1. INTRODUCTION

1.1. Wood and its usage

Wood is a rigid, fibrous structural tissue found in the stems and roots of trees and other woody plants and composed of biopolymers (celluloses, hemicelluloses and lignin) together with some minor components such as terpenoids, resin and fatty acids, pectin, proteins and in-organics (Sjöström and Alén 1999, Baeza and Fleer 2001, Rowell 2005). It is very important basic material; among others like plastics, glass and metals those are serving the society for decades. In ancient times, it was used besides for fire production already for making tools and as a building timber. Since this early beginning, the applications of wood and wood made products have expanded drastically and today wood and its derivatives can be seen in almost in every sphere of life. Indeed, its widespread availability, renewable nature, porous fibrous structure with remarkable mechanical strengths, low cost, easy handling and processing makes it a material of choice for various applications. Beside its numerous conventional usages, it has been shown potential even for some new applications e.g. as a filler for plastics to prepare so called wood plastics composites WPC (Bledzki et al. 1998, Rowell 2005, Niska and Sain 2008, Müller et al. 2012) and as a raw material for bio-fuel production (Deverell 1983, Ragauskas et al. 2006, Kumar et al. 2009).

1.2. Traditional wood preservation and related challenges

Undoubtedly, wood is a high performance material with excellent engineering properties but on the other hand, its drawbacks e.g. dimensional instability in humid atmosphere, low resistance against UV-radiation, heat, fire and biological degradation caused by insects, fungi and other organisms are very critical and cannot be ignored. Therefore, an additional treatment is crucial as a remedial measure to increase its service life for end use. Early developed classical wood preservatives like creosote (oil based), pentachlorophenol (solvent based) and chromated copper arsenate or CCA (water based) prevent wood from biological attack caused by many wood destroying organisms (Levi 1973, Leightley 2003, Schultz et al. 2007). Unfortunately, creosote and pentachlorophenol have been restricted to some USA localities only and they are no longer permitted in many European countries (Schultz et al. 2007). During late 1990’s growing environmental concerns over using heavy metals in the preservatives and their leaching during service and disposal after use have been increased rapidly (Freeman et al. 2003). Consequently, use of CCA for wood preservation was decreased in considerable length in most of Europe and Asia and CCA treated wood was restricted to industrial applications only in USA (Green and Clausen 2005, Schultz et al. 2007). CCA substitutes such as azoles, alkaline copper quaternary ammonium (ACQ), copper azoles, Cu-HDO which are free of chromium and boron based preservatives (Hughes 2004, Schultz and Nicholas 2003, Schultz et al. 2007) are even more problematic in terms of their leaching rates (Humar et al. 2005, Temiz et al. 2006, Pankras et al. 2012). Furthermore, these formulations are more expensive, corrosive and less mould resistant than CCA (Barnes 2008). Therefore, now to address above mentioned problems especially environmental concerns, one is seeking environmentally friendly alternatives to traditional wood preservatives available at low cost.

1.3. Scope of wood modification

Wood modification is a promising approach to overcome the problems described and to introduce multi-functionalities to non-durable wood. Unlike to conventional wood preservation processes which are based on biocides, wood modification relays on non-toxic chemicals and other inputs that enhance the properties of wood without containing any harmful residues in the end product. For effective modification, a chemical reaction with the reagent and cell wall components do not necessary but it is essential that the reagent infiltrates the cell wall and that it is non-leachable in service (Hill 2011). A meaningful enhancement in wood properties can be achieved either by modifying the wood substrate with mechanical, enzymatic, thermal or chemical means (Stefke and Teischinger 2002). Several heat treatment processes (thermal modifications) which are performed in inert atmosphere or in oil at temperatures in between 180 and 260 °C (Sailer et al. 2000, Militz 2002), severely degrade the hydrophilic cell wall polymers. This cleavage and subsequent conversion of cell wall components into new water insoluble polymers leads hydrophobation that lowering water sorption (Schneider and Rusche 1973), enhancing decay resistance (Stamm and Baechler 1960) and dimension stability (Stamm et al. 1946). However, cell wall damage during the thermal treatment seriously affects the strength properties (Stamm et al. 1946, Jones et al. 1999, Militz 2002). That is why;

application of this process above 240 °C is very limited due to severe strength losses (Militz 2002).

In classical sense, chemical wood modification is any chemical interaction between the reactive cell wall components and a chemical reagent at the molecular level, with or without a catalyst that can establish a chemical bond between them (Hon and Shiraishi 1991, Militz et al. 1997, Rowell 2004, Mai and Militz 2005). However, in many cases, it is very hard to fulfill this demand because of the different mode of action of several reagents used (Hill et al. 2004). Various chemical compounds have been investigated for the modification of wood such as anhydrides, acid chlorides, carboxylic acids, isocyanates, aldehydes, alkyl chlorides, lactones, nitriles and epoxides (Rowell 1983, Militz et al. 1997, Norimoto 2001). Silanes, silicones, siloxanes and titanium alkoxides are among those which have been studies explicitly in recent years (Saka and Ueno 1997, Bücker et al. 2003, Donath et al. 2004, Panov and Terier 2009, Hübert et al. 2010). Generally, as a result of successful chemical modification, a broad spectrum of properties such as durability against fungi and insects, dimension stability, strength, hardness, resistance against discoloration and weathering as well as flammability of treated wood have been improved considerably in relation to un-modified wood (Mai and Militz 2004). Acetylated wood (wood treated with acetic anhydride) with around 20 ma.% weight gains showed good durability as well as dimensional stability (up to 75 %) without sacrificing its mechanical properties (Hadi et al. 1995, Larsson-Brelid et al. 2000). Wood modified with various silicones displayed resistance against brown and soft rot (Ghosh et al. 2008, Weigenand et al. 2008), blue stain and moulds (Ghosh et al. 2009) and against natural weathering (Ghosh et al. 2009a). In addition, dimension stability and water related properties were also improved (Weigenand et al. 2007).

In brief, wood modifications are novel processes to prepare eco-friendly wood based materials that may potentially replace traditional products in near future. High cost and comparatively less performance than conventional treatments are assumed to be the main obstacles in their commercialization. More focus in future research demands on address these issues by introducing new substances for modification, improving relevant process design and by optimizing the properties of the respective end products.

1.4. Sol-gel approach for wood modification

The application of silicon and titanium compounds for wood modification based on sol-gel process is already known for 20 years (Saka et al. 1992, Saka and Yakake 1993). A comprehensive review article on wood applications of alkoxysilanes is available (Mai and Militz 2004). Three strategies are described in the literature on the using mode of these systems for efficient wood modification. In one approach, tetraethoxysilane (TEOS) was applied to preconditioned and water-soaked wood by using its bound and free water to initiate the sol-gel process in the wood matrix. It was reported that silica gels were formed in the wood cell walls in the moisture-conditioned wood and were localized mainly in the lumina of the water-soaked samples. Moisture-conditioned impregnating wood was non-leaching and showed improvement in ASE (up to 42 % with WPG 10 ma.%) and in flame retardance in a certain extent in comparison to untreated wood. No improvements were realized for water-soaked impregnated wood (Saka et al. 1992, Ogiso and Saka 1993). Later on, this work was followed up by many other investigators using various silane based agents as well as their combinations with fire, decay and leach resistant agents for tailoring wood properties (Miyafuji and Saka 1996, Saka and Tanno 1996, Saka and Ueno 1997, Tanno et al. 1997, Miyafuji et al. 1998,Tanno et al. 1998, Miyafuji and Saka 2001, Donath et al. 2004, Panov and Terier 2009, Feci et al. 2009) and were reported substantial increase in water, fire, decay and leach resistant properties of the treated wood.

In the second approach, silanes were applied to wood in pre-hydrolyzed (sol) state (Böttcher et al. 1999, Bücker et al. 2001, Reinsch et al. 2002, Bücker et al. 2003, Donath et al. 2004, Mahltig et al. 2008, Unger et al. 2012). This state was achieved by hydrolyzing the basic silane based precursor prior to wood impregnation. For infiltrating such precursors, preconditioning of wood was not required. SiO_2 wood-inorganic composites were prepared by vacuum impregnation to the oven dried wood with freshly prepared silica sol followed by a defined curing treatment. Micro-analysis of the resultant composite structure revealed that silica sols were penetrated the whole wood matrix and silica gels formed therein uniformly coated the wood interior (Bücker et al. 2001). Gels were located mainly in the lumen but also in the cell walls (Bücker et al. 2003). Composites demonstrated worth considering enhancement in a number of properties like leach reduction, lowering the moisture absorption, increasing decay resistance against brown rot fungi and improving ASE and flame resistance while mechanical properties were remained unchanged.

In third approach, silanes mixtures of different molecular weights e.g. methyltrimethoxysilane (MTMOS), hexadecyltrimethoxysilane (HDTMOS) were applied to wood to enhance its surface related properties. During treatment, being lower molecular weight silane MTMOS absorbed into the wood matrix while HDTMOS remained at the surface and formed hydrophobic thin layer. This HDTMOS based film was well intact to the surface by forming chemical network with MTMOS and showed more resistance against surface erosion and discoloration in accelerated weathering trails (Tshabalala and Gangstad 2003, Tshabalala et al. 2003, Tshabalala and Sung 2007).

Relatively, very little attention has been focused on the application of titanium alkoxides for wood modification. TiO_2-wood-inorganic composites were tailored very similar to SiO_2-wood-inorganic composites via sol–gel processing using titanium based precursors as starting materials applied to moisture conditioned or oven dried wood samples (Miyafuji and Saka 1997, Hübert et al. 2010, Wang et al. 2012). Remarkable improvements in some mechanical properties, fire retardancy and moisture and water uptake reductions were achieved for TiO_2-wood-inorganic composites in comparison to un-modified wood.

1.5. Motivation and objectives

Numerous silicon alkoxides / silanes studies in relation to wood modification (see in section 1.4) uncover many aspects related to these systems like their suitability to impregnate wood matrix, their performance to upgrade the properties of the normal wood and related drawbacks and limitations etc. in the context of specific property enhancement and process development. As a consequence of continuous research, now there is no ambiguity in the results documented in this area except some results in relation to fire performance (Saka et al. 1992, Saka and Ueno 1997). In contrast, titanium alkoxides which possess very similar properties have been used rarely till now for wood modification focusing only on few properties like moisture sorption, fire resistance and some mechanical properties (Miyafuji and Saka 1997, Hübert et al. 2010, Wang et al. 2012). Nevertheless, these early investigations of organo-functional titanium compounds are not the substitute of a comprehensive study to get deep rooted information about their potential in improving wood in a multi-dimensional way. Especially, detailed investigations for evaluating their anti-fungal efficacy are of special interest because these have not been tested yet against any of wood destroying fungi to assess their abilities to eradicate them. A mixed precursor (derived from both silicon and titanium alkoxides and has a tendency to introduce into the wood in single step) is one of the promising potential candidates for wood modification because of containing qualities of both the precursors. Its application for wood treatment in single step has not been reported yet. Thus, it is worthwhile to test this system as well through explicit investigations for wood modifying purposes.

Generally, the objective of this study is to investigate the suitability of titania, silica and mixed precursors for wood modification through detailed inspections starting from basic precursors to wooden end products.

Under the framework of this study, efforts are made to answer the following questions with pertinence:

1. What is the effect of particle size, composition and viscosity of precursor on the composite structure and properties?
2. What is the effect of drying and curing treatments on the composite structure and properties?
3. Does any chemical link establish between the deposited material and wood cell wall components of sol-gel derived titania/silica/mixed-wood composite?
4. Does titania/silica/mixed-wood composite offer resistance against fire of different length scales? Which fire retardancy mechanism is active in these materials?
5. Does sol-gel treatment based on titania, silica and mixed precursor protect wood from biological attack and how does it avoid this?
6. Is any sol-gel derived titania/silica/mixed deposition capable in preventing the leachability of active agents embedded therein? What is the cause of this leach resistance?

2. MATERIALS AND METHODS

2.1. Metal alkoxides and their sol-gel chemistry

Metal alkoxides are compounds in which metal is attached to one or more than one alkyl groups through an intermediate oxygen atom. The general formula for metal alkoxide is $M(OR)_n$ where M stands for metal, R is the alkyl group and n is the valence number. Physical and chemical properties of these compounds depend on metal atom and the alkyl group attached. The addition of water results in the conversion of metal alkoxides to their respective metal oxides following sol-gel process that proceeds in three basic steps: (1) partial hydrolysis of alkoxides to form reactive species, (2) condensation of these reactive monomeric species to form oligomers (sol formation), (3) advancing hydrolysis to promote polymerization and cross linking of the oligomers leading to a 3-dimensional network (gel formation). Hydrolysis is usually carried out in non-aqueous medium in the presence of an acid or base catalyst. Hydrolysis speeds up when the pH of the mixture decrease from 7 while a minimum pH 2 is crucial for polycondensation reaction (Keefer 1984). As a result of cross linking (networking), the viscosity of sol increases gradually until sol-gel transition point is reached. At this point, viscosity increases drastically and gelation of the sol takes place (Bradley et al. 1978, Klein 1988).

Formation of reactive species (partial hydrolysis)

$$M(OR)_n + H_2O \longrightarrow (RO)_{n-1}MOH + ROH$$

e.g. $$Si(OC_2H_5)_4 + H_2O \longrightarrow (C_2H_5O)_3SiOH + C_2H_5OH$$

$$Ti(OC_3H_7)_4 + H_2O \longrightarrow (C_3H_7O)_3TiOH + C_3H_7OH$$

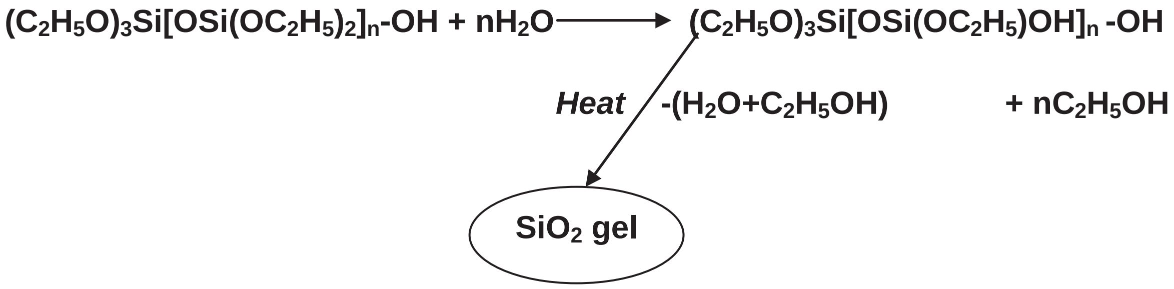
Sol formation (polycondensation)

$$2\,(RO)_{n-1}MOH \longrightarrow (RO)_{n-1}OM(OR)_{n-2}OH + ROH$$

$$(RO)_{n-1}OM(OR)_{n-2}OH \longrightarrow (RO)_{n-1}OM[OM(OR)_{n-2}]_nOH + ROH$$

e.g. $$n(C_2H_5O)_3SiOH \longrightarrow (C_2H_5O)_3Si[OSi(OC_2H_5)_2]_nOH + nC_2H_5OH$$

Gel formation (cross linking)



$$(C_2H_5O)_3Si[OSi(OC_2H_5)_2]_n\text{-}OH + nH_2O \longrightarrow (C_2H_5O)_3Si[OSi(OC_2H_5)OH]_n\text{-}OH + nC_2H_5OH$$

$$\xrightarrow[\text{Heat}]{-(H_2O+C_2H_5OH)} \boxed{SiO_2 \text{ gel}}$$

2.2. Description of materials

2.2.1. Wood specimens

Pine sapwood (*Pinus sylvestris* L.) was used as a model matrix for all investigations of wood modification. Wood specimens were prepared for different standard tests as well as for basic characterization of treated wood samples. Details of these standard tests and relevant specimen dimensions are given in Table 1. Used samples were of same densities and orientations and were free of defects, cracks, imperfections as well as biological infections. For calculating weight percentage gains (WPG) / solid uptake and bulking, all the samples were oven dried (18 h, 103 °C) to get their reference (initial) masses and volumes prior to impregnation.

Table 1 Preparation of specimens for various investigations

Investigation	Standard	Specimen dimensions
Soil bed test	ENV 807	5 mm × 10 mm × 100 mm
Basidiomycete test	Modified EN 113	5 mm × 30 mm × 30 mm
Blue stain test	EN 152	40 mm × 10 mm × 75 mm
MOE	DIN 52186	5 mm × 10 mm × 100 mm
ASE	In-house standard	25 mm × 25 mm × 10 mm
Leaching tests	EN 84 & OECD 313	15 mm × 25 mm × 50 mm
LOI	ISO 4589	4 mm × 10 mm × 80 mm
Cone calorimetery	ISO 5660	10 mm × 100 mm × 100 mm
UL 94	IEC 60695-11-10	1.6 mm × 13 mm × 125 mm
Water sorption	-	5 mm × 30 mm × 30 mm
Moisture sorption	-	5 mm × 30 mm × 30 mm
Others	-	15 mm × 25 mm × 50 mm

2.2.2. Chemicals used

All chemicals used in this research project are listed in Table 2 along with their purity details and name of their supplier / manufacturer. These chemicals were used as per received without further purification.

Table 2 Chemicals used in this study

Chemical	CAS-No.	Purity / %	Supplier
Titanium (IV) isopropoxide (TIP)	546-68-9	97	Alfa Aeser
Tetraethoxysilane (TEOS)	78-10-4	>99	Fluka
Ethanol	64-17-5	99.8	AppliChem GmbH
2-propanol (ISP)	67-63-0	99.5	Sigma-Aldrich
37 % HCl	7647-01-0	>99	AppliChem GmbH
65 % HNO_3	7697-37-2	>99	AppliChem GmbH
$CuCl_2$	7447-39-4	>98	Merck

2.3. Preparation of precursor solutions

Titania and silica based precursors were prepared by mixing basic alkoxides like titanium(IV) isopropoxide (TIP) and tetraethoxysilane (TEOS) in 2-propanol and ethanol respectively in the presence of acid catalysts like HCl or HNO_3 (sol-gel route). Base catalysts e.g. ammonia can be used as well however base catalysts are not favored because of accelerating the coagulation of colloidal particles formed during the synthesis (Yamane 1988). Titania based precursor (T1) was prepared by dropping 1 mole of TIP into 120 mole of 2-propanol under vigorous stirring. 65 % HNO_3 was added to the solution to adjust its pH to 2. TIP is highly reactive with water therefore; it can readily partially hydrolyze during the synthesis by absorbing moisture from the atmosphere. Furthermore, some water in the catalyst can be used for hydrolyzing the basic alkoxide. As a consequence of TIP-water interaction, a fraction of TIP can be converted into titania nano-particles suspended in the solvent or un-reacted precursor (Shabir Mahr et al. 2012). Similarly, titania based precursors of other concentrations (solid contents from 6.5 to 21 ma.%) were prepared accordingly. Characteristic details of these syntheses are shown in Table 3a.

Table 3a Characteristic syntheses of titania and silica based precursors

Precursor solution	Alkoxide: solvent / molar ratio	Equivalent TiO_2/SiO_2 solid content / ma.%
T1	1:120	1
T2	1:15	6.5
T3	1:10	9
T4	1:6	12
T5	1:3	16
T6	1:1	21
S1	1:110	1
S2	1:27	4
S3	1:13	7
S4	1:7	11

Silica based precursor (S1) was prepared by heating the mixture of 1 mole TEOS, 120 mole ethanol and 1 mole of water (acidified with 37 % HCl to a pH of 2); for 1-7 h to 50-70 °C. Similar syntheses (S2 to S4) were carried out to prepare TEOS derived silica based precursors of varied solid contents (see Table 3a). A series of mixed precursors (M1-M3) of various concentrations was derived from titania and silica based precursors when these were mixed drop wise in the ratio of 1:1 (by mass). Basic information related to these syntheses is given in Table 3b. Particle sizes and viscosities of the precursors were measured immediately after the synthesis. Solutions were stored at 17 °C in a storage container until impregnation finished (within a week).

Table 3b Syntheses of mixed precursor

Precursor solution	Precursors mixed by mass in 1:1 ratio	Equivalent TiO_2/SiO_2 solid content / ma.%
M1	T2, S2	5
M2	T3, S4	10
M3	T5, S4	13.5