embedded within a lignin/polysaccharide matrix. The ingress of water may expand the present- and create new-micropores within the matrix, thereby resulting in cell wall swelling.

The size and volume of micropores in the cell walls of lignocellulosic materials have been surveyed by various techniques (Hill and Papadopoulos 2001), including differential scanning calorimetry (Park et al. 2006), atomic force microscopy (Fahlén and Salmén 2005), and scanning electron microscopy (Wallström and Lindberg 1999; Persson et al. 2004). The pore size measured using these techniques varies from 2 to 10 nm in diameter, depending on the measuring method and plant species used. The drying process can result in collapse of micropores, thereby reducing the pore size and volume in the cell walls (Park et al. 2006; Suchy et al. 2010a, b). The collapsed micropores in the cell wall interior can be reopened in a moist environment by breaking the hydrogen bond network formed during micropore collapse (Hill et al. 2004b).

Delivery of reactive chemicals with a molecular size small enough to penetrate the cell walls and to chemically modify the cell wall polymers has been recognized as a strategy for improving the properties of wood and other lignocellulosic/cellulosic materials. By incorporating reactive chemical monomers or oligomers into lignocellulosic cell walls, the covalent bonding of chemicals with the hydroxyl groups of cell wall polymers can be established and/or the chemicals deposited and subsequently polymerized so that they are sterically fixed in the cell wall. As a result of in situ modification, the cell wall properties are permanently changed (Hon and Shiraishi 2001; Hill 2006). To date, the chemicals extensively used for lignocellulosic cell wall modification are various anhydrides (Hill 2008), furfuryl alcohols (Baysal et al. 2004), N-methylol compounds (Xie et al. 2005), glutaraldehyde (Xiao et al. 2010), and vinyl esters (Jebrane et al. 2009). Some of these studies have revealed that these functional chemicals can bulk the cell walls, indicating that their molecular sizes are smaller than the openings of cell wall micropores so that these molecules can penetrate and thus react with the cell walls.

Organofunctional silanes are recognized as efficient coupling agents that are extensively used in composites and adhesive formulations (Plueddemann 1991; Xie et al. 2010). Silanes have a generic chemical structure $R_3-Si-R'X$, where R is alkoxy, X represents an organofunctionality, and R' is an alkyl bridge (or alkyl spacer) connecting the silicon atom and the organic functionality. The bifunctional structure of a silane also makes it possible to use them as potential modifying agents for lignocellulosic materials, since these materials' cell wall polymers bear reactive hydroxyl groups (Mai and Militz 2004a,b). The silane organofunctional groups such as vinyl and glycidyl groups may react in the presence of initiator or catalyst with the hydroxyl groups of cell wall polymers, and the silanol produced by hydrolysis of the alkoxy moiety can condense, thereby forming a bridge between the cell wall polymers (Xie et al. 2010). Generally, the silanes need to be hydrolyzed before application in order to effectively establish the

stable Si-O-Si bonds. The kinetics of the hydrolysis and condensation of silanes have been reviewed previously (Osterholtz and Pohl 1992).

The silanes have been extensively reported to use for modifying natural fibers to improve the properties of fiber/polymer composites (Bledzki and Gassan 1999). In addition, silanes are also potential wood modifying agents because most of them are reactive and can be grafted onto or crosslink the cell wall polymers, thereby imparting wood highly hydrophobic characteristics, dimensional stability, and durability (Mai and Militz 2004a,b). Although in some of studies the researchers have observed issues related to penetration (Donath et al. 2004; Hill et al. 2004a), few of them have made a systematic investigation on penetrability, which is a basic knowledge to develop a workable silane modification technique for wood. The objective of this study is thus to establish the effect of the aging process (hydrolysis and condensation) of three commonly used organofunctional silanes in aqueous solution on their penetrability into wood and accordingly evaluate the feasibility of silanes used as a cell wall modifying agent in wood.

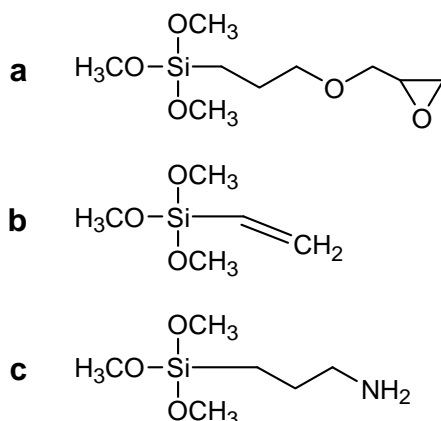


Fig. 1. Chemical structures of (3-glycidyloxypropyl)trimethoxysilane (a), vinyltrimethoxysilane (b), and (3-aminopropyl)trimethoxysilane (c)

EXPERIMENTAL

Materials

Wood pieces measuring 10 mm (longitudinally) x 5 mm (tangentially) x 1.5 mm (radially) were cut from a rotary peeled veneer of Norway spruce (*Picea abies*). Norway spruce is a coniferous species being constituted with tracheids (over 90% of total volume of wood) and small part of parenchyma and ray cells. The tracheids have an average diameter of 30-40 μm and cell wall thickness of 2-7 μm , with plenty of bordered and half-bordered pits in the cell walls (Brändström 2001).

Three organofunctional silanes (3-glycidyloxypropyl)trimethoxysilane (GPS, refractive index 1.429), vinyltrimethoxysilane (VTS, refractive index 1.392), and (3-aminopropyl)trimethoxysilane (APS, refractive index 1.424) were purchased from Sigma-Aldrich Ltd (Gillingham, United Kingdom), and their chemical structures are

shown in Fig. 1. These representative silanes were selected because they are extensively used as coupling agents in the composites and bear reactive functional groups, which can potentially react with the hydroxyl groups of wood polymers.

Ethanol and acetic acid were of analytical purity grade.

Preparation of Silane Solution

Silane solutions with a relatively high concentration of 20 wt% were prepared in this study, at which concentration bulking may be observable if the silane can penetrate the cell walls. The preparation procedures were as follows:

(1) GPS solution: Distilled water was adjusted with addition of acetic acid to obtain a pH of 2.5. Then 20 g GPS was added into 80 g of the acidified water and the solution was stirred immediately;

(2) VTS solution: 20 g VTS was added into 80 g of aqueous ethanol solution (the weight ratio of ethanol and distilled water was 70:30) and the silane solution was stirred immediately;

(3) APS solution: 20 g of APS was mixed with 80 g distilled water directly and stirred immediately. The pH value of the final solution was 11.5.

All the silane solutions were stirred with a magnetic stirring bar at 300 rpm for 0.5 h until the mixtures became transparent (fully dissolved) before any measurement.

In addition, the GPS, VTS, and APS solutions with a concentration of 5% were also prepared for dynamic light scattering analysis to determine if the change in the silane concentration caused great influence on the particle size distribution. In this context the concentration of silanes used was 20% unless otherwise stated.

Particle Size Distribution Analysis

The changing dynamics in the silane particle size distribution was determined using a Zetasizer Nano ZS (Malvern Instruments Ltd, Worcestershire, United Kingdom) with a 4 mW He-Ne laser (632.8 nm) as the light source, which could determine the hydrodynamic diameter of particles in the range of 0.3 nm to 10 μm using dynamic light scattering. The equipment was calibrated using a zeta potential transfer standard DTS 50 (carboxylated polystyrene latex) in the first instance. An aliquot of 2.5 mL was taken from the fully dissolved silane solution and measured at various aging periods. By using the proprietary Zetasizer Software 6.12, tests were started with a 120 s thermal equilibration period at 20 °C and then the particle size distribution and peak intensity were recorded.

Treatment of the Wood

Before impregnation with silane solutions, wood pieces were oven dried at 105 °C for 24 h. The weight of samples was determined, and their radial sizes were measured using a digital micrometer (Mitutoyo UK, East Kilbride). For each impregnation process, ten wood pieces were placed in a 150 mL glass bottle filled with 50 mL silane solution that had been aged for a specific period of time. The wood was impregnated under vacuum at 0.01 MPa for 30 min and subsequently in a pressure vessel at 0.4 MPa for 12 h in order to ensure the completion of silane penetration in the wood in a short period. After impregnation, the excess treatment solution was blotted off the wood pieces with

filter paper. The wood pieces were air dried for 2 days followed with 24 h oven drying at 105 °C. The weight and radial size of dried wood pieces were measured, as above. The bulking of wood is expressed in terms of the retained swelling in the radial direction compared to dry untreated wood,

$$\text{Bulking} = \frac{L_1 - L_0}{L_0} \times 100 \quad (1)$$

where L_0 and L_1 are the radial size of wood pieces untreated and treated with silane in the oven dry state (mm), respectively.

Determination of Dynamic Water Vapour Sorption Behaviour of Wood

The wood pieces (untreated and treated with silanes solutions respectively aged for 0.5 h and 15 days) were ground to a flour and passed through a 20-mesh sieve. Isotherm analysis of the prepared wood flour was carried out using a Dynamic Vapour Sorption apparatus (DVS Intrinsic, Surface Measurement Systems Ltd, London, United Kingdom) as previously described (Xie et al. 2011a,b). Approximately 20 mg of wood flour was placed in a sample holder that was connected to a microbalance and located in a thermostatically controlled cabinet. The pre-set RH increased in 5% steps from 0 to 95% and then decreased to 0% RH in the reverse order with the same step size. The sorption processes were run at a constant temperature of 25 °C over the full RH range. The instrument maintained a constant target RH until the sample moisture content change per minute (dm/dt) was less than 0.002% over a 10 min period. The running time, target RH, actual RH, and sample mass were recorded at 20 s intervals throughout each isotherm run. Since a highly reproducibility has been validated in our previous work (Hill et al. 2009), the measurement of each sample was carried out once for each treatment. The equilibrium moisture content of treated wood at a given RH was calculated based on the mass of wood before modification,

$$EMC = \frac{m_2 - m_1}{m_0} \times 100 \quad (2)$$

where EMC is the measured equilibrium moisture content of untreated and treated wood; m_0 is the dry mass of wood before modification; m_1 is the dry mass of wood after modification; m_2 is the equilibrium mass of wood at a given RH. For the untreated wood, m_1 equals m_0 .

SEM-EDX Integrated Analysis

The cross-sectional structure and elemental distribution of wood samples both treated and untreated with silanes were investigated. Each wood piece was carefully sliced to a thin film of approximately 300 µm using sharp razor blades and affixed to an aluminium stub. The samples were subsequently dried at 25 °C overnight and then carbon-coated before observed using a field-emission scanning electron microscope (SEM, Hitachi S-4800, Hitachi Ltd, UK), which was equipped with an energy-dispersive

X-ray detector (INCA X-act, Oxford instruments, UK). The accelerating voltage and the working distance were set as 16 kV and 17 mm, respectively. INCA microanalysis suite (v4.09) software was used for elemental analysis and mapping.

RESULTS AND DISCUSSION

Particle Size Distribution in Silane Solution

After adding silane into water and stirring briefly with a glass rod, the GPS, VTS, or APS solutions (20%) were immediately measured using the Zetasizer Nano ZS. The resulting size distributions exhibited only a main peak centered at ca. 200 nm, as shown in Fig. 2, which may be derived from the micelles of non-hydrolyzed silane monomers (Plueddemann 1991; Almanza-Workman et al. 2004). Through the dynamic light scattering test, 20% silane solution exhibited a particle dispersion index (PDI) range of 0.3 to 0.8, showing that the silanes were appropriately dispersed in the water.

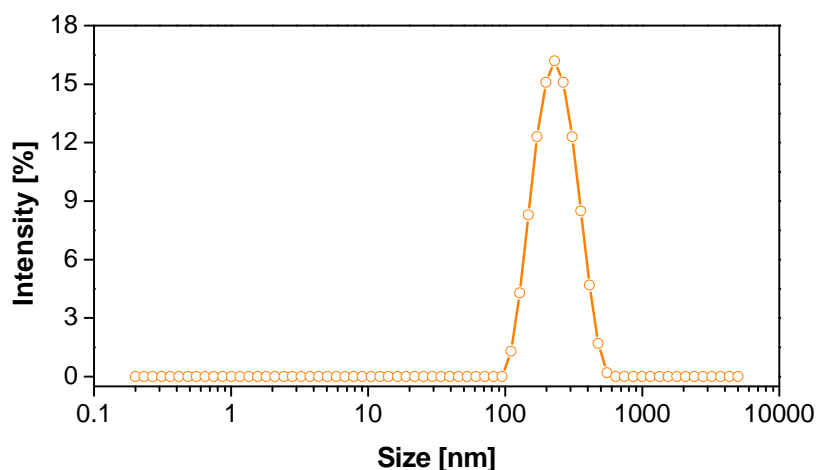


Fig. 2. Size distribution in 20% fresh GPS solution determined immediately after mixing silane and water.

The GPS solution that had been aged for 0.5 h exhibited two size distribution peaks with comparable intensity centred at 0.7 and 200 nm, respectively (Fig. 3a). The peak located at 0.7 nm is not expected to represent the silanol monomers produced by liberating alkoxy groups from GPS during hydrolysis, because the highly polar silanols are soluble and therefore should not be detected. Continuous changes in the peak intensity were observed with aging time (Fig. 3). Therefore, the peak may be assigned to the unhydrolyzed monomer. This is possible because the lowest detection limit of the Zetasizer Nano is 0.3 nm, which is at a molecular level (Note: water molecule has a diameter of 0.278 nm); in addition, the contrast of refractive index between water (1.33) and GPS (1.429) is high, so that the detector may identify the light signals scattered from GPS monomers. However, the typical molecular size of silane monomers was previously reported to be 3 to 6 nm (Plueddemann 1991), which is 4 to 8 times larger than 0.7 nm obtained herein. The great differences may be attributed to detection deviation in the low

limitation range of instrument. The peak at 200 nm exhibited a rapid decrease in intensity with aging time, which may be attributed to hydrolysis of GPS in the acidic aqueous solution (Osterholtz and Pohl 1992). After aging for 4 h, a new peak can be observed at 2800 nm, of which the intensity further increased up to 7% after 144 h aging. This increased size distribution shows that the size of particles formed in the GPS solution increased during the aging process, which can be ascribed to the formation of a polysiloxane network resulting from the condensation of silanol groups (Xie et al. 2010). Acetic acid catalyzes both the hydrolysis of silane by liberating the alkoxy group and condensation of silanols, thereby forming silica (Salon and Belgacem 2010). In this study the silane concentration (20%) was relatively high, and accordingly the silanol obtained after hydrolysis can have a greater probability to collide with others, thereby quickly forming polysiloxane structures. There was some turbidity visible in the GPS solution after 4 h aging, which could be due to the presence of large polysiloxane particles.

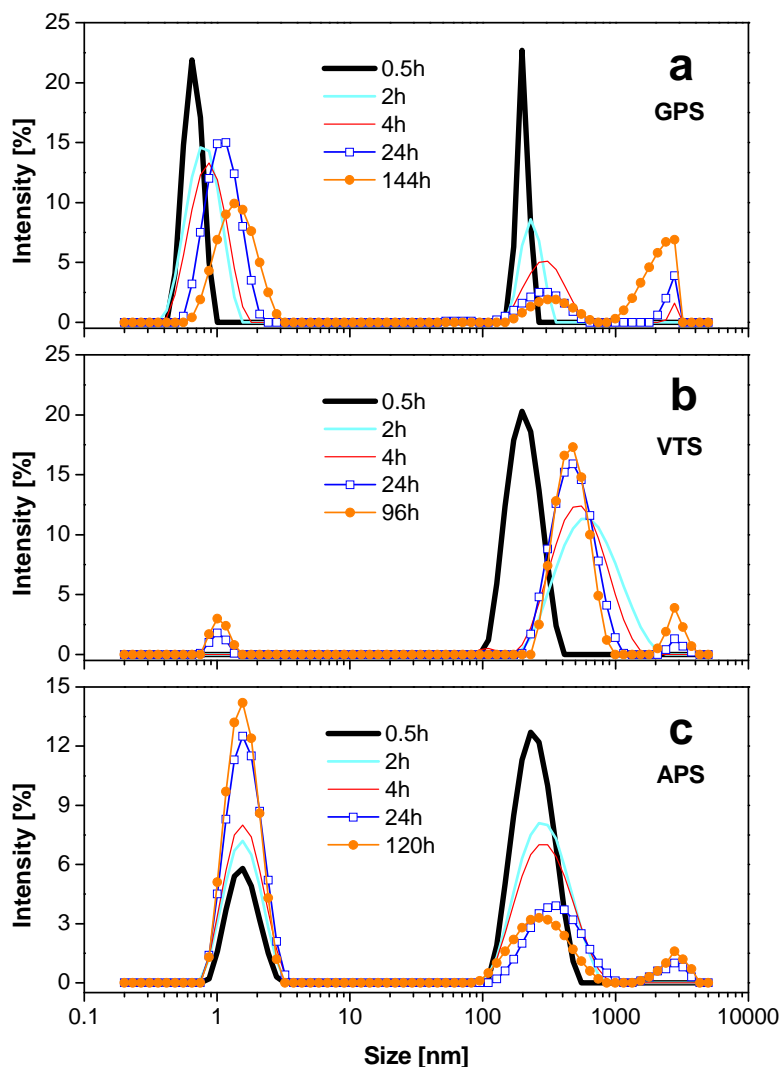


Fig. 3. Size distribution determined by light scattering for 20% GPS (a), VTS (b), and APS (c) solution, respectively, at variable aging periods

VTS did not dissolve in distilled water, and the 20% VTS/water mixture still appeared as a white viscous suspension after one week stirring, even at a pH value of 2.0 (not shown). The mixture of 20% VTS in 70wt% ethanol and 30wt% distilled water, however, turned transparent very quickly under stirring. After stirring for 0.5 h, the solution only exhibited a size distribution peak centred at 200 nm, which was probably due to the small micelles of dispersed non-hydrolyzed VTS (Fig. 3b). Micelles of VTS may be formed with the C=C groups in the centre and methoxysilanes in contact with ethanol (Plueddemann 1991). After 24 h aging period, two new peaks occurred at 1 nm and 2900 nm, respectively. Similar to the peaks of GPS, the peak centered at 1 nm may be assigned to non-hydrolyzed VTS monomer and the peak at 2900 nm to condensed silica particles. The peak at 2900 nm occurred later for VTS (24 h) than for GPS (4 h), suggesting slower hydrolysis and a lower condensation rate of VTS. The slower aging of VTS may be due to highly hydrophobic characteristics of VTS, which may result in more difficulty in dispersing them from ethanol into water for hydrolysis. In addition, a lower water level in the solution and a higher pH value may also reduce the hydrolysis reaction rate (Díaz-Benito et al. 2010; Salon and Belgacem 2010).

APS aged for 0.5 h exhibited two size distribution peaks centred at 1.8 nm (monomer) and 250 nm (micelle) with intensities of 6 and 13%, respectively (Fig. 3c). The peak located at 250 nm may be assigned to the micelles of non-hydrolyzed APS monomers with amine groups at the water interface and trimethoxysilane groups encapsulated by the micelles (Plueddemann 1991; Scruggs 2008). Previous studies of silane hydrolysis have found that APS can be quickly dispersed in ethanol/water (80/20) mixture, and ¹H NMR spectroscopy revealed that 50 and 90% of APS were hydrolyzed in 40 min and 3 h, respectively, by determining the change in amount of methanol liberated during hydrolysis (Salon et al. 2005). A new peak located at 3000 nm occurred after 24 h stirring and increased slightly after an aging period of 120 h, showing that the condensation process is simultaneously proceeding. Salon and Belgacem (2010) have recently reported using in situ ²⁹Si NMR spectroscopy that the increase of water content in the reaction solvent can hinder the condensation reactions of the amino-bearing silanes. In this study, the only solvent for APS was water, and therefore the hydrolysis process would be favored and condensation would be inhibited.

The GPS, VTS, and APS solutions at 5% concentration level exhibited similar size distribution spectra to those of 20% solutions, but the peaks shifted slightly to a smaller size range and new peaks occurred faster during the test (not shown). This minor difference in spectra may be due to faster hydrolysis, fewer particle-particle collisions, and reduced multiple scattering at the low concentration level (Urban and Schurtenberger 1998; Pusey 1999).

Weight Percent Gain and Cell Wall Bulking of Wood

The weight percent gain (WPG) of wood treated with silane solutions aged for different periods was determined in order to check whether aging had any influence on the penetration of silane into the wood structure. The WPG of wood treated with GPS, VTS, and APS did not apparently change with the aging time of treating solution (not shown). The unchanged WPG may be explained by the fact that the big particles formed during silane aging can still penetrate the grosser structure of the wood and deposit in the

wood lumens under vacuum-pressure impregnation condition even though they cannot penetrate the cell walls. The large particles in the treating solution may precipitate during the impregnation process, therefore resulting in an effective decrease in the concentration of silane used, which is closely related to WPG. The amount of precipitated particles (if any), however, is probably relatively small compared to the high silane concentration (20%). The wood treated with GPS and APS showed a WPG of 18%, but the WPG of VTS treated wood was only 14% (Fig. 4a). The difference in WPG was generally within the error bars and the minimal difference may be due to the different volume concentration, or a partitioning effect between solution and wood substance. The VTS was dissolved in the mixed solvent of ethanol and water (70:30 in weight). Since the density of ethanol is lower than water, the effective concentration of VTS in per volume unit was lower than that of GPS and APS, which both used water as the solvent.

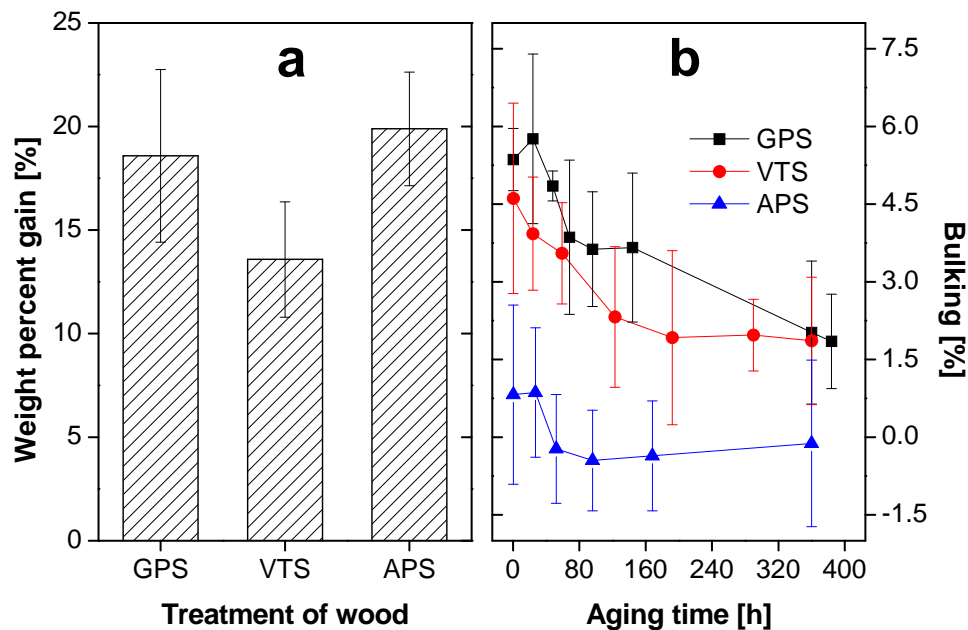


Fig. 4. Weight percent gain of wood impregnated with 20% silane solutions which had been aged for 2 h (a) and bulking in radial direction of wood samples treated with 20% silane solutions at variable aging periods (b) (n=10, bars show the standard deviation)

At the initial aging stage of 0.5 h, the wood treated with GPS and VTS solutions, respectively, produced the greatest bulking of 5.0 and 4.5% through the aging run (Fig. 4b). It was, however, observed that the size distribution in GPS and VTS solutions mainly located at 200 nm (size of micelles), which is much greater than the micropore size of cell wall. Therefore, the greater bulking at the initial stage may be mainly explained by the behavior of the silane monomers/oligomers, which are dispersed from the micelles and then delivered into the wood cell walls under vacuum-pressure impregnation process, because the molecular size of silane monomers are typically 3 to 6 nm (Plueddemann 1991), which is in the accessible range of micropores in the cell walls. Treatment with GPS caused apparently higher bulking of wood than with VTS

with varying aging periods, which may mainly be attributed to higher WPG in the GPS treated wood (Fig. 4b). In addition, water has previously been found to exhibit a greater ability in swelling the wood cell wall structure than ethanol, which may also increase delivery of GPS into the cell walls (Mantanis et al. 1994). The difference in silane chemical structures may also contribute to the bulking variation. The pendant glycidyloxy ring-opening product of GPS may possess relatively more hydrogen bonding sites and greater polarity than the hydrophobic C=C backbone of VTS. As a result, the former may exhibit greater affinity and resultant penetrability towards cell wall interiors (Ishimaru and Maruta 1996).

The bulking decreased for the wood treated with both GPS and VTS solutions with an increase of the aging period. This may mainly be attributed to the increased particle size during aging, thereby making it difficult to penetrate the cell wall. The other reason may be precipitation of big particles during impregnation resulting in a lower silane (monomers and/or oligomers) concentration in the treating solution. Lower penetrability of silane due to hydrolysis and condensation in the wood cell walls was also observed by Donath et al. (2004) and Hill et al. (2004a), although they did not reveal the dynamic penetration behavior of silanes in the wood cell walls. Donath et al. found that beech wood (*Fagus sylvatica*) treated with pre-hydrolyzed tetraethoxysilane, methyl triethoxysilane, and propyl triethoxysilane had higher weight percent gain, but less cell wall bulking, than wood treated with non-hydrolyzed silane monomers; the SEM-EDX analysis exhibited that the hydrolyzed silanes were deposited in both the cell walls and lumens, but the non-hydrolyzed silanes were mainly located in the cell walls. Comparably, Hill et al. (2004a) found that as the weight percent gain of Corsican pine (*Pinus nigra*) sapwood treated with 3-(methacryloxy)propyl trimethoxy- and vinyltrimethoxy-silanes increased over 30%, with the wood volume change maintained at a constant level of 7%, which is less than the maximum swelling (water saturated) of the order of 15%. This indicates that only part of the silane can penetrate the cell wall and the other part locates itself in the cell lumen. The reason may be due to the increased molecule size of silane due to condensation of silanols in the treating process, thereby resulting in potential difficulties in penetrating the cell walls.

Treatment with APS did not produce any apparent bulking in the wood, although the treated wood had a WPG of 18%. The analysis of the particle size distribution of the APS solution revealed that even after 120 h aging there was a size distribution peak at 3 nm with an intensity of 13%; the particle size is comparable to or even smaller than the diameter of cell wall micropores (generally smaller than 10 nm). The APS should thus penetrate the wood cell walls. The SEM-EDX analysis also confirms the penetration of APS into the wood cell walls where the dense signals of silicon elements were observed (Fig. 6). The treated wood had a brown appearance and visible deformation/contraction mainly in the tangential direction (not shown). Therefore, the lack of bulking in the APS treated wood may be attributed to the high pH (11.5) of APS solution. Under strong alkaline condition the wood cell wall components such as lignin and hemicelluloses may be dissolved from the cell wall structure to some extent, offsetting the bulking produced by incorporation of APS. As the result, the treated wood does not exhibit any apparent bulking.

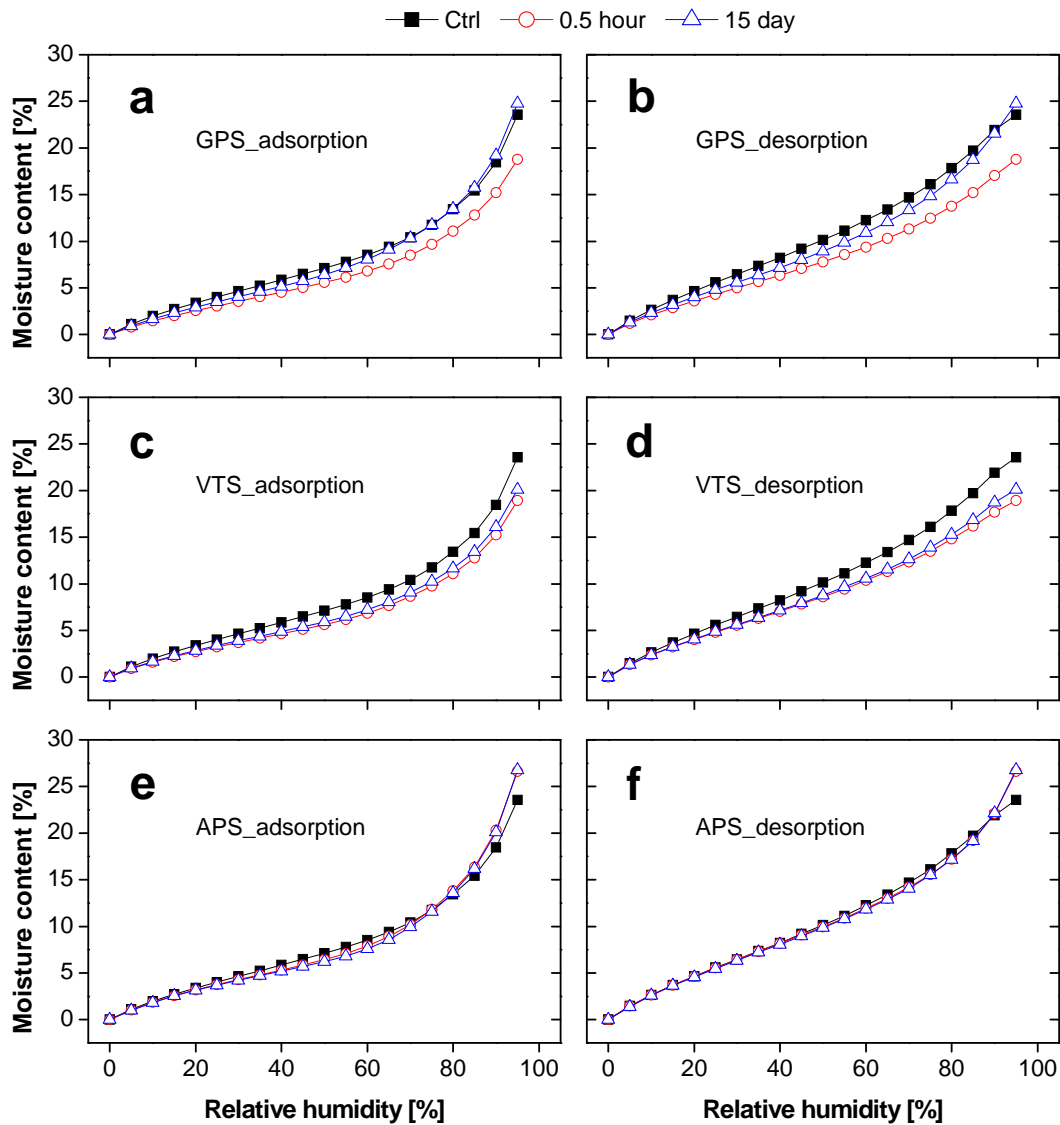


Fig. 5. Equilibrium moisture content in the adsorption (a, c, & e) and desorption processes (b, d, & f) of wood untreated control and treated with GPS, VTS, and APS solutions aged for 0.5 h and 15 day, respectively

Isotherm Sorption of Wood

Due to incorporation of silane into the wood structure, the moisture content is underestimated. This is because the mass of treated wood is increased due to the presence of silane (Hill 2006). Therefore, in this study the moisture content was calculated based on the mass before treatment in order to exclude the effect of silane incorporation and to compare the moisture content with the untreated control. The typical sigmoidal characteristics of the isotherm sorption curve of wood were not influenced by silane treatments (Fig. 5). With the stepwise increase of RH, the moisture content of untreated wood increased (Fig. 5a) due to the abundant hydroxyl groups and elastic swelling of cell walls by sorbed water. Treatment of wood with 0.5 h GPS solution apparently reduced

the equilibrium moisture content (EMC) during the adsorption (Fig. 5a) and desorption (Fig. 5b) processes, but especially for desorption. The reduction in EMC may be explained by the reduced free space of the micropores and increased cell wall stiffness due to incorporation of silane in cell walls. The reduced micropore space may accommodate less water in the cell walls; the stiffer cell wall due to bulking may swell less during moisture adsorption compared to the untreated wood, thereby providing less new space available for water (Xie et al. 2011b). Wood treated with GPS aged for 15 days exhibited a comparable EMC for the adsorption process and slightly lower EMC through the desorption process compared to unmodified wood. This suggests that the amount of GPS penetrated the cell walls was reduced and the cell wall interior was hardly influenced by the increased particle size after aging.

Compared to the untreated control, wood impregnated with both VTS solutions respectively aged for 0.5 h and 15 days displayed an obvious decrease in EMC in both the adsorption and desorption processes (Fig. 5 c&d). Treatment with solution which had been aged for 15 days only imparted to the wood a slightly higher EMC through the isotherm run compared with solution that had been aged for 0.5 h. The decrease in the EMC can be due to penetration of VTS monomers and/or oligomers in the cell walls, thereby reducing the cell wall volume that is available for the sorbed water molecules (Hill 2008). VTS exhibited a lower hydrolysis and condensation rate, as evidenced by the result of particle size distribution analysis (Fig. 3b). As a result, the difference in amount of big particles in the solutions may not have been obvious between 0.5 h and 15 days. Therefore, the penetration of VTS in the cell wall was not influenced remarkably by the aging time as compared to GPS. In comparison with GPS and VTS, APS treatment did not cause any apparent change in the EMC of wood in the RH range of 0 to 85% (Fig. 5 e&f). At higher RH levels, the EMC of APS treated wood was even higher than the untreated controls. This can be explained by the hygroscopic characteristics of amino groups in the APS. The treated wood has a WPG of 18%, and part of APS located on the cell lumen surface can absorb moisture and therefore offset the decrease of moisture caused by cell wall filling with APS. Based on the observations that there were not obvious changes, compared to untreated wood, in both the cell wall bulking (Fig. 4b) and equilibrium moisture content (Fig. 5e&f) due to APS treatment, an argument may be given accordingly that APS may not penetrate the cell wall and it ends up in the cell lumens. This argument may not, however, be in line with the following facts: (1) The molecular size of APS is small enough to penetrate the cell wall; (2) The silicon signal in the cell wall is visible according to SEM-EDX mapping analysis (Fig. 6f); and (3) The treated wood becomes brown and deformed. Consequently, penetration of APS into the cell wall and simultaneous damage of cell wall structure may be the reasons for the minor change in bulking and isothermal sorption.

SEM-EDX Analysis

The cell wall inner surface of wood treated with all silanes exhibited comparable intensity of silicon signals, and there were no visible particles detected (images not shown), suggesting that the silane in the lumens may form an invisible coating-like film covering their the inner surfaces. The cross section of wood samples treated with GPS, VTS, and APS solutions after 0.5 h aging showed strong signals corresponding to the

silicon element distributed throughout the cell walls (Fig. 6 a, c, & e), suggesting that GPS, VTS, and APS can penetrate wood cell walls. The density of silicon element signal obviously decreased for the wood treated with silane solution aged for 15 days (Fig. 6 b, d, & f), showing less accessibility of silane to cell wall interior.

It is worth considering whether the use of razor blades for preparing SEM samples may have brought the silane located the cell wall inner surface to the cutting surface, thereby causing artifacts on the observed surfaces; however, observation of three replicate samples showed a similar result of reduction in signal intensity with increased aging duration. In addition, this observation is also consistent with reduced cell wall bulking. Consequently, the information given by the EDX analysis may be partially believable. The evolution of reduced accessibility can be proposed as: the cell wall is first swollen by the solvent (water or aqueous ethanol in this study), following (1) by delivery of the non-hydrolyzed silane monomers and hydrolyzed silanol monomers into the swollen cell wall interior; (2) further condensation results in the formation of oligomers, linear Si-O-Si structure, and ultimately three-dimensional polysiloxane network in the aqueous solution, and hence penetration of the cell wall by these particles is inhibited accordingly.

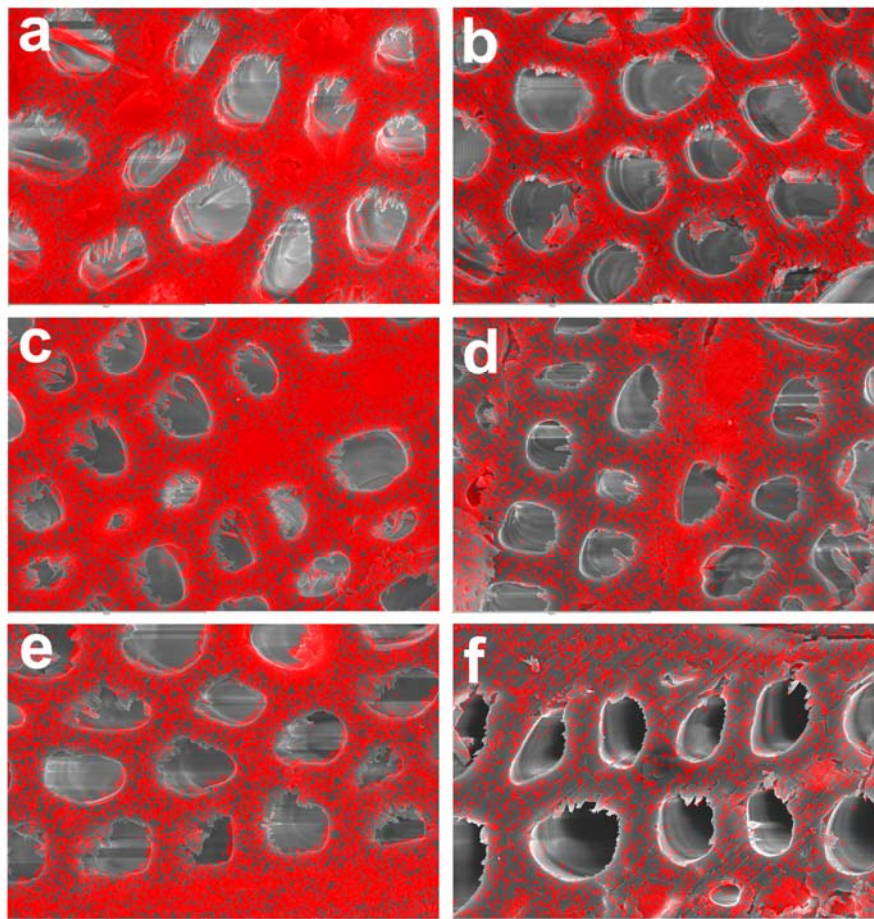


Fig. 6. Silicon element (red dot) mapping of wood cross-section treated with silane solutions aged for 0.5 h (a, c, e) and 15 days (b, d, f), respectively. (1) wood treated with GPS solution (a, b); (2) wood treated with VTS solution (c, d); (3) wood treated with APS solution (e, f).

CONCLUSIONS

1. Silanes bearing different functionalities exhibit distinct hydrolysis and condensation dynamics. Compared to GPS and VTS, the hydrolysis of APS is relatively simple and fast, but it causes greater damage to wood cell walls due to highly alkaline conditions.
2. The accessibility of silanes to wood cell wall interior in the aqueous solutions decreases with aging time, as evidenced by the cell wall bulking effect. This process will accordingly limit the shelf life of silane aqueous solutions.
3. Understanding the relationship between increased aging (hydrolysis/condensation) and the reduced chemical reactivity of silanes is of importance for the development of workable silane treatment techniques for wood.

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