

Effect of Y-Methacryloxypropyltrimethoxysilane (MPS) and Tetraethoxysilane (TEOS) Towards Preparation of Oil Absorbent Foams from Polyvinyl Alcohol (PVA) Reinforced with Microfibrillated Cellulose (MFC)

Dzun Noraini Jimat^{*}, Sharifah Shahira Syed Putra, Parveen Jamal, Wan Mohd Fazli Wan Nawawi and Mohammed Saedi Jami

Department of Biotechnology Engineering, Kulliyyah of Engineering, International Islamic University Malaysia, Kuala Lumpur, 50728, Malaysia

*Corresponding Author: Dzun Noraini Jimat. Email: jnoraini@iium.edu.my Received: 28 February 2020; Accepted: 22 April 2020

Abstract: Increasing usage of foams in various industry sectors had causing serious disposal problems once it reaches the end of its life-cycle. Herein, PVA-MFC foam was prepared by freeze-drying using polyvinyl alcohol (PVA) and microfibrillated cellulose (MFC) as a reinforced material from sugarcane bagasse (SCB). In this study, the PVA-MFC foam was chemically silvlated with Y-methacryloxypropyltrimethoxysilane (MPS) and tetraethoxysilane (TEOS). The wetting ability and mechanical strength of the silvlated 2.20 PVA-MFC foam was greatly enhanced compared with unmodified 2.20PVA-MFC foam. The silane chemicals (MPS and TEOS) had been confirmed grafted on 2.20PVA-MFC foam due to the presence of Si-C and Si-O-C stretching vibration as showed in Fourier Transform Infrared (FTIR) spectra and cloud-like coating of porous pore was observed in scanning electron microscopy (SEM) images. The silvlated 2 20 PVA-MFC foam (MPS and TEOS) exhibited a series of desirable properties such as lower swelling ratio and high absorption capacity of solvents and oils but had low thermal stability in thermogravimetric (TGA) analysis. The characterization of 2,20PVA-MFC foam using TEOS was further investigated. A significant difference in morphology was clearly observed between the unmodified and silvlated 2.20 PVA-MFC-TEOS foam through field emission scanning electron microscopy (FESEM) images. The X-ray photoelectron (XPS) analysis of silvlated 2.20 PVA-MFC-TEOS foam confirmed the presence of C, O and trace amount of Si elements. These synthesized 2.20 PVA-MFC foam could be a promising material for broad range of polymer foam applications.

Keywords: Polyvinyl alcohol foam; microfibrillated cellulose; sugarcane bagasse; Y-methacryloxypropyltrimethoxysilane; tetraethoxysilane and oil absorbent

1 Introduction

Polymer foams have attracted considerable attention toward various applications such as thermal and acoustic insulation, energy dissipation, packaging, shock protection and many more [1]. However, these polymer foams are made from non-degradable polymers which are inevitably brought substantive waste



This work is licensed under a Creative Commons Attribution 4.0 International License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

and serious environmental pollution [2]. Recently, trend toward fabrication of degradable polymer foams reinforced with renewable resources such as natural fibers is considerable increased due to the demand of ecofriendly and non-toxic material. Hence, the use of natural fibers such as microfibrillated cellulose (MFCs) is considered to be a promising material as an alternative to inorganic fillers in porous composite materials [2]. MFC is also known as nanocelluloses which can be extracted from lignocellulosic materials through chemical and/or mechanical disintegration methods [3]. Typically, it is in the range of 20–40 nm since it usually consists of aggregates of cellulose microfibrils [4]. They are usually used as reinforced materials in composites due to its desirable properties such as lightweight, nontoxic and biodegradable. In this study, the microfibrillated cellulose was extracted from sugarcane bagasse (SCB). SCB is a by-product which is generated after juice extraction from sugarcane mills [5] and have dry weight basis of cellulose approximately 43.8% [6]. It has been extensively applied in various industries such as in pulp and paper production [7], textiles [8] and furniture industry [9]. Due to its intrinsic mechanical and chemical properties, it can be used to build hierarchical structures which can enhance the performance of traditional polymeric materials [10–12].

In this respect, the development of 'green foams' from biodegradable polymer reinforced with natural fibres from renewable resources is necessity as an alternative to non-degradable polymer foams. Polyvinyl alcohol (PVA) is consider as one of the polymers that is nontoxic, biodegradable, biocompatible and water soluble synthetic polymer. In presence of suitable microorganisms, PVA is easily susceptible to biodegradation [1,13]. PVA and SCB are highly hydrophilic which rich in pendant hydroxyl groups that act as attachment sites for biomolecules [14] and have low thermal stability that can limit the choice of polymer matrices as well as processing technologies for production of foam composites [15]. Thus, incorporating MFC-SCB into PVA foam will be less attractive as it lacks fine interfacial adhesion, low melting point and poor resistance towards moisture which may lead to fibers agglomeration and cause poor mechanical properties [16]. Therefore, the most feasible solution to this problem is increasing the hydrophobicity of PVA-MFC composite foams by chemically modification using coupling agents such as alkoxysilane.

Alkoxysilane is one example of organosilicon compounds which particularly effective in hydrophobizing hydroxylated substrates [17] and improved degree of cross-linking in the interface region besides offering a perfect bonding [18]. After silanols react with hydroxyl groups of MFC and PVA, they can form stable covalent bonds to the cell wall that are chemisorbed onto the foam surface [18]. Hence, the swelling ratio of the PVA-MFC composite foams (i.e., creation of a crosslinked network) due to covalent bonding between the matrices can be restrained by modification with silane.

PVA foam has poor dimensional stability and mechanical properties, while pure fibrillar cellulose foam has loose characteristics [2]. Therefore, in this study, the microfibrillated cellulose of sugarcane bagasse (MFC-SCB) was incorporated with PVA in order to prepare composite foam and chemically modified with Y-methacryloxypropyltrimethoxysilane (MPS) and tetraethoxysilane (TEOS). The best silane concentration and reaction time in preparing the silylated PVA-MFC composite foams were determined. The characteristics such as morphology, chemical structure, thermal, mechanical and wetting ability of PVA-MFC composite foams before and after treatment were investigated. The swelling ratio and absorption capacity of the unmodified and silylated foams were also compared. The silylated $_{2,20}$ PVA-MFC-TEOS_{10,2} foams showed a good characterization in terms of morphology, absorption capacity, wetting ability, thermal and mechanical properties. Thus, further examinations of this foam were performed in respects of morphology, chemical compositions and specific surface area using FESEM, XPS and BET surface area, respectively.

2 Experimental

2.1 Materials

The agricultural residues (SCB) were obtained from Sri Gombak market, Selangor. Sodium hydroxide (NaOH) pellets, 35% hydrogen peroxide (H₂O₂), 95% sulphuric acids (H₂SO₄) and polyvinyl alcohol (PVA)

with degree of hydrolysis (87–89%) at molecular weight 50 k were purchased from Sigma-Aldrich. Two silane coupling agent Y-methacryloxypropyltrimethoxysilane (MPS) and tetraethoxysilane (TEOS) were purchased from Merck and Fisher Scientific (Malaysia) respectively. Others reagent such as ethanol (HmbG chemical) and glacial acetic acid (CH₃COOH) were purchased from Merck (Malaysia). All the reagents are analytical grade and were used as received without further purification.

2.2 Extraction of Microfibrillated Cellulose (MFC) from Sugarcane Bagasse (SCB)

Extraction of cellulose from SCB was adapted from Anchor et al. [19] with slightly modification as described by Asem et al. [20]. The SCB was sun-dried and ground-using grinder until it achieved 100 μ m size. The SCB powder (25 g) were mixed with 500 ml of 2% (w/v) of NaOH and water bath for 5 h at 80°C. The treated SCB were filtered, then bleached with 500 ml of H₂O₂ in 1:1 aqueous dilution at 75°C. The samples were further treated with 12% (w/v) of NaOH solution and incubated in water bath at 80°C for 15 min. In order to breakdown the chemical bond of hemicellulose and lignin of SCB completely, the SCB was treated two times using NaOH. The treated SCB sample was vacuum filtered and washed for few times to ensure there were no NaOH and H₂O₂ residues in the cellulose fibers suspension. The treated SCB samples were then further treated with 1% v/v of H₂SO₄ at 80°C. The extracted samples were cleaned with distilled water until achieved neutral pH value. The samples were sonicated using probe sonicator (B.Braun Biotech International, Germany) for few hours at amplitude of 70. The MFC-SCB samples were centrifuged for 15 min at 6000 rpm and stored in the refrigerator at 4°C until further used.

2.3 Preparation of PVA-MFC Foams

The PVA-MFC foams were prepared with 2 w/w% concentration of MFC-SCB suspension, 20 w/v% concentration of PVA (MW: 50 k). The mixtures were slowly stirred at room temperature for 4 h and frozen at -22° C freezer (Polar 530SV, AS biomedical division, Italy) for 24 h. The frozen samples were subsequently dried for 4 days in ALPHA 1–4 LD Plus freeze-dryer (Christ, Germany) to sublimate the water under vacuum. This method is adapted from Dash et al. with slightly modification [21]. The PVA-MFC foam was denoted as $_{2,20}$ PVA-MFC foam, where 2 denotes as concentration of MFC-SCB suspension (w/w%) and 20 as concentration of PVA (w/v%).

2.4 Modification of PVA-MFC Foams

The freeze dried PVA-MFC foam was firstly cut with diameter of 1.6 cm and 1 cm of thickness. The coupling agents, MPS and TEOS were gently stirred in ethanol/water mixture in ratio of 80:20 at different concentrations (5 wt%, 10 wt% and 15 wt%). In order to ensure efficient coating of MPS/TEOS on PVA-MFC foam, the mixture was gently stirred at room temperature and pH of the solution was adjusted to 5 using acetic acid as described in previous studies [22]. The PVA-MFC foam was immersed into 1 mL of MPS/TEOS and 1 mL of deionized water at different reaction time (2 h, 4 h and 6 h) in the conical flasks. These flasks were tightly sealed and placed in an oven at 70°C. Then, the silylated sample was taken out and placed in oven for another 24 h at 60°C. The silylated PVA-MFC foams were stored in desiccator until further used. The silylated PVA-MFC foams are denoted as PVA-MFC-MPSx,y foam and PVA-MFC-TEOSx,y foam. The x and y are denoted as silane concentration and reaction time, respectively.

2.5 Characterization

2.5.1 Morphology Observation of the MFC-SCB and PVA-MFC Foam

Field emission scanning electron microscopy (FESEM, MERLIN ZEIS) analysis was performed to investigate the dimension of the MFC-SCB. A drop of the MFC-SCB suspension was placed on conductive carbon tape and left it dry. The, the tape was mounted on the aluminium studs and sputter coated with irradium for 15 s.

The scanning electron microscopy (SEM) analysis of 50 mg unmodified and silylated PVA-MFC foam were determined using JEOL (JSM IT 100, Japan) at an accelerating voltage of 8 kV. The foam samples were fixed on sample holders using carbon pad and sputter-coated with a thin layer of platinum.

2.5.2 Structural Characterization by Fourier Transform Infrared (FTIR) of PVA-MFC Foam

Fourier transform infrared (FTIR) spectra of unmodified and silvlated PVA-MFC foams were recorded on IRAffinity-1S FTIR (ShimadzuTM Corporation, Japan) in the transmittance mode in range of 4000–400 cm^{-1} using KBr pellets with resolution of 4 cm⁻¹.

2.5.3 Wetting Ability of PVA-MFC Foam

The surface wettability of unmodified and silylated PVA-MFC foams were evaluated by contact angle measurement, using Static Contact Angle (Data Physics Instruments, Germany) combined with high speed camera. At the top surface of the sample, 0.1 μ L/s of water droplet were deposited directly using a precision stainless steel tip at room temperature. Three measurements of each sample were taken after contact angle measurement had reached a stable value after 30 s.

2.5.4 Thermogravimetric Analysis (TGA) of PVA-MFC Foam

Thermal stability measurements of unmodified and silylated PVA-MFC foam were carried out using simultaneous thermal analyzer (TG2, STA7300 HITACHI, Japan) at a heating rate of 10 °C/min, under argon atmosphere (flow rate about 100 mL/min) from 25°C to 600°C.

2.5.5 Compression Test Analysis of PVA-MFC Foam

Compression testing of foam sample was performed on an electronic universal tensile machine (LR10K Plus, LLYOD Instruments, Germany) with thickness 1 cm and diameter of 1.6 cm. The preload for each sample was 0.5 N with a speed of 1 mm/min to 50% of its original thickness for 10 s. The samples were prepared according to the American Society for Testing and Materials, ASTM D3574 Part C. Five different experiments of unmodified and silylated $_{2,20}$ PVA-MFC foams were performed.

2.5.6 Swelling Ratio of PVA-MFC Foam

For swelling ratio (Sr) test, three measurements of each PVA-MFC foam (thickness 1 cm, diameter 1.6 cm) were performed and the average values were calculated. Each foam sample was immersed into distilled water until its weight remained constant. Calculation of PVA-MFC foams swelling behavior were evaluated using Eq. (1) [13]:

$$Sr = 100 \times \frac{W_s - W_d}{W_d} \tag{1}$$

where, W_s is the weight of the sample in the swollen state and W_d represent the dried weight of the sample.

2.5.7 Solvent and Oil Absorption Capacities of PVA-MFC Foam

The solvent and oil absorption capacities (Cm) of PVA-MFC foam were determined by dipped the unmodified and silylated PVA-MFC foams (thickness 1 cm and diameter of 1.6 cm) into 20 mL of solvents (phosphate buffered saline, ethanol, dichloromethane, dimethyl sulfoxide) and oil (castor oil, synthetic oil, cooking oil) for 5 s. The average of Cm obtained by measuring three different foam samples and was calculated as follows [17]:

$$C_m(w/w) = \frac{m_1 - m_0}{m_0}$$
(2)

where m_0 and m_1 are the weights of the sample before and after absorption, respectively.

2.6 Further Characterization of the Silylated 2,20 PVA-MFC-TEOS 10,2 Foam

2.6.1 Field Emission Scanning Electron Microscopy (FESEM)

The unmodified and silylated $_{2,20}$ PVA-MFC-TEOS $_{10,2}$ foam were further observed by field emission scanning electron microscopy (FESEM, MERLIN, ZEISS, Germany). The foams samples (10 mg) were mounted on the aluminium studs and sputter-coated with a thin layer of iridium.

2.6.2 X-Ray Photoelectron Spectrometer (XPS)

XPS was performed using Axis Ultra DLD (Kratos, SHIMADZU, Japan) with an aluminum anode (AlK α = 1486.6 eV) operating at 150 W with a background pressure 1–10 torr. The low-resolution survey scans were taken with 50 eV analyzer pass energy and high-resolution spectra was taken with 20 eV analyzer pass energy. The atomic ratio of oxygen-to-carbon (O/C) was calculated from their normalized peak areas as [23]:

$$\frac{O}{C} = \frac{I_0}{I_c} \times \frac{S_c}{S_0} \tag{3}$$

where I_o and I_c are the normalized integrated area of the peaks for oxygen and carbon, respectively while SC/SO is the corrected term for the sensitivity factor. The quantitative data on the surface chemical composition are acquired primarily from the O/C atomic proportion and the relative quantity of each carbon type (C 1 s). For example, the oxygen-to-carbon (O/C) nuclear ratio was calculated using region sensitivity variables as an original indication of _{2.20}PVA-MFC foam surface treatment.

2.6.3 Brunauer-Emmet-Teller (BET) Specific Surface Area

The BET specific surface area of the best silvlated PVA-MFC foam (silvlated $_{2,20}$ PVA-MFC-TEOS $_{10,2}$ foam) was determined by nitrogen adsorption using surface area and pore size analyzer (Autosorb-1, Quantachrome, USA). 30 mg of foam sample was dried under a nitrogen gas flow at 105°C for 18 h and measured at -196°C, under a range of relative vapor pressures between 0.05 and 0.2. The BET surface area and pore size were evaluated from the obtained adsorption isotherm.

3 Results and Discussion

3.1 FESEM Analysis of Microfibrillated Cellulose of Sugarcane Bagasse (MFC-SCB)

Fig. 1 showed the even surface morphology of sugarcane bagasse microfibrillated cellulose (MFC-SCB) at 90 k magnification. It is clearly showed that the individualized forms of MFC covering the whole area. These fibrillated microcelluloses with high entangled-structure that is several microns in length but 1–100 nm in diameter.



Figure 1: FESEM micrograph of microfibrillated cellulose of sugarcane bagasse (MFC-SCB) with magnification of 90 k X

3.2 Determination of Appropriate Parameters (Silane Concentration and Reaction Time) of Silane Modification on PVA-MFC Composite Foam

The density and porosity obtained from unmodified 2.20 PVA-MFC foams (Mw: 50 k) were 0.49 g/cm³ and 68%, respectively. However, the density values of silylated 2.20PVA-MFC-MPS foams and 2.20PVA-MFC-TEOS foams were higher compared to unmodified 2,20PVA-MFC foams. This is because, increased in density values lead to the decrement of porosity values of the silylated 2.20PVA-MFC foams. From the result obtained, the porosity values of silylated 2,20PVA-MFC-MPS foams were decreased from 68% to 32% when increasing in silane concentration and reaction time. Meanwhile, silylated 2.20PVA-MFC-TEOS foams also showed a decreasing of porosity values (68% to 26%), when increasing in silane concentration and reaction time. Previous study reported that a gradual decreased in porosity of both silylated foams (MPS and TEOS) indicated that the void volume fraction progressively decreased within the silvlated foams due to the thickening of the cellulosic scaffold after silvlation [18]. Moreover, this phenomenon may also due to the number of hydroxyl groups of PVA and cellulose decreased with increasing of silane concentration which resulted an increased in density values of silylated 2.20 PVA-MFC foam [24]. Both porosity of silvlated foams (MPS and TEOS) also showed a decreased value when the reaction time was increased. It might be due to longer reaction time in complex interactions between cellulose, PVA compounds and solvents may affect the physical properties of 2.20PVA-MFC foams [25,26]. Therefore, these two parameters (silane concentration and reaction time) need to control carefully in order to optimize the surface modification of 2,20 PVA-MFC foams. The highest porosity values achieved in this work were 65% (2.20PVA-MFC-MPS foam) and 67% (2.20PVA-MFC-TEOS foam). The appropriate conditions to achieve this porosity value were observed at conditions of 10 wt% of silane concentration and 2 h of reaction time.

3.3 Characterization of PVA-MFC Foams before and after Silane Modification

3.3.1 Scanning Electron Microscopy (SEM)

SEM micrograph of unmodified _{2,20}PVA-MFC foam with open pore structure is shown in Fig. 2. SEM micrographs of silylated _{2,20}PVA-MFC composite foam surface are illustrated in Fig. 3.

As can be seen, the modification of foams with silane resulted in a continuous and cloud-like coating unlike unmodified $_{2,20}$ PVA-MFC foam. The unmodified $_{2,20}$ PVA-MFC foam showed a random three-dimensional network structure. This formation might be due to the nucleation and growth of large ice crystals within the network when the MFC are pushed out from its original location during the freeze-drying process [27]. When coupling agent (MPS or TEOS) were introduced, the $_{2,20}$ PVA-MFC foam



Figure 2: SEM micrograph of unmodified 2.20 PVA-MFC foam with magnification of 5 k X



Figure 3: SEM micrographs surface of (a) silvlated $_{2,20}$ PVA-MFC-MPS $_{10,2}$ foam, and (b) silvlated $_{2,20}$ PVA-MFC-TEOS $_{10,2}$ foam with magnification 5 k X

pores become smaller and the texture of foams surface were quite different before and after silvlation as can be seen in Fig. 3. This difference showed that MPS and TEOS had successfully been grafted on the surface of $_{2,20}$ PVA-MFC foam as the porous pores of the silvlated $_{2,20}$ PVA-MFC foam were almost covered and closed by silane chemicals.

3.3.2 Fourier Transform Infrared (FTIR) Analysis

Fig. 4 shows the FTIR spectra of $_{2,20}$ PVA-MFC foams before and after silanization ($_{2,20}$ PVA-MFC-MPS_{10,2} foams and $_{2,20}$ PVA-MFC-TEOS_{10,2} foams). As observed, bands at 3340 cm⁻¹, 2940 cm⁻¹, 1646 cm⁻¹, 1429 cm⁻¹, 1143 cm⁻¹, 1096 cm⁻¹ and 895 cm⁻¹ were presence in all samples. The band at 3340 cm⁻¹ is attributed to O-H vibration which mainly results from hydrogen bonds in cellulose [25]. Meanwhile, the bands at 2940 cm⁻¹, 1429 cm⁻¹ and 1143 cm⁻¹ are associated with C-H, C-H₂ and C-O stretching vibrations, respectively. The shoulder band presence at 1096 cm⁻¹ is attributed to C-O stretching, which could be detected in PVA nanocomposites [28]. From the spectra, it was observed that the band at 1594 cm⁻¹ and 895 cm⁻¹ associated to C-NH₂ bending vibration [29] and β-1,4-glucosidic bond vibration [30], respectively. Further inspection of these spectra reveals the presence of two small peaks around 950 cm⁻¹ and 800 cm⁻¹ in both silylated $_{2,20}$ PVA-MFC-MPS_{10,2} foams and silylated $_{2,20}$ PVA-MFC-TEOS_{10,2} foams. These bands were attributed to Si-O stretching vibration and deformation of Si-OH stretching vibrations, respectively [31].



Figure 4: FTIR spectra of (a) silvlated $_{2,20}$ PVA-MFC-MPS $_{10,2}$ foam, (b) silvlated $_{2,20}$ PVA-MFC-TEOS $_{10,2}$ foam and (c) unmodified $_{2,20}$ PVA-MFC foam

3.3.3 Wetting Ability of Unmodified and Silylated PVA-MFC Foams

 $_{2,20}$ PVA-MFC foam is easily to absorb moisture and swell in water due to high density of the hydroxyl groups present at the surface of PVA and MFC-SCB [27]. Therefore, this hydrophilicity features were modified with silane coupling agents (MPS and TEOS). The resulting wetting properties were evaluated by measuring contact angle of a water droplet (WCA) deposited directly at the top surfaces of the unmodified and silylated $_{2,20}$ PVA-MFC foams.

Fig. 5a shows a distinct hydrophilic character of unmodified $_{2,20}$ PVA-MFC because WCA could not be measured as it was immediately absorbed within the foam structure in less than 1 s. This is due to the amphiphilic character of cellulose [32] and hydrophilic properties of PVA [33,34]. In contrast, the water droplets could stand on the surfaces of the silylated $_{2,20}$ PVA-MFC-MPS $_{10,2}$ (123.3° ± 0.4°) foams and $_{2,20}$ PVA-MFC-TEOS $_{10,2}$ (99.6° ± 0.6°) foams. Both silylated $_{2,20}$ PVA-MFC foams kept their original shapes well without significant absorption within 30 s (Figs. 5b and 5c). The difference in contact angle might also be attributed at least in part to the different surface chemistry as reported in previous studies [34–36]. TEOS has short pendant group compared to MPS [37], thus extent of silane hydrolysis and its degree of polymerization are known to exert a great influence on the silane adsorption at the foam surface [38]. The improved in WCA measurements of both silylated $_{2,20}$ PVA-MFC foams (MPS and TEOS) can be attributed to the formation of a thin and interpenetrated silane coating network on the surface of the



Figure 5: Contact angle measurements of (a) unmodified _{2,20}PVA-MFC foam, (b) silylated _{2,20}PVA-MFC-MPS_{10,2} foam, and (c) silylated _{2,20}PVA-MFC-TEOS_{10,2} foam using water droplets

foam [27]. In this respect, the hydrophobic nature of alkoxy groups on the surface of the silane coatings can influence the WCA measurements of silane treated $_{2,20}$ PVA-MFC-MPS $_{10,2}$ foams and $_{2,20}$ PVA-MFC-TEOS $_{10,2}$ foams [27,39].

3.3.4 Thermal Properties of Unmodified and Silylated PVA-MFC Foams

Figs. 6a and 6b show the thermo gravimetric (TG) and derived curves (DTG) of unmodified $_{2,20}$ PVA-MFC foams, silylated $_{2,20}$ PVA-MFC-MPS $_{10,2}$ foams and silylated $_{2,20}$ PVA-MFC-TEOS $_{10,2}$ foams, respectively. The starting curve was not stable due to different moisture uptake that different sample exhibits. Modification with silane was not only reduced ambient moisture uptake but also acted as barrier preventing inherent available bound water within PVA/MFC foam from easily evaporated (or diffused out) at the beginning of TGA test. This can be seen clearly in Fig. 6 when unmodified sample experienced faster weight loss from ambient up to 100°C). Based on the observation, the initial weight loss in the range of 30–150°C for silylated $_{2,20}$ PVA-MFC-MPS $_{10,2}$ foams and silylated $_{2,20}$ PVA-MFC-TEOS $_{10,2}$ foams were attributed to the removal of intermolecular H-bonded water [25,40]. However, without modification with silane, the unmodified $_{2,20}$ PVA-MFC foams showed an initial and slow weight loss until around 200°C, which might be attributed to the loss of residual moisture in the MFC as well as the slow degradation of MFC [41]. This phenomenon also occurs due to the evolution of water produced by elimination of hydroxyl side groups [13,42] and formation of some volatile products which yields predominantly macromolecules with a polyene structure in PVA [13,43].



Figure 6: TG (a) and DTG (b) curves of unmodified $_{2,20}$ PVA-MFC foam, silvlated $_{2,20}$ PVA-MFC-MPS $_{10,2}$ foam and silvlated $_{2,20}$ PVA-MFC-TEOS $_{10,2}$ foam

The degradation temperature for unmodified $_{2,20}$ PVA-MFC foams was 237°C. Upon treated the foam samples with silane, the degradation temperatures for silylated $_{2,20}$ PVA-MFC-MPS $_{10,2}$ foams and silylated $_{2,20}$ PVA-MFC-TEOS $_{10,2}$ foams shifted to lower temperature which is 158°C and 191°C, respectively. This might be due to the agglomeration of silane treated inside the silylated $_{2,20}$ PVA-MFC foams. This phenomenon occurred due to the agglomeration of silane treated composites that could result in poor interfacial adhesion with the polymer matrix [43]. Thus, due to poor dispersion of silane treated composites can cause the formation of aggregates in the matrix and the thermal stability of the polymer nanocomposites was reduced. Furthermore, other studies reported that addition of silane can decrease the crystalline, and thereby decreased the thermostability [24].

As seen from DTG curves (Fig. 6b), for silylated $_{2,20}$ PVA-MFC-MPS $_{10,2}$ foams and silylated $_{2,20}$ PVA-MFC-TEOS $_{10,2}$ foams, both weight loss started at around 30.3°C, followed by a drastic weight loss at 119°C and 134°C. In contrast, the unmodified $_{2,20}$ PVA-MFC foams showed a slow weight loss in range of 201°C-243°C. By comparing both types of silylated foams, a better improvement of thermal stability was observed

on silvlated $_{2,20}$ PVA-MFC-TEOS $_{10,2}$ foams. This result could be attributed to the better retardation of PVA thermal decomposition by covalent bonds formed between PVA and silane chemical [27] during silane modification using TEOS.

3.3.5 Compressive Properties of Unmodified and Silylated PVA-MFC Foams

In this study, unmodified _{2,20}PVA-MFC foams were easily loose and fragmented while silvlated _{2,20}PVA-MFC foams (MPS and TEOS) could be manipulated without breaking and showed higher flexibility based on the mechanical properties results. All samples; unmodified _{2,20}PVA-MFC foams, silvlated _{2,20}PVA-MFC (MPS and TEOS) were compressed to 50% of their original thickness.

Based on compressive stress-strain curves presented in Fig. 7, all samples exhibited typical characteristics of elasto-plastic foams, showing an elastic behavior at low stress, followed by collapse region and then the stress increased steeply. The deformation mechanism of the foam could be separated into three different phases during compression [44,45]. At the early stage, a linear-elastic region appears where the cell walls start to bend. Then, there is a plateau-like state which corresponds to the buckling of cell walls. When the foam was further compressed to higher strain, its volume decreased and the cell walls began to collapse, which showed a significant increase in the stress. The compressive strength of the foams lies in the order of silylated $_{2,20}$ PVA-MFC-TEOS_{10,2} foam > silylated $_{2,20}$ PVA-MFC foam in the elastic region of the curves. It showed that the compression strength of the silylated foams were higher than unmodified $_{2,20}$ PVA-MFC foams.



Figure 7: Compressive stress-strain curves of unmodified and silylated _{2,20}PVA-MFC foams (MPS and TEOS) compressed to 50% strain

The compression stress of unmodified $_{2,20}$ PVA-MFC foams was 0.31 MPa at 50% strain. Meanwhile, the compressive strength of silylated $_{2,20}$ PVA-MFC-MPS $_{10,2}$ foams and silylated $_{2,20}$ PVA-MFC-TEOS $_{10,2}$ foams were 0.43 MPa and 0.64 MPa, respectively (as shown in Tab. 1). It is clearly showed that the silane treatment could improve the mechanical properties of $_{2,20}$ PVA-MFC foams which opposite to the thermal properties results. This result could be attributed to the increase in the degree of hydrogen bonding within the PVA-MFC network after silylation, which incite an increase in the arrangement of networks between PVA and MFC [17].

Materials	Compressive strength (MPa)	
Unmodified 2,20PVA-MFC foam	0.31 ± 0.1	
Silylated 2,20PVA-MFC-MPS10,2 foam	0.43 ± 0.2	
Silylated 2,20PVA-MFC-TEOS10,2 foam	0.64 ± 0.3	

Table 1: Compressive strength of unmodified and silylated 2.20 PVA-MFC (MPS and TEOS) foams at 50% strain

3.3.6 Swelling Ratio of Unmodified and Silylated PVA-MFC Foams

As observed in Fig. 8, all foams reached an equilibrium swelling state within 24 h. The highest swelling ratio observed in unmodified $_{2,20}$ PVA-MFC foams was 10.8%. This result can be ascribed to the hydrophilicity feature of PVA and MFC. The swelling behavior can be explained by taking into account that hydrogen-bonding interactions between PVA and MFC free hydroxyl groups occurs in $_{2,20}$ PVA-MFC foams [13]. After 2 h water immersion, silane treated sample exhibited ~2.5 times less absorption (2–3% swelling ratio) compared to unmodified sample (10% swelling ratio). The low values of swelling ratios in silylated $_{2,20}$ PVA-MFC-MPS_{10,2} foams (3.95%) and silylated $_{2,20}$ PVA-MFC-TEOS_{10,2} foams (2.65%) were observed. This might be due to the silane treatment was successfully carried out to enhance the hydrophobicity of the foam. These differences occurred due to the origin of silylated $_{2,20}$ PVA-MFC foams (MPS and TEOS) in specific ionic or hydrogen bonding phenomena [46]. The interaction H-bond networks between PVA and MFC-SCB are occurred due to both PVA and MFC-SCB are hydrophilic [47]. In this respect, the silane chemicals (MPS and TEOS) have removed the H-bond networks. Hence, the ionic charges are no longer active when the surface of the $_{2,20}$ PVA-MFC foams are silylated and soaked into water. This phenomenon of hydrophobicity of silylated $_{2,20}$ PVA-MFC foams was confirmed by water contact angle analysis.



Figure 8: Swelling ratios of unmodified _{2,20}PVA-MFC foam, silvlated _{2,20}PVA-MFC-MPS_{10,2} foam and silvlated _{2,20}PVA-MFC-TEOS_{10,2} foam

3.3.7 Solvents and Oils Absorption Capacity of Unmodified and Silylated PVA-MFC Foams

Through the silanization using MPS or TEOS, the $_{2,20}$ PVA-MFC foams exhibited decreasing of theirs inherent hydrophilicity features. Hydrophobizing of hydroxylated PVA-MFC by silylating agents (MPS and TEOS), were expected to serve as absorbents for effective clean and collection of organic solvents and oils [48]. As seen in Fig. 9, the silylated $_{2,20}$ PVA-MFC foams were kept floating on the water surface, whereas the unmodified $_{2,20}$ PVA-MFC foams was sank into water rapidly.



Figure 9: The unmodified and silvlated 2,20 PVA-MFC foams were immersed in water

The absorption capacity of unmodified $_{2,20}$ PVA-MFC foams could not be measured as it was easily to absorb water as well as solvents and oils during the absorption capacity tests. Silane-treated samples were also selectively absorb organic solvent and oil (Figs. 10 and 11) in water-oil environment. Figs. 10a–10c showed the results of removal of genuine engine oils (0.5 mL) from water using unmodified $_{2,20}$ PVA-MFC foam, silylated $_{2,20}$ PVA-MFC-MPS $_{10,2}$ foam and silylated $_{2,20}$ PVA-MFC-TEOS $_{10,2}$ foam. As observed, the unmodified $_{2,20}$ PVA-MFC foam was quickly absorbed water while the silylated $_{2,20}$ PVA-MFC-MPS $_{10,2}$ foam and silylated $_{2,20}$ PVA-MFC-foams with degrad the genuine engine oil. Based on this observation, there was no residual of genuine engine oils left after these tests, revealing that the excellent absorption capacity of the silylated $_{2,20}$ PVA-MFC foams with MPS and TEOS. These behaviors clearly demonstrated the cooperative hydrophobic interaction is favored over hydrophilic absorption in silylated $_{2,20}$ PVA-MFC foams.

The absorption capacity of silylated $_{2,20}$ PVA-MFC-MPS $_{10,2}$ foams and silylated $_{2,20}$ PVA-MFC-TEOS $_{10,2}$ foams for different oils and organic solvents were measured and presented in Fig. 11. The absorption capacity of solvents and oils in silylated $_{2,20}$ PVA-MFC-TEOS $_{10,2}$ foams were range from 0.41 g/g to 48.59 g/g and 16.42 g/g to 23.7 g/g, respectively. It shows that the highest absorption capacity compared to silylated $_{2,20}$ PVA-MFC-MPS $_{10,2}$ foams. While, the range of solvents and oils in silylated $_{2,20}$ PVA-MFC-MPS $_{10,2}$ foams were from 0.78 g/g and 14.56 g/g to 22 g/g, respectively. In general, the absorption capacity of the silylated $_{2,20}$ PVA-MFC foams increased with the density of the liquids, as reported for other absorbent materials [49–51]. The chemical functionalization by MPS and TEOS could cause the modification of surface chemistry of the pores and led to increment of the oleophilicity, which due to an increase in the capillary pressure of the medium and low pore connectivity foams [52]. As expected lower absorption values obtained for deionized water could be linked to the hydrophobicity of silylated $_{2,20}$ PVA-MFC foams.

3.4 Characterization of Silylated_{2,20} PVA-MFC-TEOS_{10,2} Foams

Based on the initial characterization of unmodified and silylated $_{2,20}$ PVA-MFC-SCB foams (MPS and TEOS), the silylated $_{2,20}$ PVA-MFC-TEOS $_{10,2}$ foams showed good characterization in terms of



Figure 10: Removal of genuine engine oil from water by (a) unmodified $_{2,20}$ PVA-MFC foam, (b) silvlated $_{2,20}$ PVA-MFC-MPS $_{10,2}$ foam, and (c) silvlated $_{2,20}$ PVA-MFC-TEOS $_{10,2}$ foam



Figure 11: Absorption capacity of the silvlated $_{2,20}$ PVA-MFC-MPS $_{10,2}$ foam and silvlated $_{2,20}$ PVA-MFC-TEOS $_{10,2}$ foam for various solvents and oils

morphology, absorption capacity, wetting ability, thermal and mechanical properties. Therefore, it was further examined in terms of morphology, chemical compositions and specific surface area using FESEM, XPS and BET surface area, respectively.

3.4.1 Field Emission Scanning Electron Microscope (FESEM) of 2,20 PVA-MFC-TEOS10,2 Foam

The FESEM micrographs (Figs. 12a and 12b) showed the surface of the prepared foams (unmodified $_{2,20}$ PVA-MFC foams and silvlated $_{2,20}$ PVA-MFC-TEOS $_{10,2}$ foams) respectively with magnification of 5 k X. A significant difference in morphology between the unmodified and silvlated foams was clearly observed. Fig. 12a show open small pores of unmodified $_{2,20}$ PVA-MFC foams. The small pores size were probably due to the removal of ice crystals in the samples during freeze-drying, which can only form very small bubbles in the polymer matrix [53]. As can be seen in the image of unmodified $_{2,20}$ PVA-MFC foams, the interior of the pores possessed a continuously three-dimensional (3D) porous structure, formed by randomly entangled MFC fibers and PVA. After $_{2,20}$ PVA-MFC foam was silvlated with TEOS, there were closed small pores and cloud-like structure observed on $_{2,20}$ PVA-MFC-TEOS_{10,2} foam surface.



Figure 12: FESEM images of (a) unmodified $_{2,20}$ PVA-MFC foams and (b) silvlated $_{2,20}$ PVA-MFC-TEOS $_{10,2}$ foams at magnification 5 k X

3.4.2 XPS Analysis of 2,20PVA-MFC-TEOS_{10,2} Foam

The change in chemical compositions after silane modification with TEOS was further characterized by X-ray photoelectron spectrometer (XPS). As shown in Fig. 13, the XPS analysis of the unmodified $_{2,20}$ PVA-MFC foams and silylated $_{2,20}$ PVA-MFC-TEOS $_{2,20}$ foams confirmed the presence of C,O and trace amount of Si elements. The Si 2p peak appeared in the silylated foam demonstrating the successful silane treatment of the $_{2,20}$ PVA-MFC-TEOS $_{10,2}$ foams. The peak spectrum in Fig. 14 showed the XPS spectrum between 108 and 98 eV of binding energy which indicated the existence of Si 2p peaks as reported in previous study [54]. The peaks at 102.1 eV and 101.5 eV are represented the Si-O-Si bond and C-O-Si bond, respectively [48,54,55].



Figure 13: The XPS curves of the unmodified 2,20 PVA-MFC foam and silvlated 2,20 PVA-MFC-TEOS10,2 foam



Figure 14: The Si 2p XPS spectrum of silvlated 2.20 PVA-MFC-TEOS foam

The XPS results provide direct proofs for the coupling of TEOS on the $_{2,20}$ PVA-MFC foams which enable to elucidate the modification process of $_{2,20}$ PVA-MFC foam in this study. As expected in unmodified and silylated $_{2,20}$ PVA-MFC foams, the main elements detected are carbon and oxygen. The O/C atomic ratio of unmodified $_{2,20}$ PVA-MFC foam and silylated $_{2,20}$ PVA-MFC-TEOS $_{10,2}$ foam was 0.91 and 0.52, respectively. The O/C atomic ratio of unmodified $_{2,20}$ PVA-MFC foam was close to the theoretical value of 0.83 based formula of cellulose [56]. The chemical shifts for C 1 s and O 1 s could be observed in the XPS spectra (Fig. 13). The binding energy of C 1 s and O 1 s for unmodified $_{2,20}$ PVA-MFC-TEOS $_{10,2}$ foams is 284.95 eV and 530.91 eV, respectively. Meanwhile, the binding energy of C 1 s and O 1 s for silylated $_{2,20}$ PVA-MFC-TEOS $_{10,2}$ foams is 284.8 eV and 529.25 eV, respectively. The binding energy of C 1 s and O 1 s for unmodified $_{2,20}$ PVA-MFC foams and silylated $_{2,20}$ PVA-MFC-TEOS $_{10,2}$ foams were shifted to lower value respectively probably due to the rise of hydrogen bonding in the MFC [23].

3.4.3 Brunauer-Emmett-Teller (BET) Specific Surface Area of 2,20PVA-MFC-TEOS10,2 Foam

The subsequent pore structure data was presented in Tab. 2. As can be seen in this table, the surface area and pore volume of silylated $_{2,20}$ PVA-MFC-TEOS $_{10,2}$ foam were 3.14 m²/g and 0.01 cm³/g, respectively. A low BET surface area of the silylated foam might be due to the characteristic of silane coupling agent (TEOS) which is easy to be self-polymerization especially on PVA-MFC foam, where it is frequently decreased the specific surface area and obstructed the inner pore structure [25,57].

Samples	S_{BET} (m ² /g)	V_{pore} (cm ³ /g)	Pore Radius Dv (r) (Å)
Silylated 2,20PVA-MFC-TEOS foam	3.14	0.01	19.32

Table 2: Pore structure data of silylated $_{2,20}$ PVA-MFC-TEOS_{10,2} foam

4 Conclusion

The successfully grafted of MPS and TEOS on the surface of foams was proven as showed in FTIR results. The WCA of both silylated foams possessed a hydrophobic characteristic than the unmodified $_{2,20}$ PVA-MFC foam. In contrast to unmodified $_{2,20}$ PVA-MFC foam, both silylated $_{2,20}$ PVA-MFC foam show low thermal properties but displayed high compressive strength. The silylated $_{2,20}$ PVA-MFC foam also exhibited low swelling ratio and excellent absorption capacity on organic solvents and oils compared to unmodified $_{2,20}$ PVA-MFC foam. Silylated $_{2,20}$ PVA-MFC foam with TEOS showed good characterization in terms of morphology, absorption capacity, wetting ability, thermal and mechanical properties compared to the $_{2,20}$ PVA-MFC foam with MPS. Perhaps this absorbent foam could be alternative materials used for oil-water separation.

Funding Statement: We acknowledged the financial support provided by the Ministry of Education of Malaysia under grant FRGS 16-044-0543 and FRGS19-091-0700.

Conflicts of Interest: The authors declare that they have no conflicts of interest to report regarding the present study.

References

- 1. Avella, M., Cocca, M., Errico, M. E., Gentile, G. (2012). Polyvinyl alcohol biodegradable foams containing cellulose fibres. *Journal of Cellular Plastics*, 48(5), 459–470. DOI 10.1177/0021955X12449639.
- Liu, D., Ma, Z., Wang, Z., Tian, H., Gu, M. (2014). Biodegradable poly (vinyl alcohol) foams supported by cellulose nanofibrils: processing, structure, and properties. *Langmuir*, 30(31), 9544–9550. DOI 10.1021/ la502723d.
- 3. Lavoine, N., Desloges, I., Dufresne, A., Bras, J. (2012). Microfibrillated cellulose—its barrier properties and applications in cellulosic materials: a review. *Carbohydrate Polymers*, 90(2), 735–764. DOI 10.1016/j. carbpol.2012.05.026.
- 4. Svagan, A. J., Azizi Samir, M. A. S., Berglund, L. A. (2007). Biomimetic polysaccharide nanocomposites of high cellulose content and high toughness. *Biomacromolecules*, *8*(*8*), 2556–2563. DOI 10.1021/bm0703160.
- Mangi, S. A., Jamaluddin, N., Wan Ibrahim, M. H., Abdullah, A. H., Abdul Awal, A. S. M. et al. (2017). Utilization of sugarcane bagasse ash in concrete as partial replacement of cement. *IOP Conference Series: Materials Science and Engineering*, 271, 1–8. DOI 10.1088/1757-899X/271/1/012001.
- 6. Pereira, P. H. F., Jacobus, C., Cioffi, M. O. H., Mulinari, R., Luz, M. D. (2011). Sugarcane bagasse pulping and bleaching: thermal and chemical characterization. *BioResources*, 6(2005), 2471–2482.
- 7. Vena, P. F., Garcia-Aparicio, M. P., Brienzo, M., Gorgens, J. F., Rypstra, T. (2013). Impact of hemicelluloses preextraction on pulp properties of sugarcane bagasse. *Cellulose Chemistry and Technology*, 47(5-6), 425-441.
- 8. Cueva-orjuela, J. C., Hormaza-anaguano, A., Merino-Restrepo, A. (2017). Sugarcane bagasse and its potential use for the textile effluent. *Dyna*, *84(203)*, 291–297. DOI 10.15446/dyna.v84n203.61723.
- Oliveira, S. L., Mendes, R. F., Mendes, L. M., Freire, T. P. (2016). Particleboard panels made from sugarcane bagasse characterization for use in the furniture industry. *Materials Research*, 19(4), 914–922. DOI 10.1590/ 1980-5373-MR-2015-0211.
- Fatona, A., Berry, R. M., Brook, M. A., Moran-mirabal, J. M. (2018). Versatile surface modification of cellulose fibers and cellulose nanocrystals through modular triazinyl chemistry. *Chemistry of Materials*, 30(7), 2424–2435. DOI 10.1021/acs.chemmater.8b00511.
- 11. Kenny, M., Peponi, L., Puglia, D., Torre, L., Valentini, L. (2014). Processing of nanostructured polymers and advanced polymeric based nanocomposites. *Material Science and Engineering R, 85,* 1–46. DOI 10.1016/j. mser.2014.08.002.
- 12. Peponi, L., Pugllia, D., Torre, L., Valentini, L., Kenny, J. M. (2014). Cellulose reinforced polymer composites and nanocomposites a critical review. *Materials Science and Engineering R*, *85*, 1–46. DOI 10.1016/j. mser.2014.08.002.
- 13. Avella, M., Cocca, M., Errico, M. E., Gentile, G. (2011). Biodegradable PVOH-based foams for packaging applications. *Journal of Cellular Plastics*, 47(3), 271–281. DOI 10.1177/0021955X11407401.
- 14. Tumala, G. K. (2018). *Hydrogels of poly (vinyl alcohol) and nanocellulose for ophthalmic applications*. Uppsala: Uppsala Universitet.
- Oksman, K., Aitomäki, Y., Mathew, A. P., Siqueira, G., Zhou, Q. et al. (2016). Review of the recent developments in cellulose nanocomposite processing. *Composites Part A: Applied Science and Manufacturing*, 83, 2–18. DOI 10.1016/j.compositesa.2015.10.041.
- 16. Orhan, M. (2010). *Polylactide foams reinforced with wood fibers or microfibrillated cellulose*. Uppsala: Uppsala Universitet.

- Zhang, Z., Rentsch, D., Zimmermann, T., Tingaut, P. (2014). Ultralightweight and flexible silvlated nanocellulose sponges for the selective removal of oil from water. *Chemistry of Materials*, 26(8), 2659–2668. DOI 10.1021/ cm5004164.
- 18. Kalia, S., Dufresne, A., Cherian, B. M., Kaith, B. S., Av, L. et al. (2011). Cellulose-based bio and nanocomposites: a review. *International Journal of Polymer Science*, 2011(8), 1–35. DOI 10.1155/2011/837875.
- 19. Achor, M., Oyeniyi, Y. J., Yahaya, A. (2014). Extraction and characterization of microcrystalline cellulose obtained from the back of the fruit of Lageriana siceraria (water gourd). *Journal of Applied Pharmaceutical Science*, 4(1), 57–60. DOI 10.7324/JAPS.2014.40109.
- Asem, M., Nawawi, W. M. F. W., Jimat, D. N. (2018). Evaluation of water absorption of polyvinyl alcohol-starch biocomposite reinforced with sugarcane bagasse nanofibre: optimization using two-level factorial design. *IOP Conference Series: Materials Science and Engineering*, 368, 012005. DOI 10.1088/1757-899X/368/1/012005.
- 21. Dash, R., Li, Y., Ragauskas, A. J. (2012). Cellulose nanowhisker foams by freeze casting. *Carbohydrate Polymers*, 88(2), 789–792. DOI 10.1016/j.carbpol.2011.12.035.
- Mihaela, D., Andi, C., Vuluga, Z., Vitelaru, C., Gabriela, C. et al. (2016). Influence of hemp fibers with modified surface on polypropylene composites. *Journal of Industrial and Engineering Chemistry*, 37, 137–146. DOI 10.1016/j.jiec.2016.03.018.
- 23. Dai, D. (2012). Hemp nanocellulose: fabrication, characterisation and application. London: Brunel University.
- 24. Tan, B., Ching, Y., Poh, S., Abdullah, L., Gan, S. (2015). A review of natural fiber reinforced poly(vinyl alcohol) based composites: application and opportunity. *Polymers*, *7(11)*, 2205–2222. DOI 10.3390/polym7111509.
- 25. Wu, Y., Cao, F., Jlang, H., Zhang, Y. (2017). Preparation and characterization of aminosilane-functionalized cellulose nanocrystal aerogel. *Materials Research Express*, 4(8), 085303. DOI 10.1088/2053-1591/aa8067.
- 26. Pircher, N., Carbajal, L., Schimper, C., Bacher, M., Rennhofer, H. et al. (2016). Impact of selected solvent systems on the pore and solid structure of cellulose aerogels. *Cellulose*, 23(3), 1949–1966. DOI 10.1007/s10570-016-0896-z.
- Javadi, A., Zheng, Q., Payen, F., Javadi, A., Altin, Y. et al. (2013). Polyvinyl alcohol-cellulose nano fibrilsgraphene oxide hybrid organic aerogels. *Applied Materials & Interfaces*, 5(13), 5969–5975. DOI 10.1021/ am400171y.
- Fahma, F., Hori, N., Iwata, T., Takemura, A. (2017). PVA nanocomposites reinforced with cellulose nanofibers from oil palm empty fruit bunches (OPEFBs). *Emirates Journal of Food and Agriculture*, 29(5), 323–329. DOI 10.9755/ejfa.2016-02-215.
- Hiyoshi, N., Yogo, K., Yashima, T. (2005). Adsorption characteristics of carbon dioxide on organically functionalized SBA-15. *Microporous and Mesoporous Materials*, 84(1-3), 357–365. DOI 10.1016/j. micromeso.2005.06.010.
- Le, M., Sedan, D., Peyratout, C., Pierre, J. (2008). Influence of various chemical treatments on the composition and structure of hemp fibres. *Composites Part A: Applied Science and Manufacturing*, 39(3), 514–522. DOI 10.1016/j. compositesa.2007.12.001.
- Kapgate, B. P., Das, C., Basu, D., Das, A., Heinrich, G. (2013). Rubber composites based on silane-treated stober silica and nitrile rubber: interaction of treated silica with rubber matrix. *Journal of Elastomers and Plastics*, 47(3), 248–261. DOI 10.1177/0095244313507807.
- 32. Wang, Y., Wei, X., Li, J., Wang, F., Wang, Q. et al. (2015). Study on nanocellulose by high pressure homogenization in homogeneous study on nanocellulose by high pressure homogenization in homogeneous isolation. *Fibers and Polymers*, 16(3), 572–578. DOI 10.1007/s12221-015-0572-1.
- Gaaz, T. S., Sulong, A. B., Akhtar, M. N., Kadhum, A. A. H. (2016). Properties and applications of polyvinyl alcohol, halloysite nanotubes and properties and applications of polyvinyl alcohol, halloysite nanotubes and their nanocomposites. *Molecules*, 20(12), 22833–22847. DOI 10.3390/molecules201219884.
- Zhang, Z., Sèbe, G., Rentsch, D., Zimmermann, T., Tingaut, P. (2014). Ultralightweight and flexible silylated nanocellulose sponges for the selective removal of oil from water. *Chemistry of Materials*, 26(8), 2659–2668. DOI 10.1021/cm5004164.

- 35. Shang, H. M., Wang, Y., Takahashi, K., Cao, G. Z., Li, D. et al. (2005). Nanostructured superhydrophobic surfaces. *Journal of Materials Science*, 40(13), 3587–3591. DOI 10.1007/s10853-005-2892-9.
- 36. Xia, B. F., Jiang, L. (2008). Bio-inspired, smart, multiscale interfacial materials. *Advanced Materials*, 20(15), 2842–2858. DOI 10.1002/adma.200800836.
- Jang, J., Bae, J., Kang, D. (2001). Phase-separation prevention and performance improvement of poly(vinyl acetate)/TEOS hybrid using modified sol-gel process. *Journal of Applied Polymer Science*, 82(9), 2310–2318. DOI 10.1002/app.2079.
- Abdmouleh, M., Boufi, S., Belgacem, N. (2005). Silane adsorption onto cellulose fibres: hydrolysis and condensation reactions. *Colloid and Interface Science*, 289(1), 249–261. DOI 10.1016/j.jcis.2005.03.070.
- Paltakari, J., Jin, H., Kettunen, M., Laiho, A., Pynn, H. et al. (2011). Superhydrophobic and superoleophobic nanocellulose aerogel membranes as bioinspired cargo carriers on water and oil. *Langmuir*, 27(14), 1930–1934. DOI 10.1021/la103877r.
- 40. Yu, H., Li, J. (2011). Ultralight and highly flexible aerogels with long cellulose I nanofibers. *Soft Matter*, 7(21), 10360–10368. DOI 10.1039/c1sm06179h.
- Turng, Y. S. L., Sabo, R., Clemons, C. (2012). Nanofibrillated cellulose (NFC) reinforced polyvinyl alcohol (PVOH) nanocomposites: properties, solubility of carbon dioxide, and foaming. *Cellulose*, 19(4), 1209–1223. DOI 10.1007/s10570-012-9726-0.
- 42. Montaudo, G., Chimiche, S., Doria, V. A., Nazwnale, C., Doria, V. A. et al. (1986). Correlation of thermal degradation mechanisms: polyacetylene and vinyl and vinylidene polymers. *Journal of Polymer Science, 24*, 301–316.
- 43. Tsuchiya, Y., Sumi, K., Section, F. (1969). Thermal decomposition products of poly (vinyl alcohol). *Journal of Polymer Science: Part A-1, 7,* 3151–3158.
- 44. Song, T., Tanpichai, S. (2016). Cross-linked polyvinyl alcohol (PVA) foams reinforced with cellulose nanocrystals (CNCs). *Cellulose*, *23(3)*, 1925–1938. DOI 10.1007/s10570-016-0925-y.
- 45. Pampolini, G., Del Piero, G. (2008). Strain localization in polyurethane foams: experiments and theoretical. *Journal of Mechanics of Materials and Structures*, 5(5), 969–981. DOI 10.2140/jomms.2008.3.969.
- 46. Gousse, C., Chanzy, H., Cerrada, M. L., Fleury, E. (2004). Surface silylation of cellulose microfibrils preparation and rheological properties. *Polymer*, 45(5), 1569–1575. DOI 10.1016/j.polymer.2003.12.028.
- Peresin, M. S., Vesterinen, A., Habibi, Y., Johansson, L., Pawlak, J. J. et al. (2014). Crosslinked PVA nanofibers reinforced with cellulose nanocrystals: water interactions and thermomechanical properties. *Journal of Applied Polymer Science*, 40334(11), 1–12. DOI 10.1002/app.40334.
- 48. Xiong, S., Zhong, Z., Wang, Y. (2016). Direct silanization of polyurethane foams for efficient selective absorption of oil from water. *AIChE Journal*, *63(6)*, 1–31. DOI 10.1002/aic.
- 49. Chuanwei, M., Hamad, W. Y. (2013). Cellulose reinforced polymer composites and nanocomposites: a critical review. *Cellulose*, 20(5), 2221–2262. DOI 10.1007/s10570-013-0007-3.
- 50. Sun, H., Xu, Z., Gao, C. (2013). Multifunctional, ultra-flyweight, synergistically assembled carbon aerogels. *Advanced Materials*, 25(18), 2554–2560. DOI 10.1002/adma.201204576.
- Dong, X., Chen, J., Ma, Y., Wang, J., Chan-Park, M. B. et al. (2012). Superhydrophobic and superoleophilic hybrid foam of graphene and carbon nanotube for selective removal of oils or organic solvents from the surface of water. *Chemical Communication*, 48(86), 10660–10662. DOI 10.1039/c2cc35844a.
- 52. Pinto, J., Athanassiou, A., Fragouli, D. (2016). Effect of the porous structure of polymer foams on the remediation of oil spills. *Journal of Physics D: Applied Physics*, 49(14), 145601. DOI 10.1088/0022-3727/49/14/145601.
- Song, T., Tanpichai, S., Oksman, K. (2016). Cross-linked polyvinyl alcohol (PVA) foams reinforced with cellulose nanocrystals (CNCs). *Cellulose*, 23(3), 1925–1938. DOI 10.1007/s10570-016-0925-y.
- Miyazaki, E., Tagawa, M., Yokota, K., Yokota, R., Kimoto, Y. (2010). Investigation into tolerance of polysiloxaneblock-polyimide film against atomic oxygen. *Acta Astronautica*, 66(5–6), 922–928. DOI 10.1016/j. actaastro.2009.09.002.

- 55. Morent, R., De Geyter, N., Axisa, F., De Smet, N., Gengembre, L. et al. (2007). Adhesion enhancement by a dielectric barrier discharge of PDMS used for flexible and stretchable electronics. *Journal of Physics D: Applied Physics*, 40(23), 7392–7401. DOI 10.1088/0022-3727/40/23/021.
- 56. Lu, J. U. E., Drzal, L. T. (2010). Microfibrillated cellulose/cellulose acetate composites: effect of surface treatment. *Journal of Polymer Science: Part B: Polymer Physics, 48(2),* 153–161. DOI 10.1002/polb.21875.
- 57. Wang, N., Ding, E., Cheng, R. (2007). Surface modification of cellulose nanocrystals. *Frontiers of Chemical Engineering in China*, 1(3), 228–232. DOI 10.1007/s11705-007-0041-5.