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A Characteristic Study of Nanocrystalline Cellulose and its Potential in Forming Pickering Emulsion

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The phenomenon of particle-stabilized emulsion was a breakthrough discovery by Ramsden and Pickering in 19's century. It has recently attracted tremendous attention among different disciplines for its potential developments in oil recovery, food industry, and biomedical application due to its high stability, better permeability, and compatibility as a delivery platform. Recently, research efforts have been shifted toward the exploration of using biologically derived materials in emulsion formation. In the current study, the extraction of nanocrystalline cellulose from oil palm empty fruit bunch was reviewed. To our knowledge, the characteristic of nanocrystalline cellulose was largely determined by the hydrolysis process. For the conventional acid hydrolysis route, acid destroyed the cellulose amorphous region, greatly reduced its degree of polymerization, and thus resulting in much smaller cellulose particles. This would be the fundamental for the later formation of sub-micron Pickering emulsion.

1. Introduction

Cellulose, a linear homo-polysaccharide of β-D-glucopyranose linked by 1,4-glycosidic bonds, was first discovered by Payen in 18's century (Payen, 1839) on the composition of wood. Over the past decades, microcrystalline cellulose (MCC) obtained from partial hydrolysis of high purity wood pulp was commonly used as a filler in drug formulations (eg. Pharmacel®, PARMCEL), due to its high stability and strong binding performance. In its nano-dimension i.e. nanocrystalline cellulose (NCC), it shows unique characteristics such as high surface area (Lu and Hsieh, 2010), high crystallinity (Kargarzadeh et. al., 2012) and a Young's modulus (~105 – 168 GPa) (Šturcová, 2005; Rusli et. al, 2008) comparable to copper and titanium. Moreover, it forms chiral nematic self-ordering liquid crystals at some specific concentration (Revol et. al., 1992), owing to its ability to switch isotropic into anisotropic behaviour. These striking characteristics have brought NCC with tremendous attentions (Lorenzo et. al., 2014). Generally, the structural complexity and the composition of the raw material determine the type of treatment in NCC extraction. Most lignocellulosic biomass including agricultural residue (e.g. rice husk, bagasse), terrestrial plant (e.g. Bamboo, wood) require delignification prior acid hydrolysis. The amorphous region is more accessible to acid (Beck et. al., 2005; Håkansson H and Ahlgren P, 2005) and subsequently degraded during hydrolysis process. The glycosidic bonds cleaved and the degradation continues during the hydrolysis process (Börjesson and Westman, 2015). Negatively charged NCC can be produced through sulfuric acid hydrolysis (van den Berg O et. al., 2007; I. A. Sacui et. al., 2014). The repulsion forces contributed by the electrical double layers allow NCC to disperse in water and form stable colloidal suspension (Lu and Hsieh 2010). It has fewer tendencies to aggregate compared to the neutral surface charged hydrochloric acid-hydrolysed NCC (van den Berg O et. al., 2007). This characteristic facilitates the formation of Pickering emulsion by using NCC as particles stabilizer. The phenomenon of particles-stabilized emulsion was first discovered by Ramsden and Pickering in early 20th century (Ramsden,

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1903; Pickering, 1907), while colloidal suspension stabilized by cellulose obtained via controlled sulfuric acid-catalyzed degradation was first reported by Ränby in the 1950s. (Habibi et. al., 2010). Pickering emulsion has a propensity to separate and stabilise two immiscible liquids at micro dimension ascribed to the nature of the liquids immiscibility, density difference, and the earth's gravity. It is notable that the diversity in particle shape, dimension and hydrophobicity determine the properties and stability of Pickering emulsion (Lam et. al., 2014). NCC tends to stabilize water-continuous (oil-in-water) emulsion due to its hydrophilic nature (Kalashnikova et. al., 2013; Capron and Cathala, 2013). Its rod like structure allows the formation of entanglement network on emulsion interfaces at low particle concentration (Capron and Cathala, 2013). It is also worth noting that the hydrophobicity of the NCC can be tuned (Andresen and Stenius, 2007; Saidane et. al, 2016) to make water-in-oil emulsion. Pickering emulsion stabilised by inorganic particles such as clay (T. Sharma et. al., 2015) and silica (D. J. French et. al., 2015) has been attempted. The focus was shifted towards biologically derived materials recently to make NCC superior in the production of particle-stabilized emulsion. In this study, NCC was extracted from palm oil biomass i.e. empty fruit bunch (EFB), as an ideal candidate for Pickering emulsion due to its inherent biodegradability, sustainability and biocompatibility. Firstly, The EFB and chemically purified cellulose (PC) were analysed using fourier transform infrared spectroscopy (FTIR) to confirm the removal of lignin and hemicellulose before acid hydrolysis. Secondly, sulfuric acid was exploited as the hydrolysis agent. The morphology of NCC was characterized using field emission scanning electron microscopy (FE-SEM), and ImageJ software was employed to estimate the particles size from FE-SEM image. The result was supported by dynamic light scattering (DLS) to confirm the overall particle size distribution of NCC in a more quantitative way. Although theoretically feasible, NCC extraction in large quantity with well size-controlled is very difficult (Shanmugarajah et. al., 2015). Moreover, the mechanism of Pickering stabilization by needle-like nanoparticles remains much enigmatic. The current work would be of helpful to address some fundamental questions in later formation of sub-micron Pickering emulsion.

2. Experimental

2.1 Material

Oil palm empty fruit bunch (EFB) fibers were received complimentary from Eureka Synergy Sdn Bhd. Sodium hydroxide (NaOH, Friendemann Schmidt Chemical), sodium chlorite ($NaClO_2$, AR Grade, Friendemann Schmidt Chemical), sulfuric acid (H_2SO_4, 95–97%, AR Grade, Friendemann Schmidt Chemical), and glacial acetic acid (CH_3COOH, 99.7%, AR Grade, Fisher Scientific) were used as received.

2.2 Empty fruit bunch (EFB) and chemically purified cellulose (PC)

The EFB fibers with a size less than 250 µm were obtained using Pulverisette 14 (Fritsch, Germany) rotor mills. The EFB fibers were then gone through several rounds of washing to remove water-soluble substances. After drying, 2 w/v% $NaClO_2$ solution was adopted for delignification at 80 °C for 2 hr, with continuous stirring. The solution pH was controlled at acidic condition (pH 4-5) throughout the process by adding equal amount of acetate buffer (mixture of sodium hydroxide and glacial acetic acid) to the solution. Removal of hemicellulose was achieved with 4 w/v% NaOH solution under continuously stirring at 80 °C for 2 hr. These processes were repeated for 3 times. The fibers were washed with deionized water during the off-treatment intervals to minimize soluble alkali remained on fibers surface. The resulting sample i.e. purified celluloses (PC) were freeze-dried for later acid hydrolysis.

2.3 Extraction of nanocrystalline cellulose (NCC)

H_2SO_4 solution (58 wt%) was attempted to hydrolyse PC to obtain NCC. With an acid-to-pulp ratio of 17.5ml/g, the temperature was controlled at 45 °C for 30 minutes. After hydrolysis, deionized water was added for quenching to cease aggressive degradation. The hydrolysed sample was centrifuged under isothermal condition of 10 °C at 14,000 rpm for 15 minutes. The resulting precipitant was re-centrifuged with deionized water for 2 times. The precipitate was then dialyzed against deionized water until a constant pH was received. The dispersed NCC obtained through ultrasonication was stored in refrigerator after addition of few drops chloroform.

2.4 Characterization

2.4.1 Fourier transform infrared spectroscopy (FTIR)

Fourier infrared spectra of EFB and PC were examined using diamond probe equipped FTIR spectrophotometer (Nicolet iS10, Thermo Scientic, USA) in the range of 525 - 4000 cm^{-1} with 64 scans for each sample.

2.4.2 Particle size measurement and zeta potential

The particle size distribution of NCC was examined using dynamic light scattering (DLS) method. The measurement of particle size and zeta potential of the NCC suspension was obtained using Malvern Nano-ZS Zetasizer (Malvern Instruments Ltd, UK).

2.4.3 Microscopy analysis

The particle size and surface morphology of NCC were studied using field emission scanning electron microscope (FE-SEM) on Hitachi SU8010 microscope at 15 kV. The sample was air-dried prior to analysis. The particles size was estimated using ImageJ software.

3. Results and Discussion

The FTIR spectra of EFB and PC are reported to confirm the delignification and alkali treatment prior hydrolysis to obtain NCC (Figure 1).

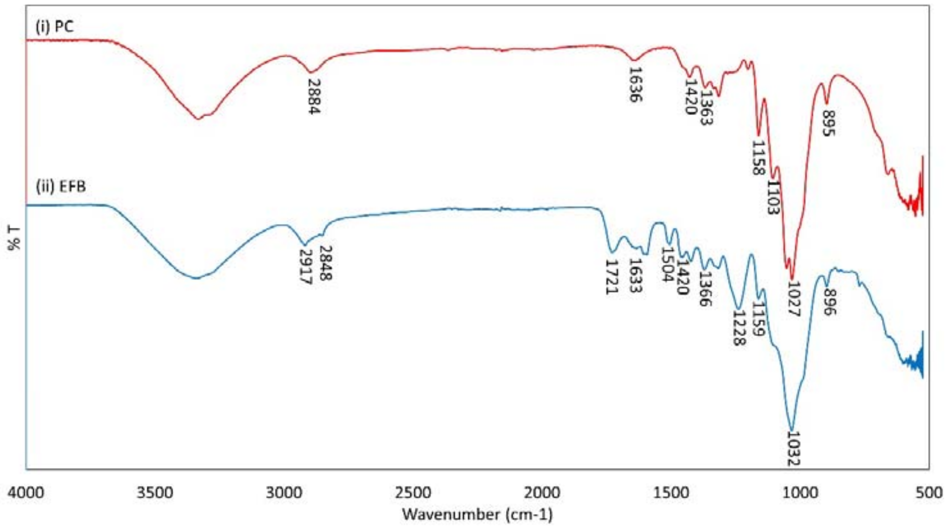

Figure 1: FTIR spectra of (i) PC and (ii) washed EFB

It was observed that the absorbance bands at 1228, 1504 and 1721 cm^{-1} on the EFB's spectra were no longer present after treatment (Table 1).

Table 1: Absorbance peaks and the corresponding functional groups of the EFB and PC

Spectra (cm^{-1})		Functional group
EFB	PC	
3046-3645	3052-3615	-OH stretching of cellulose molecules (Mo et. al., 2009)
2848-2917	2884	C-H stretching (Sain and Panthapulakkal, 2006)
1721	-	C=O stretching vibration of the acetyl and uronic ester groups from hemicellulose or the ester linkage of carboxylic group of ferulic and p-coumaric acids of lignin or hemicellulose. (Sain and Panthapulakkal, 2006; Sun et al., 2005)
1633	1636	-OH bending of the absorbed water (Mandal and Chakrabarty, 2011)
1504	-	aromatic C=C vibration from the aromatic ring of lignin (Sun et al., 2005)
1420	1418	C-H_2 bending (Jonoobi et al., 2009)
1366	1364	Bending vibration of C-H and C-O bonds in the polysaccharide aromatic rings. (Jonoobi et al., 2009)
1228	-	C-O-C (aryl-alkyl ether), which is commonly observed in ether, ester, and phenol groups are present (Xiao et. al, 2001)
1032	1027	Stretching vibration of C-O groups, asymmetric stretching vibrations of pyranose rings and bridge C-O-C bonds (Krassig HA, 1993)
896	895	Glycosidic C-H deformation, with a ring vibration contribution and -OH bending (Elanthikkal et. al., 2010; Fortunati E, 2013)

The disappearance of these peaks strongly indicated the success of removal of hemicellulose and lignin through $NaClO_2$ delignification and NaOH alkali treatment, respectively, as these peaks are corresponding to the functional groups of hemicellulose and lignin.

NCC was obtained from PC after acid hydrolysis. The dimension of NCC was estimated using ImageJ software (Figure 2), which showed that NCC has a rod-like structure with 15 – 25 nm in width and 200 – 500 nm in length; while particle size distribution obtained from DLS shows 97.5 % of particles fall within nano dimensions (up to 400 nm), as showed in Figure 3. Noting that, DLS is an ideal tool for the measurement of spherical particles' hydrodynamic diameter. However, for non-spherical particles like NCC, DLS could only provide an estimation of the equivalent hydrodynamic diameter, thus suggesting a slightly deviate length and width. Nevertheless, the broadness of the particles size distribution and the presence of large particles species can still be observed through the distribution stats, albeit the limitation of particle shapes. Due to its high sensitivity to detect particles aggregation, agglomeration, and large particles, a broad distribution over nano-range implies a relatively high yield of NCC.

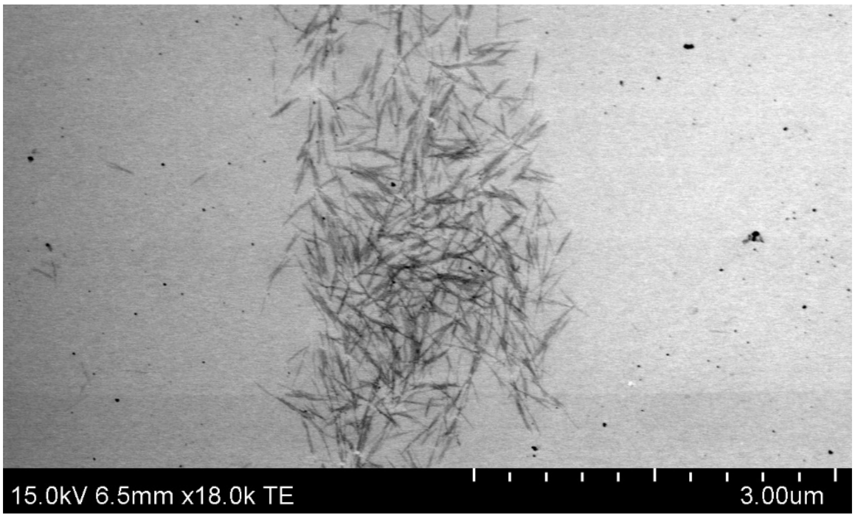

Figure 2: FE-SEM micrographs of NCC extracted from EFB at 3 µm scale.

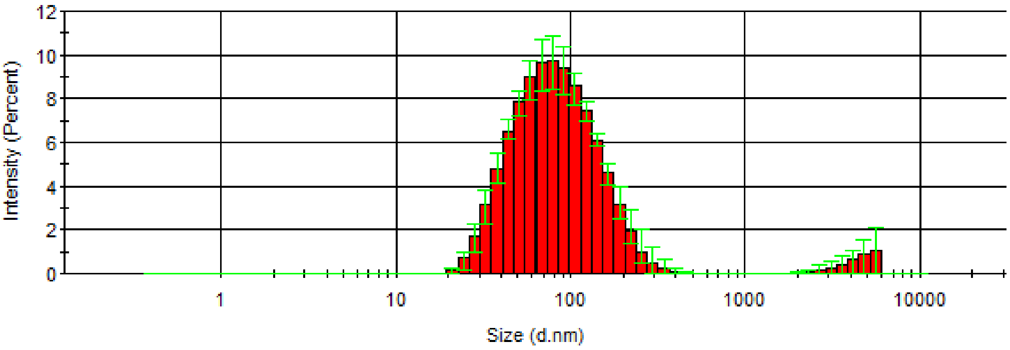

Figure 3: Particle size distribution of NCC obtained from DLS measurements

The zeta potential of the NCC was examined to predict suspension colloidal stability. Generally, particles having a zeta potential larger than positive or negative 30 mV is suggested to contribute a stable suspension (Hunter, 2013). In this study, the mean zeta potential was obtained at a value of – 48.7 mV, suggesting the resulted NCC could be a very good candidate to stabilize colloid in aqueous media. We have postulated that the high negative zeta potential was attributed to the negatively charged sulfate groups introduced to NCC during acid hydrolysis (van den Berg O et. al., 2007; I. A. Sacui et. al., 2014). Subsequently, it is speculated that the NCC extracted from EFB would disperse and remain stable in Pickering emulsion. It is believed that the dimension of the NCC can be further reduced (Börjesson and Westman, 2015), as well as a lower polydispersity, which is desirable for better control over its applications.

4. Conclusions

In this work, NCC was extracted from oil palm EFB in two steps. In the first step, the delignification and alkali treatment were successfully conducted to obtain PC from EFB. This was confirmed through the analysis of FTIR, from the disappearance of absorbance bands at 1228, 1504 and 1721 cm^{-1} on PC's FTIR spectra. In the second step, acid hydrolysis is proceeded by employing sulfuric acid as hydrolysis agent to obtain NCC. The FE-SEM micrograph shows the extracted NCC exhibits a rod-like structure, with size ranged from 15–25 nm and 200–500 nm, for particle width and length, respectively, as confirmed by ImageJ software. The measurement was supported by DLS analysis. A high zeta potential of -48.7 mV was recorded for the receiving NCC, postulating the extracted NCC would be an ideal candidate for the future Pickering emulsion study. Properties such as crystallinity, wettability, and morphology will be further studied to understand their role in the later formation of NCC-stabilized emulsion.

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Reference

Andresen M. and Stenius P., 2007, Water-in-oil Emulsions Stabilized by Hydrophobized Microfibrillated Cellulose, Journal of dispersion science and technology 28, 837-944.

Beck-Candanedo S., Roman M. and Gray D.G., 2005, Effect of reaction conditions on the properties and behavior of wood cellulose nanocrystal suspensions. Biomacromolecules 6, 1048-1054.

Börjesson M. and Westman G., 2015, Crystalline Nanocellulose - Preparation, Modification, and Properties. In Cellulose-Fundamental Aspects and Current Trends. InTech, Croatia, EU.

Capron I. and Cathala B., 2013, Surfactant-free high internal phase emulsion stabilized by cellulose nanocrystals, Biomacromolecules 14, 291-296.

Fortunati E., Puglia D., Monti M., Peponi L., Santulli C., Kenny J.M., Torre L., 2013, Extraction of cellulose nanocrystals from Phormium tenax fibres, J Polym. Environ. 21, 319-328.

French D.J., Taylor P., Fowler J. and Clegg P.S., 2015, Making and breaking bridges in a Pickering emulsion, J. Colloid Interface Sci. 441, 30-38.

Habibi Y., Lucia L.A. and Rojas O.J., 2010, Cellulose nanocrystals: chemistry, self-assembly, and applications, Chem. Rev. 110, 3479-3500.

Hunter R.J., 2013, Zeta potential in colloid science: principles and applications, vol. 2, Academic press, London, UK.

Jonoobi M., Harun J., Mishra M. and Oksman K., 2009, Chemical composition, crystallinity and thermal degradation of bleached and unbleached kenaf bast (Hibiscus cannabinus) pulp and nanofiber, BioResources 4, 626-639.

Kalashnikova I., Bizot H., Bertoncini P., Cathala B. and Capron I., 2013, Cellulosic nanorods of various aspect ratios for oil in water Pickering emulsions, Soft Matter 9, 952-959.

Kargarzadeh H., Ahmad I., Abdullah I., Dufresne A., Zainudin S.Y. and Sheltami R.M., 2012, Effect of hydrolysis conditions on the morphology, crystallinity, and thermal stability of cellulose nanocrystals extracted from kenaf bast fibers, Cellulose 19, 855-866.

Krassig H.A., 1993, Cellulose: structure, accessibility and reactivity. Gordon and Breach Science Publishers, Philadelphia PA, USA.

Lam S., Velikov K.P. and Velev O.D., 2014, Pickering stabilization of foams and emulsions with particles of biological origin, Curr. Opin. Colloid Interface Sci. 19, 490-500.

Lorenzo Z., Destro M., Curtil D., Chaussy D., Penazzi N., Beneventi D., Gerbaldi C., 2014, Flexible Cellulose-Based Electrodes: Towards Eco-friendly All-paper Batteries, Chemical Engineering Transactions 41, 361-366.

Lu P. and Hsieh Y.L., 2010, Preparation and properties of cellulose nanocrystals: rods, spheres, and network, Carbohydr. Polym. 82, 329-336.

Mandal A. and Chakrabarty D., 2011, Isolation of nanocellulose from waste sugarcane bagasse (SCB) and its characterization, Carbohydr. Polym. 86, 1291-1299.

Mo Z.L., Zhao Z.L., Chen H., Niu G.P. and Shi H.F., 2009, Heterogeneous preparation of cellulose-polyaniline conductive composites with cellulose activated by acids and its electrical properties. Carbohydr. Polym. 75, 660-664.

Payen, 1839, Relatif à la composition de la matière ligneuse, Comptes rendus, 8, 51-53.

Pickering S.U.J., 1907, Emulsions, Chem. Soc. 91, 2001-2021.

Ramsden W., 1903, separation of solids in the surface-layers of solutions and 'suspensions' (Observations on surface-membranes, bubbles, emulsions, and mechanical coagulation), Proceedings of the Royal Society of London 72, 156–164.

Revol J.F., Bradford H., Giasson J., Marchessault R.H. and Gray D.G., 1992, Helicoidal self-ordering of cellulose microfibrils in aqueous suspension, Int. J. Biol. Macromolec. 14, 170-172.

Rinaldi R. and Schüth F., 2009, Acid hydrolysis of cellulose as the entry point into biorefinery schemes, ChemSusChem 2, 1096-1107.

Rusli R. and Eichhorn S.J., 2008, Determination of the stiffness of cellulose nanowhiskers and the fiber-matrix interface in a nanocomposite using Raman spectroscopy, Applied Physics Letters 93.

Sacui I.A., Nieuwendaal R.C., Burnett D.J., Stranick S.J., Jorfi M., Weder C., Foster E.J., Olsson R.T. and Gilman J.W., 2014, Comparison of the properties of cellulose nanocrystals and cellulose nanofibrils isolated from bacteria, tunicate, and wood processed using acid, enzymatic, mechanical, and oxidative methods, ACS Appl. Mater. & Interfaces 6, 6127-6138.

Saidane D., Perrin E., Cherhal F., Guellec F. and Capron I., 2016, Some modification of cellulose nanocrystals for functional Pickering emulsions, Phil. Trans. R. Soc. A. 374, DOI: 10.1098/rsta.2015.0139

Sain M. and Panthapulakkal S., 2006, Bioprocess preparation of wheat straw fibers and their characterization. Ind. Crops Prod. 23, 1-8.

Shanmugarajah B., Kiew P.L., Chew I.M.L., Choong T.S.Y. and Tan K.W., 2015, Isolation of nanocrystalline cellulose (NCC) from palm oil empty fruit bunch (EFB): Preliminary result on FTIR and DLS analysis, Chemical Engineering Transactions 45, 1705-1710.

Sharma T., Kumar G.S., Chon B.H. and Sangwai J.S., 2015, Thermal stability of oil-in-water Pickering emulsion in the presence of nanoparticle, surfactant, and polymer, Ind. Eng. Chem. Res. 22, 324-334.

Šturcová A., Davies G.R. and Eichhorn S.J., 2005, Elastic modulus and stress-transfer properties of tunicate cellulose whiskers, Biomacromolecules 6, 1055-061.

Sun R.C., Tomkinson J., Wang Y.X. and Xiao B., 2000, Physico-chemical and structural characterization of hemicelluloses from wheat straw by alkaline peroxide extraction, Polymer 41, 2647-2656.

Van den Berg, O., Capadona J.R. and Weder C., 2007, Preparation of homogeneous dispersions of tunicate cellulose whiskers in organic solvents, Biomacromolecules 8, 1353-1357.

Xiao, B., Sun, X. and Sun, R., 2001, Chemical, structural, and thermal characterizations of alkali-soluble lignins and hemicelluloses, and cellulose from maize stems, rye straw, and rice straw, Polym. Degrad. Stabil., 74, 307-319.