

**THE EFFECT OF FILLER CONTENT AND
CHEMICAL MODIFICATIONS ON PROPERTIES OF
COCONUT SHELL REGENERATED CELLULOSE
BIOCOMPOSITE FILMS**

FARAH NORAIN BINTI HAHARY

UNIVERSITI MALAYSIA PERLIS

2016

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OF COCONUT SHELL REGENERATED
CELLULOSE BIOCOMPOSITE FILMS**

by

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LIST OF ABBREVIATIONS

AA	Acetic acid
ACCs	All-cellulose composites
BMA	Butyl methacrylate
Ca(OH) ₂	Calcium hydroxide
CrI	Crystallinity index
COOH	Carboxylic group
CO ₂	Carbon dioxide
CS	Coconut shell
DMAc	N,N-dimethylacetamide
DMSO	Dimethylsulfoxide
DP	Degree of polymerization
FTIR	Fourier Transform Infrared
H ₂ SO ₄	Sulphuric acid
ILs	Ionic liquids
IR	Infrared Spectroscopy
LiCl	Lithium chloride
LA	Lactic acid
MAA	Methylacrylic acid
MCC	Microcrystalline cellulose
MW	Molecular weight
NMMO	N-methylmorpholine-N-oxide
NMR	Nuclear Magnetic Resonance
NaOH	Sodium hydroxide
OH	Hydroxyl group
p <i>K</i> _a	Acid dissociation constant
PLA	Poly(lactic acid)
PF	Paraformaldehyde
RC	Regenerated cellulose
RTILs	Room temperature ionic liquids
SEC	Size exclusion chromatography
SEM	Scanning Electron Microscopy

TBAF	Tetrebtylammonium fluoride
TGA	Thermogravimetric Analysis
UV	Ultraviolet
XRD	X-Ray diffraction

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Kesan Kandungan Pengisi dan Modifikasi-Modifikasi Kimia ke atas Sifat-sifat Biokomposit Filem Tempurung Kelapa Selulosa Dijana Semula

ABSTRAK

Filem-filem biokomposit tempurung kelapa (TK) selulosa dijana semula (SDS) dihasilkan dengan TK dan selulosa berbahlur mikro (SBM) menggunakan N,N-dimetilasetamida (DMAc) dan lithium klorida (LiCl) melalui teknik larutan penuangan. Kesan kandungan TK dan jenis modifikasi-modifikasi kimia yang berbeza dengan menggunakan asid butilmetakrilat (ABM), asid laktik (AL) dan asid asetik (AA) ke atas sifat-sifat tegangan, pembelauan X-Ray, morfologi, sifat-sifat terma, dan FTIR telah dikaji. Penambahan TK ke dalam matrik selulosa dijana semula meningkatkan kekuatan tegangan dan modulus elastisiti sehingga 3 wt% kandungan TK tetapi berkurang pada 4 wt% kandungan TK. Pemanjangan pada takat putus bagi filem-filem biokomposit TK-SDS berkurang dengan peningkatan kandungan TK hingga 3 wt% dan meningkat pada 4 wt% TK. Indeks penghabluran dan sifat-sifat terma juga meningkat dengan kandungan TK sehingga 3 wt% dan berkurang pada 4 wt% TK. Kajian morfologi filem-filem biokomposit TK-SDS menunjukkan penyebaran kandungan TK yang baik di dalam matrik SDS pada 3 wt% kandungan TK. Suhu penguraian maksimum (T_{dmax}) dan baki filem-filem biokomposit TK-SDS meningkat dengan peningkatan kandungan TK. Pengurangan berat pada suhu 300 dan 600 °C menurun dengan meningkatnya kandungan TK dalam filem-filem biokomposit SDS. Modifikasi-modifikasi kimia ke atas filem-filem biokomposit TK-SDS meningkatkan indeks penghabluran, sifat-sifat tegangan dan terma filem-filem biokomposit TK-SDS pada 3 wt% kandungan TK. Filem-filem biokomposit TK-SDS yang dirawat dengan ABM, AL and AA menunjukkan kekuatan tegangan, modulus elastisiti, indeks penghabluran dan kestabilan terma yg lebih tinggi berbanding filem-filem biokomposit TK-SDS tidak di rawat. Interaksi antara muka yang lebih baik diantara TK dan matrik SDS telah disokong dengan kajian SEM yang menunjukkan permukaan yang lebih licin pada permukaan tegang patah filem-filem biokomposit SDS yang dirawat. Spektra FTIR filem-filem biokomposit TK-SDS yang dirawat menunjukkan pembentukan tindak balas estrifikasi di antara TK dan modifikasi kimia. TK yang dirawat dengan AA menunjukkan kekuatan tegangan dan indeks penghabluran yang lebih tinggi dibandingkan dengan filem-filem biokomposit yang dirawat dengan ABM dan AL. Namun tetapi, kestabilan terma yang lebih baik filem-filem biokomposit ditunjukkan pada TK yang dirawat dengan BMA.

The Effect of Filler Content and Chemical Modifications on Properties of Coconut Shell Regenerated Cellulose Biocomposite Films

ABSTRACT

The coconut shell (CS) regenerated cellulose (RC) biocomposite films were produced with CS and microcrystalline cellulose (MCC) using N,N-dimethylacetamide/lithium chloride by solution casting technique. The effect of CS content and different types of chemical modifications using butyl methacrylate acid (BMA), lactic acid (LA) and acetic acid (AA) on tensile properties, X-ray diffraction, morphology, thermal properties and FTIR were investigated. The addition of CS into the regenerated cellulose matrix increased the tensile strength and modulus of elasticity up to 3 wt% of CS content but reduced at 4 wt% of CS. The elongation at break of CS-RC biocomposite films reduced with increasing CS content up to 3 wt% and increased at 4 wt% of CS. The crystallinity index (CrI) and thermal properties also increased with the incorporation of CS content up to 3 wt% and reduced at 4 wt%. The morphological study of CS-RC biocomposite films exhibited at 3 wt% CS content has better dispersion into the RC matrix. The decomposition at maximum temperature (T_{dmax}) and residue of CS-RC biocomposite films increased with increasing of CS content. Weight loss at temperature 300 and 600 °C decreased with increment of CS content in RC biocomposite films. The chemical modifications of CS-RC biocomposite films improved crystallinity index, tensile and thermal properties of CS-RC biocomposite films at 3 wt% of CS content. Treated CS-RC biocomposite films with BMA, LA and AA exhibit higher tensile strength, modulus elasticity, crystallinity index and thermal stability compared to the untreated CS-RC biocomposite films. The better interfacial interaction between the CS and RC matrix was supported by SEM study which showed smooth surface on the tensile fracture surface of treated RC biocomposite films. The FTIR spectra of treated CS-RC biocomposite films indicated the formation of esterification reaction between CS and chemical modifying agent. The CS treatment with AA has the highest tensile properties and CrI compared with the treatment with LA and BMA of biocomposite films. However, the better thermal stability of CS-RC biocomposite films was found with CS treated with BMA.

CHAPTER 1

INTRODUCTION

1.1 Research Background

Currently, bio-based composites are preferred materials that present a good compromise between final performance and that can substitute and compete with traditional petroleum-based materials while reducing environmental harm and maintaining economic viability. Industries are developing and manufacturing “greener” materials; government is encouraging bio-based product research; researchers are searching for eco-friendly materials; and the public is coming to value the benefit of environmentally friendly products (Smithipong et al., 2014). The developments in emerging bio-based composite leads to their rapid growth in the market place. The worldwide capacity of bio-based plastics is expected to increase from 2.23 million metric ton (2013) to 3.45 million metric ton in 2020 (Faruk et al., 2012). Despite being consumer favorite demands, bio-based composites from petroleum-based polymer are non-biodegradable in structure which they are non-recyclable. Petroleum is not sustainable or renewable resources. As thousands of tons of these non-degradable petroleum-based polymers and composites are discarded daily, leads to significant environment concerns and serious ecological problems (Huang & Netravali, 2009; Lu et al., 2014).

More effort on exploitation of new materials from biomass resources as alternative for petroleum-based materials have been made in recent years, resulting the production of

sustainable and environmental friendly sources of energy known as green materials which caught enormous attention and interest in both academic and industrial field (Haafiz et al., 2013; Pang et al., 2015). In recent years, there is newly developed all-cellulose composites (ACCs) represent an approaches to formulating green composites that aim to eliminate the chemical incompatibility between matrix and reinforcement phases by utilizing cellulose for both components. Consequently, not only some all-cellulose composites exhibit mechanical properties superior than those cellulose-reinforced thermoplastic, but also biodegradable in nature (Duchemin et al., 2009; Huber et al., 2012).

Biocomposites made from plant based polymer such as lignocellulosic materials referred to as green composites (Vilaplana et al., 2010). Cellulose is one of the most abundant, never ending biopolymer on earth with outstanding properties such as high flexibility, biocompatibility, good thermal stability, high mechanical strength and chemical stability (Flieger et al., 2003; Geng et al., 2014; Li et al., 2014; Soheilmoghaddam et al., 2014). However, due to the crystalline form and the hydrogen bonds of native cellulose, which is naturally occurring cellulose involved as well as lignin that binds the cellulose makes it difficult to process thus restricting its applications (Fang & Feng, 2013). Therefore, the conversion of native cellulose into regenerated cellulose is essential for structure that is more thermodynamically stable material. Regenerated cellulose is a class of materials produce when cellulose is regenerated chemically to a cellulose solution by regeneration process (Pullawan, 2012). Regeneration of cellulose by coagulation with anti-solvent provides a simple pathway to transform native cellulose to useful material in many forms such as fibres, beads and hydrogel (Zhou, 2010).

Cellulose composed of $\beta(1\rightarrow4)$ linked glucose repeating units. Because of the stiff molecules and close chain packing through numerous intermolecular and intramolecular hydrogen bonds, it is extremely difficult to dissolve cellulose in water and most conventional solvent (Zhang et al., 2013). The ability to disrupting the inter-chain hydrogen bonds of cellulose determines the dissolution efficiency of solvent (Hameed & Guo, 2009; Liu et al., 2015). Several processes were introduced to developed regenerated cellulose such as viscose and Lyocell process. Viscose process rendered possible the utilization of cellulose in different field such as construction, textile industry, paint, ceramics, cosmetics or food industry. Lyocell process uses direct dissolution of cellulose to produce lyocell fibres mainly for textile industry. The major problem associated with this process is that the amine oxide solvent suffers from the drawback that the regeneration involves dangerous and potentially explosion conditions (Isik et al., 2014). Meanwhile, cellulose dissolution processes, such as cuprammonium and xanthate processes are often cumbersome or expensive and require the use of unusual solvents, typically with high ionic strength and use relatively harsh conditions. Moreover, these processes sometimes cause serious environmental problems because these solvents cannot be recovered and reused (Zhu et al., 2006).

In recent time, new class solvent, ionic liquids (ILs) have recently received much attention as green solvents because of its potential to regenerate and chemically modify the cellulose (Hameed & Guo, 2009; Soheilmoghaddam et al., 2014). ILs is a kind of organic salt with melting temperature lower than 100 °C, substantially lower than normal salt. An ionic liquid that has melting temperature lower than room temperature are coined as room temperature ILs (RTILs) (Gupta & Jiang, 2015; Liu et al., 2015). RTILs have been used as “eco-friendly” solvent for cellulose dissolution and regeneration due to their unique properties such as non-volatile, negligible vapor

pressure, non-flammability, outstanding solvation ability, wide temperature for liquid, chemical and thermal stability and ease of recycling (Hameed & Guo, 2010; Liu et al., 2011; Liu et al., 2015; Shibata et al., 2013; Soheilmoghaddam et al., 2014). The most common ILs for cellulose dissolution are 1-butyl-3-methylimidazolium chloride ([Bmim]Cl) (Sun et al., 2015; Tian et al., 2015), 1-ethyl-3-methylimidazolium chloride ([Emim]Cl) (Soheilmoghaddam et al., 2014), 1-butyl-3-methylimidazolium acetate ([Bmim]Ac) (Liu et al., 2015), N-allyl-N-methylmorpholinium acetate ([AMMorp][OAc]) (Raut et al., 2015), 1-allyl-3-methylimidazolium chloride ([Amim]Cl) (Yang et al., 2013). Solvent system such as dimethyl sulfoxide/paraformaldehyde (DMSO/PF) (Gupta & Jiang, 2015, Jiang et al., 2012), N,N-dimethylacetamide/lithium chloride (DMAc/LiCl) (Yousefi et al., 2015, Zhang et al., 2012), N-methylmorpholine-N-oxide (NMMO) (Erdman et al., 2015; Zhao et al., 2007) and NaOH/urea solution (Chen et al., 2015; Kuo & Lee, 2009) also have been proven capable of dissolving cellulose.

These developments regarding the novel solvents for cellulose offer the possibilities to prepare cellulose biocomposite through solution processing. Nishino et al. (2004) prepared an all-cellulose composite from pure cellulose and ramie fiber in DMAc/LiCl system. This method eliminates the overheating of incorporated fibers during the thermal processing, and thereby the high mechanical performance of plant fibers has been remained greatly. Gindl et al., (2007) prepared an optically transparent cellulose biocomposite from microcrystalline cellulose (MCC) through partial dissolution of cellulose surface with the same solvent system.

N,N-dimethylacetamide (DMAc) containing lithium chloride is very frequently used solvent system in cellulose chemistry (Potthast et al., 2002). This solvent can dissolve

cellulose with a molecular weight of more than 10^6 under ambient conditions without severe degradation or other undesirable reactions. Due to the fact that the mixture is able to effect dissolution of cellulose within a certain concentration range of LiCl and cellulose, DMAc/LiCl has been utilized in an analytical use to investigate the molecular properties of cellulose, such as the chain dimension and flexibility in the dissolved state (Ishii et al., 2008; Potthast et al., 2002). One of the several methods have been developed for cellulose dissolution in DMAc/LiCl, solvent exchange which consist procedure of the immersion of cellulose in water, acetone and further by DMAc. Some researchers have explained the effect of solvent exchange as activation (Ishii et al., 2008; Raus et al., 2012). Skipping the activation step may lead to the dissolution of cellulose to take up to several months to proceed regardless of the crystallinity of the cellulose (Huber et al., 2012). The uses of DMAc/LiCl with natural filler in cellulose biocomposites system have been reported by some researcher. Chen at al., (2015) studies the combined effect of four different cellulosic materials (microcrystalline cellulose, cotton linter pulp, bamboo pulp and bleached softwood sulfite dissolving pulp) in DMAc/LiCl solvent system. Obradovic et al., (2014) reported the use of softwood dissolving pulp swelling in DMAc/LiCl solvent system. Yousefi et al., (2015) used the canola straw as cellulose fibres to make all-cellulose nanocomposite and DMAc/LiCl as a direct solvent.

Lignocellulosic are produced in billions of tons around the world every year. Lignocellulosic agro waste such as oil palm trunks, coir, bamboo, kenaf, hemp and sisal exhibit some excellent properties due to their low density, good thermal insulation and mechanical properties, durability, sustainability and biodegradability. Natural lignocellulosic such as coconut shell has outstanding potential as reinforcement in cellulose biocomposites (Hakeem et al., 2014; Liu et al., 2012).

Coconut (*cocos nucifera*), a member of the palm family, grows broadly in tropical and sub-tropical regions and is employed for a range of applications including decoration, culinary and non-culinary uses; virtually every part of the coconut palm. Coconut shell is non-food part of coconut which is hard lignocellulosic agro waste. Coconut shell is 15-20% part of coconut (Bledzki et al., 2010; Jang et al., 2012). Lignocelluloses present in the shells are tougher than wood. First, coconut shells had little or no economic value, and their disposal was not only costly but harm to the environment (Chun et al., 2012). Nowadays, coconut shell is used as activated carbon, mosquitos coil and as lignocellulosic filler in polymer composite (Bledzki et al., 2010; Chun et al., 2012; Husseinsyah et al., 2012). Several studies have been made regarding the utilizing of coconut shell with petroleum-based polymer (Agunsoye et al., 2012; Bledzki et al., 2010; Chun et al., 2013; Husseinsyah et al., 2013; Husseinsyah & Mostapha, 2011; Jang et al., 2012; Pradhan et al., 2004; Singh et al., 2013).

1.2 Problem Statement

The problems with majority of plastic today are their end-of-life disposal of plastic waste and the reducing number of landfill sites that leads to environment and ecological problems. Besides, the gradual depletion of fossil fuels have become an impact factor to the growing interest in using more environmentally friendly materials and naturally occurring polymer for new materials. Thus, the utilizing of cellulosic fibres in biocomposite films gives alternative routes to environmentally friendly green products as they are renewable with low density, high mechanical properties, lower in cost and one of the ways to reduce the major used of plastic in the world. The different approach has been made to develop biocomposites such as incorporation of cellulose with