



# Influence of alkali and Si-based treatments on the physical and chemical characteristics of miscanthus stem fragments



Estefania Boix, Frederic Georgi, Patrick Navard\*

MINES ParisTech, PSL Research University, CEMEF<sup>1</sup>—Centre de mise en forme des matériaux, CNRS UMR 7635, CS 10207 rue Claude Daunesse, 06904 Sophia Antipolis Cedex, France

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## ABSTRACT

Lignocellulosic materials in the form of miscanthus stem fragments were treated in order to limit their drawbacks (hydrophilicity, degradability, compatibility) when willing to use them as fillers for new bio-based concrete composites. This included a pre-alkaline soaking of the stem fragments followed by sol-gel tetraethoxysilane treatments in aqueous solutions. Since a modification of miscanthus using these methods has not been previously reported, the efficiency of the reactions was investigated at different pH conditions. The hydrolysis and condensation reactions of silane were monitored through the colorimetric silicomolybdenum method; the miscanthus structural changes, surface topography and the evidence of silica deposition on the fragments' surface were investigated by X-ray diffraction, X-ray photoelectron spectroscopy, electron microscopy and infrared spectroscopy. Results showed that the highest hydrophobicity, calculated by the water absorption of the stem fragments, was obtained for silane treatments in acidic and basic media. However, silica condensation followed different kinetics for each media conditions and headed to different morphology of the miscanthus coating. The alkali pre-treatment led to more hydrophilic products but with a more fibrillated surface, which may be potentially useful for its application in concrete.

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## 1. Introduction

Composites made of a filler or a reinforcing agent embedded into a matrix have properties influenced by the properties of the individual components and by the interface between components. When dealing with lignocellulosic fillers mixed with cements or polymers, the hydrophilic/hydrophobic character of the lignocellulosic components can be a critical parameter for ensuring a proper compatibility with the matrix. When the matrix is based on cement, treatments like boiling water, alkali, silane, titanium alkoxide were tried (Vo and Navard, 2016). In most of the cases, the objective is to increase the hydrophobicity of the filler and improve the affinity between the inorganic matrix (cement) and the plant filler.

Treatment with alkalis is a major step in the treatment of biomass for producing cellulose as it can remove some lignins, hemicelluloses, pectins and other minor components like wax (Mwaikambo and Ansell, 2002; Sun et al., 2000). In addition to

removing chemicals, and also due to the swelling induced by the treatment, the structure and mainly the surface of a lignocellulosic object is changed, being rougher. These leads to better mechanical interlocking due to the increase of the surface area and also the exposition of more hydroxyl groups, increasing the number of possible reactions. All these effects are increasing interface strength (Valadez-Gonzalez et al., 1999).

Aside having been obviously used as a coupling agent for glass fibres and silica particles in polymer matrices, silanes were extensively tested as a compatibilisation agent for natural fillers. For polymers, the reason is the possibility to create silanol moieties grafted onto the O–H bonds, always present at the surface of a lignocellulosic material, in order to decrease its hydrophobicity and improve the compatibility with hydrophobic polymers as polyolefins. It is recognized that the chemical reactions leading to this improvement follow four steps, hydrolysis, self-condensation, then a stage of adsorption which can be followed by the formation of Si–O–C bonds under heating, leading to a grafting of silanol onto the natural stem surface (Bilba and Arsene, 2008; Xie et al., 2010). Such coverage of the filler surface reduces the number of hydroxyl groups, decreasing thus hydrophilicity. But it has also the advantage of forming a link between the filler (one end of silanol reacts with hydroxyl groups) and the matrix (the other end form a bond

\* Corresponding author.

E-mail address: [patrick.navard@mines-paristech.fr](mailto:patrick.navard@mines-paristech.fr) (P. Navard).

<sup>1</sup> Member of the European Polysaccharide Network of Excellence ([www.epnoe.eu](http://www.epnoe.eu)).

with a matrix functional group). Silane treatments were applied for bio-based concrete materials. Such treatment applied on bagasse fibres resulted in a decrease in water absorption by the fibres, an improvement in the affinity between the cement matrix and natural filler, and also shortened the setting time of the composite (Bilba and Arsene, 2008).

Sol-gel processes have been widely used for material synthesis, such as metalloid oxides or materials coating. In the case of Si-species, alkoxyxilanes ( $\text{Si}(\text{OR})_4$ ) are typically used as a precursor. The hydrolysis of alkoxyxilanes is generally performed in a mixture of alcohol, water and an acid or base catalyst. The role of the alcohol is to favour the miscibility of the alkoxyxilane with the aqueous media. However, the hydrolysis of these precursors at low concentration can also be performed in aqueous media, specially under acid or basic catalysis to produce silicic acid ( $\text{Si}(\text{OH})_4$ ), which subsequently form oligomers and other species with other monomeric silicic acid or silicates ( $\text{Si}(\text{OR})_x\text{O}_y^{-(4-x)}$ ). The partial or total hydrolysis of the alkoxyxilane precursor ( $\text{Si}(\text{OR})_4$ ) into  $[\text{Si}(\text{OR})_x(\text{OH})_y]$  is required for the further condensation of silica ( $\text{SiO}_2$ ) (Iler, 1979) and/or the reaction between silanol groups ( $\text{Si}-\text{OH}$ ) and cellulose hydroxyl groups (Castellano et al., 2004). The subsequent condensation reaction has been shown to be faster at circumneutral pH (between pH 6 and 8) (Iler, 1979). Nonetheless, their response to silane treatments and the resulting materials properties in the presence of natural plants depends on the nature of the stem (Pehanich et al., 2004).

The main advantages of using miscanthus plants as a source of renewable materials are its environmental performances and its high yield. Moreover, from the point of view of materials application, the structure of miscanthus fragments provide thermal insulating properties, firmness and it is considered a strong plant when compared to other lignocellulosic materials such as straw (Pude et al., 2005). The presented work consists of an optimised processing of miscanthus plants based on alkoxyxilane treatments under mild conditions. The investigation focuses on resolving three main incompatibilities when using miscanthus as materials filler: i) to reduce water absorption by the natural stems that may result in materials dimensional instability, ii) to provide the stem fragments with a coating acting as a protection against degradation by the material matrix such as polymer or cement and iii) to modify the plant surface in order to increase the affinity between the natural plant and the matrix.

The final objective of this work is to find ways to improve the manufacturing of miscanthus-based concrete by pre-treating the biomass. To this end, a first study, reported here, was performed where miscanthus stem fragments were treated with Si based compounds together with an alkali pre-treatment. The present article reports the details of this pre-treatment. The alkoxyxilane used in this study for the miscanthus stem fragments treatment is tetraethoxysilane (TEOS). This silica precursor was selected due to the possibility to be hydrolysed completely into silicic acid, which allows monitoring the hydrolysis and condensation reactions through the silicomolybdenum method (Belton et al., 2012). Besides, the absence of alkyl groups gives a lower hydrophobic character to the molecule and therefore aqueous media of low concentrations of TEOS can be used for its hydrolysis without needing an organic solvent such as ethanol (Bilba and Arsene, 2008).

## 2. Experimental

### 2.1. Materials

Miscanthus X giganteus stems were harvested from Seine-et-Marne region (France) on March 2014 by the BES group (Biomass Environment System) and grinded by SD Tech SA

(Alès, France). The resulting miscanthus objects received are thus stem fragments. Tetraethoxysilane (TEOS, 99.99%), ammonia solution ( $\text{NH}_3$ , 28–30%), potassium sulphate ( $\text{K}_2\text{SO}_4$ ,  $\geq 99\%$ ) sodium acetate ( $\text{CH}_3\text{COONa}$ ,  $\geq 99\%$ ) and Aquanal™-plus silicon/silicium (Si) 0.01–0.25 mg/l  $\text{Si}^{4+}$  (vis) test kit were purchased from Sigma-Aldrich. Sodium hydroxide pellets ( $\text{NaOH}$ ,  $\geq 97\%$ ) were purchased from Merck and glacial acetic acid ( $\text{CH}_3\text{CO}_2\text{H}$ , 99.83%) was purchased from Fisher Scientific. All experiments were performed with distilled water.

### 2.2. Alkali pre-treatment

Alkali treatment of the stems was applied to some untreated, as received miscanthus stem fragments. Alkali treatment was conducted by submerging untreated stem fragments in a 5% sodium hydroxide solution during 30 min under stirring. Afterwards, stems were filtered and rinsed with acidified water (1% acetic acid glacial) followed by abundant water until rinsing water had a neutral pH and a conductivity lower than  $50 \mu\text{S}/\text{cm}$ . Samples were finally dried in oven (Salvis Lab Vacucenter, Switzerland) at  $80^\circ\text{C}$  and vacuum.

### 2.3. Silane treatment of the stems

The silane emulsion treatment was applied to both untreated and previously alkali treated miscanthus stem fragments by using a 2.6% v/v (115 mM) of silica precursor tetraethoxysilane (TEOS) in aqueous media: a) water (pH  $\approx 6$ ), b) acid (pH 4) or c) basic (pH 10). The acidic media was a pH 4 buffer prepared with a mixture of 0.1 M glacial acetic acid and 0.1 M sodium acetate. The basic media consisted of a 0.06 M ammonia solution. TEOS aliquot was added into the aqueous solution and five minutes later, stem fragments were submerged and kept under stirring for two hours. Alternatively, other stem fragments were also stirred in distilled water for two hours to prepare the untreated miscanthus sample aiming a better comparison to treated samples. The experimental setting consisted of 6 g of stem fragments added into 81.6 ml solution. The amount of miscanthus was chosen after preliminary tests in which increasing amounts of stem fragments were submerged in water in a 100 ml volumetric flask and stirred. The selected ratio stem mass/solution volume was the highest allowing a homogeneous stirring of the mix. Following the water soaking or silane treatment; samples were filtered in a round mesh sieve, air dried for four hours and further dried in oven at  $80^\circ\text{C}$  and under vacuum to allow condensation of silanol groups ( $\text{Si}-\text{OH}$ ) without degrading the stem fragments. Once dried, stem fragments were rinsed with water several times to remove unreacted species or salts and dried again at  $80^\circ\text{C}$  under vacuum.

The hydrolysis/condensation of the silica precursor was monitored using the Aquanal™ test kit. Aliquots of 0.2 ml were extracted from the treatment solution at 20, 45, 70, 100 and 120 min and diluted as required to reach a concentration within the detection range of the analytical silicomolybdenum kit.

### 2.4. Optical microscopy

The size distribution of grinded miscanthus stem fragments was determined using optical microscopy (Leica DM4500 P, Leica microsystems GmbH, Germany) operating in transmission mode and coupled with an image analysis software Archimed 4.2 (Microvision Instruments, France). The length and width of the fragments were measured using Image J software. The weighted arithmetic average and corresponding standard deviations of the fragment diameter, length and aspect ratio were calculated from the measurement of 350 fragments.

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