UNIVERSITI PUTRA MALAYSIA

SUPERHEATED STEAM PRETREATMENT OF OIL PALM BIOMASS FOR IMPROVING NANOFIBRILLATION OF CELLULOSE AND PERFORMANCE OF POLYPROPYLENE/CELLULOSE NANOFIBER COMPOSITES

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FBSB 2018 33

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By

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Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfilment of the Requirements for the Degree of Doctor of Philosophy

August 2018

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirement for the degree of Doctor of Philosophy

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August 2018

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Cellulose isolation from lignocellulosic materials is a crucial step prior to cellulose nanofiber (CNF) production. Previous studies exhibited that the presence of some amount of hemicellulose would give advantage in the nanofibrillation of cellulose. Superheated steam (SHS) pretreatment has been portrayed as a green approach to partially remove the hemicellulose from lignocellulosic materials. In this research, SHS was used to pretreat three types of oil palm biomass (OPB): oil palm mesocarp fiber (OPMF), oil palm empty fruit bunch (OPEFB) and oil palm frond (OPF). Potassium hydroxide (KOH) pretreatment was used as control experiment. Two processing methods for CNF production were used *i.e.* wet disk milling (WDM) and electrospinning. CNF obtained was characterised and later, CNF-reinforced polypropylene (PP) biocomposites were prepared using melt-blending method. SHS pretreatment caused partial removal of hemicellulose, producing cellulose with residual hemicellulose of 9 – 14 wt%. This residual hemicellulose assisted in the formation of smaller diameter size CNF from both of the processing methods; compared to the CNF from KOH-pretreated OPB. This can be explained by the role of hemicellulose which facilitated fiber beating and avoided the coalescence of cellulose fibrils. Overall observation showed that WDM managed to produce smaller diameter CNF (20-100 nm) compared to electrospinning (100-150nm). The influence of residual hemicellulose in CNF on PP/CNF biocomposites was evaluated. Several PP:CNF ratio were tested, ranging between 100:0 – 95:5 (wt/wt), with the addition of 3wt% of MA-g-PP as compatibiliser. It was found that 3wt% CNF gave the best improvement in term of mechanical properties, in which tensile and flexural strengths were increased by ~31% and ~28%, respectively, compared to the neat PP. It was interesting to note that PP/SHS-pretreated CNF and PP/KOH-pretreated CNF had almost similar performances; showing that residual hemicellulose left in the CNF did not influence the performance of the PP/CNF biocomposites produced. This finding suggests that complete hemicellulose removal is unnecessary for preparing CNF to be used in biocomposites making; and hence a less harsh pretreatment step is sufficient. In the preparation of nanofiber-plastics compound such as PP/CNF for biocomposites

production, the conventional method would involve two separate unit operations for nanofibrillation and melt-compounding, respectively. The ability to combine these two steps in one-pot would add value to the whole process, considering the instability of CNF which is easily agglomerated, and the low productivity due to the downtime in between the two-unit operations. In this research, nanofibrillation of cellulose and melt-compounding of PP and the CNF produced were conducted in an extruder with specially-designed screw for nanofibrillation. Results showed that PP/CNF biocomposites produced through this approach had almost similar performances as PP/CNF biocomposites produced by the conventional method. This finding contributes greatly to PP-based biocomposites processing, since this indicates that the overall biocomposites making could be shortened due to the absence of downtime between the two processes (nanofibrillation and melt-compounding). Overall, the findings from this study are beneficial for cellulose-based nanomaterials research and industries; since the results contributed to an effective, simpler, easier and shorter duration process for CNF and nanofiber-plastics compounding.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk Ijazah Doktor Falsafah

SISA BIOJISIM KELAPA SAWIT TERAWAT DENGAN STIM PANAS LAMPAU UNTUK MENAMBAH BAIK NANOFIBRILLASI SELULOSA DAN PRESTASI KOMPOSIT POLIPROPILENA/NANOFIBER SELULOSA

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Pengasingan selulosa daripada bahan lignoselulosa adalah langkah penting untuk penghasilan CNF. Kajian sebelum ini menunjukkan kehadiran sejumlah kecil hemiselulosa mampu memberi kebaikan kepada nanofibrilasi selulosa. Rawatan stim panas lampau (SHS) telah terbukti sebagai kaedah rawatan secara hijau untuk menyingkirkan sebahagian hemiselulosa daripada bahan lignoselulosa. Di dalam kajian ini, SHS telah digunakan untuk merawat tiga jenis sisa biomas kelapa sawit (OPB): serat mesokarp kelapa sawit (OPMF), tandan kosong kelapa sawit (OPEFB) dan pelepah kelapa sawit (OPF). Rawatan kalium hidroksida (KOH) digunakan sebagai eksperimen kawalan. Dua kaedah penghasilan CNF telah digunakan iaitu penspinan elektro dan pengilingan cakera basah (WDM). CNF yang dihasilkan telah dinilai serta digunakan untuk penghasilan biokomposit CNF-diperkuatkan polipropilena (PP) dengan menggunakan kaedah campuran-lebur. Rawatan SHS telah menyingkirkan hemiselulosa secara separa, dengan menghasilkan selulosa dan hemiselulosa berbaki sebanyak 9 – 14 % berat. Baki hemiselulosa membantu dalam penghasilan CNF bersaiz yang lebih kecil untuk kedua-dua kaedah pemprosesan, jika dibandingkan dengan CNF daripada OPB terawat KOH. Ini boleh dijelaskan dengan fungsi hemiselulosa yang membantu untuk lonjakan fiber dan menghalang perlekatan semula fibril selulosa. Secara keseluruhanya, WDM menghasilkan CNF yang berdiameter lebih kecil (20-100 nm) jika dibandingkan dengan penspinan elektro (100-150 nm). Kesan terhadap baki hemiselulosa pada CNF dalam PP/CNF biokomposit telah dinilai. Beberapa nisbah untuk PP:CNF telah diuji dalam lingkungan 100:0 – 95:5 (berat/berat), dengan tambahan 3% berat MA-g-PP sebagai bahan serasi. Hasil menunjukkan bahawa 3% berat CNF memberikan kadar penambahbaikan yang terbaik untuk sifat mekanikal dengan peningkatan kadar kekuatan tegangan dan fleksur masing-masing sebanyak ~31% dan ~28%, jika dibandingkan dengan PP. Menariknya, PP/CNF terawat SHS dan KOH mempunyai prestasi yang sama; menunjukkan bahawa kehadiran sejumlah kecil hemiselulosa pada CNF tidak mempengaruhi prestasi biokomposit PP/CNF. Penemuan ini mencadangkan bahawa rawatan pengasingan hemiselulosa sepenuhnya adalah tidak diperlukan untuk penghasilan CNF untuk digunakan di dalam biokomposit; oleh itu, rawatan yang kurang menggunakan bahan kimia boleh digunakan. Dalam penghasilan bahan campuran nanofiber-plastik seperti PP/CNF biokomposit secara konvesional melibatkan dua jenis unit operasi iaitu nanofibrilasi dan campuran-lebur. Kebolehan untuk menggabungkan dua proses ini di dalam satu-pot akan menyumbangkan kebaikan kepada keseluruhan proses, dengan mengambil kira ketidakstabilan CNF yang mudah beraglomerasi dan produktiviti yang rendah disebabkan oleh tambahan masa peralihan di antara dua unit operasi. Dalam kajian ini, nanofibrilasi selulosa dan campuran-lebur di antara PP dan CNF dihasilkan dengan menggunakan extrusi dengan skru yang direka khas untuk nanofibrilasi. Keputusan telah mendapati bahawa PP/CNF biokomposit yang dihasilkan secara kaedah ini mempunyai prestasi yang sama dengan komposit yang dihasilkan secara kaedah konvensional. Penemuan ini telah menyumbang kebaikan kepada pemprosesan biokomposit berasaskan PP, dimana ia membuktikan bahawa keseluruhan proses penghasilan biokomposit boleh dipercepatkan dengan menyingkirkan masa peralihan di antara dua proses (nanofibrilasi dan campuran lebur). Secara keseluruhannya, penemuan di dalam kajian ini memberi kebaikan kepada industri dan kajian nanomaterial berasaskan selulosa. Kajian ini telah menyumbang kepada proses penghasilan biokomposit dan nanofiber yang efektif, ringkas, mudah dan pantas.

ACKNOWLEDGEMENTS

First and foremost, I would like to say Alhamdulillah and thank my Lord, Allah S.WT. for His mercy and guidance for which I have completed my research. Many people have contributed in their own way in the progress of my research study.

Firstly, I would like to express my utmost gratitude to my supervisor, Associate Prof. Dr Hidayah Ariffin, for her kind support, patience, motivation, enthusiasm, enlightening lectures, and for many valuable discussions. I also would like to express my deepest gratitude to my co-supervisors Prof. Dr. Mohd Ali Hassan, Prof. Emeritus Dato' Dr. Wan Md. Zin, Associate Prof. Dr. Nor Azowa Ibrahim, and Associate Prof. Dr. Janet Lim Hong Ngee for their detailed and constructive comments, guidance, suggestion and unconditional support that greatly eased my progress throughout this study.

I also would like to express my greatest gratitude to my father, Norrrahim Ibrahim and other family members for their love, prayer, and moral support. They prevented me from feeling lost and give up during my study and helped me by giving me unconditional supports.

My condensed thanks go to Prof. Dr. Yoshito Shirai, Prof. Haruo Nishida, and Associate Prof. Yoshito Ando, from Kyushu Institute of Technology, Japan for their kind help, and supports, during my study.

I also wish to extend my sincere gratitude to all my friends, Mohd Fadli Kharian, Mohd Shahlizar Rosli, and others who helped and gave me support, guidance, helpful suggestions as well as proof-read my publications and thesis.

This list is far from exhaustive, I pray for forgiveness from those I did not mention by name and include then in my heart-felt gratitude.

I certify that a Thesis Examination Committee has met on 9 August 2018 to conduct the final examination of Mohd Nor Faiz b. Norrahim on his Doctor of Philosophy thesis entitled "Superheated Steam Pretreatment of Oil Palm Biomass for Improving Nanofibrillation of Cellulose and Polypropylene/cellulose Nanofiber Composites Performances" in accordance with the Universities and University Colleges Act 1971 and the Constitution of the Universiti Putra Malaysia [P.U.(A) 106] 15 March 1998. The committee recommends that the student be awarded the Doctor of Philosophy.

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LIST OF ABBREVIATIONS

BNC	Bacterial nanocellulose
CNC	Cellulose nanocrystal
CNF	Cellulose nanofiber
DMF	di-methyl formamide
FE-SEM	Field emission- scanning electron microscopy
FTIR	Fourier transform infrared spectrometry
GPa	Giga pascal
kJ	kilo joule
KOH	Potassium hydroxide
kV	Kilo volt
kW	Kilo watt
MA-g-PP	Maleic anhydride grafted PP
MAH	Maleic anhydride
MFC	Microfibrillated cellulose
MPa	Mega pascal
$NaClO_2$	Sodium chlorite
NaOH	Sodium hydroxide
nm	Nanometer
OPB	Oil palm biomass
OPEFB	Oil palm empty fruit bunches
OPF	Oil palm fronds
OPMF	Oil palm mesocarp fiber
p.p.m	Part per million
PEO	Polyethylene oxide
PET	Polyethylene terepthalate
phr	Part per hundred
PLA	Polylactic acid
PP	Polypropylene
PU	Polyurethane
RPM	Rotation per minute
RSM	Response surface methodology
SEM	Scanning electron microscopy
SHS	Superheated steam
T_c	Crystallization temperature
TCD	Tip to collector distance
T_d	Degradation temperature
TG	Thermogravimetry
TGA	Thermogravimetry analyser
$\mathrm{T_m}$	Melting tempearature
WDM	Wet disk milling
XRD	X-ray powder diffraction
ΔH_m	Melting enthalpy

CHAPTER 1

INTRODUCTION

1.1 Research overview

Malaysia is one of the top producers of palm oil in the world with a total oil palm plantation area of 5.39 million hectares (Awalludin *et al*., 2015). It is estimated that 80 million dry tons of solid oil palm biomass (OPB) residues are produced during the palm oil extraction process which comprises of 54% of empty fruit bunch (OPEFB), 30% of shell and 18% of mesocarp fiber (OPMF) (Warid *et al*., 2016; Chiew and Shimada, 2013). This value is expected to rise exponentially by the year 2020 as the palm oil industry keeps expanding. Malaysian government has launched many initiatives to capitalise biomass potential to demonstrate its commitment towards reducing global warming and climate change effects (The Sun Daily,2016).

In recent years, there are raising concerns by the public in creating environmental sustainability of the industry through utilisation of biomass. Various OPB such as OPMF, OPEFB and oil palm fronds (OPF) are suitable candidates for development of bio-based products such as biocomposites, biofuels, biosugars and particularly nanocellulose (Fahma *et al*., 2011; Nordin *et al*., 2013; Wu *et al*., 2017). According to Chen et al. (2011), nanocellulose is a fiber with a dimension of 100 nanometer (nm) or less with extremely high specific area and high porosity with excellent pore interconnectivity. Nanocellulose can be classified into cellulose nanofiber (CNF), cellulose nanocrystals (CNC) and bacterial nanocellulose (BNC). Nanocellulose has been listed as focused nanomaterial in the 11th Malaysia Plan under strategic research. It can be used for several applications such as plastic production, packaging, biocomposites, food, cosmetics, and healthcare.

There have been several reports on CNF production from OPB (Yahya *et al*., 2015; Syamsu, 2016; Yasim-Anuar *et al*., 2017), indicating its suitability as starting material. Prior to CNF production, pretreatment process is needed to isolate cellulose from OPB since OPB contains other components such as lignin, hemicellulose and extractives. Selection of pretreatment process may influence the characteristics of the CNF produced. For instance, it has been reported that wood powder pretreated with sodium chlorite ($NaClO_2$) for delignification resulted in holocellulose pulp, in which hemicellulose in the sample was found to facilitate nanofibrillation. This gave smaller diameter CNF as compared to cellulose pulp which has undergone pretreatment *i.e.* delignification and complete hemicellulose removal by potassium hydroxide (Iwamoto *et al*., 2008). According to the Iwamoto et al. (2008), this observation was due to the presence of hemicellulose inhibiting coalescence of microfibrils. This is supported by a report by Duchesne et al. (2001), where degree of hornification can be correlated with hemicellulose content of pulp.

Superheated steam (SHS) is considered as a promising pretreatment method for fiber due to its ability in removing hemicellulose (Nordin *et al.*, 2013; Zakaria *et al.*, 2014; Warid *et al.*, 2016). It is a green fiber pretreatment method since it does not involve harsh chemicals and is conducted at atmospheric pressure (Nordin *et al.*, 2013). Another advantage of using SHS is that it removes hemicellulose partially, since small amount of recalcitrant hemicellulose usually remains in the sample after SHS pretreatment. This could be an advantage for cellulose nanofiber production as it may assist in nanofibrillation of the nanocellulose. To clarify this, the effect of SHS pretreatment on nanofibrillation of CNF from OPB was studied in this research, using two methods for nanofiber production which are electrospinning and wet disk milling (WDM).

CNF has been widely studied as reinforcement material in biocomposites. Polyolefins such as polypropylene (PP) is the commonly used polymer matrix in biocomposites, due to its low density, low production cost, and design flexibility. There are several factors which may affect the production of PP/CNF biocomposites such as blending technique, the form of CNF used and the amount of CNF loaded during blending. Twin screw extrusion has been extensively used as a method for melt-blending for biocomposites production (Ho *et al.*, 2015). Nevertheless, in the case of nanofiber, reports have shown that too much of CNF used during melt-blending has led to agglomeration which eventually affected the mechanical properties of the biocomposites produced (Lani *et al.*, 2014). It is therefore the effect of cellulose concentration (wt %) was clarified in this study.

On the other hand, Oksman and colleagues (2014) and Nishida et al. (2017) have demonstrated that wood fibers can be directly fibrillated into nanofiber using a twin-screw extruder, proving the feasibility of having CNF formation and melt-compounding in one-pot. In this study, SHS-pretreated OPB which contained hemicellulose was used as starting material; and a specially-designed twin-screw extruder was used to fibrillate the pretreated fibers into CNF, and subsequently compounded with PP in the same extruder. Effects of hemicellulose on nanofibrillation during this process and the resultant biocomposites were studied.

1.2 Problem statements

Pretreatment is required to isolate cellulose from OPB prior to CNF production. It was shown that types of pretreatment methods may influence the hemicellulose content which eventually affected the characteristics of the CNF produced. Current pretreatment method using chemical is not only removing the hemicellulose completely, but also causing environmental issue. SHS has been shown to be a better alternative to chemical pretreatment (Nordin *et al.*, 2013) and at the same time is advantageous in partially removing hemicellulose from OPB. Since hemicellulose may contribute to better nanofibrillation, SHS was postulated to be a better pretreatment method for CNF production as compared to chemical pretreatment. In this study, the optimised parameters of SHS pretreatment was used to pretreat the OPB fibers. Two processing methods for CNF production were used *i.e.* by using WDM and electrospinning. WDM is chosen due to its advantages; no chemical usage, high efficiency and low cost. For electrospinning, the effect of hemicellulose in the fiber to the parameters such as cellulose solution viscosity and surface tension was unknown, and it is imperative that the effects be studied to further improve the method for use with lignocellulosic biomass.

Characteristics of biocomposites can be affected by the composition and the properties of the reinforcement material. The form of CNF used and the amount of CNF loaded during blending may also affect the properties of the biocomposites. Furthermore, the effect of hemicellulose on the biocomposites properties needs to be clarified to mitigate any negative effect it has to the biocomposites.

Combined nanofibrillation and melt-compounding processes in twin screw extruder would be beneficial in reducing the time taken to prepare biocomposites, and subsequently increase the productivity. The use of wood powder and cellulose pulp as starting material in this process have been tested (Oksman *et al*., 2014; Nishida *et al*., 2017). While, the use of holocellulose pulp (cellulose + hemicellulose) is still lacking. Since, the presence of hemicellulose was found advantageous in wet nanofibrillation, it is important to see whether the same situation applied in thermal nanofibrillation (*i.e.* in twin-screw extruder). For this process, the role of hemicellulose needs to be clarified, and subsequently its effect on the biocomposites produced.

1.3 Objectives

The overall objective of this study was to determine the influence of superheated steam pretreatment on the CNF formation and the characteristics of the biocomposites reinforced with the produced CNF.

The specific objectives of this research were:

1. To characterise the oil palm biomass cellulose isolated using optimised parameters of superheated steam and chemical pretreatments.
2. To evaluate the effect of superheated steam pretreatment on cellulose nanofiber formation via electrospinning and wet disk milling.
3. To investigate the effect of superheated steam-pretreated cellulose nanofiber on the performance of polypropylene / cellulose nanofiber biocomposites.
4. To determine the effect of residual hemicellulose on one-pot nanofibrillation and melt-compounding in twin-screw extruder.

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