APPLIED SURFACE SCIENCE

Hydrophobicity of Hemp Shiv treated with Sol-gel Coatings

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Abstract

This is the first time sol-gel technology is used in the treatment of hemp shiv to develop sustainable thermal insulation building materials. The impact on the hydrophobicity of hemp shiv by depositing functionalised sol-gel coatings using hexadecyltrimethoxysilane (HDTMS) has been investigated. Bio-based materials have tendency to absorb large amounts of water due to their hydrophilic nature and highly porous structure. In this work, the influence of catalysts, solvent dilution and HDTMS loading in the silica sols on the hydrophobicity of hemp shiv surface has been reported. The hydrophobicity of sol-gel coated hemp shiv increased significantly when using acid catalysed sols which provided water contact angles of up to 118° at 1% HDTMS loading. Ethanol diluted sol-gel coatings enhanced the surface roughness of the hemp shiv by 36% as observed under 3D optical profilometer. The XPS results revealed that the surface chemical composition of the hemp shiv was altered by the sol-gel coating, blocking the hydroxyl sites responsible for hydrophilicity.

Keywords

Sol-gel, hydrophobicity, coatings, surface roughness, hemp shiv

1. Introduction

Wettability of a solid surface is governed by a combination of chemical composition and geometric structure of the surface [1,2]. The interplay between surface chemistry and surface roughness has been an active research topic for enhancing the hydrophobicity of cellulose based materials.

The woody core of the hemp plant (*Cannabis Sativa* L.) known as shiv has gained interest in the building industry during the recent years for production of lightweight composites. Hemp shiv based composites have interesting properties such as thermal [3], hygroscopic [4], mechanical, acoustic [5] and biodegradability [6].

Hemp shiv are generally very porous with low density tending to absorb large amounts of water. Previous studies have reported that hemp shiv not only has higher water absorption rate but also absorb high amounts of water in the very first minutes compared to different plant materials [7]. Moreover, the presence of cellulose, hemicellulose and lignin in bio-based materials contributes to the presence of hydroxyl groups in their structure. This leads to certain disadvantages of using bio-based materials making them incompatible with hydrophobic thermoset/thermoplastic polymers [8]. High moisture uptake also encourages colonial fungal growth resulting in cell wall degradation and lower durability of the material [9].

The major constituents of industrial hemp shiv are: cellulose (44%), hemicellulose (18-27%), lignin (22-28%) and other components such as extractives (1-6%) and ash (1-2%) [10,11]. Cellulose is a semi crystalline polysaccharide consisting of linear chain of several D-glucose units linked together by β (1–4) glucosidal bond. Cellulose contains free hydroxyl groups, and since they form the major structural component of hemp shiv, they are responsible for the extreme hydrophilic behaviour.

One of the mechanism to convert cellulose–based material from hydrophilic to hydrophobic involves chemical modification to block the hydroxyl groups of the cell wall thereby reducing water sorption sites. Treatments include acetylation [12], silanization [13] and in situ polymerization [14] that involve incorporation of materials into the cell wall blocking the voids accessible to water molecules. Other treatments methods that are known to enhance the water repellence are plasma etching, lithography, electrospinning and sol-gel treatment that endow the material with nano-scale surface roughness [15].

Chemical pre-treatment of natural plant materials have reported better bonding with polymer matrix interface due to improvement of their hydrophobic characteristics [16]. There is a need to develop a novel treatment method for hemp shiv to enhance its water resistance thereby improving the shiv-binder interfacial adhesion and reduce its susceptibility to decay. The sol-gel technique is a highly versatile method to deposit silica based coatings possessing single or multi functionality [17]. These thin mesoporous coatings have high structural homogeneity and their adhesion can be tailored to different substrates.

Sol-gel based hydrophobic and water repellent coatings have been investigated on different bio-based materials such as wood [18] and cellulosic fibres [19], however for hemp shiv this is the first time. The reactive hydroxyl groups present in the polysiloxane network of the sol-gel combine with the hydroxyl groups of cellulose through a covalent bond. This study successfully delivers a sol-gel modified hemp shiv material of hydrophobic character through a simple and inexpensive, one step dip-coating method.

2. Experimental

2.1 Materials

Hemp shiv used in this study was received from MEM Inc., manufacturer of ecological materials based in Rimouski, Canada. Tetraethyl orthosilicate (TEOS, 98%) and hexadecyltrimethoxysilane (HDTMS, 85%) were obtained from Sigma-Aldrich. Anhydrous ethanol was purchased form Commercial Alcohols, Canada. Hydrochloric acid (HCl, 38%) and nitric acid (HNO_3, 70%) were obtained from Anachemia, VWR, Canada. All chemicals were used as received without further purification.

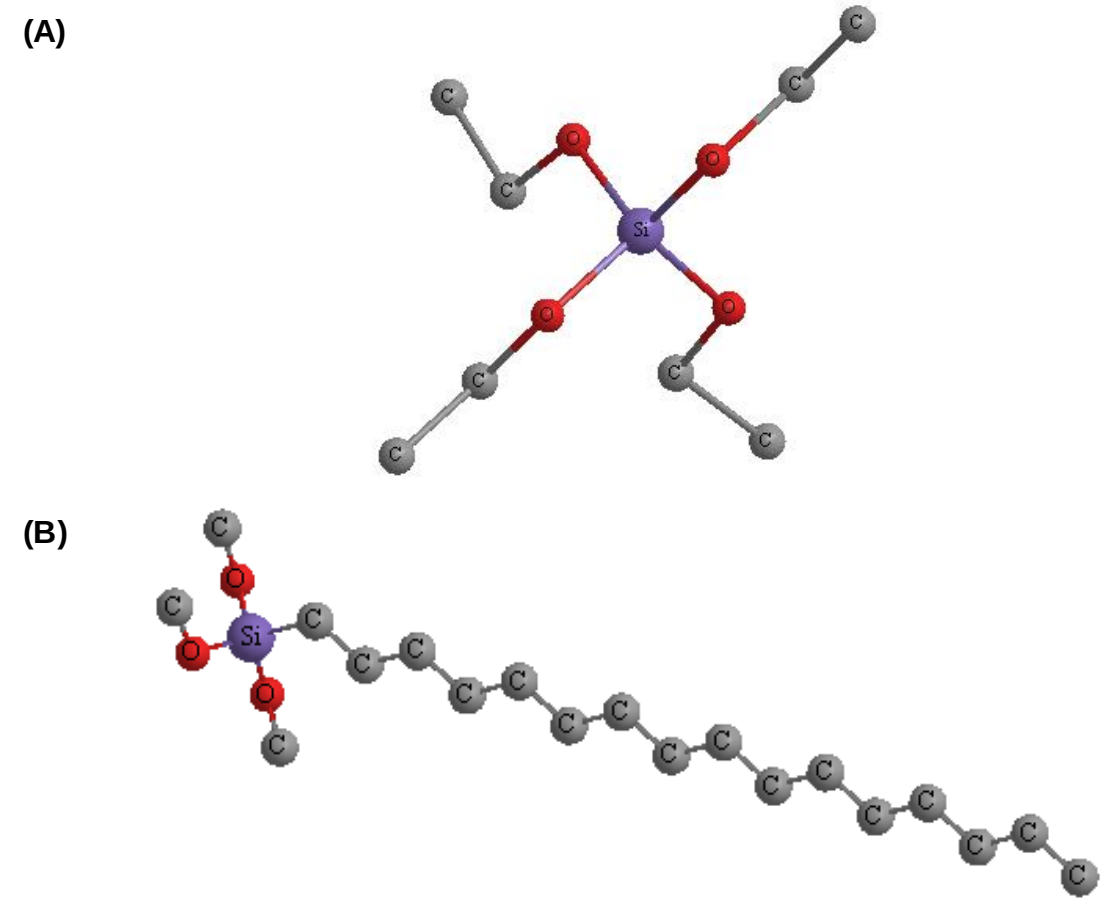


Figure 1. 3D structure of a (A) TEOS molecule, (B) HDTMS molecule; and (C) water on coated hemp shiv samples.

It is known that HDTMS may not be able to penetrate the outer surface layers of the cell wall due to its high molecular weight [18]. Due to this, the hydrophobicity would be compromised and it can be predicted that the coating might not be robust. Moreover, using only HDTMS would be highly expensive and would not be of interest to the construction industry. For these reasons, it was considered inappropriate to make a comparative study using purely HDTMS.

2.2 Preparation of the hydrophobic coatings

The silica based sol-gel was synthesised by hydrolysis and condensation of TEOS in ethanol and water. The reaction was catalysed using 0.005M acid (HCl/ HNO_3). Two sets of silica sols were prepared based on the difference in concentration of ethanol. The first set of formulations (sols A) were prepared stirring 1M TEOS in a mixture of 4M water and 4M ethanol. For the preparation of the second set of formulations (sols B), 1M TEOS was added to 4M water and 16M ethanol. After the preparation of both sets of silica formulations, the hydrophobic agent HDTMS was added in concentrations of 0.5-4 wt% of the sol. These mixtures of silica sol and HDTMS were stirred at 300 rpm for at least 20 minutes before performing the dip-coating process. All the sols were prepared at 40 °C and atmospheric pressure. The sols were allowed to cool down to room temperature and the pH was recorded.

The sols aged for 48 hours in closed container at room temperature before the dip-coating process. Gelation took place in-situ in which pieces of hemp shiv were dipped in the sol for 10 min and then carefully removed and transferred onto a Petri dish. The samples were placed at room temperature for one hour and then dried at 80 °C for one hour. A schematic illustration of the HDTMS modified silica sol-gel coating is shown in Figure 1.

As for the preparation of the pure sol-gel specimen, the sol aged in a container at room temperature until gel point. The gel-point was taken as the time when the sol did not show any movement on turning the container upside down. The gel-time and pH for all the prepared sols are reported in Table 1.

Table 1. Composition of the prepared sol-gel formulations and their properties.

FORMULATION	CATALYST	ETHANOL CONC. (M)	HDTMS CONC. (wt%)	GEL TIME (DAYS)	pH
sol A-1	HCl	4.0	4.0	178	1.87
sol A-2	HCl	4.0	2.0	116	1.82
sol A-3	HCl	4.0	1.0	101	1.78
sol A-4	HCl	4.0	0.5	101	1.85
sol A-5	HNO_3	4.0	4.0	150	1.73
sol A-6	HNO_3	4.0	2.0	112	1.87
sol A-7	HNO_3	4.0	1.0	101	1.92
sol A-8	HNO_3	4.0	0.5	101	1.92
sol B-1	HCl	16.0	4.0	>180	1.64
sol B-2	HCl	16.0	2.0	>180	1.68
sol B-3	HCl	16.0	1.0	>180	1.67
sol B-4	HCl	16.0	0.5	>180	1.72
sol B-5	HNO_3	16.0	4.0	>180	1.70
sol B-6	HNO_3	16.0	2.0	>180	1.76
sol B-7	HNO_3	16.0	1.0	>180	1.81
sol B-8	HNO_3	16.0	0.5	>180	1.83

2.3 Contact Angle Measurements

The water contact angle (WCA) of uncoated and coated hemp shiv samples were measured using a contact angle meter (First Ten Ångstroms USA, FTA200 series). The sessile drop method was employed and the contact angle was determined on at least three different positions for each sample (coated substrate). The volume of the water droplets was 5µl for the contact angle measurements. The average value was adopted as a final value. Images were captured and analysed using the FTA32 Video 2.0 software. All the measurements were performed at room temperature (24 ± 1 °C).

2.4 Surface Roughness

The topography and surface roughness of the samples was obtained using a 3D optical profilometer (Bruker Nano GmbH Germany, ContourGT-K series). The surface roughness was measured over an area at 0.25*0.30 mm^2 in non-contact mode at 20X magnification. Vision 64 on board software was then employed to analyse these data and calculate the roughness parameters. The readings were taken on at least three different positions for each sample and the average value was reported as the final value.

2.5 X-ray photoelectron spectroscopy (XPS)

The surface elemental and chemical composition of the samples were analysed using XPS. Prior to XPS analysis, samples were oven-dried at 80 °C for 96 hours. XPS spectra of uncoated and sol-gel coated hemp shiv were recorded with an X-ray photoelectron spectrometer (Kratos Axis Ultra, UK). All spectra were collected using a monochromatic Al Kα X-ray source operated at 300 watts. The lateral dimensions of the samples were 800 microns × 400 microns, corresponding to those of the Al Kα X-ray used, and probing depth was approximately 5 nanometres. For each sample, two spectra were recorded: (i) survey spectra (0–1150 eV, pass energy 160 eV, and step size 1eV) recorded for apparent composition calculation; and (ii) high-resolution C1s, O1s and Si 2p spectra (within 20 eV, pass energy 20 eV and step size within 0.05eV) recorded to obtain information on chemical bonds. Calculation of the apparent relative atomic concentrations is performed with the CasaXPS software. Peak fitting is performed with CasaXPS, which automatically and iteratively minimizes the difference between the experimental spectrum and the calculated envelope by varying the parameters supplied in a first guess.

2.6 Scanning Electron Microscopy

The surface morphology of the specimens was characterised using a scanning electron microscopy (SEM), JEOL corporation - Japan Model JSM-6360 operating at 25 kV. The specimens were coated with gold to achieve maximum magnification of textural and morphological characteristics.

3. Results

3.1 Hydrophobicity of sol-gel coatings

The water contact angle was determined as soon as the water droplet encountered the sol-gel coated hemp shiv surface. The sol-gel coatings with high HDTMS loadings (4 wt%) and varying concentration of ethanol are compared in Figure 2. It can be seen that uncoated shiv has an extremely hydrophilic surface and water droplet sinks into the substrate reducing the WCA in a short time. The sol-gel coatings yield hydrophobicity to the hemp shiv by maintaining a stable contact angle over 60 seconds.

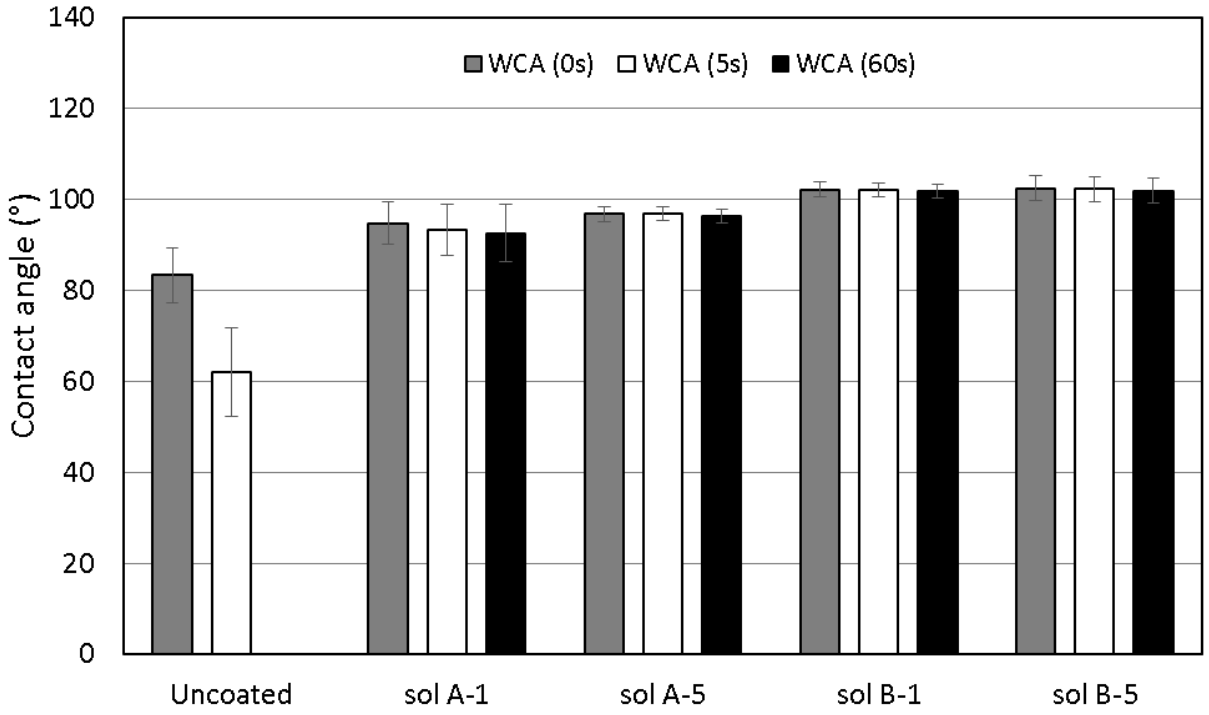


Figure 2. Hydrophobicity of hemp shiv surface treated with different sol-gel coatings over 60 seconds of water contact.

Considering the coating compositions with 4% HDTMS loading listed in Table 1, it was observed that ethanol diluted sols (sol B series) performed better in terms of providing hydrophobicity to hemp shiv surface compared to undiluted sols (sol A series). Sol B-1 and sol B-5 coatings had higher contact angles (up to 105°) compared to sol A-1 and sol A-5 coatings (up to 100°).

Ethanol helps the HDTMS to be fully dissolved in water thereby promoting the hydrolysis reaction [20,21]. Figure 2 shows the WCA measurements of sol coatings containing 4 wt% HDTMS. Sol A-1 and sol A-5 contain only 4M ethanol whereas sol B-1 and sol B-5 contain 16M of ethanol. At 4 wt% HDTMS concentration, using 16M of ethanol favours the hydrolysis of HDTMS. In this way HDTMS molecules are able to self-assemble on the silica network, hence providing enhanced hydrophobicity to the material. In general, it was observed that sol-gel coatings with HNO_3 as catalyst perform slightly better in terms of hydrophobicity than coatings with HCl as catalyst.

The changes in water contact angle as a function of HDTMS loading (0.5-4.0 wt%) is presented in Figure 3. The contact angle measurements had a standard deviation between 1.1° and 6.0°. The hydrophobic performance of the coatings is not reduced on lowering the HDTMS loading down to 1%. Surfaces coated with sol B series showed good water repellence with contact angles ranging between 96° to 108°.

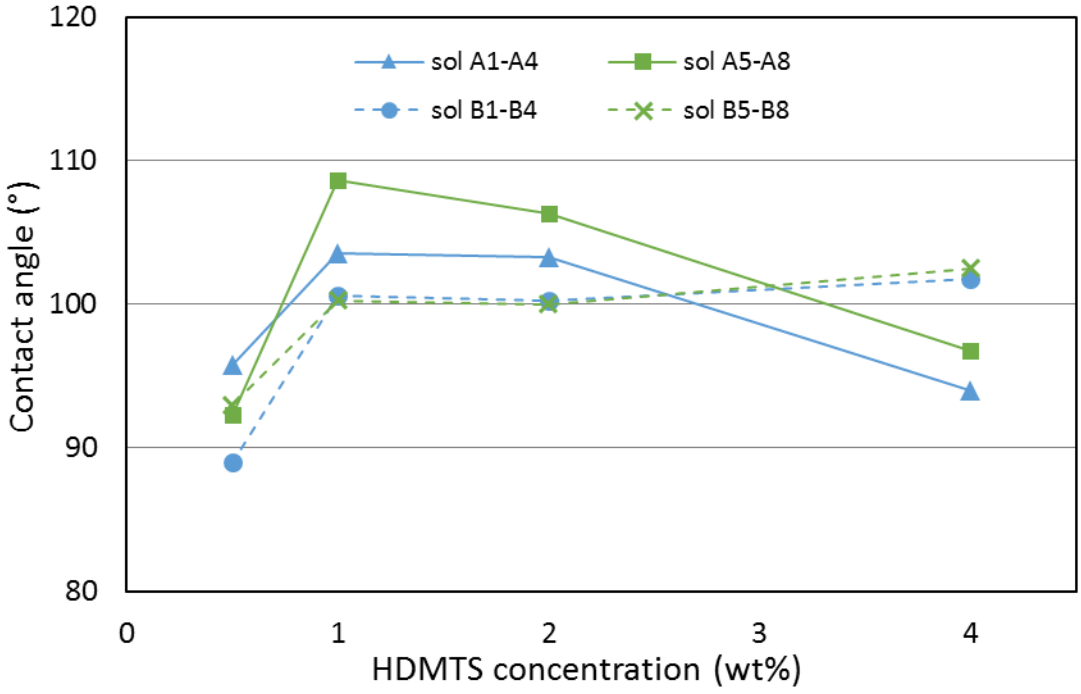


Figure 3. Effect of ethanol dilution and varying HDTMS concentration in the sol-gel coating on hydrophobicity of hemp shiv surface.

3.2 Surface roughness of the coatings

The samples were analysed for their surface microstructure and roughness by the Vision64 software using a Robust Gaussian Filter (ISO 16610-31 2016) and a short wavelength cut-off 0.025mm. The use of such filters helps to reduce the anatomical influence and optimizes the roughness profile data for evaluation of the sample surface [22,23]. The robust Gaussian filter avoids the distortions produced by some filters when applied in profiles with deep valleys [24]. Mean surface roughness (*Sa*) was calculated according to ISO 4287 (1997). *Sa* gives the description of the height variations in the surface and it is the most widely used parameter to measure the surface roughness profile of the sample. The surface roughness parameters for sol-gel coated hemp shiv with 1% and 4% HDTMS loadings are shown in Figure 4.

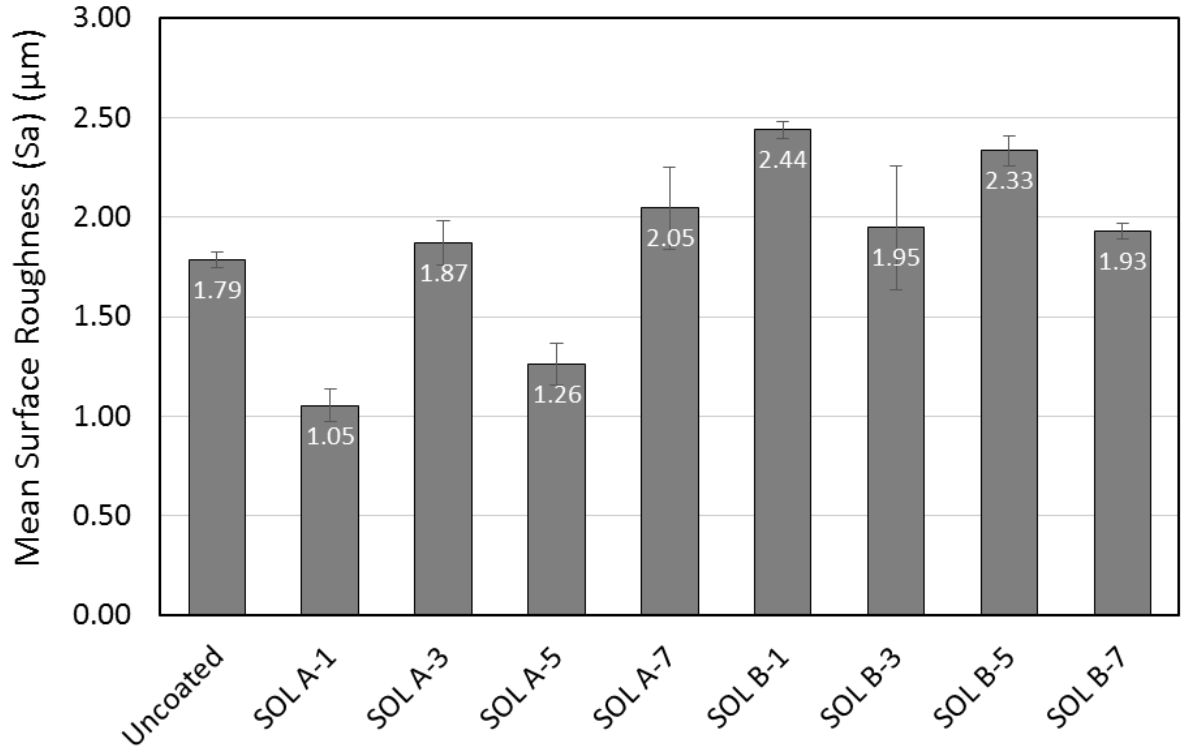
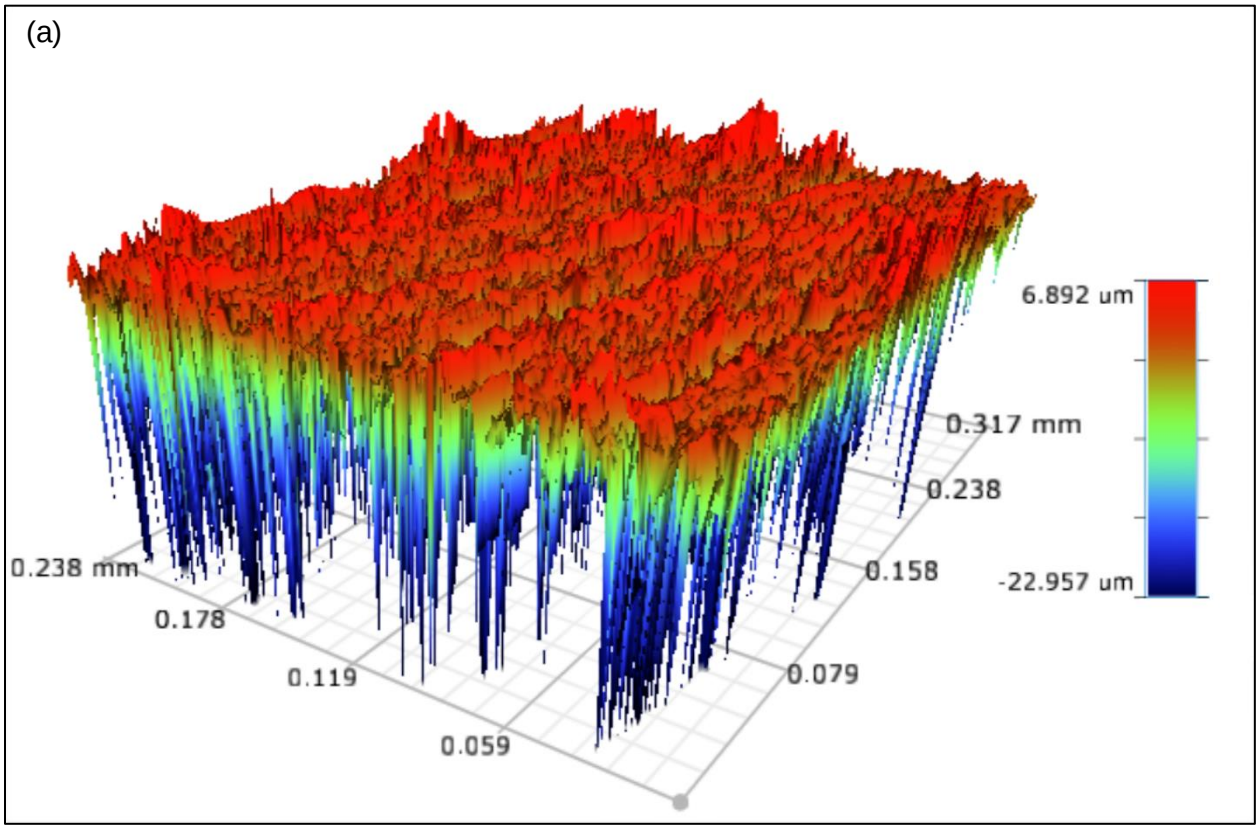


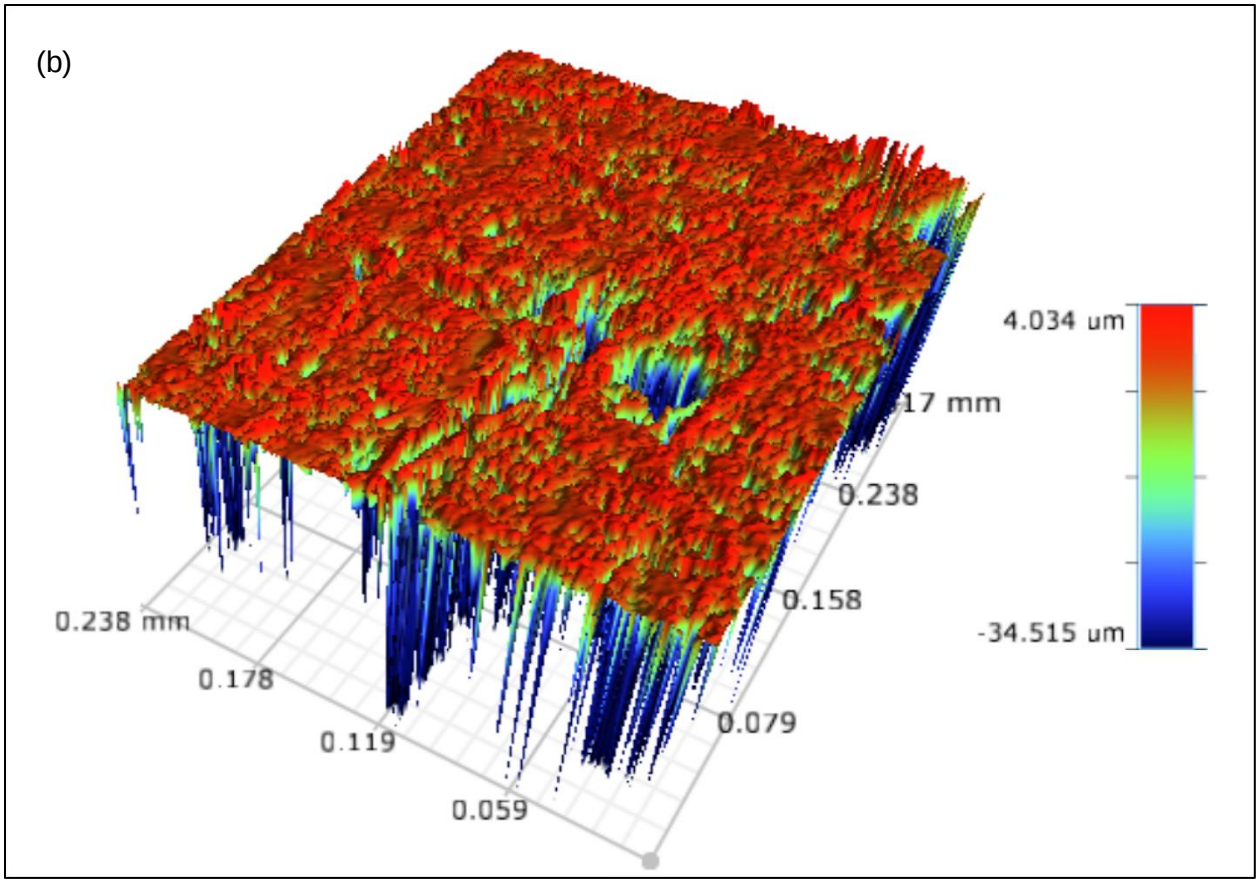
Figure 4. Mean surface roughness (Sa) measurement of uncoated and sol-gel coated hemp shiv surfaces.

The influence of different sol-gel coatings on the surface roughness of hemp shiv can be seen in Figure 5. The 3D surface roughness profile showed that the sol A-5 coating on the hemp shiv lowered the surface roughness providing a smoother surface as seen in Figure 5b. The non-uniform coating was also cracked, which in turn can facilitate water penetration into the hemp shiv. On the other hand, sol A-7 (contemning lower HDTMS loading) enhanced the surface

roughness of hemp shiv. Overall ethanol diluted sol-gel coatings had enhanced the surface roughness of hemp shiv. Sol B-5 had the highest mean surface roughness as seen in Figure 5c.



(b)



(c)

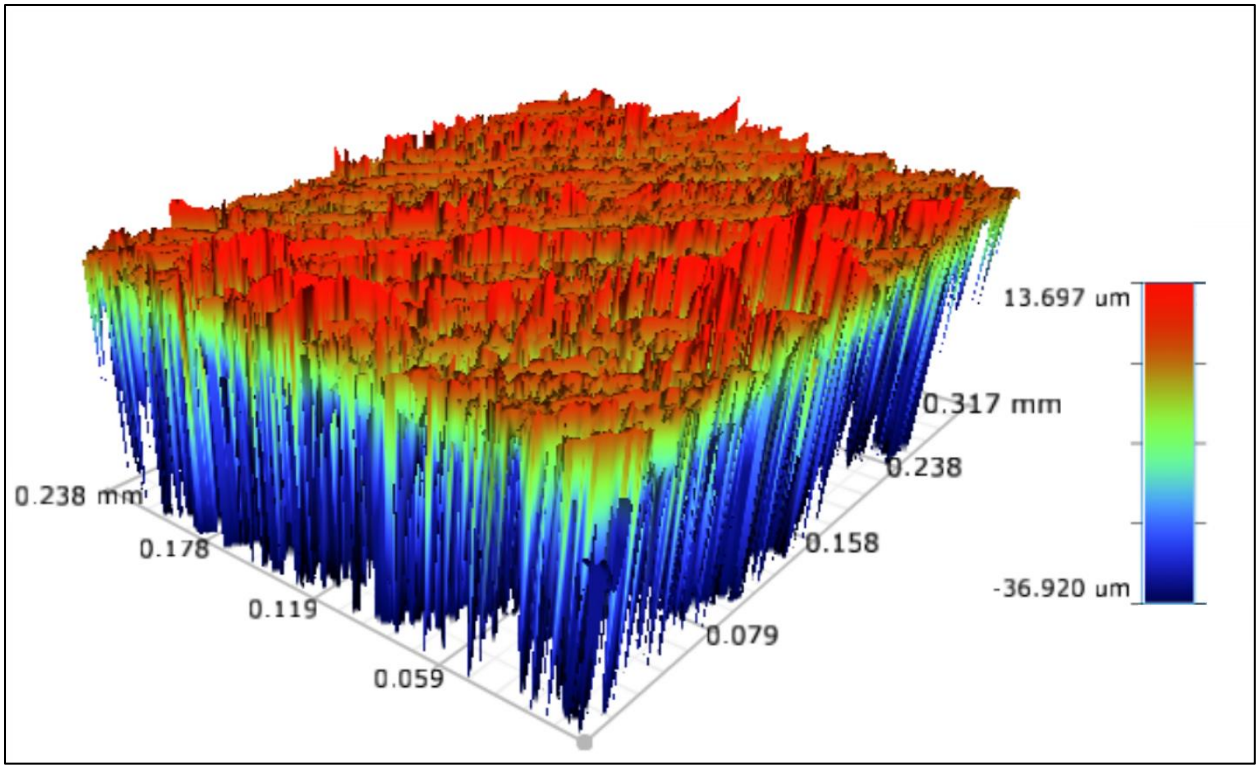
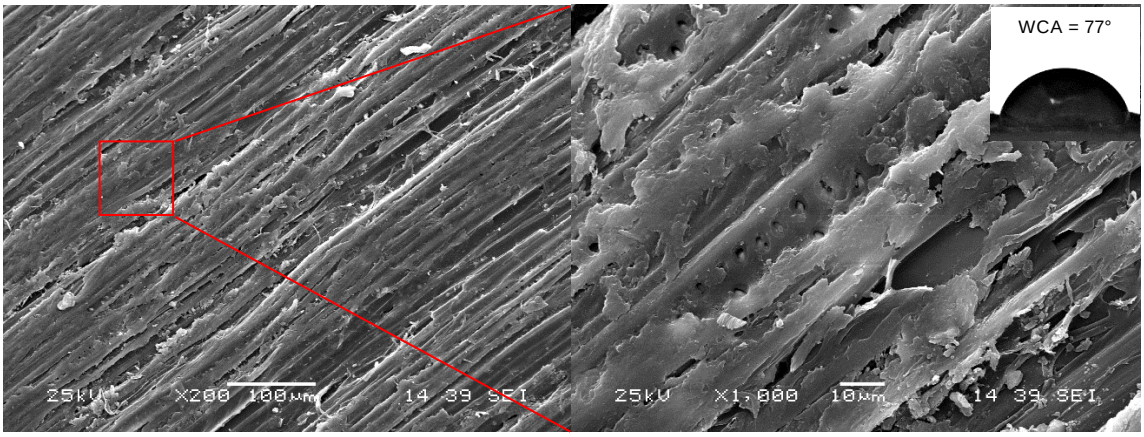


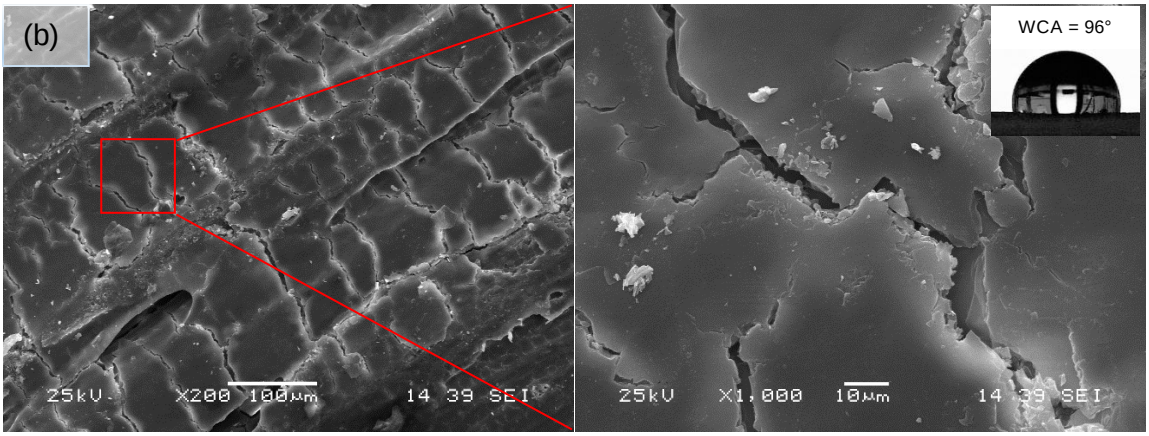
Figure 5. Surface roughness of (a) uncoated, (b) sol A-5 and (c) sol B-5 coated hemp shiv surface.

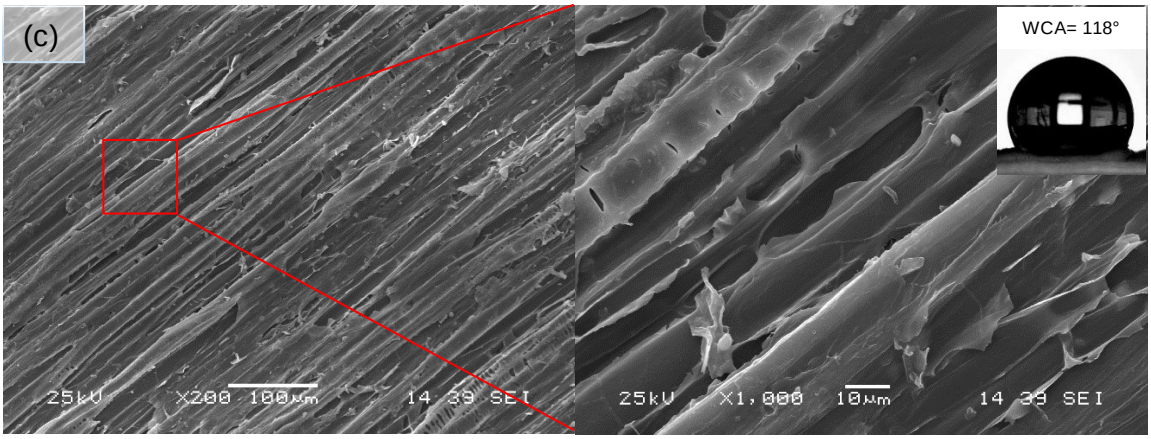
3.3 Surface Morphology

Roughness parameters alone cannot describe the surface morphology and therefore microscopy analysis is beneficial to improve surface evaluations. The morphology of the uncoated and sol-gel coated surfaces was studied by scanning electron microscopy (SEM). Figure 6 shows the micrographs of hemp shiv surface before and after modification with different sol-gel coatings. Sol A-5 and sol B-7 (Figures 6b and 6e) formed a thick coating layer and changed the morphology of the shiv surface. This resulted in coating with major cracks which could be a result of shrinkage after drying the treated sample (sol-gel coated hemp shiv). On the other hand, sol A-7 and sol B-5 (Figures 6c and 6d) showed uniformly coated surfaces without significantly altering the morphology of the hemp shiv.

(a)


WCA = 77°
25kV X200 100µm 14 39 SEI
25kV X1,000 10µm 14 39 SEI


(b)
WCA = 96°
25kV X200 100µm 14 39 SEI
25kV X1,000 10µm 14 39 SEI


(c)
WCA= 118°
25kV X200 100µm 14 39 SEI
25kV X1,000 10µm 14 39 SEI

(d)

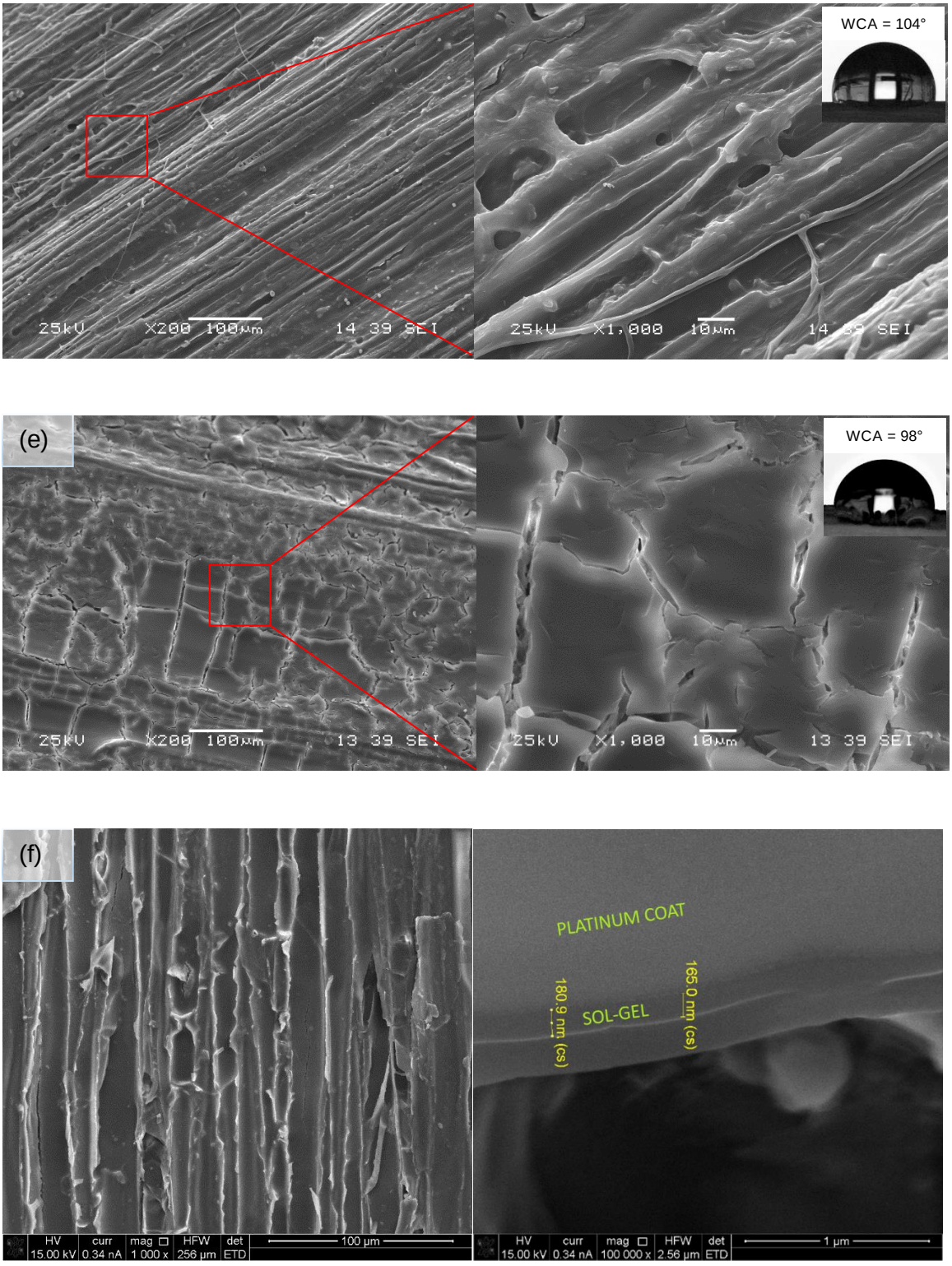


Figure 6. Surface morphology and WCA of (a) uncoated, (b) sol A-5, (c) sol A-7, (d) sol B-5 (e) sol B-7 coated hemp shiv surface and (f) thickness of sol-gel coating.

Conventional SEM techniques proved unsuccessful in determining the coating thickness, but SEM-FIB (Focused Ion Beam) imaging of an early iteration of the formulation (Figure 6f) measured a thickness in the range 160-180nm. It is expected that the current formulations (sol A-7 and sol B-5) would have a similar thickness.

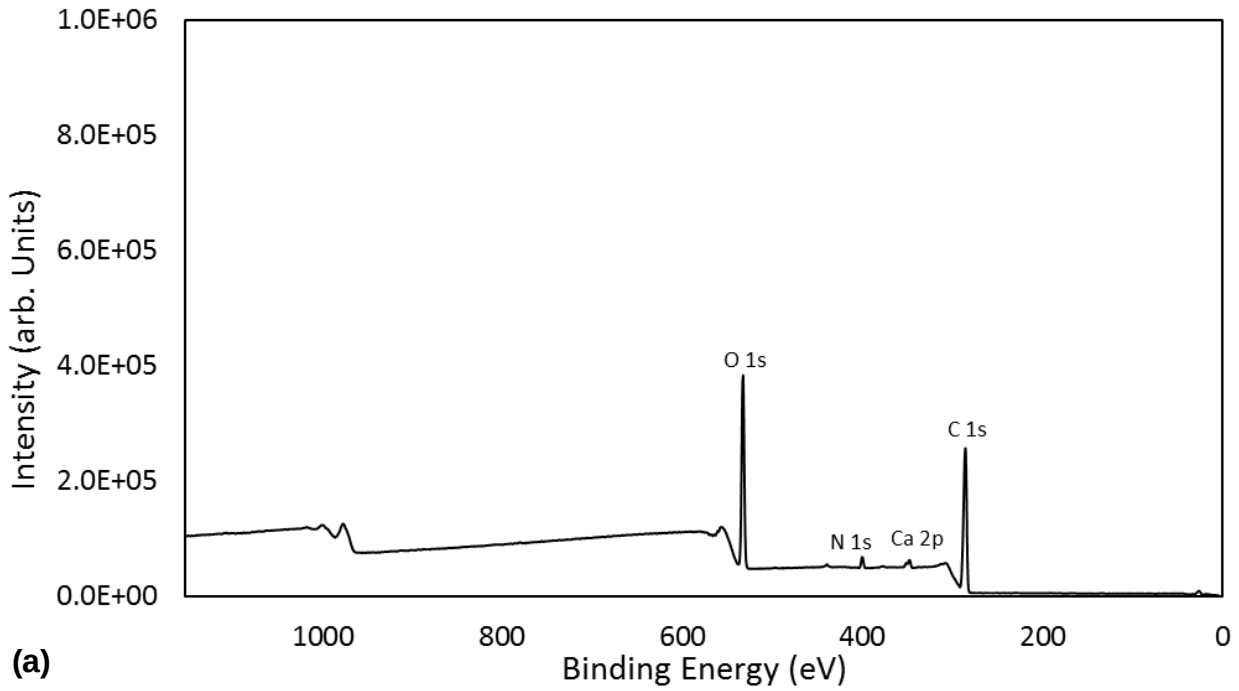
3.4 Chemical Composition

The surface chemical composition was determined by X-ray photoelectron spectroscopy. A low-resolution survey scan determined the atomic percentage of various elements present at the sample surface (Figure 7). The relative elemental composition of the uncoated and sol-gel coated hemp shiv surface is listed in Table 2.

Table 2. Relative amount of atoms at sample surface determined by low-resolution XPS scan.

Element	Relative Conc. (atomic %)	
	Uncoated Hemp shiv	Sol A-7 Coated Hemp Shiv
C	69.61	28.33
O	27.06	53.57
N	2.06	-
Ca	0.64	-
P	0.14	-
K	0.30	-
S	0.09	-
Na	0.04	-
Cl	0.04	-
Co	0.03	-
Si	-	18.10

The main elements detected for uncoated hemp shiv were carbon and oxygen. Small amounts of other elements were present either possibly arising from the epidermal cell wall or from contamination during sample preparation. The sol-gel coated hemp shiv additionally showed high content of silicon arising from the silica based membrane on the surface (Figure 7b).



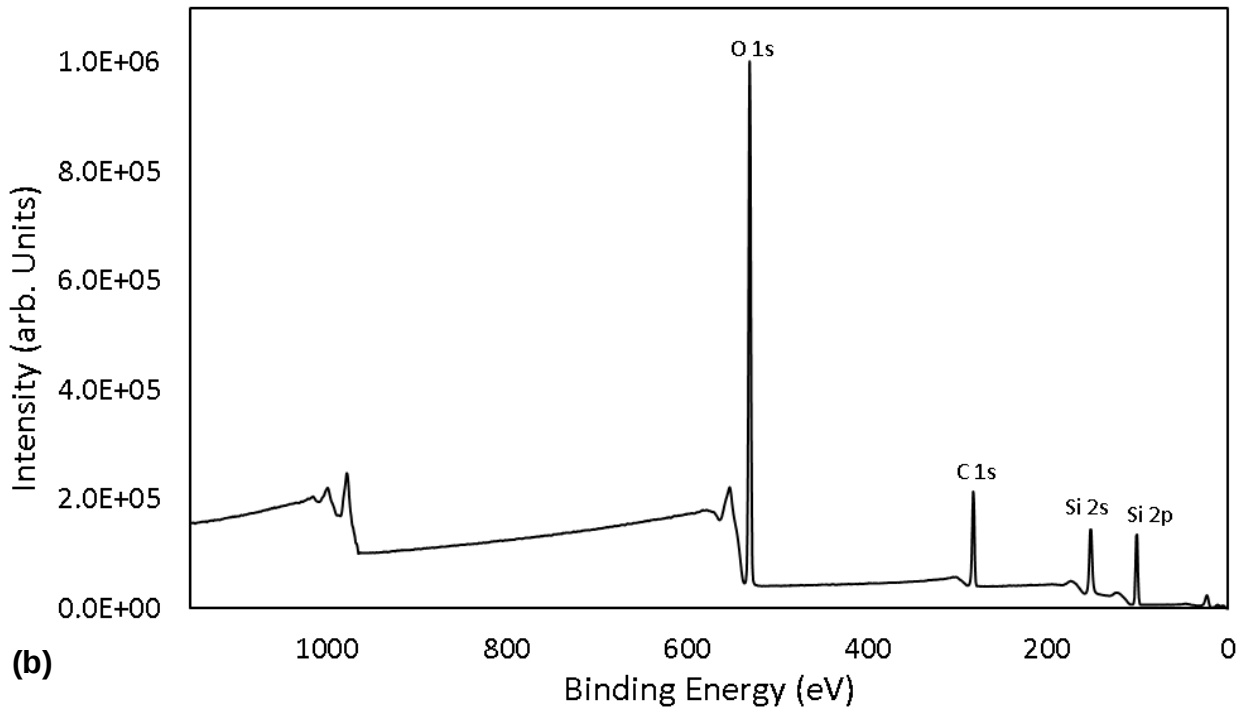


Figure 7. XPS survey can for (a) uncoated hemp shiv, (b) sol A-7 coated hemp shiv.

A high-resolution scan was performed on the C1s region for the uncoated and sol-gel coated hemp shiv samples to determine the type of oxygen-carbon bonds present. The chemical bond analysis of carbon was performed by curve-fitting the C1s peak and deconvoluting it into four sub peaks corresponding to unoxidized carbon C1, and various oxidized carbons C2, C3 and C4. A ratio between oxidized carbon (C_{ox}) and unoxidized carbon (C_{unox}) was calculated by the equation [25]:

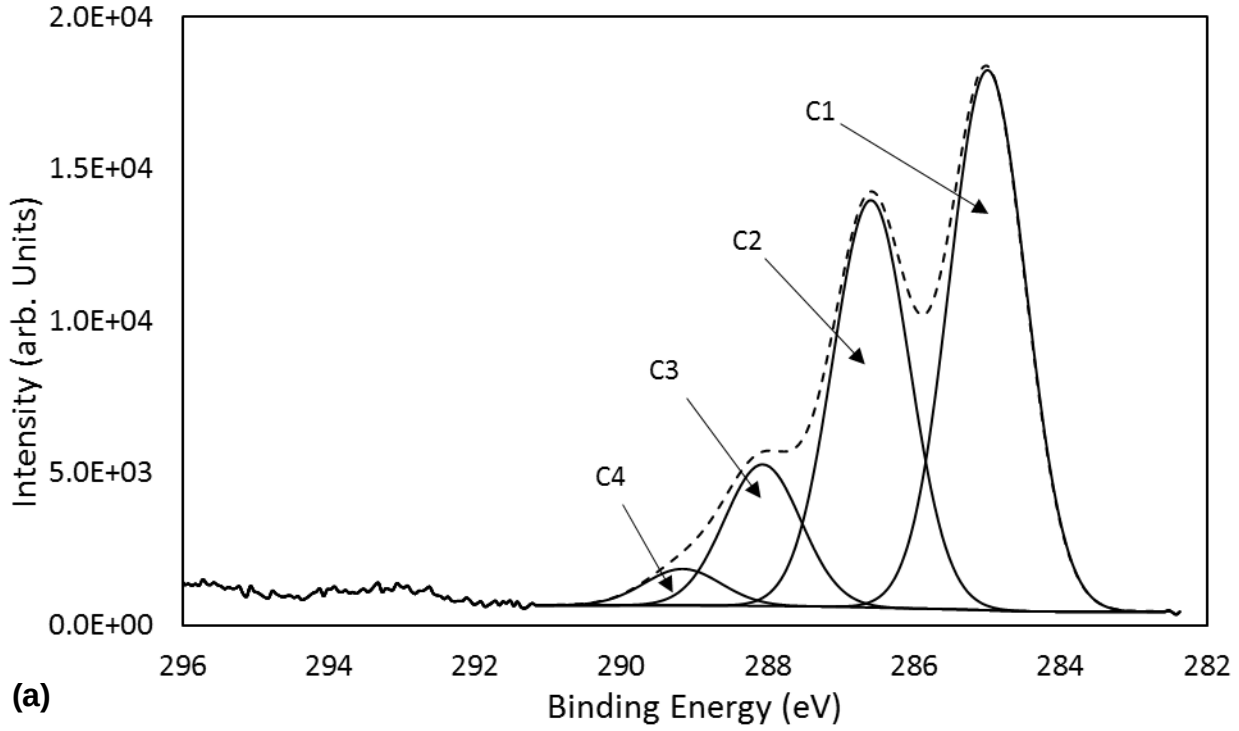
$$C_{ox/unox} = \frac{C_{ox}}{C_{unox}} = \frac{C2+C3+C4}{C1} \qquad \text{Equation 1}$$

The binding energy, corresponding bond type and their relative percentage are listed in Table 3. The ratio of $C_{ox/unox}$ has dropped significantly for sol-gel coated hemp shiv indicating that the carbon oxygen bonds have decreased on the surface of the samples.

Table 3. Deconvoluted peak parameters and relative amount of different carbon-to-oxygen bonds at sample surface determined by high-resolution XPS.

Carbon Group	Peak parameters		Relative amount (% area)	
	Binding Energy (eV)	Bond	Uncoated	Sol A-7 Coated
C1	285.0	C-C or C-H	48.01	91.09
C2	286.6/286.8	C-OH	36.18	8.91
C3	288.0	O-C-O or C=O	12.56	0.00
C4	289.2	O-C=O	3.24	0.00
$C_{ox/unox}$	-	-	1.08	0.09

The C1s high resolution spectra with the deconvoluted peaks for uncoated and sol-gel coated surfaces are represented in Figure 8. The C1 peak represents carbon-carbon or carbon-hydrogen bonds whereas C2, C3, and C4 peaks possess carbon-oxygen bonds.



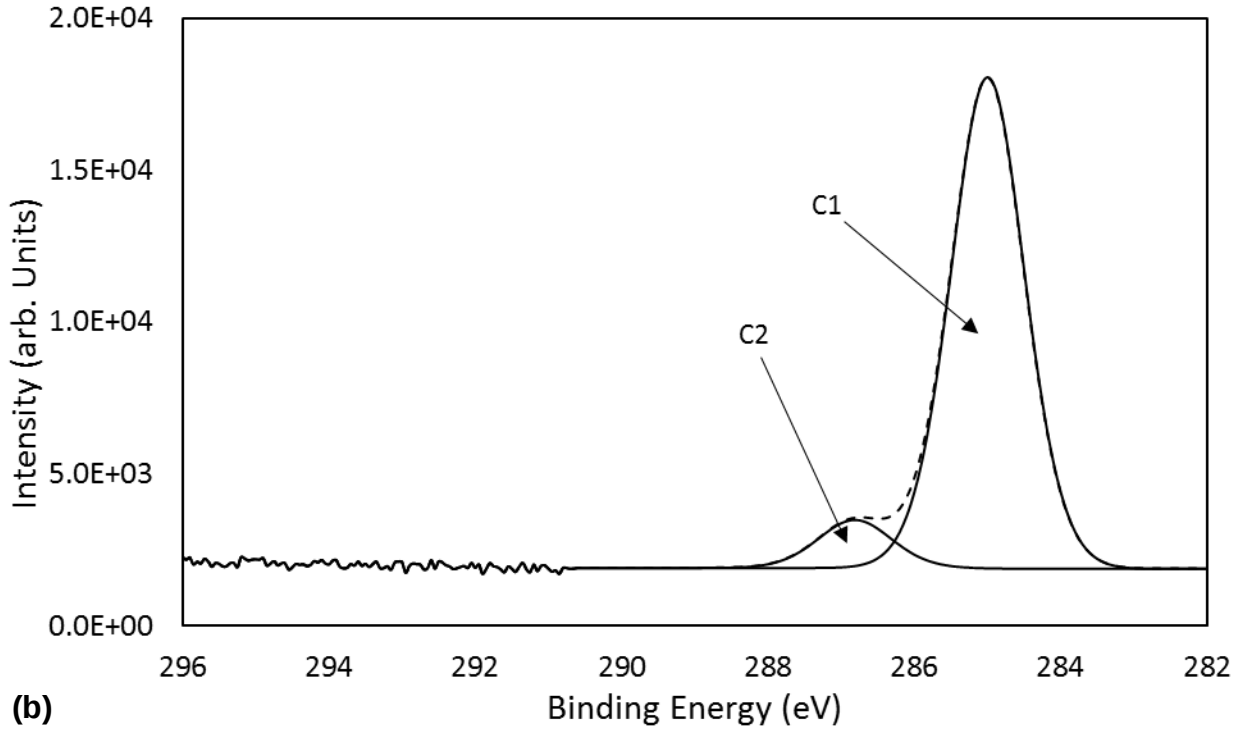


Figure 8. XPS scan of C_{1s} region for (a) uncoated hemp shiv, (b) sol A-7 coated hemp shiv.

4. Discussion

The sol-gel coatings were functionalised using HDTMS as the hydrophobic additive during the sol-gel synthesis. The co-precursor method of sol-gel synthesis was followed based on the simplicity of the process. In the sol-gel process, TEOS is hydrolysed and condensed to form a SiO_2 network which is covalently bonded to cell wall through the hydroxyl sites of cellulose present in the hemp shiv. On addition of hydrophobic agent as a co-precursor during the sol-gel processing, the hydroxyl groups on the silica clusters are replaced by the $–Si–C_{16}$ groups through oxygen bonds as illustrated in Figure 9. The hydrophobicity of the sol-gel coatings is due to the attachment of these long alkyl chains on the silica network thereby providing water resistance to the hemp shiv surface.

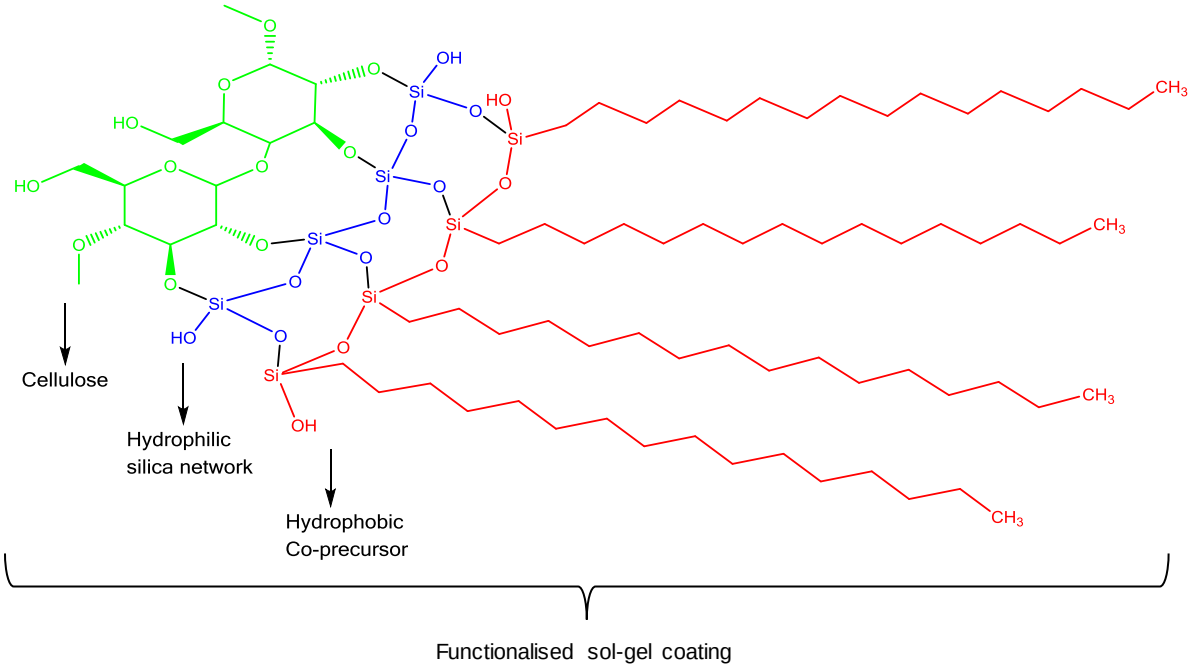


Figure 9 Schematic illustration of sol-gel deposition on glucose units of cellulose.

Overall, the acid catalysed sol-gel coatings enhance the water repellence of hemp shiv making the surface hydrophobic (WCA>90°). The wettability of the surface is controlled by the surface chemical composition as well as by the morphology of the microstructure. Surfaces with a similar chemical composition may have different wettability behaviour due to the surface topology [26]. In this study, the surface of hemp shiv underwent microstructural changes via deposition of an organo-functionalised silica coating.

Ethanol diluted sol series enhanced the surface roughness of the hemp shiv. At higher HDTMS loading, undiluted coatings (sol A-1 and sol A-5) lowered the surface roughness of the shiv which could explain the reason for lower contact angles compared to diluted coatings. Sol A-1 and sol A-5 have HDTMS molecules that are not fully hydrolysed and being deposited onto the membrane as a flat thick film as seen in Figure 6b. The reduced surface roughness can be attributed to the extra HDTMS molecules on the coated surface [27].

Since an organic-inorganic hybrid coating was used, the ratio of TEOS: HDTMS was critical to control the roughness of the coatings resulting in variable water repellent properties of the coated hemp shiv. Most of the coatings enhanced the surface roughness except sol A-1 and sol A-5. These coatings had smooth surfaces with cracks which could explain the lower contact angles even though it had the highest loading of hydrophobic agent. It was observed that the TEOS: HDTMS molar ratio in the coating formulations affected the hydrophobicity of the coated hemp shiv. From Figure 3 it can be seen that varying the concentration of HDTMS in the formulations affects the water contact angle. When TEOS: HDTMS was 1: 0.01 corresponding to 0.5 wt% HDTMS, the contact angle was below 100° which suggests the concentration of the hydrophobic agent was too low to provide sufficient level of hydrophobicity . The best results were obtained with TEOS: HDTMS ratio 1: 0.02 (1 wt% HDTMS) with contact angles up to 118°. However, when the TEOS: HDTMS ratio was increased to 1: 0.06 (4 wt% HDTMS), the hydrophobicity was decreased for the undiluted sol coatings. These results can be explained by the combined effect of surface roughness and energy. TEOS is hydrophilic whereas HDTMS is hydrophobic and changing their molar ratio can affect the surface roughness and energy of the coated material. Increasing the HDTMS concentration would reduce the surface energy. However the surface roughness can be reduced if the HDTMS concentration is high enough as the extra silane fills the inter-particle gap. Similar results have been reported in different coating systems [27,28]. Although sol B-7 coating enhanced the surface roughness, it had developed cracks which lowered the water contact angle to 98°. The presence of surface cracks arising as a result of shrinkage after drying the coated shiv is a significant factor to be considered when hydrophobic properties are concerned. The hydrophobicity of modified hemp shiv can be compromised as the water molecules can penetrate through the cracked coating wetting the bulk of the material over time. Therefore, sol-gel coatings chemically modified the surface of hemp shiv which overall improved the hydrophobicity of the material. The high water repellence can be attributed to the long alkyl chains of HDTMS that provide high hydrophobicity.

The chemical composition of hemp shiv is mainly composed of cellulose, hemicellulose and lignin, which altogether contain a large percentage of oxidized carbon in their structure. Hydroxyl groups are known to contribute towards majority of the carbon-oxygen bonds in bio-based materials [29]. The XPS data confirmed that the sol-gel deposition on hemp shiv significantly altered the surface chemistry. The surface carbon content of the coated hemp shiv decreased by 41.28% (from 69.61 to 28.33%). On the other hand, the oxygen content increased by 26.51% (from 27.06 to 53.57%). This change in C/O ratio and increase in surface oxygen concentration can be attributed to O-CH3 bonds present in the polysiloxane coating on the surface of the sol-gel coated hemp shiv. Moreover, the decrease in the surface carbon concentration of the sol-gel coated shiv can be attributed to the masking effect of the polysiloxane coating which reduces the detectability of surface cellulose and hemicellulose.

The C1s high resolution XPS spectra indicate that the surface has been modified by the silica based coating that led to disappearance of C3 and C4 components of the C1s peaks. A shift in the binding energy of C2 component (from 286.6 to 286.8 eV) was observed along with the decrease in the intensity of the C2 component for the sol-gel coated sample. This shift indicates the presence of a carbon atom linked to an oxygen and silicon atom (O-C-Si or C-O-Si) [18]. It has also been shown [16,30–32] that curing above room temperature drives the dehydration reaction at the adsorption sites between hydroxyl groups of the cellulose and the silanols forming –Si-O-C- bonds. These bonds are formed by the linkage between polysilanol network with the cellulose hydroxyl groups via polycondensation as illustrated in Figure 9. The increase in the intensity of C1 component for sol-gel coated sample from 48.01% to 91.09% indicates the presence of C-H and C-C bonds from the HDTMS hydrocarbon chain.

5. Conclusion

A simple one step dip-coating process was successfully applied to form a hydrophobic surface onto an extremely hydrophilic bio-based aggregate construction material. The hydrophobic properties were achieved through a combination of topological alteration and chemical modification of the hemp shiv by the modified silica based sol-gel coatings.

The treated material (hemp shiv coated with silica based membrane) delivered the following properties when compared to the untreated hemp shiv:

- Delivered water repellence by maintaining stable water contact angles over 60 seconds.
- Controlled surface wettability through microstructure modification.
- Uniform and crack-free coated surface.
- Enhanced surface roughness providing water contact angles up to 118°.

It can be concluded that water based sol-gel coatings with low HDTMS precursor loading (sol A-7) would be of interest to the bio-based building industry due to its hygroscopic properties, long shelf life, reduced cost and lower environmental impact.

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