The effect of chemically treated all-cellulose composites (ACCs) with dodecyltriethoxysilane (DTES) solution on the structural-property relationship

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Abstract. Cellulose is the most abundant natural polymer on the Earth that is widely used in bio-based composites due to its high mechanical properties, availability and biodegradability. All-cellulose composites (ACCs) are known as a new class monocomponent of biocomposites due to both reinforcing and matrix phases that are based on cellulose. However, a technical challenge for ACCs is observed due to their propensity for high moisture absorption (water uptake), leading to the instability and deterioration of the mechanical properties. Therefore, this research focused towards the improvement of the surface of ACCs in order to increase the resistance to water absorption. Prior to the characterizations, ACCs were chemically treated using dodecyltriethoxysilane (DTES) coating solution by dip coating method. In this present study, the effects of two control factors: (i) DTES concentration (1.5, 7.5, and 12.5 vol%), and (ii) heating temperature (50, and 100 °C), were investigated on the ACCs. Upon completion of this treatment, three possible characterizations were conducted including of Fourier Transform Infrared (FTIR) spectroscopy analysis, scanning electron microscopy (SEM), and water absorption (WA) testing. Creation of polysiloxane layer was expected to reduce the tendency to absorb water in ACCs while being applied in the outdoor applications.

1. Introduction
Cellulose was the most abundant natural polymer on the Earth that was widely used in bio-based composites due to its high mechanical properties, availability and biodegradability [1, 2]. All-cellulose composites (ACCs) are composed of a cellulose for the reinforcement and matrix phases. The concept of using the same polymer for both phases was aimed at facilitating the recyclability and improving mechanical performance of the final composite [3]. Nishino et al. first reported on the terminology, processing and mechanical properties of ACCs [4]. Gindl et al. reported that ACCs may be manufactured by the partial (or selective) dissolution of cellulose I with a suitable solvent, where the portion of dissolved cellulose was then subsequently regenerated (via solvent exchange with a coagulant) to form a cellulose II matrix phase in-situ [5]. The advantages of ACCs had been reported previously, including of its superior mechanical properties and more rapid biodegradability as compared to other bio-based composites [6, 7]. Previous research also showed that ACCs were intended to overcome the problem with chemical incompatibility due to the use of cellulose, for both phases, with the expectation of producing of interfaceless ACCs [8].
However, a technical challenge for ACCs was observed due to their propensity for high water absorption, leading to the instability and deterioration of the mechanical properties. These results had been shown by the previous studies of other bio-based composite materials [9, 10]. It happened due to the hydrophilic behaviour of cellulose which was attributed by hydroxyl (OH) groups that are located on the surface of cellulose. The OH groups tended to bind with water molecules which rendered to a higher water absorption. Therefore, ACCs surfaces had to be chemically treated in order to prevent the attachment of water molecules with the OH groups.

Several approaches had been studied in order to reduce the hydrophilic character of the cellulose surface. Previous studies reported that the use of fluorine-based or alkyl-based silane coupling agents was found to be efficient due to their high water resistance and ability to couple both hydrophilic and hydrophobic groups, which had been widely applied in various fields [11, 12]. Based on the previous study by Xie et al., silanes were classified as extensively used coupling agents in composites and adhesive formulations [11]. The advantages of silanes included of the large-scale commercial availability with several chemical functional groups, and the ability to couple with any polymer or mineral in composites. The organofunctional group was responsible for bonding with any polymer through a covalent reaction with other phases. In addition, silane coupling agents were also used to enhance the compatibility and dispersion of nanocellulose in the polymer matrix [13]. These silane coatings also had excellent compatibility and high adhesion to the wide range of inorganic and organic interfaces [14, 15]. The silane compounds used for coating applications contain at least one non-hydrolysable functional group (amino, epoxy, etc) that chemically interacted with overlying organic coating and also hydrolysable portions that were responsible for forming covalent bonds with the substrate surface. Besides, a hybrid silane coating’s primary protective mechanism was to build a barrier siloxane network, which was obtained by condensing silanol (Si-OH) groups [16–18].

In this present study, DTES was used to impart water repellency to ACCs. Upon completion of this treatment, the structural-property relationship of chemically-treated ACCs was examined with FTIR spectroscopy, SEM, and WA testing. To the best of our knowledge, no report related to the chemically-treated ACCs produced via sodium hydroxide (NaOH)/urea with DTES had been published previously.

2. Experimental procedures

A rayon fiber textile (Cordenka GmbH, Obernburg Germany) in the form of a K2/2 twill weave was used. The textile was based on a multifilament yarn (Cordenka 700, 1840 dtex, f1000) with a filament diameter of 12 µm and final areal weight of 450 g/m². The NaOH, urea, DTES, and ethanol were commercially available and used without further purification.

The solvent was prepared by mixing 7/12/81 wt.% of NaOH/urea/distilled water in a glass beaker. The mixture is stirred by using magnetic stirrer at room temperature until clear. The solvent is referred to as NaOH/urea.

The procedures to the chemically treated ACCs with DTES were followed, as described by Yousefi et al. [12]. A mixture solution of DTES and the ratio 80:20 of ethanol/distilled water was prepared by vigorous stirring for 2 h. The ACCs specimen was immersed into three different concentrations of
DTES (1.5, 7.5, and 12.5 vol%) using dip coating method. The ACCs specimen was immersed in DTES solution for 1 h. Then, the samples were dried at room temperature, followed by further heating temperature of 50, and 100 °C for 1 h each different temperature. All treated samples were stored in sealed plastic bag prior to the characterisations.

Both treated and untreated ACCs were characterized using a Perkin Elmer (Waltham, MA, USA) FT-IR spectrometer Frontier with universal ATR sampling accessory. Wavenumbers ranging from 4000 to 650 cm$^{-1}$ were scanned 24 times at 0.4 cm$^{-1}$ resolution. Microscopy samples were cut from ACCs laminae into a rectangular shape with dimensions of (10 (l) × 10 (w) mm). The specimen was firstly dried under 0.2 MPa external pressure in vacuum state at 60 °C temperature. Then the sample surface was sputtered-coated with gold film at 25 mA for 180 s. Gold sputter-coated (180 s, 25 mA) samples were imaged using a TM3000 scanning electron microscopy (SEM) at an accelerating voltage of 5 kV.

Water absorption testing were conducted in accordance with ASTM D570-98 in which the specimens were immersed in water for 7 days at a room temperature. The weight gain was then measured until the samples attained equilibrium. The water absorption was measured as the weight gain over the oven-dry of samples, and calculated by using the following equation [10]:

$$WA(\%) = \frac{m_t - m_o}{m_o} \times 100$$  (1)

where $m_o$ and $m_t$ are the oven-dry weight and weight after time, respectively. The equilibrium moisture content (EMC) of the specimens is the moisture content when the daily weight change of sample was less than 0.01% and thus to be reached the equilibrium state.

3. Results and discussion
The effect of various DTES concentrations (1.5, 7.5, and 12.5 vol%) and heating temperatures (50 and 100 °C) on ACCs were presented. These results were examined using several characterisations, including of FTIR, SEM, and WA testing.

The FTIR spectrums of untreated and treated ACCs with various DTES concentration are presented in Figure 1. The untreated ACCs shows several typical characteristic bands for cellulose, including of the hydrogen bonded OH stretching, CH stretching, OH bending of absorbed water, CH bending, CH$_2$ stretching, and OH out of plane bending at 3420.7, 2900, 1632.3, 1371, 900, and 791.68 cm$^{-1}$, respectively (Figure 1). The spectrum for untreated ACCs is labelled as raw ACCs, as shown in Figure 1. The observation of the pristine cellulose characteristic band in untreated ACCs is expected due to no changes occur in the ACCs structure prior to the DTES treatment.

The narrow range of FTIR spectrum is carried out in order to clearly observe the presence of silane on the cellulose structure following the DTES treatment. It was observed that the strong peak at 1061.5 cm$^{-1}$ in 1.5 vol% DTES (50 °C), 1059.3 cm$^{-1}$ in 1.5 vol% DTES (100 °C), 1077 cm$^{-1}$ in 7.5 vol% DTES (100 °C), and peak at 1077 cm$^{-1}$ in 7.5 vol% DTES (50 °C), 12.5 vol% DTES (50 °C), and 12.5 vol% DTES (100 °C) was attributed to the Si-O-C bands. This result indicated that the silane was completely attached with the carbon group in the cellulose structure, resulting in a formation of covalent bond in treated ACCs. The Si-O-C peaks for the treated ACCs with 7.5 vol% DTES (50 °C) and 12.5 vol% DTES (100 °C) showed a significant increase in their intensity due to the increasing DTES concentration. It was exhibited by the narrower and sharper peak in the wavenumber range of 1077-1078 cm$^{-1}$. This finding indicated that the silane has successfully attached to the carbon component in ACCs structure, as aforementioned previously. Meanwhile, for Si-O-Si peak, the peak appears after the DTES treatment in ACCs at 1100 cm$^{-1}$, resulting in a formation of polysiloxane layer on ACCs surface structure. However, these strong two bands that occurred between regions 1000-1200 cm$^{-1}$ make it difficult to completely assigned Si-O-Si (siloxane) and Si-O-C band which might be due to the overlapping of Si-O-Si band and C-O stretching of cellulose.
Besides, the effect of heating temperature on the formation of Si-O-C was considerably varied for each DTES concentration. It was observed that the heating temperature of 50°C produced a broader peak as compared to heating temperature of 100°C at DTES concentration up to 7.5 vol%. However, the sharper peaks were found at DTES concentration of 12.5 vol% for both temperatures, as compared to the others. These results showed that the increasing Si-O-C formation was evidenced with the increasing DTES concentration rather than that of the heating temperature.

Figure 2 show the SEM images of surface for treated and untreated ACCs with DTES. Based on Figure 2 (a), the surface for untreated ACCs was considerably smooth, and large gap between the fiber and matrix phases was also observed. The large gap between fiber and matrix indicated that the poor interfacial bonding in ACCs structure, resulting in the existence of the intermolecular crack. This may be due to the insufficient pressure at the pressing machine, leading to the poor arrangement of fiber and matrix phases in ACCs. The untreated ACCs also exhibited a large void in the cross-sectional view. These voids were produced due to the small volume of air that trapped during the SIP of ACCs laminates, as also discussed by Jan et al. [1].

For the treated ACCs with DTES which are presented in Figure 2 (b-g), it was observed that the surface of ACCs significantly changed after the silane treatment, resulting in a rougher surface of treated ACCs, as compared to the untreated ACCs. This morphology changes can be attributed to the removal of impurities on the surface of ACCs after the formation of silane treatment. In addition, the formation of thin silane layer and granular-like structure on the ACCs surface were evidenced upon completion of DTES treatment. However, a larger void was not completely removed after the silane treatment, whereas a thin layer of DTES was observed due to the presence of a polysiloxane layer, as presented by the FTIR analysis.
Figure 2. SEM images for (a) untreated and (b-g) treated ACCs (surface view).
Figure 3 demonstrates the effect of untreated and treated ACCs with DTES concentration of 1.5, 7.5, and 12.5 vol% and heating temperatures of 50 and 100 °C of the WA. It is observed that the WA increased with immersion time until equilibrium states were reached. The WA of untreated ACCs increased rapidly with immersion time in the initial state. This result was expected due to the hydrophilicity of ACCs that consisted of cellulose for both fiber and matrix phases. It has been reported that the numerous accessible hydroxyl groups in cellulose structure led to the binding of water molecules with the hydroxyl groups [9, 10]. Thus, a higher WA was significantly found in untreated ACCs. In addition, the increasing of WA for untreated ACCs also may be also attributed due to the occurrence of voids and microcracks in ACCs. A higher void content and microcracks of untreated ACCs has resulted in a higher water absorption within the more confined free space of the microstructure defects.

For the DTES treated ACCs, the WA decreased significantly due to the OH-rich surface that was covered by a layer of polysiloxane, thus preventing the water penetration into the cellulose structures. By increasing the DTES concentration, the decreasing water absorption was observed in the treated ACCs. The maximum of WA after 7 days of the testing for the untreated ACCs was 140 % It was followed by the treated ACCs of 1.5 vol% DTES (50 °C) and 1.5 vol% DTES (100 °C) with WA of 119.58%, and 116.67%, respectively. It was found that the maximum WA exceeded 100% for untreated and treated ACCs with 1.5 vol% DTES (50 °C) and 1.5 vol% DTES (100 °C). This is probably due to the larger void that was existed in untreated ACCs and insufficient amount of DTES concentration for both treated ACCs with 1.5 vol% DTES at 50 and 100 °C.

Apart from that, a significant decrease in water absorption was observed for treated ACCs with 7.5, and 12.5 vol% DTES. The consumption of sufficient DTES can enhance the bonding in ACCs, resulting in the formation of multilayer silanol groups that led to the existence of polysiloxane layer on the ACCs surface. The maximum WA for treated ACCs with 12.5 vol% DTES (50 °C) was 67.11%. Meanwhile, it was reduced to 67.24% for 12.5 vol% DTES (100 °C). It can be concluded that a higher
DTES concentration resulted in a lower the percentages of water absorption. However, the effect of heating temperature on the WA seemed to be comparable in each DTES concentration. It is difficult to observe any significant changes of various heating temperature on WA. Therefore, it could be concluded that the heating temperature has little effect on the WA at specified DTES concentration.

4. Conclusion
As a conclusion, ACCs were successfully treated with DTES in this present study. Several findings can be drawn as discussed below.

FTIR spectroscopy was used to examine the peak of functional group that appeared through this silane treatment which was expected in the formation of covalent bonds. The presence of silane functional groups (Si-O-C bonds) on the ACCs was observed at the range 1059.3-1078 cm⁻¹. The silanol groups was formed a multilayer on ACCs, thus the formation of rigid polysiloxane layer on the surface. The increasing DTES concentration showed a significant increase in the peak associated with the Si-O-C functional group, representing by a narrower and sharper peak at the specified wavenumber 1077-1078 cm⁻¹. This result indicated that the presence of silane was successfully attached on ACCs surface structure, thus preventing the water absorption into the ACCs structures.

SEM images showed that the microstructural analysis of untreated and treated ACCs with DTES. The surface of ACCs that treated with 12.5 vol% DTES concentration produced rougher surface structures as compared to the others. In addition, the presence of DTES were also evidenced by the observation of granule-like structure and thin layer of DTES on ACCs structures.

WA results exhibited that the treated ACCs with 12.5 vol% DTES provided a lower percentage of water absorption, as compared to the others with the increasing DTES concentration. This finding showed that the water barrier was formed upon the completion of DTES surface treatment, indicating the successful implementation of coating procedures in this present study.

The effect of DTES concentration was rather significant as compared to the effect of heating temperature. It was showed by an improvement in reducing the WA rather than that of heating temperature. However, several future works are required in order to examine the hydrophobic behaviour of treated ACCs in the future.

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