Preparation and Characterization of Natural *Citrus aurantifolia* Crosslinked Tapioca Starch/Nanocellulose Biocomposites

by

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LIST OF ABBREVIATIONS

ASTM	American Society for Testing and Materials
CA	Citric acid
DCMC	Dialdehyde carboxymethyl cellulose
DDE	Degree of di-esterification
DMSO	Dimethyl sulfoxide
DS	Degree of substitution
DSC	Differential scanning calorimetry
FTIR	Fourier transform infrared spectroscopy
LDPE	Low-density polyethylene
LJ	Lime juice
MA	Moisture absorption
MC	Microcellulose
NC	Nanocellulose
OPEFB	Oil palm empty fruit bunch
PA	Polyamide
PE	Polyethylene
PET	Polyethylene terephthalate
PHA	Polyhydroxyalkanoate
phs	Part per hundred starch
PLA	Polylactic acid
PP	Polypropylene
pph	Part per hundred
PS	Polystyrene
PVC	Polyvinylchloride
RH	Relative humidity
rpm	Revolutions per minute
SA	Succinic acid
SEM	Scanning electron microscopy
SPI	Soy protein isolate
TEM	Transmission electron microscopy
TGA	Thermogravimetry analysis
TS	Tapioca starch
UV-vis	Ultraviolet-visible

WS	Water solubility
WVP	Water vapor permeability
WVT	Water vapor transmission
XRD	X-ray diffraction

LIST OF SYMBOLS

A_{600}	Absorbance value at 600 nm
a*	Chromaticity parameters (red-green)
b*	Chromaticity parameters (yellow-blue)
I_{002}	Crystallinity index for crystalline and amorphous region
I_{am}	Crystallinity index for amorphous region only
I_{cr}	Crystallinity index
L*	Luminosity
MW	Molecular weight of ester group
M_{AGU}	Molar mass of one anhydroglucose unit
M_{CA}	Molar mass of citric acid
m_{CA}	Amount of citric acid added into starch film
m_{TS}	Amount of tapioca starch in film
N_a	Normality of H_2SO_4 solution
Q	Swelling ratio
$R1$	Relative humidity in the humidity chamber
$R2$	Relative humidity in the glass test cup
S	Saturation vapor pressure
T value	Transparency value
T_5	Initial weight loss of about 5% temperature
$T_{DTGpeak}$	Degradation temperature
T_{eva}	Evaporation temperature
T_m	Melting temperature
T_{on}	Initial (onset) degradation temperature
V_1	Molar volume of solvent
V_2	Volume fraction of specimen in swollen network at equilibrium
V_a	Volume of H_2SO_4 solution used (for crosslinked film)
V_{blank}	Volume of H_2SO_4 solution used (for non-crosslinked film)
W_f	Final weight of the specimen
W_i	Initial weight of the specimen
W_s	Weight of specimen
W_t	Weight of specimen at any given time, t
$w_{diester}$	Weight fraction of citric acid taking part in a di-ester linkage
(W/t)	Rate of change of weight
X	Thickness of the film

$\%Transmittance$	Transmittance value in percentage
ε	Crosslinked density
ρ	Density
ρ_1	Density of specimen
ρ_2	Density of solvent
χ	Flory-Huggins TS-solvent interaction parameter

LIST OF NOMENCLATURE

CH_3COOH	Acetic acid glacial
C_2H_6O	Ethanol
$C_3H_8O_3$	Glycerol
$C_6H_8O_7$	Citric acid
$C_8H_8N_6O_6$	Murexide
$C_{20}H_{14}O_4$	Phenolphthalein
$CuSO_4$	Copper (II) sulfate
H_2SO_4	Sulphuric acid
KBr	Potassium bromide
KOH	Potassium hydroxide
K_2SO_4	Potassium sulfate
$NaBr$	Sodium bromide
$NaCl$	Sodium chloride
$NaClO_2$	Sodium chlorite
$NaHSO_4$	Sodium hydrogen sulfate
$NaOH$	Sodium hydroxide
$Na_2B_4O_7 \cdot 10H_2O$	Sodium tetraborate decahydrate

Penyediaan dan Pencirian Biokomposit Kanji Ubi Kayu/Nanoselulosa Berangkai Silang dengan *Citrus aurantifolia* Semula Jadi

ABSTRAK

Saput biokomposit berasaskan kanji dalam aplikasi pembungkusan makanan telah menarik perhatian umum disebabkan kombinasi menarik sifat-sifatnya seperti kos rendah, mesra alam dan mudah didapati. Walau bagaimanapun, penggunaan saput biokomposit berasaskan kanji dalam aplikasi perindustrian dihadkan oleh sifat tegangan yang lemah, rintangan terhadap air yang lemah serta sifat sukar dikawal yang semulajadi. Tujuan kajian ini adalah untuk menghasilkan saput biokomposit berasaskan kanji berangkai silang serta mengkaji kesan nanoselulosa (NC) dan ejen rangkai silang terhadap ciri-ciri tegangan, fizikal, rintangan air, terma serta biodegradasi saput kanji ubi kayu (TS). NC telah diekstrak daripada tandan kosong kelapa sawit (OPEFB) melalui hidrolisis asid. Analisis dari spektroskopi inframerah jelmaan Fourier pada NC mengesahkan rawatan kimia dan hidrolisis asid menyingkirkan unsur-unsur bukan selulosa seperti hemiselulosa dan lignin daripada OPEFB. Difraktogram sinar-X mendedahkan peningkatan kehabluran NC dari 43.1 % bagi OPEFB mentah ke 65.8 %. Imej mikroskop elektron transmisi mengesahkan diameter NC adalah bersaiz nano dengan struktur menyerupai jarum. Biokomposit TS/NC dengan gliserol sebagai pemplastik disediakan menggunakan kaedah tuangan larutan dengan mempelbagaikan jumlah NC. Ejen rangkai silang, iaitu *Citrus aurantifolia*, juga dikenali sebagai jus limau (LJ), diperkenalkan untuk merangkai silang TS. Pada masa yang sama, asid sitrik komersial (CA) digunakan sebagai ejen rangkai silang bagi tujuan perbandingan. Rangkai silang diantara TS dan LJ melalui pengesteran telah disahkan melalui keputusan dari spektroskopi inframerah jelmaan Fourier, darjah penggantian dan darjah di-pengesteran. Sepuluh bahagian per seratus kanji (bsk) LJ meningkatkan kebolehlenturan biokomposit TS seperti yang ditunjukkan menerusi pemanjangan putusannya yang sebanyak 106 % adalah tertinggi, manakala NC (1 bsk) meningkatkan kekuatan tegangan dengan nilai tertinggi sebanyak 13.5 MPa. Ejen rangkai silang tidak menjejaskan sifat optik biokomposit TS tetapi penambahan NC mengurangkan kelutsinarannya. Saput biokomposit TS dengan kedua-dua LJ dan NC mempunyai kebolehtelapan wap air (WVP) yang lebih rendah. WVP bagi saput TS yang berangkai silang-LJ dengan 1 bsk NC dikurangkan kira-kira 55 % berbanding dengan saput TS bersih. Kehabluran saput TS meningkat dari 43.5 % untuk TS bersih ke 51.6 % untuk saput TS dengan penambahan NC. Saput TS yang berangkai silang-LJ serta mengandungi 1 bsk NC memiliki penyerapan kelembapan dan nisbah pembengkakan yang paling rendah, ini menunjukkan peningkatan rintangan terhadap air oleh TS. Saput biokomposit TS dengan kedua-dua LJ dan NC juga mempunyai ciri-ciri terma dan biodegradasi yang lebih baik. Hasil kajian ini menunjukkan bahawa LJ boleh digunakan untuk merangkai silang kanji kerana keputusan-keputusan ujian yang diperoleh adalah standing dengan CA komersial. Peningkatan ciri-ciri seperti tegangan, rintangan terhadap air dan terma pada biokomposit TS berangkai silang-LJ membolehkannya digunakan sebagai pembungkus makanan terutamanya untuk makanan kering.

Preparation and Characterization of Natural *Citrus aurantifolia* Crosslinked Tapioca Starch/Nanocellulose Biocomposites

ABSTRACT

Starch-based biocomposite films have drawn considerable attention on food packaging due to their attractive combination of low price, environmental friendly, and abundance. Nevertheless, the use of starch-based biocomposite films in industrial application were restricted by its poor tensile properties, poor water resistance and naturally intractable behavior. The aims of this research work were to develop crosslinked starch-based biocomposite films and to investigate the effects of nanocellulose (NC) and crosslinking agent on tensile, physical, water resistance, thermal and biodegradation properties of tapioca starch (TS) biocomposite films. The NC was extracted from oil palm empty fruit bunch (OPEFB) via acid hydrolysis. Fourier transform infrared spectroscopy analysis on NC verified that the chemical treatments and acid hydrolysis removed non-cellulosic constituents including hemicelluloses and lignin from OPEFB. X-ray diffractograms revealed that the crystallinity of NC increased from 43.1% of raw OPEFB to 65.8%. Transmission electron microscope image confirmed the diameter of NC was in nano-sized with needle like structure. TS/NC biocomposites with glycerol as plasticizer were prepared using solution casting method by varying amounts of NC. Crosslinker, namely *Citrus aurantifolia*, also known as lime juice (LJ), was introduced for TS crosslinking. At the same time, commercial citric acid (CA) was used as crosslinker for comparison purposes. Crosslinking between TS and LJ through esterification were validated through the Fourier transform infrared spectroscopy, degree of substitution and degree of di-esterification results. Ten parts per hundred starch (phs) of LJ enhanced the flexibility of TS biocomposite as its break elongation of 106 % was the highest, while NC (1 phs) increased its tensile strength with the highest value of 13.5 MPa. Crosslinkers did not considerably affect the optical property of TS biocomposites but the addition of NC reduced its transparency. TS biocomposite films with both LJ and NC have lower water vapor permeability (WVP). The WVP of LJ-crosslinked TS film with 1 phs NC reduced about 55%, compared to neat TS film. The crystallinity of TS film increased from 43.5 % for neat TS to 51.6 % for TS film with addition of NC. LJ-crosslinked TS film with 1 phs of NC had the lowest moisture absorption and swelling ratio, indicating the improvement of water resistance of TS. TS biocomposites with both NC and LJ also had better thermal and biodegradation behavior. This outcome showed that LJ is usable in starch crosslinking as the results obtained were comparable to those of the commercial CA. The developed LJ-crosslinked TS biocomposites with enhanced tensile properties, water resistance and thermal properties could be used as food packaging, especially for dry food.

CHAPTER 1 : INTRODUCTION

1.1 Research background

Polymer composites have been employed worldwide for several years, yet their market share still grows continuously. It is widely known that the utilization of a polymer with one or more solid fillers have some advantages such as improvement of mechanical properties, thermal properties and reduction of cost of materials. The goals of designing composites are to combine the properties that is not displayed by individual material and to incorporate the best characteristics of the component materials (Zafar et al., 2016). Few instances among the solid fillers used are silica, graphite, carbon, etc.

However, the combination of two different materials leads to one of the restrictions of polymer composites that is the difficulty to reuse and recycle (La Mantia & Morreale, 2011). Hence, the preferred method to handle these polymer composites after being used is either direct disposal in a dump or incineration. Both methods is considered to be unsatisfactory due to the high cost, technical difficulties and environmental problems. In addition, it is worsened by the fact that most polymer composites used especially for food packaging are practically non-biodegradable. Petrochemical-based plastics such as polyethylene terephthalate (PET), polyvinylchloride (PVC), polyethylene (PE), polypropylene (PP), polystyrene (PS) and polyamide (PA) have been increasingly used as packaging materials because of their good mechanical performance such as tensile strength, good barrier to oxygen, carbon dioxide and heat seal ability (Siracusa, Rocculi, Romani, & Rosa, 2008).

The rising concerns towards environmental issues created by petroleum products and non-renewability of fossil resources have led researches to focus on new bio-based materials in order to develop biodegradable films as a big effort to extend shelf life, to improve quality of food and at the same time to reduce packaging waste (Azeredo, 2009; Dai, Zhang, & Cheng, 2019). Moreover, this century has witnessed remarkable green technology achievements in the field of materials science via the development of biocomposites because of the environment and sustainability issues.

According to Ivanič, Jochec-Mošková, Janigová, & Chodák (2017), starch is applied in a wide range of products, such as different applications of food, pharmaceutics, textiles and plastics from renewable resources especially biodegradable plastics. In food industry, the two major applications of the starch-based biocomposites are food packaging (Goudarzi, Shahabi-Ghahfarrokhi, & Babaei-Ghazvini, 2017; Liu et al., 2017; López-Córdoba, Medina-Jaramillo, Piñeros-Hernandez, & Goyanes, 2017; Moustafa, Youssef, Darwish, & Abou-Kandil, 2019; Salehudin, Salleh, Mamat, & Muhamad, 2014) and edible films (Basiak, Lenart, & Debeaufort, 2018; Mantovan, Bersaneti, Faria-Tischer, Celligoi, & Mali, 2018; Piñeros-Hernandez, Medina-Jaramillo, López-Córdoba, & Goyanes, 2017). This could be because of the products developed from starch are isotropic, odorless, tasteless, colorless, non-toxic, and biodegradable (Belibi et al., 2014; Prakash Maran, Sivakumar, Sridhar, & Prince Immanuel, 2013).

The properties of biocomposites are manipulated by a number of variables comprising the type of fiber, environmental aspects, and processing methods. Recently, there are an increasing interest in the industries for composites involving biofibers and biopolymers. The greatest challenge when dealing with biocomposites based on natural fibers is the variation in properties and characteristics of natural fibers. Nowadays, researches on using biodegradable starch as alternative material to replace or minimize the use of petrochemical-based plastic, particularly for food packaging, are being carried out. Piñeros-Hernandez et al. (2017) stated that about 39.6 % of total plastics are used for packaging application, which constitute the largest market share. In addition, production of green materials from bio-based substances is now very crucial due to issues of global warming and depletion of fossil fuel (Kengkhetkit & Amornsakchai, 2014).

Among the natural polymers, starch proved to be attractive due to its low price, wide availability, renewability and compostability without toxic residue (Nakthong, Wongsagonsup, & Amornsakchai, 2017; F. Xie, Pollet, Halley, & Avérous, 2013). Many researchers had reported the good quality of starch-based films from different crops, such as corn (Qin et al., 2016; Teacă, Bodîrlău, & Spiridon, 2013; K. Wang et al., 2017; Xu, Canisag, Mu, & Yang, 2015), potato (Ghosh Dastidar & Netravali, 2012), wheat (Goudarzi et al., 2017), rice (Colussi et al., 2015), cassava (Chuang, Panyoyai, Shanks, & Kasapis, 2017; López-Córdoba et al., 2017; Mei, Zhou, Jin, Xu, & Chen, 2015), etc.

Plasticizer such as glycerol are usually added to improve the processing of starch-based film by softening the polymer. Despite the interesting and promising potential uses of starch to replace conventional polymers such as low-density polyethylene (LDPE), the uses of starch-based materials are limited to some applications due to its natural intractability, brittleness, poor mechanical properties, poor water barrier properties and poor resistance to water (Al-Hassan & Norziah, 2012). According to Li et al. (2018a), the poor resistance to water can be attributed to the existence of numerous hydroxyl groups