Effect of temperature on the silylation of nanocrystalline cellulose from oil palm empty fruit bunch with 3-aminopropyltriethoxysilane

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Abstract. Nanocrystalline cellulose (NCC) was obtained through the oxidation reaction of oil palm empty fruit bunch (OPEFB) pulp and 4-acetamido-2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO) followed by ultrasonication. The aim of this study the effects of temperature on the silylation of nanocrystalline cellulose (NCC) using OPEFB-NCC and 3-aminopropyltriethoxysilane (APS). The reaction temperatures used in the silylation process were 60, 70, 80, 90 and 100°C. FTIR of the distinctive peaks resulting from the silylation process at 810 cm⁻¹, broad peaks at 1028-1157 cm⁻¹ and at 2928 cm⁻¹ were used as the basis for investigating the influence of temperature on the silylation reaction. In addition, a visual examination of the final product was also carried out. Based on the FTIR analyses and aided by visual assessment, it can be deduced that a medium temperature of 80°C is the optimum silylation reaction temperature.

1. Introduction
Natural fibers have garnered greater attention both in the industry and research due to their specific properties which include excellent biocompatibility, mechanical strength, low density, biodegradability, renewability, and low cost [1, 2, 3, 4, 5]. Cellulose which can be derived from these fibers can be transformed into nanoscale dimension with various potential application such as paper additive [6], drug carrier [7], enzyme immobilizer [8], and food packaging [9]. Because of their remarkable mechanical properties, cellulose has become a prominent candidate to replace the use of synthetic reinforcing fillers in bio-nanocomposites, polymeric matrices and biodegradable composites [4, 10].

Cellulose nanocrystals are usually produced by acid hydrolysis process which leads to the preferential digestion all of cellulose amorphous region resulting in low yield of NCC of between 20-30% [11]. An alternative method which found prominence is the TEMPO-mediated oxidation where carboxyl acid groups are introduced to the surface of cellulose nanoparticles and has a higher yield (80-90%) compare to acid hydrolysis [12].

The TEMPO treatment mainly oxidizes the primary alcohol groups (C6 hydroxyl along the cellulose structure) with minimal reaction with the secondary and tertiary hydroxyl groups to carboxylate groups. The regioselective reaction on the outer side of the primary hydroxyl groups in cellulose chain lead to loosening of the adhesion between the fibrils by hindering the strong interfibril hydrogen bonds [13].
To obtain the NCC, these TEMPO-oxidized fibers undergo a vigorous mechanical treatment, such as sonication which is basically an acoustic cavitation process, whereas sonic radiation breaks the chemical bonds. The main occurrence in sonochemistry is creation, growth and collapse of a bubble that is formed in a liquid [14] the collapse results startle waves which lead mechanical effect. This phenomenon increases the splitting of polymers to smaller fragment by generating shear forces.

However, since NCC has OH on its outer surface and very hydrophilic, its industrial application is limited because of poor interfacial adhesion [15] and low compatibility with nonpolar polymer matrices [16]. To overcome those problems, the modification of nanocellulose has become important for further high interest. There are several methods that have been applied on the surface modification; chemical modification to form covalent bonds between cellulosic and the grafting agent, or by the physical interaction, or adsorption, of molecules on the macromolecular surface. The success of these surface modifications can be verified via several analysis such as, appearance new functional groups of modification agent, stability dispersion on nonpolar solvent [17, 18], compatibility with polymer matrix [19].

Several studies have reported the modification of nanocellulose with silane coupling agent; for example, NCF form softwood pulp was modified using chlorodimethyl isopropylsilane that gave better dispersion in nonpolar solvent [20], NCF modified using isopropyl dimethylchlorosilane gave stable suspensions without fluctuation [21]. The use of organosilane fiber is useful since it has been proved to render nanocellulose surface hydrophobic and to improve matrix-filler interactions. However, there is no report regarding the effect of reaction temperature on the silylation of nanocellulose. In this study, we investigated these effects by using nanocrystalline cellulose obtained from oil palm empty fruit bunch (OPEFB-NCC) and modified using 3-aminopropytriethoxysilane (APS) as a coupling agent at 60, 70, 80, 90 and 100°C. The modified NCC was analysed by FTIR to find the better performance of typical peak functional groups and the appearance of modified NCC powder.

2. Materials and Methods

2.1 Materials

The OPEFB strand were obtained from SABUTEK Sdn. Berhad, Perak, Malaysia, and were used as a raw material. The 4-acetamido-TEMPO (2,2,6,6-tetramethylpiperidin-1-oxyl) was procured from Sigma Aldrich (USA). Sodium hydroxide (NaOH) pellets, sodium bromide (NaBr), sodium hypochlorite (NaOCl) and other reagents used in the experiment were purchased from Bendosen Chemicals and QRec (Kuala Lumpur, Malaysia).

2.2 Preparation of OPEFB-NCC

Nanocrystalline cellulose was isolated directly from OPEFB pulp via TEMPO mediated oxidation process as described by [12]. The OPEFB pulp was prepared through prehydrolysis and soda pulping [22]. The 3 g OPEB pulp was placed in a 1 L reactor and added 500 mL distilled water to maintain in aqueous condition. A 0.115 g of TEMPO and 0.3175 of sodium bromide was mixed with OPEFB pulp and a 10 mL NaOCl (10%) reaction was held at 25°C for 4 hours. A subsequent post oxidation process was carried out by adding NaClO2 at 70°C for 2 hours in water bath. After completing reaction, the mixture was washed with distilled water and followed by sonication process to disintegrated TEMPO-oxidized pulp. The sonication process was carried out using a sonicator with a 7 micro tip for 15 min in an ice bath to avoid overheating. Separation of the nanosize of NCC was carried using a centrifuge (Kubota 5100) at 3500 rpm for 1 h.

2.3 Modification of NCC

The NCC surface was modified by 3-aminopropytriethoxysilane (APS) using the method reported by [23]. The NCC in water suspension with 1% (wt%) was mixed with APS (10%) with dried ratio 1:4 (w/w). Before mixing with NCC, APS was diluted in water ethanol (10:90 v/v). The reaction was held in round bottle flask with four neck and placed into a jacket mantel. The pH was maintained at 10 by adding NaOH 1% and mixed at 300 rpm. The reaction was first carried out at room temperature for 2 hours, followed by refluxing at 5 different temperatures of 60, 70, 80, 90 and 100°C for 3 hours and the temperature was controlled with a thermocouple. After completion of reaction, the mixture was washed
with 300 mL water ethanol solution (10/90) to remove the excess APS, and then dried at 40°C in oven for 24 hours.

2.4 Characterization of Modified NCC

Fourier transform infrared (FTIR) spectroscopy performance of nanocrystalline cellulose was used to determine the functional groups of the materials using FTIR spectrometer (Nicolet iS10, Thermo Scientific). In brief, a 0.2 mg NCC sample were mixed thoroughly with 0.98 mg potassium bromide (KBr) which is then pressed into thin pellets for transmittal spectra analysis at a wavenumber range of 4000–400 cm\(^{-1}\) and a resolution of 4 cm\(^{-1}\) at an accumulation of 32 scans.

3. Results and Discussion

3.1 Fourier Transform Infrared Analysis

Fourier transform infrared (FTIR) spectroscopy shows the intensity of the peak absorbance or transmittance of the functional groups, which can then help to identify the chemical bond in materials. It’s intensity could directly relate to the amount present; for transmittance the higher the intensity, the more is the amount present, however for absorbance it is the opposite.

In this study, FTIR was employed to analyze the effects of temperature on the surface modification of NCC using APS which is shown in Figure 1. It has been reported earlier [23] that FTIR evidences of a successful silylation are from the existence of several peaks, notably peak in the vicinity of 810 cm\(^{-1}\) which is attributed to the Si-CH\(_3\) stretching, broad peaks at 1028-1157 cm\(^{-1}\) (Si-O-Si and Si-O-C), 1510 cm\(^{-1}\) which is related to a typical amine group (N-H), and at 2928 cm\(^{-1}\) which can be assigned to C-H (bond with NH\(_2\)). All these said peaks are present in the FTIR spectra in Figure 1 indicating the successful silylation reaction. It represents the full FTIR spectra of the modified NCC at different reaction temperatures with regions emphasized in blue dotted lines for the purpose of identification of the distinctive bands resulting from the silylation process. The magnified regions are shown in Figure 2.

![Figure 1](image_url)

**Figure 1.** FT-IR spectra of modified NCC spectra at 60°C (blue line); 70°C (green line); 80°C (pink line); 90°C (red line); and 100°C (black line)

A broad peak in the range between 3600 and 3000 cm\(^{-1}\) are ascribed to -OH is stretching of all cellulose, irrespective whether it is has been modified or not. What is worth highlighting is that there are some changes in the intensity at different reaction temperatures. During silylation, hydroxyl groups are replaced by the carboxylic groups, thus reducing the number of free hydroxyl groups, which is then reflected in the transmittance intensity of the peak. As can be seen from Figure 2(a), the spectrum
corresponding to 80°C (pink) has the lowest intensity, indicating that there are less free hydroxyl groups available, thus silylation is higher at this temperature.

The peak at 2980 cm\(^{-1}\) (Figure 2(a)) which can be assigned to C-H (bond with NH\(_2\)) is interesting since it is only present in the modified NCC [23], hence it’s intensity will have a direct correlation on the extent of reaction. It indicates the reaction between ethoxy groups of APS and the free hydroxyl groups on the surface of the NCC. The intensity of the peak is an indication of the possible formation of a stable bonding of silane with cellulose (polysiloxanes) [24] on the surface of NCC. As can be seen from the figure, the temperatures of 80°C and 90°C gave the highest reaction (highest intensity), with the latter (red spectrum) a better one.

The peak at 1515 cm\(^{-1}\) in Figure 2(b) is ascribed to the vibrating N-H of the amine group [18, 25, 26] which originates from the APS. Again, it can be seen from the intensity that the temperature of 80°C is best. Another evidence of a successful silylation can be seen from the broad peaks at 1028-1157 cm\(^{-1}\) (Figure 2(c)) which is associated to Si-O-Si and Si-O-C) bonding. Here also, based on the transmittance intensities, it can be seen that the reaction temperatures of 80°C (pink) and 90°C (red) presented the best conditions. From these FTIR spectral peaks and their intensities, it can be deduced that the temperatures which are desirable for the silylation reaction are in the range of 80–90°C, with 80°C most preferable. This is in contrary to the expected outcome as outlined by the Arrhenius equation [27] as shown in Equation (1), that relates the dependence of reaction rates on temperature.

\[
k = A \cdot e^{-\frac{E_a}{R \cdot T}}
\]  

where \(k\) is the rate constant at temperature \(T\) (K), \(A\) is a constant called ‘frequency factor’, \(E_a\) is the activation energy for the reaction (J/mol), and \(R\) is the universal gas constant (8.314 J/mole/K). The higher the temperature, the greater is thermal energy available and it is thus expected that chemical reactions will proceed at a faster rate in conditions with higher thermal energy.

However as can be seen from the spectra in Figure 2, this is not the case. Lowest intensities are at reactions that occur at 100°C (black), followed by 60°C and 70°C (blue and green), with temperatures of 80°C and 90°C are the best with 80°C most preferable, which means very high and low temperatures are not conducive for silylation reaction. It is assumed that at lower temperatures as can be extrapolated from the Arrhenius equation, it will not give sufficient energy for the reaction to complete, whilst at higher temperatures (100°C and to a lesser extent 90°C) as will be discussed later. It is probable that the modified cellulose were “burnt” or “charred” due to the overheating of the silane group, hence even though silylation might go to completion at these temperatures, the resultant product is not the silylated

**Figure 2.** FT-IR spectra of modified NCC: (a) 4000-2800 cm\(^{-1}\) region; (b) 1600–1450 cm\(^{-1}\) region, in which the amino bending is appreciable; (c) 1200-1000 cm\(^{-1}\) region and (d) 830–740 cm\(^{-1}\) region.
NCC but a “burnt” residue. This can be observed from the spectrum at 100°C where at almost all of the important designated peaks, the transmittance intensity is the lowest thus indicating there is only a small amount (if there exists at all) of the functional group.

![Figure 3. Modified nanocrystalline cellulose powder at 60°C (a), 70°C (b), 80°C (c), 90°C (d), and 100°C (e).](image)

3.2 Physical Appearance of Modified NCC Powder

The dried modified NCC was pulverized followed by sieving it using a 400 mesh sieve to obtain a powdered NCC of < 49 µm and visually analysed for its appearance as shown in Figure 3. The color changes from white, cream, yellow to brown. Both NCC and APS has white initial color (picture not shown) before cellulose modification with APS, but changes to different shades of color as reaction temperature increases. It should be noted that even though at temperatures of 60-70°C, there is no much of color difference as seen from the naked eye, it is nevertheless assumed such reactions do occur as can be seen from the FTIR spectra discussed above. Dark colored compounds are normally associated with “burning” of the product. It is believed that the dark brown product at temperatures of 100°C are a result of this “burning” and hence as had been discussed above, even though the reaction might have gone to completion, the product is not a pure silylated NCC but a mixture of it and the “burnt” silylated NCC. At 90°C, the effect of such “burning” is noticeable by the light brownish color, nevertheless the product is mostly silylated NCC as seen from Figure 2.

4. Conclusion

The effects of temperature on the silylation of nanocrystalline cellulose (NCC) was studied using OPEFB-NCC and 3-aminopropyltriethoxysilane (APS). FTIR of the distinctive peaks were used as the basis for investigating the influence of temperature on the silylation reaction. In addition, a visual examination of the final product was also carried out. Based on the FTIR analyses of the silylation distinctive peaks, it can be concluded that a medium temperature of 80°C is the optimum reaction temperature. Lower temperatures do not give substantial amount of the silylated NCC as observed from the transmittance intensities. Conversely, higher temperatures not only gave a colored product, but also a much smaller amount of the silylated NCC as seen from the spectra. Even though a temperature of 90°C is still considered satisfactory, however because of silylated NCC being slightly colored and also considering more thermal energy is required for reactions to occur at 90°C as compared 80°C, it is thus recommended that 80°C is the optimum temperature for silylation of OPEFB-NCC with APS.

References

[1]  Azizi Samir M A S, Alloin F and Dufresne A  2005 Biomacromolecules, 6 612-26
[2]  Mishra R K, Sabu A and Tiwari S K  2018 J. Saudi Chem. Soc. 22 949-78
[3]  Ali M E, Yong C K, Ching Y C, Chuah C H and Liou N-S  2015 BioResources, 10 822-38
[4]  Tan B K, Ching Y C, Gan S N and Rozali S  2015 BioResources, 10 5532-43
[5]  Ching K Y, Chee C Y, Afzan M, Kang L Z and Eng C K  2015 J. Biobased Mater. Bio. 9 231-5
[6] Sehaqui H, Allais M, Zhou Q and Berglund L A 2011 Compos. Sci. Technol. 71 382-7
[7] Jackson J K, Letchford K, Wasserman B Z, Ye L, Hamad W Y and Burt H M 2011 Int. J. Nanomed. 6 321
[8] Mahmoud K A, Male K B, Hrapovic S and Luong J H 2009 ACS Appl. Mater. Inter. 1 1383-6
[9] Bideau B, Loranger E and Daneault C 2018 Prog. Org. Coat. 123 128-33
[10] Cherian B M, Leão A L, de Souza S F, Costa L M M, de Olyveira G M, Kottaisamy M, Nagarajan E and Thomas S 2011 Carbohydr. Polym. 86 1790-8
[11] Börjesson M and Westman G 2015 Crystalline Nanocellulose - Preparation, Modification and Properties ed. Polletto M Intech Open
[12] Rohaizu R and Wanrosli W D 2017 Ultrason. Sonochem. 34 631-9
[13] Saito T, Kimura S, Nishiyama Y and Isogai A 2007 Biomacromolecules 8 2485-91
[14] Rattaz A, Mishra S P, Chabot B and Daneault C 2011 Cellulose 18 585
[15] Kalia S, Kaith B and Kaur I 2009 Polym. Eng. Sci. 49 1253-72
[16] Hubbe M A, Rojas O J, Lucia L A and Sain M 2008 BioResources 3 929-80
[17] Laitinen O, Suopajärvi T, Österberg M and Liimatainen H 2017 ACS Appl. Mater. Inter. 9 25029-37
[18] Lu J, Askeland P and Drzal L T 2008 Polymer, 49 1285-96
[19] Raquez J-M, Murena Y, Goffin A-L, Habibi Y, Ruelle B, DeBuyl F and Dubois P 2012 Compos. Sci. Technol. 72 544-9
[20] Andresen M, Johansson L-S, Tanem B S and Stenius P 2006 Cellulose 13 665-77
[21] Gousse C, Chanzy H, Cerrada M and Fleury E 2004 Polymer 45 1569-75
[22] Rosli W W, Leh C, Zainuddin Z and Tanaka R 2003 Holzforschung 57 106-13
[23] Indarti E, Rohaizu R and Wanrosli W 2019 Int. J. Biol. Macromol. 135 106-12
[24] Robles E, Csöka L and Labidi J 2018 coatings, 8 139 1-14
[25] Abdelmouleh M, Boufi S, ben Salah A, Belgacem M N and Gandini A 2002 Langmuir, 18 3203-8
[26] Pacaphol K and Aht-Ong D 2017 Surf. Coat. Technol. 320 70-81
[27] Arrhenius S 1889 Z. Phys. Chem. 4 226-48