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Modification of NanoCrystalline Cellulose (NCC) by Hyperbranched Polymer

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Abstract

Objectives: The surface modification of NanoCrystalline Cellulose (NCC) recently has been paid attention due to the increasing opportunities in the application. The objective of this paper is to modify the surface of NCC by the HyperBranched Polymer (HBP) with hydroxyl terminal groups ends. **Methods/Statistical Analysis:** The NCC surfaces were modified with HBP using solvent evaporation methods. First, the NCC was synthesized via ultrasound assisted acid hydrolysis process and the obtained NCC was surface coated by using HBP with different concentration through solvent evaporation technique. Finally, the obtained NCC and Modified NCC were characterized by using FTIR, XRD and TGA. **Findings:** Results revealed that there are significant differences of FTIR pattern analysis indicated that the NCC has been modified, however the modification NCC with HBP under various conditions did not change the X-ray patterns of NCC which indicates that the HBP only coated on the surface of NCC. **Application/Improvements:** This modification of NCC showed promising results which can be used for various applications.

Keywords: Adsorption, Hyper-Branched Polymer (HBP), Modification, Nanocrystalline Cellulose (NCC)

1. Introduction

NanoCrystalline Cellulose (NCC) can be defined as the needle or rod shaped crystalline which has 1-10 nm in width and hundreds of nanometers in length. NCC also by chance is known as Cellulose NanoWhiskers (CNW)[1], Cellulose Nanocrystals (CNs)[2] and nanocrystals. In literature, NCC has been widely producing from cotton[3], bamboo fiber[4,5], MCC[6], pineapple leaves[7], pandause leave[8,9], coconut fiber[10] and others. Recently NCC, have gained considerable interest as a promising biomaterial due to their outstanding properties such as high surface area, high mechanical property, hydrophilic, biocompatibility, and biodegradability. The NCC also has good stability in water which compatible for mixing of water base polymer solution or emulsions with NCC. However, the NCC also exhibits the disadvantages of aggregate due to highly hydrophilic in nature which limits the application of NCC.

In order to improve the compatibility and barrier properties of NCC, the modification of NCC is used by utilizing the available hydroxyl group on the surface of NCC. Two modification approaches such as covalent and non-covalent have been developed to functionalize the NCC and to improve the dispersion the NCC. Among these approaches, the non-covalent attachment by HyperBranched Polymer (HBP) on the surface of NCC can be one of the promising techniques to modified NCC.

HBP or dendrimer, is known in a family of macromolecules, have a huge potential in developing new synthetic routes in various applications for HBP. The HBP offer unique abilities which led to the design of novel HBP materials for a various application such as bio imaging, drug, adsorption waste and gene delivery, cancer diagnosis and sensors.

Considering these advantages, the present work is modified the surface of NCC by HBP with different concentration through solvent evaporation technique.

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2. Materials and Methods

Oil Palm Empty Fruit Bunch (REFB) was provided by MPOB Bandar Lama Bangi, Malaysia. The Polyester-16-hydroxyl-1-acetylenebis-MPA Dendron (Generation 4, 96%) as HBP with chemical structure and properties shown in Figure 1 and Table 1, Sodium hydroxide (NaOH), Sulphuric acid (H_2SO_4), (95-98 wt%) and Tetrahydrofuron (THF) and the dialysis bags (MW cut off 12,000-14,000, 25mm) were purchased from Sigma-Aldrich. Deionised Water (DW) was used throughout all experiment.

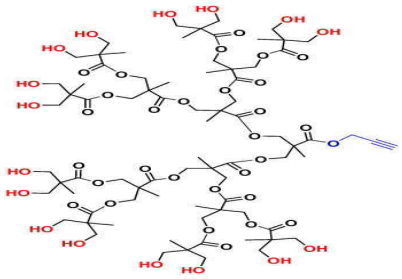


Figure 1. Molecular structure of HBP.

Table 1. Physical properties of HBP

Structure	Hyperbranched polyster acetylene
Appearance	White Powder or crystal
Molecular weight End group	1,797.79g/mol Secondary OH

2.1 Preparation of NCC

The hydrolysis of Treated Empty Fruit Bunch Pulp (TEFBP) slurry was carried out with 64% (w/v) H_2SO_4 solution in an ultrasound bath (Elma 37kHz, power capacity 320 W, Germany) at 45°C for 2 hours. At the end of hydrolysis process, the suspension of NCC was centrifuged and washed with DW for several times. The washed NCC was dialyzed using dialysis membrane (MWCO 12,000-14,000; 25mm) against DW for three days. Finally, the dialyzed NCC was exposed in an ultra sound bath for 30 min to disentangle them and oven dried at 60°C for characterization.

2.2 Modification of NCC

The surface modification of NCC (Mod-NCC) was prepared according to A. K. M, M. A. et al.2006with modification. Briefly, the HBP and 90mg of NCC were dissolved in 50ml of THF. The solution was stirred for another 15min until the HPB and NCC dissolved in THF. Then, the solution was sonicated for 30min. After that, the solution was poured into Petri dish and placed into fume hood in order to eliminated THF solvent. Finally the Mod-NCC was dried in vacuum oven at 100 °C for post analyses. The HBP coated NCC was prepared by different concentration of 0.1mmol/g, 0.3mmol/g and 0.5mmol/g. The unmodified NCC was denoted as NCC while the modified NCC was denoted as 0.1Mod-NCC, 0.3Mod-NCC and 0.5Mod-NCC for the concentration of 0.1mmol/g, 0.3mmol/g and 0.5mmol/g respectively.

2.3 Characterization

2.3.1 Fourier Transform Infrared Spectroscopy (FTIR)

The sample of NCC, 0.1Mod-NCC, 0.3Mod-NCC and 0.5Mod-NCC were characterized using a Fourier transform infrared spectroscopy (FTIR GX 2000, Perkin-Elmer, USA). FT-IR spectra were recorded in a spectral range of 4000–450 cm-1 with a resolution of 2 cm-1, with10 scans for each sample.

2.3.2 X-Ray Diffraction (XRD)

X-Ray Diffraction (XRD) data was collected by using a Rigaku Mini Flex II, Japan, operated at 30 kV and 15mA. The specimens were step-wise scanned over the operational range of scattering angle (2θ) between 3 to 50°, with a step of 0.02°, using CuKα radiation of wavelength λ=1.541Å. The degree of crystallinity (Xc) was calculated using equation (1)

$$\%\ Crsytallinity = \left(\frac{Icr - Iam}{Icr}\right) \times 100 \quad (1)$$

2.3.3 ThermoGravimetric Analysis (TGA)

The thermal stability of the NCC, 0.1Mod-NCC, 0.3Mod-NCC and 0.5Mod-NCC were analyzed using Thermal Gravimetric Analysis (TGA - Pyris 1, Perkin Elmer). A total of 5 mg of sample (dried) was analyzed under nitrogen supply with 50mL/min of gas flow rate, heating rate of 10°C/min with a temperature range of 30 to 700 °C

3. Results and Discussion

3.1 Chemical Structure

Figure 2 shows the FT-IR spectra of a) NCC, b) 0.1Mod-NCC, c) 0.3Mod-NCC and d) 0.5Mod-NCC

respectively. The absorption of NCC at 3300.0, 2892.6, 1637.1, 1426.4, 1029.0, and 895.77 cm^{-1} are associated with native cellulose in the spectrum. The strong absorption at 3300 cm^{-1}associate was associated to OH groups. This band is shifted to 0.5Mod-NCC due to the attachment of HBP on the surface of NCC thus increase the amount of hydroxyl group. The adsorption at 2800 cm^{-1} is due to the stretching vibration of and C-H, respectively. The peak at 1637 $cm^{-1}$for all corresponds to the absorbed water in cellulose[11]. characteristic The peak appeared at 1730 cm^{-1} in 0.1Mod-NCC, 0.3Mod-NCC and 0.5Mod-NCC indicated the shows C=O stretching vibration band due to oxidation during the modification of NCC[12].A strong peak at 1030 cm^{-1}indicated C–O stretching. A sharp band at 890 is characteristic of ß– glucosidic linkages between the sugar units[13]. The Characteristics peaks of NCC, 0.1Mod-NCC, 0.3Mod-NCC and 0.5Mod-NCC are shown in Table 2.

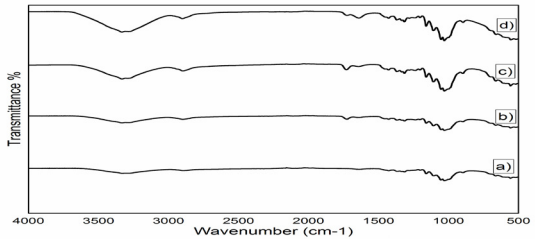


Figure 2. Chemical structure of (a) NCC (b) 0.1Mod-NCC (c) 0.3Mod-NCC and (d) 0.5Mod-NCC.

Table 2. Physical properties of HBP

Bond	Sample			
	NCC	0.1Mod-NCC	0.3Mod-NCC	0.5Mod-NCC
OH group	3300.0	3332.5	3332.5	3333.5
C-H C=O stretching absorbed water C–O stretching C–OH stretching	2892.6 - 1637.1 1029.0 895.77	2898.6 1726.0 1637.1 1029.0 895.77	2898.6 1726.0 1637.1 1029.0 895.77	2901.3 1726.0 1640.4 1052.5 895.66

3.2 Crystallinity

Figure 3 illustrate the XRD patterns of raw NCC, 0.1Mod-NCC, 0.3Mod-NCC and 0.5Mod-NCC. The NCC represents the scattering angle at 14.97°, 22.50° and 34.24°shows the crystal planes of (101), (002) and (040) respectively. The 0.1Mod-NCC also shows the scattering angles at 15.51°22.54° and 34.50°. However, the0.3Mod-NCC and 0.5Mod-NCC shows the appearance of four scattering angles indicates that the surface modification of HBP might be observed due to high concentration of HBP. The FWHM (δ), average crystal size (D) in the direction normal to the reflecting plane, the lattice spacing d, and crystallinity index (Ci) are summarized in table 2. The Full Width at Half Maximum (FWHM) values in Table 3 illustrates that scattering peaks of NCC are narrower as compared to the 0.3Mod-NCC and 0.5Mod-NCC. The crystals size and the lattice spacing of each of the mod-NCC for every plane are increased as compared to NCC. Moreover, the crystallinity of 0.3 Mod-NCC and 0.5 Mod-NCC were slightly increased as compared to NCC.

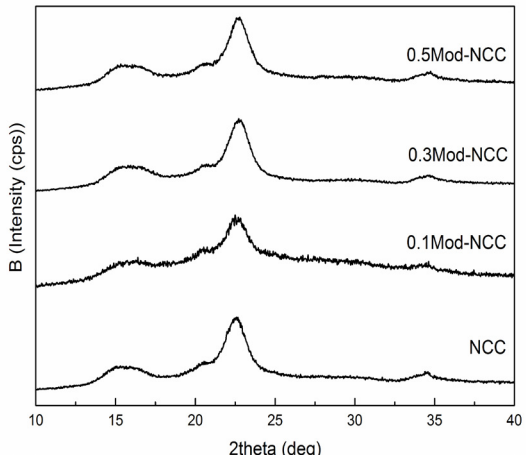


Figure 3. Crystallinity NCC, 0.1, Mod-NCC, 0.3Mod-NCC and 0.5Mod-NCC.

Table 3. Physical properties of HBP

Sample	2θ (°)	FWHM (Δ2θ) (°)	D(Å)	d(Å)	C_i (%)
NCC	14.97	2.26	37.1	5.91	62
	22.50	1.73	48.8	3.95	
	34.24	1.16	75.0	2.62	
0.1 Mod-NCC	15.51	2.36	36.0	5.71	56.04
	22.54	3.82	22.1	3.94	
	34.50	5.90	15.0	2.04	

0.3Mod-NCC	15.84	3.26	25.7	5.59	64.0
	21.16	4.41	19.1	4.19	
	22.66	1.41	60.2	3.92	
	34.37	1.31	66.0	2.61	
0.5 Mod-NCC	15.38	2.63	31.8	5.76	62.0
	20.93	3.45	24.4	4.24	
	22.63	1.41	60.2	3.93	
	34.62	1.35	65.0	2.59	

3.3 Thermal Stability

The TG and DTG of NCC, 0.1Mod-NCC, 0.3Mod-NCC and 0.5 Mod-NCC are presented in Figure 4.Thermal decomposition of NCC took place at around 348.36°C.

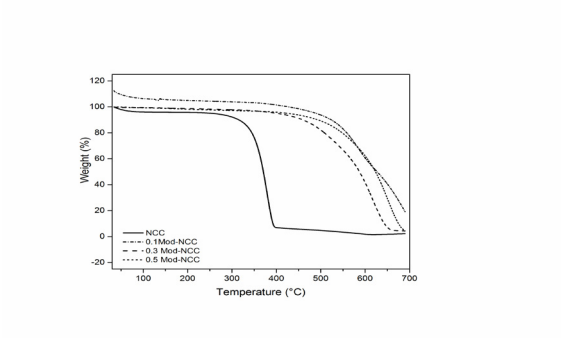
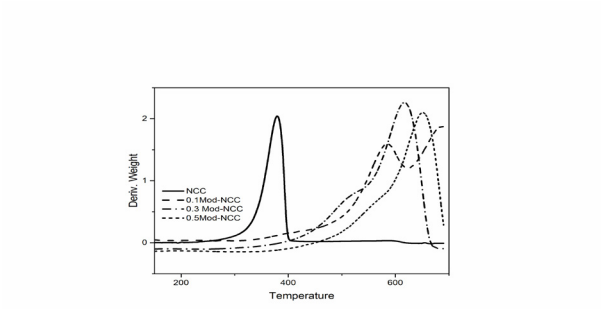


Figure 4. DTG of NCC, 0.1Mod-NCC, 0.3Mod-NCC and 0.5 Mod-NCC.



In contrast, the 0.1Mod-NCC, 0.3Mod-NCC and 0.5Mod-NCC degradation started at relatively higher temperature than NCC.

4. Conclusion

The surface modification by appropriate amount of HBP was beneficial for the improvement of NCC. The result of FTIR shows the existence of HBP on the surface of NCC. The XRD pattern of NCC and mod-NCC remain same which indicated that the HBP are only attached on the surface of NCC. The International Conference on Fluids and Chemical Engineering (FluidsChE 2017) is the second in series with complete information on the official website[14] and organised by The Center of Excellence for Advanced Research in Fluid Flow (CARIFF)[15]. The publications on products from natural resources, polymer technology, and pharmaceutical technology have been published as a special note in volume 2[16]. The conference host being University Malaysia Pahang[17] is the parent governing body.

5. Acknowledgement

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