PREPARATION AND CHARACTERIZATION OF POLYVINYL ALCOHOL/CHITOSAN COMPOSITE FILMS REINFORCED WITH CELLULOSE NANOFIBER

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PREPARATION AND CHARACTERIZATION OF POLYVINYL ALCOHOL/CHITOSAN COMPOSITE FILMS REINFORCED WITH CELLULOSE NANOFIBER

ABSTRACT

Natural nanocellulose reinforced polymer composites are recently gaining interest in various applications. Much more attentions have been focused to replace petroleum-derived polymers with sustainable natural biopolymers due to their unique properties. In many instances, the fabrication of composites through blending approach of natural and synthetic polymers does not meet the satisfaction on their properties. Thus, the reinforcement of nanofiller into the composite could be a promising way to produce biomaterials with desired properties. The purpose of this project is to discover the effect of cellulose nanofiber (CNF) reinforced on the characteristics of polyvinyl alcohol (PVA)/chitosan (CS) composite. In this study, microcrystalline cellulose (MCC) was oxidized by 2,2,6,6-tetramethylpiperidine-1-oxyl radical (TEMPO)-mediated oxidation method. Bio-nanocomposite films were then prepared from PVA/CS polymeric blends with different TEMPO-mediated oxidized cellulose nanofiber (TOCN) contents (0, 0.5, 1.0 and 1.5 wt%) via the solution casting method. The composite films were characterized in terms of crystallinity, morphological, mechanical, chemical and thermal properties. The morphology results from field emission scanning electron microscopy (FESEM) analysis justified that homogenous dispersion of TOCNs was achieved up to 1.1 wt% in the PVA/CS composite. For the tensile profile of pure PVA/CS composite, it was observed that the optimum tensile strength and elongation at break has been achieved in PVA/CS/TOCNs = 75/25/0.5 composite. For the thermal study by thermogravimetric analysis (TGA) and differential thermogravimetric (DTG) analysis, there was improvement of 4°C and 6°C in onset temperature and maximum degradation temperature, respectively when 1.0 wt% of TOCNs was added into the PVA/CS = 50/50 composite. As evidenced by Fourier transform infrared (FTIR) analysis, itshowed the well interaction between the functional groups of TOCNs and PVA/CS composite matrix due to strong hydrogen bonding. Based on the crystallinity study by x-ray diffraction (XRD), the addition of TOCNs has successfully enhanced the molecular ordering in the amorphous phase of the composite. Hence, the improved characteristics of TOCNs reinforced composites could be strongly beneficial in numerous applications in the future.

Keywords: bio-nanocomposite films, polyvinyl alcohol, chitosan, TEMPO-oxidized cellulose nanofiber, solution casting

PENYEDIAAN DAN PENCIRIAN POLYVINYL ALCOHOL/CHITOSAN KOMPOSIT FILEM BERTETULANG DENGAN SELULOSA NANOFIBER

ABSTRAK

Kebelakangan ini, nanoselulosa semulajadi bertetulang komposit polimer telah mendapat perhatian dalam pelbagai aplikasi. Lebih perhatian telah diberikan untuk menggantikan polimer yang diperolehi daripada petroleum dengan bio-polimer semulajadi disebabkan oleh ciri-ciri yang unik. Dalam banyak keadaan, fabrikasi komposit melalui pencampuran antara polimer semulajadi dan sintetik tidak memenuhi kepuasan terhadap ciri-ciri mereka. Oleh itu, pengukuhan nanofiller ke dalam komposit boleh menjadi cara yang menjanjikan untuk menghasilkan biomaterial dengan sifat yang dikehendaki. Tujuan projek ini adalah untuk mengetahui kesan-kesan selulosa nanofiber (CNF) yang ditambah terhadap ciri-ciri komposit polyvinyl alkohol (PVA)/ chitosan (CS). Dalam kajian ini, selulosa mikrokristal (MCC) telah dioksida oleh 2,2,6,6-tetramethylpiperidine-1-oxyl radikal (TEMPO) yang menjadi pengantara kepada kaedah pengoksidaan. Filem bio-komposit yang terdiri daripada saiz nano ini kemudiannya disediakan daripada PVA/CS polimer yang dicampurkan dengan TEMPO-oxidized cellulose nanofiber (TOCNs) dalam kandungan yang berbeza (0, 0.5, 1.0 dan 1.5 wt%) melalui kaedah penuangan larutan. Filem komposit ini akan dicirikan dari segi kristal, sifat morfologi, mekanikal, kimia dan terma. Keputusan morfologi daripada analisis field emission scanning electron microscopy (FESEM) menjustifikasi bahawa TOCNs telah tersebar secara seragam dan homogen dengan tahap pembebanan kandungannya sehingga 1.0 wt% dalam gabungan PVA/CS. Bagi profil tensil filem PVA/CS yang tulen, didapati bahawa kekuatan tensil dan pemanjangan pada takat putus telah mencapai optima di komposit PVA/CS/TOCNs = 75/25/0.5. Berdasarkan kajian haba melalui thermogravimetric analysis (TGA) dan analisis differential thermogravimetric (DTG), peningkatan sebanyak 4°C dan 6°C pada suhu permulaan dan suhu maxima degradasi masing-masing apabila 1.0 wt% TOCNs dicampurkan dalam komposit PVA/CS = 50/50. Seperti yang dibuktikan oleh Fourier transform infrared (FTIR), analsis ini menunjukkan interaksi yang baik di antara kumpulan berfungsi TOCNs dankomposit matriks PVA/CS disebabkan oleh ikatan hidrogen yang kuat. Berdasarkan kajian penghabluran melalui x-ray diffraction (XRD), penambahan TOCNs telah berjaya meningkatkan penyusunan molekul dalam fasa amorfus di komposit. Oleh itu, ciri-ciri yang dipertingkatkan berikutan pengukuhan komposit bertetulang TOCNs boleh menjadi sangat bermanfaat dalam pelbagai aplikasi pada masa akan datang.

Kata kunci: filem bio-nanokomposit, polyvinyl alkohol, chitosan, TEMPO-oxidized cellulose nanofiber, penuangan larutan

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LIST OF ABBREVIATION

ASTM	:	American standard test method
CAB	:	Cellulose acetate butyrate
CNC	:	Cellulose nanocrystal
CNF	:	Cellulose nanofiber
CNT	:	Carbon nanotube
CNW	:	Cellulose nanowhisker
CS	:	Chitosan
DNA	:	Deoxyribonucleic acid
DTG	:	Differential thermogravimetric analysis
EDC	:	(3-dimethylaminopropyl)-3-ethylcarbodiimide
FESEM	:	Field emission scanning electron microscopy
FTIR	:	Fourier transform infrared spectroscopy
GMS	:	Glyceryl monostearate
HNT	:	Halloysite nanotubes
LDPE	:	Low density polyethylene
MCC	:	Microcrystalline cellulose
MFC	:	Microfibrilated cellulose

PCL : Polycaprolactone

PEG : Polyethylene glycol

PHA : Polyhydroxyalkanoates

PHB : Polyhydroxybutyrate

PHV : Polyhydroxy-valerate

PLA : Polylactic acid

PP : Polypropylene

PVA : Polyvinyl alcohol

PVAc : Polyvinyl acetate

RNA : Ribonucleic acid

$Sn(Oct)_2$: Tin (II) acetate

TEMPO : 2,2,6,6-tetramethylpiperidine-1-oxyl radical

TFA : Trifluoroacetic acid

TGA : Thermogravimetric analysis

TMOCC : TEMPO-mediated oxidized microcrystalline cellulose

TOCN : TEMPO-mediated oxidized cellulose nanofiber

TS : Tensile strength

UF : Urea-formaldehyde

UV-Vis : Ultraviolet-visible

XRD : X-ray diffraction

%E : Elongation at break

LIST OF SYMBOLS

T_g	:	Glass transition temperature
x g	:	Gravity
T_{max}	:	Maximum temperature of degradation
T_{onset}	:	Onset temperature
θ	:	Theta
x	:	Times
λ	:	Wavelength
w/v	:	Weight per volume
w/w	:	Weight per weight (wt)

CHAPTER 1 INTRODUCTION

1.1 Background

Recently, there is an increased attention to develop eco-friendly polymers derived from natural resources in the academic and industrial research areas (Fortunati et al., 2012). Much more efforts have been given to decrease or replace petroleum-based polymers with sustainable biopolymers derived from natural fibers and renewable natural resources because they are biodegradable, environment-friendly and renewable with lower energy consumption (Goffin et al., 2011). The biopolymer also displays its potential in decreasing the severe pollution caused by continuous accumulation of conventional petroleum-based polymer products in the environment.

Polyvinyl alcohol (PVA) is one of the synthetic polymers with interesting physical and chemical properties. PVA is a biodegradable and non-toxic material with proper mechanical strength (Lu et al, 2009), and suitable for biomedical application such as bone tissue engineering scaffold, artificial cartilage as well as cell micro-capsulation (Guo and Xu, 2005). PVA-based composites have also been used for food packaging applications due to good barrier properties, transparency, toughness and flexibility (Qiu and Netravali, 2012). PVA has good film-forming ability due to abundance of hydroxyl groups, resulting in the formation of intermolecular hydrogen bonding (Bonilla et al., 2014). However, one of the efficient ways to broaden the application of PVA is to further enhance its physical and chemical properties.

Chitosan (CS), the second most abundant natural polysaccharide after cellulose, is a partially deacetylated derivative of chitin derived from crabs, shrimps and fungi. CS is a biocompatible polymer with excellent film-forming ability and oxygen barrier properties due to its high crystallinity and strong intermolecular bonding (Kjellgren et al., 2006). At relatively low pH (pH < 6), CS is positively charged (-NH_3^+) and tends to be soluble in dilute aqueous solutions, but at higher pH, it tends to lose their charge and may precipitates from solution due to deprotonation of amino groups (Kumirska et al., 2011; Rinaudo, 2006). CS also shows some unique properties such as non-toxicity, biodegradability, and good antimicrobial properties (Darmadji and Izumimoto, 1994; Jo et al., 2001). CS has been reported for its applications in packaging (van den Broek et al., 2015) and biomedical fields (Dash et al., 2011). In food packaging industry, CS has been used to produce biodegradable composite films to prevent contamination and prolonged shelf-life of foods due to its good antimicrobial properties and ability to chelate bivalent minerals (Chen et al., 2002). One of disadvantages of CS is poor solubility in neutral water and in common organic solvents which has limited its potential applications.

In general, biopolymers are very sensitive to various environmental conditions. Although the biopolymers displayed their own potential, it is important to improve some properties to an acceptable level that can compete with the petroleum-derived polymers, especially their poor mechanical, barrier, processing and thermal properties, which are the desired properties for packaging applications (Kanmani and Rhim, 2014; Rhim and Ng, 2007; Rodríguez-González et al., 2012).

Numerous researches have been done to produce composite by the blending of two or more natural biopolymers such as CS, starch, etc. and synthetic polymers such as PVA, polycaprolactone (PCL), polylactic acid (PLA), low density polyethylene (LDPE), etc. (Alix et al., 2013; Bonilla et al., 2013; Kanatt et al., 2012; Tripathi et al., 2009; van den Broek et al., 2015). For example, PVA has been blended with starch and LDPE to produce composite films as packaging materials for intermediate moisture foods (Holton et al., 1994). Blending approaches are a very promising way to produce novel eco-friendly biomaterials with desired thermal, mechanical, optical and barrier properties. (Avella et al., 2005; Chen et al., 2003; Mensitieri et al., 2011; Rhim et al., 2013; Rhim and Ng, 2007). This may also improve the cost effectiveness of the composite films because most synthetic polymers can be easily obtained and have a relatively low production cost (Bahrami et al., 2003).

Several studies have been done on the properties of PVA/CS composites especially in biomedical applications (Costa-Júnior et al., 2009; Sundaramurthi et al., 2012). Since PVA/CS composite shows good compatibility, it is a promising strategy to blend PVA and CS to obtain the combined properties of both polymers. It has been reported to be an effective technique by blending PVA and CS using solution casting method to produce composite films with desired characteristics such as good antimicrobial properties, tensile strength, barrier properties and formability (Bonilla et al., 2014; Tripathi et al., 2009). However, their poor elongation at break and thermal properties are still the main limiting factors for medical and packaging application as reported by researchers (Lewandowska, 2009; Srinivasa et al., 2003; Vidyalakshmi et al., 2004). Unfortunately, the poor performance of most biopolymer composites, especially their low cost effective ratio, material processing problems and barrier properties, has limited their potential application such as in packaging industry.

Alternatively, the blends of natural biopolymer and synthetic polymer are reinforced with various nanofillers to overcome their limitation as reported by researchers (De Azeredo, 2009; Rhim et al., 2013; Saba et al., 2014). Several studies on the bio-nanocomposite with low amount of nanofillers have been reported as an excellent method to produce biomaterials for packaging applications (Reddy et al., 2013; Rhim et al., 2013). The incorporation of well-dispersed nanofillers into polymer matrix may improve their physiochemical properties such as mechanical, thermal, barrier and optical properties. Numerous studies have been reported on the reinforcement of PVA/CS composite using nanofillers such as carbon nanotubes (CNTs), nanoclays and halloysite nanotubes (HNTs). Particularly, some desired properties could be greatly enhanced by the incorporation of only a small amount of nanofillers due to their significantly large surface area.

Cellulose is used to develop one of the promising bio-reinforcing materials known as cellulose nanofiber (CNF). Cellulose can be obtained from variety of sources such as plants and bacteria (Moon et al., 2011). The smaller the filler particles, the better are the interaction of filler and matrix (Luduena et al., 2007), and usually the better is the cost price efficiency (Sorrentino et al., 2007). CNFs are recognized as being more effective than their micro-sized counterparts to reinforce polymers due to the interaction between the nano-sized elements and polymer matrix that form a percolated network through hydrogen bonding, assumed there is a good dispersion of the nanofibers in the matrix (Angles and Dufresne, 2000; Nakagaito et al., 2009).

CNFs have been gaining much more attentions in recent years because they can be used as natural nanofillers to produce bio-nanocomposites due to their renewability, low cost, low density and non-abrasive nature. TEMPO-mediated oxidized cellulose nanofiber (TOCN) can be produced through 2,2,6,6-tetramethylpiperidinde-1-oxy radical (TEMPO)-mediated oxidation of cellulose followed by the mechanical disintegration of the oxidized cellulose slurry (Fujisawa et al., 2011). TOCN as a reinforcing phase, shows higher crystallinity, larger aspect ratio (>50) and mostly uniform widths (3-4 nm) as compared to other nanocelluloses. TOCNs can be homogeneously dispersed in water due to their effective electrostatic repulsion on the anionic charges present on the surfaces of TOCNs (Fujisawa et al., 2011). This allows the formation of nanofillers reinforced bio-nanocomposites with easy processability. The synergetic effects of nanoreinforcements would be a great contribution for many technological and industrial applications in the future.

1.2 Problem Statement

Generally, biopolymer films are very sensitive to environmental conditions and generally have low physical properties such as barrier, thermal and mechanical properties, which are the important properties for packaging materials. Polymer blending is a promising method by mixing two or more natural polymers and synthetic polymer to produce new commercially viable biomaterials. In fact, it is always difficult to obtain compatible polymer blends with desired properties. It was previously reported that chitosan (CS)/polylactic acid (PLA) blends are incompatible based on the mechanical and thermal studies, consistent with the results of FTIR analysis that showed the absence of specific interaction between CS and PLA (Suyatma et al., 2004). It was also reported that the elasticity of CS/polyethylene glycol (PEG) composite membranes was better than that of pure CS membranes, however the tensile strength decreased in most cases (Kolhe and Kannan, 2003). The PEG component tends to solubilise in aqueous solution due to the physical and weak interactions between CS and PEG, leading to weight loss and worsening of the composite membrane performances (Zivanovic et al., 2007).

On the contrary, the blending of polyvinyl alcohol (PVA) and CS has been proven to be an effective way to improve the mechanical properties as reported by researchers (Costa-Júnior et al., 2009; Islam and Yasin, 2012). PVA/CS composite also represents novel bio-material processing better thermal, mechanical properties and biocompatibility than the characteristics of single components (Cascone, 1997). Although PVA/CS composites showed great changes in their characteristics, there is still a huge gap to achieve the desired properties in order to be commercialized in the market.

To further improve their properties, nanocellulose such as cellulose nanofibers (CNFs) will be introduced to PVA/CS composite. Previous study showed the mechanical and water vapour barrier properties of CS films were improved by the addition of CNFs (Azeredo et al., 2010). It was found that the CNF improved the tensile strength and Young's modulus with values 2.8 and 2.4 times larger as compared to neat PVA. The composites exhibited good better thermal stability and excellent transparency with a visible light transmittance of 73.7% (Tan et al., 2015). Similar improvement on PVA/CNF was also reported (Liu et al., 2013). A paper also proved that the incorporation nanocellulose improved the barrier properties but reduced the swelling properties of PVA/CS composite (Samzadeh-Kermani and Esfandiary, 2016).

1.3 Objective of Study

This study is aimed to produce bio-nanocomposites films based on PVA/CS/TOCN with enhanced chemical, mechanical and thermal properties. The main purpose of this research is to improve the dispersion and bonding between the filler and the matrix for enhancing mechanical, chemical and thermal behaviours by modifying the functional groups on the surface of the cellulose. Mechanical, morphological, chemical, thermal and spectroscopic behaviours of the resulting bio-nanocomposite films at various nano-filler and polymer matrix compositions are evaluated.

The objectives of study are listed as below:

(a) To isolate cellulose nanofiber (CNF) from microcrystalline cellulose (MCC) using TEMPO-mediated oxidation method.

(b) To investigate the effect of TEMPO-mediated oxidized cellulose nanofiber (TOCN) loading on the morphology, mechanical, chemical and thermal properties of the PVA/chitosan (CS)/TOCN composite films.

1.4 Scope of Study

In this study, cellulose nanofiber (CNF) was used as the nanoreinforcement or nanofiiler for the polymer matrix. Various mixing ratios of polyvinyl alcohol (PVA) and chitosan (CS) were used as matrix for fabrication of composites. The bio-nanocomposite films were prepared using solution casting method. Microcrystalline cellulose (MCC) was chemically treated with TEMPO-mediated oxidation method to obtain a better dispersion of nanofibers in PVA/CS composite matrix. Field emission scanning electron microscopy (FESEM) analysis was carried out to observe the degree of dispersion and adhesion of TEMPO-oxidized cellulose nanofiber (TOCN) within PVA/CS matrix in the composites. The mechanical properties of bio-nanocomposites were proved by tensile test that include tensile strength and elongation at break of the samples. Thermogravimetric analysis (TGA) and differential thermogravimetric (DTG) analysis were conducted to evaluate the thermal stability of the resulting bio-nanocomposites. Fourier transform infrared (FTIR) spectroscopy was also carried out on each composite to confirm the chemical reactions between the CNF and PVA/CS matrix as well as in the matrix itself. Lastly, X-ray diffraction (XRD) analysis was performed to study the crystallinity of the PVA/CS/TOCN composites.

1.5 Thesis Outline

This thesis has been organized into five chapters, which provides information regarding the research interests. Thesis frame illustrates the summary of each chapter from chapter 1 to chapter 5.

Chapter 1 consists of introduction of the project. It covers brief introduction about the background of research, problem statements, objectives and scopes of study of the project.

Chapter 2 presents a literature review on previous work in different field of areas related to this project. This chapter covers brief explanations of biopolymers and their classification and polymer matrices in terms of properties, structure and application. The utilization of cellulose nanofiber (CNF) as source for reinforcement is also highlighted. This chapter also covers the short explanations of biopolymer composite. The overviews of nano-reinforcement of CNF in biopolymer composite are addressed as well.

Chapter 3 describes the information about the methodology including materials and chemicals and procedures used to prepare the TEMPO-mediated oxidized cellulose nanofiber (TOCN) and PVA/CS/TOCN composite films. It is followed by the characterization tests carried out on the resulting bio-nanocomposite films.

Chapter 4 reports the results and discussion of this study. It covers the characterization tests of the bio-nanocompites in terms of morphology, mechanical, thermal and chemical properties of TOCNs reinforced PVA/CS composite films. The effect of TOCN loadings on the characteristics are examined and correlated to the previous works by other researchers.

Chapter 5 provides the important findings and overall conclusions and also suggests recommendations for the future study.

CHAPTER 2 LITERATURE REVIEW

2.1 Biopolymer

Biopolymer is a chain-like polymer which consists of repeating chemical blocks and can be very long in length. The prefix ―bio‖ shows that they are derived from living organisms such as plants and animal. Generally, biodegradable polymers can be classified into four types: (i) natural polymers, such as cellulose, starch, chitosan (CS), protein and lipids; (ii) synthetic polymers from genetic manipulation, such as polylactic acid (PLA); and (iii) polymers from microbial synthesize, such as polyhydroxyl-valerate (PHV), polyhydroxyalkanoates (PHA), polyhydroxybutyrate (PHB), xanthan, pullan and bacterial cellulose; and (iv) produced from non-renewable sources such as polyvinyl alcohol (PVA), aliphatic and aromatic polyesters, modified polyolefins and polycaprolactone (PCL), which are sensitive to light and temperature, as shown in Figure 2.l (Chandra and Rustgi, 1998). Biopolymer or polymers from renewable natural resources have gained much more attention on the last few decades, mostly owing to two main reasons: concerns over its environmental-friendliness while secondly the fact that our petroleum resources are limited due to its non-renewability. Biopolymers consist of complex molecular structure that adopts defined and precise 3D structure while synthetic polymers have simpler and more random structure.

Advantages of petroleum-derived polymers are: (i) increased cost effectiveness; (ii) good barrier properties; (iii) high mechanical performance; and (iv) enhanced thermal stability. In contrast, it has few disadvantages such as: (i) reducing amount of petroleum resources; (ii) rising of prices of oil and gas during last few decades; (iii) risks of consumer over the toxicity of edible materials derived from their monomers or oligomers; (iv) expensive costs and cross-contamination in their recycle processes and

(e) environmental concerns after degradation and global warming (Amass et al., 1998; Chandra and Rustgi, 1998; Mohanty et al., 2000; Siracusa et al., 2008).

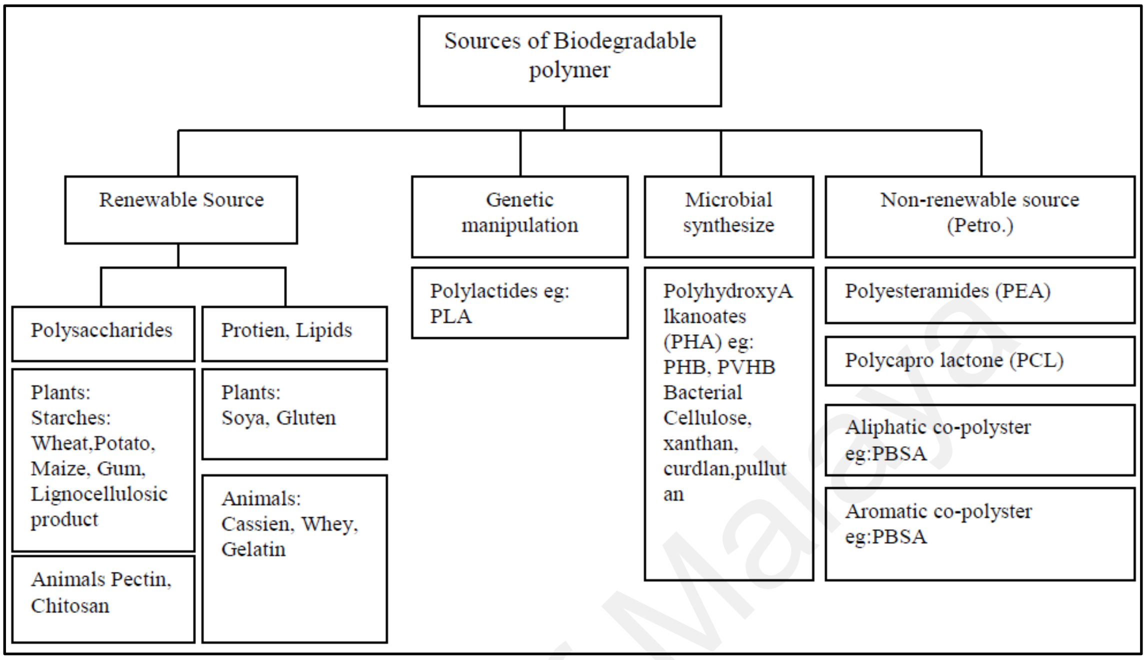

Figure 2.1 : Classification of potential biopolymers in composite fabrication.

Adapted from ―Biocomposites based on plastisized starch: Thermal and mechanical behaviours,‖ by Averous and Boquillon, 2004, *Carbohydrate Polymers*, 56, p. 111-122.

Due the disadvantages specified above, it is critical to replace those non-renewable polymers with biopolymers concerning the biodegradation that happens in nature. Biodegradation is about the degradation of a polymer in natural environments that gives transition in chemical structure, damage of structural and mechanical properties, and lastly, converting into another compounds like carbon dioxide, water, minerals or partially-degradable products like humic materials and biomass (Siracusa et al., 2008). Several desired properties of biopolymers can also be enhanced through polymer blending of petroleum-derived polymers to form a new composite. Current advances give powerful devices to explain microstructures at various levels as well as to comprehend the connections amongst structure and properties. These breakthroughs could convey chances to create bio-materials for novel applications. The biodegradable characteristic of natural polymers implies it is vital to optimize the environment in which the polymers are utilized, to avoid incomplete degradation.

2.2 Polyvinyl alcohol (PVA)

2.2.1 Properties

Polyvinyl alcohol (PVA) is one of the largest products of synthetic water-soluble polymer in the world. The world production of PVA is about 65,000 tons per annum (Lin et al., 2014). PVA is resistance to oil, grease and solvent. PVA is a translucent, odourless and tasteless, white coloured granular powder. The aqueous solution of PVA is slightly acidic or neutral. However, it can decompose immediately beyond 200°C as it will undergo pyrolysis at elevated temperature. Thus, it is more preferable to store PVA in a dry and cool condition.

In addition, PVA shows good mechanical properties such as tensile strength and flexibility and aroma barrier properties. It will absorb the moisture in high humidity condition and thus, reduce its tensile strength but increase its flexibility. PVA can be classified into two types: the fully and partially hydrolyzed grades based on the applications. The melting point of PVA is around 180-190°C for partially hydrolyzed grade and about 230°C for fully hydrolyzed grade. The degree of solubility, biodegradability and other properties of PVA can be optimized through differing their molecular weight as well as the hydrolysis degree during the saponification process (Bohlmann, 2005). The hydrolysis degree depends particularly on the amount of residual acetate groups in the backbone of PVA. Hence, the partially hydrolyzed PVA can be recognized as copolymers of vinyl alcohol and vinyl acetate due to incomplete saponification or alcoholysis (Goldschmidt and Streitberger, 2003). In fact, the mechanical, chemical properties of PVA including its reactivity and physical characteristics such as its solubility will ultimately affected by the degree of hydrolysis (Ng et al., 2014). Hence, PVA can be utilized in wide applications especially as the polymer matrix for bio-nanocomposites.

2.2.2 Structure

PVA is an atactic polymer that consists of crystallinity. From the microstructure view, it contains primarily of 1,3-diol units [-CH_2-CH(OH)-CH_2-CH(OH)-]. The amount of 1,2-diol units [-CH_2-CH(OH)-CH(OH)-CH_2-] is only less than 1-2%, based on the polymerization conditions of the vinyl ester precursor (Hallensleben et al., 2000). Generally, most polymers can have polymerization through its own monomer. However, PVA can be prepared industrially through hydrolysis of polyvinyl acetate (PVAc) because of the unstable condition of vinyl monomer. Thus, PVA can be produced by mixing PVAc with methanol or by a saponification technique from PVAc (Odian, 2004). Figure 2.2 shows the chemical reaction equation of hydrolysis of PVAc.

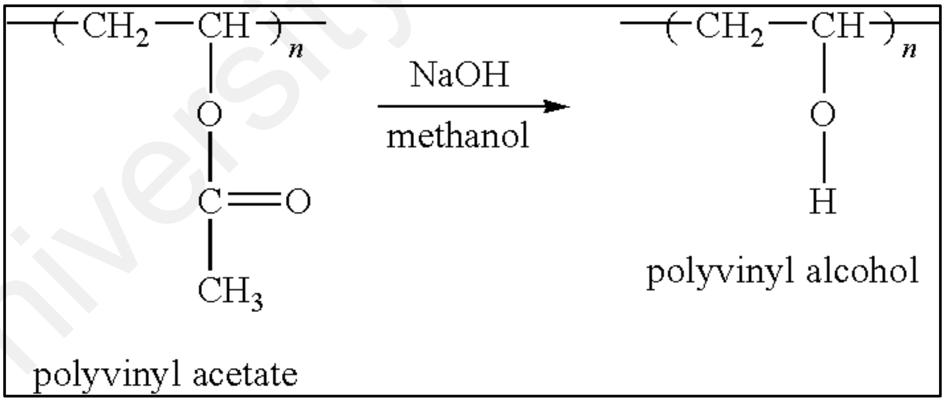

Figure 2.2: Hydrolysis of polyvinyl acetate to form PVA. Adapted from ―Binder for an electrode of an electrochemical system, electrode comprising this binder, and electrochemical system comprising this electrode,‖ by Medlege et al., 2017, U.S. Patent No. 9,673,480.

2.2.3 Selection of PVA as a Matrix

PVA is one of the most promising polymers due to its (a) non-toxicity, (b) ease-of-use, (c) high chemical resistance, (d) high crystallinity, (e) biodegradability and (f) biocompatibility. It also has interesting physical and chemical properties and good film-forming property due to the abundant of hydroxyl groups and thus, formation of intermolecular hydrogen bonding (Bonilla et al., 2014). PVA is one of the synthetic polymers which is easily obtained and has a relatively low cost of production.

2.2.4 Application

Owing to the excellent mechanical, physical properties and high chemical stability at room temperature, PVA is a highly promising polymer commonly used for various applications such as in textile, cosmetic, pharmaceutical, medical, food, paper and packaging industries. For example, Food and Drug Administration (United State) has allowed the polymer to have close contact with products of food. Hence, it can be applied in packaging systems of food due to good barrier characteristic (Baker et al., 2012). In food industries, it has been applied as coating and binding agent and as a barrier film for dry foods and supplement of food in tablet forms to avoid moisture uptake.

Besides that, PVA is often applied as a bio-material in medical devices owing to its non-toxicity, non-carcinogenicity, swelling properties and bio-adhesive characteristics (Hassan and Peppas, 2000). PVA also show its potential applications in field of medical like haemodialysis, implantable medical devices and artificial pancreas. PVA has also been utilized in the formation of composites with various natural and renewable biopolymers such as cellulose nanofiber (CNF), chitosan (CS), starch and etc. PVA is a synthetic polymer that also gained much attention for its use in drugs and cosmetics. PVA has been involved in the formulation of skin lotions, cream hair dressings and liquid make-ups. PVA functions as emulsifier and thickener for lotions as well as peel-off facial masks. PVA has been used for years in both drugs and cosmetics and has an excellent record regarding its safety. It is not a primary irritant, and there is no prove of its causing sensitization. It can be considered as innocuous (Ward and Sperandio, 1964). In summary, PVA is a safe and versatile polymer with a broad range of potential applications especially in the packaging and medical industry.

2.3 Chitosan (CS)

2.3.1 Properties

Chitosan (CS) is a natural biopolymer and most essential derivative of chitin. It is the second most abundant natural polysaccharides after cellulose and next to lignin in the universe. CS is derived from natural resources such as arthropods including exoskeleton of insects, crustacean shells, crabs, prawns, cell walls of fungi, shellfish like shrimp and beaks of cephalopods (Hirano et al., 1990). Owing to the abundance of intermolecular hydrogen bonding, it will undergo degradation before melting. The physiochemical properties of CS are mainly depend on its molecular weight and degree of deacetylation. Most CS is insoluble in organic solvents and pure water with a neutral pH of 7.0. Nonetheless, it can be easily soluble in acidic mediums at less than pH 6.3 while it became very viscous at concentration >2wt% (Kaur and Dhillon, 2014). CS is a highly basic polymer while the majority of naturally occurring polysaccharides including pectin, agar and cellulose are acidic in nature.

Due to its origin of polycationic in nature, it has the ability to protect against contamination and antimicrobial characteristics against yeasts, bacteria, fungi and moulds (Kim et al., 2003). The antimicrobial actions of CS are proposed in three ways including (a) the electrostatic attractions between the positively charged amino groups in CS and the negatively charged on the surfaces of cell residues (Benhabiles et al., 2012); (b) Low molecular weight CS enters the nucleus of cell and blocks the transcription of RNA through DNA by stacking to molecules of DNA (Jing et al., 2007) and (c) as a chelating agent of essential minerals (Goy et al., 2009). Hence, it is important to have more protonated amino groups in CS by increasing the degree of deacetylation (Elsabee and Abdou, 2013).

2.3.2 Structure

Chitosan (CS) is a linear copolymer comprising of 1,4-linked 2-amino-2-deoxy-β-D-glucopyranose units and low amount of 1,4-linked 2-acetamido-2-deoxy-β-D-glucopyranose units. Thus, it consists of a strong crystalline structure through intra and inter-molecular hydrogen bonding (Dash et al., 2011). CS is a partially de-acetylated derivative of chitin containing the reactive amino groups. CS is formed by eliminating an acetate moiety from chitin through hydration such as amide hydrolysis by alkaline treatment or enzymatic hydrolysis by chitin deacetylase (Suh and Matthew, 2000). Figure 2.3 illustrates the deactylation of chitin to produce CS.

2.3.3 Selection of Chitosan as a Matrix

CS has unique properties such as (a) non-toxicity, (b) biodegradability, (c) bio-renewability, (d) biocompatibility, (e) good mechanical properties, and (f) barrier properties. CS is more suitable for the bio-applications as compared to chitin due to the improved solubility in water and in organic solvents (Mima et al., 1983). CS composes of some unique characteristics such as polyelectrolyte properties, mucoadhesivity, solubility in different media, viscosity, metal chelations, polyoxysalt formation, optical and structural behaviours. It also has the ability to adhere antagonistically with microbial and mammalian cells. It also favours the production of CS films, membranes or coating material that are partially permeable to gases due to great film-forming ability of CS as reported by researcher (Aider, 2010).

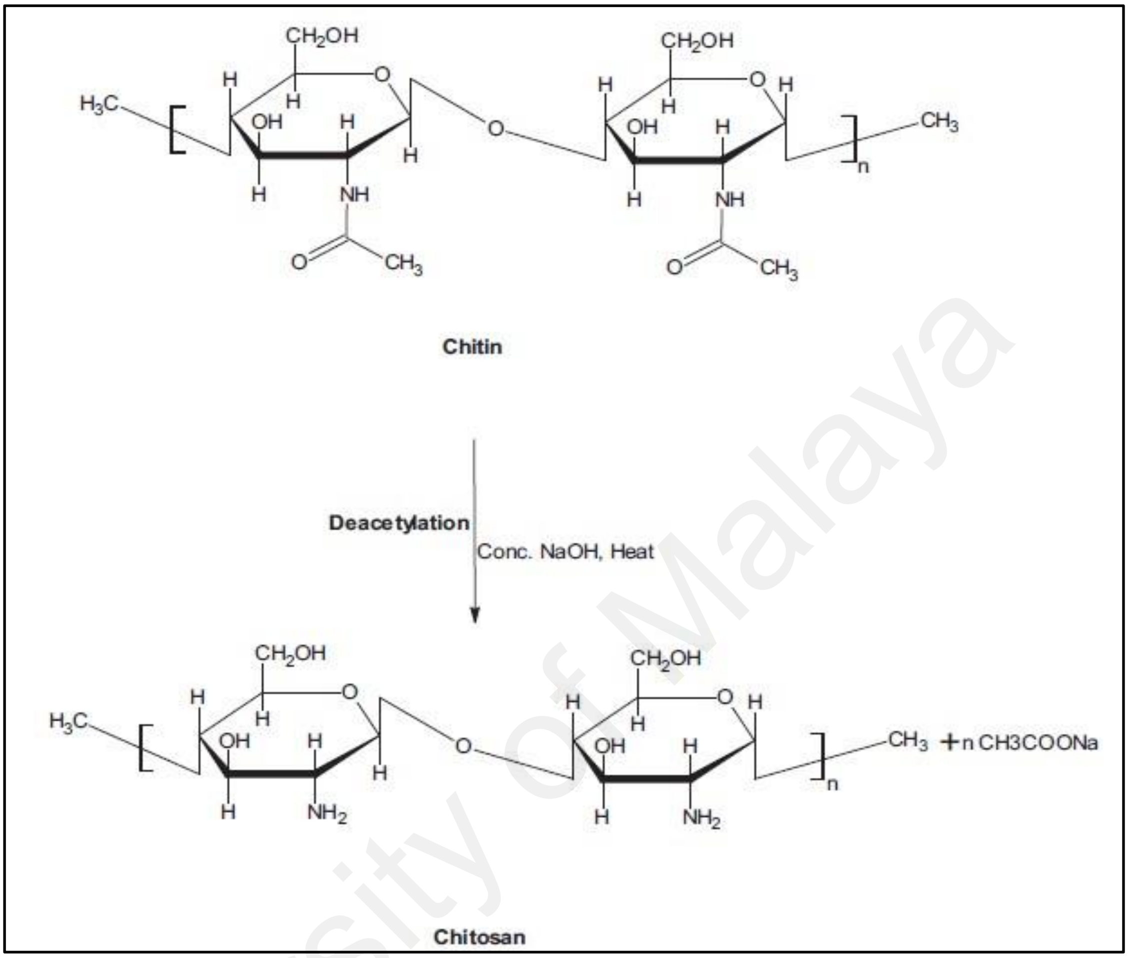

Figure 2.3: Deacetylation of chitin to produce CS. Adapted from ―Chitosan-based nanomaterials: A state-of-the-art review,‖ by Shukla et al., 2013, *International Journal of Biological Macromolecules*, 59, p. 46-58.

2.3.4 Applications

For last 20 years, many researchers have reported on CS and its potential in numerous applications. CS is very important in pharmaceutical fields as compared to other natural biopolymers owing to the presence of primary amine groups. It also has potential application in tissue engineering, due to its regenerative effect on connective gum tissue (Jayakumar et al., 2010). CS also plays a crucial part in helping for bone regeneration due to the formation of osteoblast. CS films have been successfully used as a packaging material for the protection against microbial attack and contamination in order to enhance food safety and shelf life (van den Broek et al., 2015). As CS is inexpensive and commercially available, it can be contributed to the low total production cost of packaging materials. The biopolymer is also a suitable material for biomedical applications such as wound healing, drug delivery, tissue engineering and numerous antimicrobial properties (Dash et al., 2011). CS provides a natural alternative to the application of chemical materials in drug and cosmetic applications that are often unsafe to humans and environment. In cosmetics, CS produces a moisturizing, protective and elastic film on the skin surface that able to bind other useful ingredients that could benefits the skin. Due to antimicrobial properties of CS, it is an important component in skin-care and hair-care products such as hairsprays and shampoos. Other properties include control moisture of skin, protect the epidermis, tone skin, treat acne, fight dandruff and make hair softer (Dutta et al., 2004). In summary, all of these useful properties could be advantageous for all potential applications such as packaging, biomedical and cosmetic applications.

2.4 Extraction and Production of Cellulose Nanofiber

Cellulose, one of the most abundant, renewable and natural biopolymer, can be widely found in many forms of biomass, such as cotton, wood and hemp among other sources. Cellulose is a very strong natural biopolymer which consists of long fibrous cells. It is a linear carbohydrate polymer consisting of D-glucopyranose units linked together by β-1,4-D-glycosidic bonds. Cellulose exists in amorphous form, but is mixed with crystalline phases through the formation of both intra- and inter-molecular hydrogen bonding and thus, it will not melt before thermal degradation (Klemm et al., 2005). It can be observed from the history that humans have utilized mechanically and chemically treated celluloses and also the cellulose fibers in numerous applications include textile and paper industries, food additives, flat board units in liquid crystals displays, medicines' components and hollow fibers for artificial kidney dialysis (Isogai et al., 2011).

Cellulose nanofibers (CNFs) are differentiated by its raw material, pre-treatment and isolation method. Nonetheless, the most important is that the CNF is influenced by disintegration reaction itself. The chemical and mechanical treatment could be combined together to enhance the isolation process by means of improving the production of cellulose. Generally, the mechanical treatments consist of refining, disintegration, cryocrushing, and high-pressure homogenization. A flow chart of the overall isolation technique of nanofiber is shown in Figure 2.4.

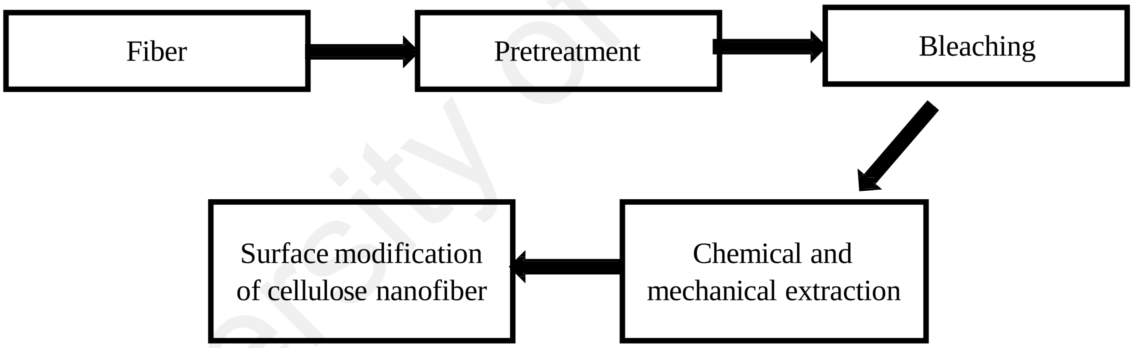

Figure 2.4: Schematic diagram of overall cellulose nanofiber isolation technique.

In the following paragraph, the extraction methods that commonly used for CNFs isolation are described in details. There are two different major ways to isolate the cellulose nanopaticles traditionally, which are acid hydrolysis and mechanical treatment. The great shear forces introduced by strong mechanical approach to cellulose fibers induce the extraction of CNFs with higher aspect ratio, resulting in formation of highly entangled networks. Meanwhile, cellulose nanocrystals (CNCs) and cellulose nanowhiskers (CNWs) can be produced by strong acid hydrolysis which promotes transversal fracture of non-crystalline parts of cellulose microfibrils. CNCs and CNWs are rod-like in shape with length in the range of 100-600 nm and 2-20 nm in diameter.

Pre-treatment is a series of treatment that is required before the isolation process of cellulose fiber. Main reasons for pre-treatments are to expel any undesirable particles before the fiber is further converted into nanofiber. Pre-treatment and washing processes tend to expel waxes, ashes and non-cellulosic compounds to fabricate a high quality and purified cellulosic products. Lignin contents in the cellulose fiber can be removed during the pre-treatment process. The removal of lignin is crucial because it is believed to give some drawbacks in composite features. Lignin will be broken down during pre-treatment and crystalline parts of cellulose fiber will be disrupted, resulting in possible removal of lignin (Mosier et al., 2005). Several types of pre-treatments have been reported during the last few decades. The alkali treatment is the most common method used in this process. In general, alkali pre-treatments can be categorized into two groups such as pre-treatments by using hydroxides of sodium, potassium or calcium and ammonia.

Pulp contains cellulose fibers, normally extracted from wood. There are three ways to obtain cellulose fibers from the wood matrix which are chemical, mechanical and enzymatic treatments. Firstly, mechanical treatments could consume high energy power because they are always requiring higher pressure or kinetic energy. Through mechanical pulping, the product obtained has the similar components as the initial feeding. A variety of cellulose sources was used to extract cellulose fibers through various major mechanical treatments such as grinders/refiners (Abe et al., 2007; Iwamoto et al., 2005), cryocrushing (Chakraborty et al., 2005; Wang and Sain, 2007), and high-intensity ultrasonic treatments (Johnson et al., 2009).

Lignin-hemicellulose matrix that surrounds the cellulose fibers can be dissolved through chemical treatment of pulp using several chemical agents. However, lower yields of products are usually obtained based on the cellulose sources which a higher degree of carbohydrate degradation always happens simultaneously. One of the main concerns of using chemical pulping is the environmental safety of the residual products of the method. Kraft process (1884) is the most common techniques used for removing lignin and hemicelluloses (Vazquez et al., 2015) which uses sodium sulphide (Na_2S) and sodium hydroxide (NaOH), followed by a bleaching step involving chlorine dioxide (ClO_2), hydrogen peroxide (H_2O_2), peracetic acid or ozone (O_3). A whiter product with lower contents of unwanted impurities and enhanced resistance to brittleness and yellowing can be obtained by the bleaching of pulp. Other bleaching agent such as potassium hydroxide (KOH) has been reported for its ability to remove hemicelluloses (Jonoobi et al., 2010). To decrease the environmental impact of the pulping technique, a few sulphide and chlorine-free treatments have been reported by researcher (Morán et al., 2008).

Besides the mechanical and chemical pulping process, enzymatic or biological pulping has gained great interests from the researcher. This process depends mainly on the capability of individual microorganisms and their produced enzymes to direct depolymerise hemicelluloses and attach to the interface of lignin/cellulose. This pulping technique facilitates the isolation of pure cellulose with the least possible degradation and relatively high quality pulps as reported by researchers (Beg et al., 2000; Techapun et al., 2003).

In general, the production of CNF is done by mechanical processes consist of high pressure homogenization and refining process. An alternative way for fabricating CNFs is called cryocrushing in which cellulose fibers are frozen using liquid nitrogen, followed by the application of high shear forces. Various preparation techniques were introduced for the isolation of CNFs as reported by researchers. Dufresne et al. (2000) utilized mechanical process on potato after bleaching and gained CNFs with a width of 5 nm. Iwamoto et al. (2005) produced CNFs with width of 50-100 nm from kraft pulp by passing through a refiner with gap of 0.1 mm for 30 times before homogenization process. Wang and Sain (2007) obtained CNFs with a dimension 50-100 nm in width through cryocrushing process for soybean stock. (Alemdar and Sain, 2008a) used cryocrushing method followed by fibrillation before the homogenization process to form CNFs from wheat straw. The width of CNFs obtained is about 20-100 nm while most CNFs are approximately 30-40 nm. Chen et al. (2011) fabricated CNFs from wood source in two different steps. Initally, wood fibers were sent to a chemical treatment to remove hemicelluloses and lignin. These fibers were then separated by mechanical process into CNFs using ultrasonication with high intensity. The dimension distributions of the nanofibers obtained are based on the output power of the ultrasonic treatment. The CNFs obtained from natural sources include bamboo, wheat straw fibers and wood showed uniform diameters of 10-40 nm. However, due to high cellulose amount of the flax fibers, they were incomplete nano-fibrillated after the whole process.

Montaño-Leyva et al. (2011) studied the potential of CNFs extracted from durum wheat straw as reinforcement phase in bio-composites via few characterization tests. CNFs were fabricated through an electrospinning technique using a specific solvent known as trifluoroacetic acid (TFA). The diameter of nanofibers obtained was approximately 270 nm. Alemdar and Sain (2008a) used a combination of chemical and mechanical method and obtained CNFs from the agricultural wastes such as soy hulls and wheat straws. The structure and morphology of CNFs were analyzed using transmission electron microscopy (TEM). The diameter of nanofibers extracted from wheat straw is in the range of 10-80 nm and up to few thousand nm in length. It is observed that diameter of nanofibers extracted from soy hull is around 20-120 nm and shorter lengths than the nanofibers extracted from wheat straw. Cherian et al. (2010) has successfully extracted CNFs from pineapple leaf by steam explosion technique. An efficient method was found in the defibrillation and depolymerisation of the pineapple leaf fibers to fabricate nanofibers by steam coupled acid process. The extracted nanofiber shows its potential as functional materials for broad range of applications in biomedical and biotechnology. Deepa et al. (2011) used steam explosion method to obtain CNFs from banana fibers. These nanofibers were thermogravimetrically examined to study the differences of degradation behaviours between the chemically treated fibers and the untreated one. Due to increased fibrillation of the pulp fibers, films made from these nanofibers showed high optical transparency and low swelling properties.

2.5 Structure and Properties of Cellulose Nanofiber

Nanofibers are characterized as fibers in nano-sized with width of <100 nm or fibers in micron-sized with at least one dimension of the structures are in nano-sized. Nanofibers show high specific surface areas which are significantly different as compared to those of the bulk materials. Due to its potential in the nanotechnology area, the research and development has been widely carried out by both academia and industry. There are some potential applications of nanofibers such as gas-barrier films, nanofiber reinforced composites, flame-resistant materials, catalysts, electro-optical films, microelectronics, cosmetics and other high performance materials (Paul and Robeson, 2008; Rusli and Eichhorn, 2008). Owing to the environmental-friendliness and the establishment of sustainable and recycle-based societies, much more attentions have been given to promote the research and development as well as application of biodegradable nanofibers since the last few decades.

Cellulose nanofibers (CNFs) have been gaining much more attentions in recent years because they are applicable as the natural nanofillers to produce bio-nanocomposites. The nanofibers, produced through the cellulose chains in plants or animals consist of long bundles of molecules and stabilized by inter- and intra-molecular hydrogen bonding. The nanofibers have nano-sized diameter of 2-20 nm based on the sources, and micron-sized lengths (Azizi Samir et al., 2005). Each nanofiber is produced through the combination of elementary fibrils, which composed of two different phases. The crystalline region, which can be separated through few methods, are the nanocrystals or whiskers which length ranging from 500 nm up to about 1-2 µm, and diameter with around 8-20 nm (Samir et al., 2004), resulting in large aspect ratios. Meanwhile, another phase in the nanofiber is known as the amorphous phase.

There are many advantages of environmental-friendly CNFs such as low density, high aspect ratio, high mechanical properties, low energy consumption in manufacturing, biodegradability, biocompatibility, easy of recycling by combustion, etc. Additionally, CNFs can be obtained from abundance of renewable natural sources. All of these unique characteristics make CNFs an attractive grade of nanomaterials to produce light, low cost and high strength nanocomposites. However, such nanofillers have to solve many problems against industrial practices due to extremely hydrophilic surface, poor dispersion due to larger aggregation ability, low yield, low thermal stability, commercially unavailability as well as relative higher price through expensive resources (Pandey et al., 2009). Figure 2.5 illustrates a schematic model of the internal structure of CNF.

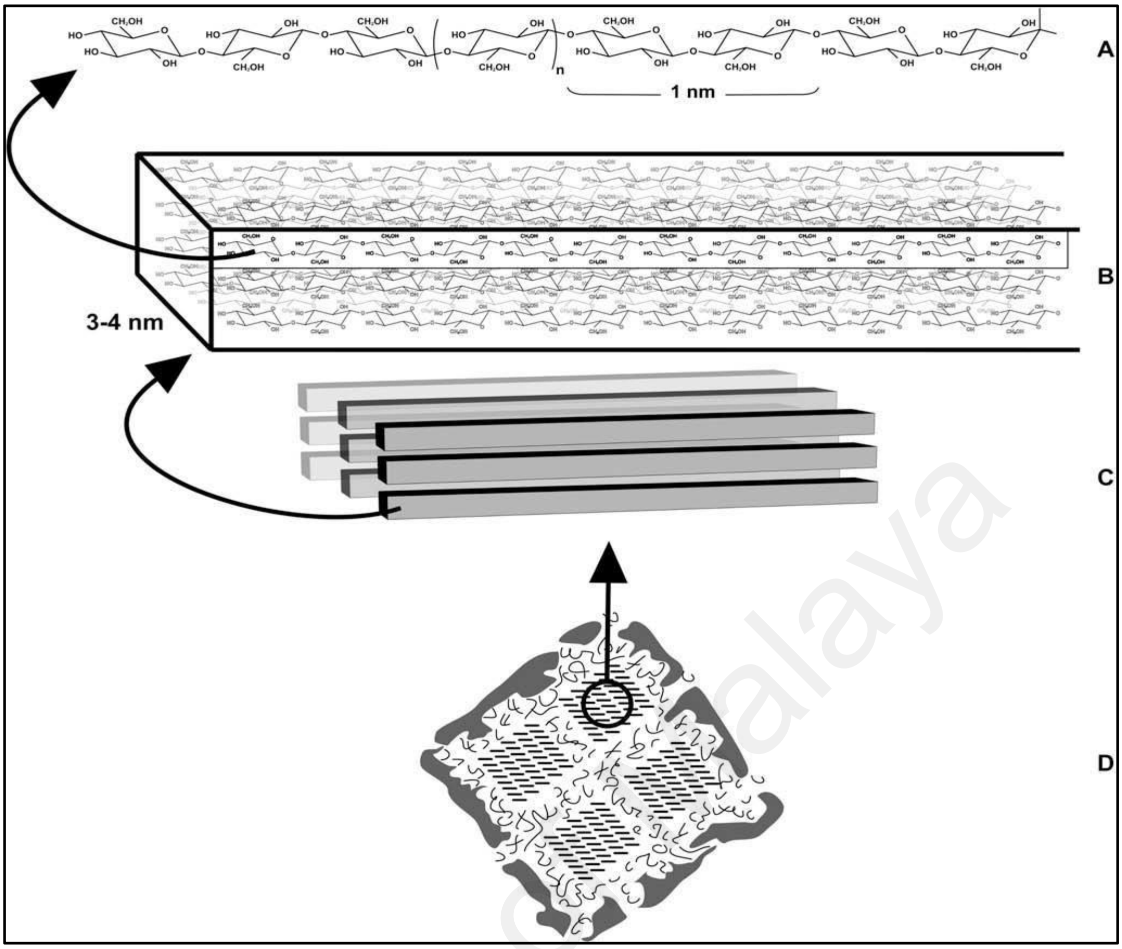

Figure 2.5: Internal structure of a CNF: (A) a chain of cellulose; (B) bundles of cellulose chains in an elementary fiber; (C) parallel elementary fibers; (D) nanofibers aggregated together with hemicelluloses and lignin. Adapted from ―The chemistry involved in the steam treatment of lignocellulosic materials,‖ by Ramos, 2003, *Quimica Nova*, 26(6), p. 863-871.

The information about the dimension of CNF can be easily obtained through a combination of microscopic methods with morphology study except for its lengths due to the entanglements and complicates in analyzing both ends of each CNF. The white and coloured nanofibers suspensions were produced by the acid hydrolysis of natural cotton fibers in white and coloured, respectively (de Morais Teixeira et al., 2010). Both the cotton nanofibers were investigated through morphology study and other characterization tests. From morphological study, the length and diameter of both nanofibers is about 85–225 nm and 6–18 nm, respectively. Based on their nanostructures from morphological study, no significant differences were observed from both cotton nanofibers. For the white nanofiber, it had higher thermal stability under dynamic temperature conditions, sulphonation effectiveness and slightly improved yield compared to the coloured nanofiber. However, in isothermal conditions, the coloured nanofiber had a higher thermal stability than the white nanofiber at 180°C.

Partially or significantly fibrillated cellulose fibers have been applied as beaten pulps in papermaking and microfibrilated cellulose (MFC), respectively. By continuous high-pressure homogenization process, MFC can be produced from wood pulp slurries at the level of industrial (Turbak et al., 1983). It has been utilized as a thickener and filter aid. In general, consumption of high energy is required for nano-fibrillation of wood and other sources of plant celluloses by incomplete cleavage of hydrogen bonds between the fibrils. Besides, it is still impossible to achieve complete separation of wood cellulose fibers to produce fibril elements with 3-4 nm in width without any loss. At the laboratory level, it is found that the mechanical fibrillation of cellulose slurries was more effective in terms of energy consumption and nano-fibrillation.

At the laboratory level, nano-fibrillations of various celluloses through chemical approach have been widely studied. A traditional acid hydrolysis method is chosen to introduce the anionically charge functional groups onto the surfaces of MFC using 64% H_2SO_4 at about 45°C for 1-4 hours (Elazzouzi-Hafraoui et al., 2007; van den Berg et al., 2007). Thus, negatively charged groups on the surfaces of MFC will now produce strong electrostatic repulsion among the MFCs in the water. Hence, the amorphous parts present in the fibers can be removed and leaving the crystalline parts. After the successive times of mechanical disintegration on the acid hydrolyzed MFC slurry, it will formed cellulose nanocrystals (CNCs) or cellulose nanowhiskers (CNWs) (van den

Berg et al., 2007). The dimensions of the CNCs or CNWs could be varied for each living organisms due to different percentages of amorphous parts in the bulk fibers.

Nonetheless, the percentages of weight recovery are only about 30-50%. Pre-treatment of cellulases or partial carboxymethylation of celluloses caused a decreased in consumption of energy for nano-fibrillation process in water using high-pressure homogenizer and refiner processes (Wågberg et al., 2008). Graft-polymerization of acrylonitrile onto celluloses followed by consecutive mechanical processes are likely to ensure the dispersion of partially negatively charged groups-grafted nanocellulose in the slurry (Lepoutre et al., 1976). Acid-hydrolyzed CNCs and enzymatically or chemically treated MFCs have been analyzed particularly for applications as nano-fillers in bio-nanocomposites and relevant review has been reported (Eichhorn et al., 2010).

The preparation method, yield and other important properties of TEMPO-mediated oxidized cellulose nanofiber (TOCN), MFC and CNC or CNW are represented in Table 2.1. The high degree of nano-dispersion, high aspect ratios and uniform widths of individual TOCNs are considered to be more benefit as compared to the others. The TOCN was clearly indicated for its potential application as bio-based nanofibers in high technology areas.

Table 2.1: Differences between TOCN, MFC and CNC or CNW. Adapted from ―TEMPO-oxidized cellulose nanofibers,‖ by Isogai et al., 2011, *Nanoscale*, 3(1), p. 71-85.

	TOCN	**MFC**	**CNC or CNW**
Preparation method	TEMPO-mediated oxidation of wood cellulose, and mechanical disintegration of the oxidized cellulose slurry	Consecutive high-pressure homogenizer process of wood cellulose slurry	Acid hydrolysis of wood cellulose with 64% H_2SO_4, and disintegration of the residues in water
Yield	More than 90%	Approximately 100%	Less than 50%
Morphology	Uniform width of 3-4 nm, <2-3 µm in length	Uneven width of 10-2000 nm forming bundles	Uneven width of 5-10 nm, <300 nm in length, spindle-like whiskers forming partial bundles
Energy consumption in nano-conversion	<7 MJ kg^{-1}	700-1400 MJ kg^{-1}	<7 MJ kg^{-1}
Potential applications	High gas-barrier films for packaging & display, fine separation filters, health care materials, nanofibers for composites	Filter aid nanofiber for composites, thickeners	Nanofiller for composites

2.6 Surface Modification of Cellulose Nanofiber

To produce composite with enhanced mechanical properties and environmental performance, it is important to improve the hydrophobicity of the cellulose nanofiber (CNF) which leads to improvement of interaction between nanofiber and polymer matrix. There are some disadvantages of using plant cellulose fiber-reinforced composite include low melting point, limited interfacial adhesion and poor moisture barrier properties. The purposes of pre-treatments of the cellulose fiber are to clear the surface of fiber, reduce the absorption of moisture by fiber, enhance the roughness of surface and chemically modify the fiber surface. Silylation, acetylation, peroxide, mercerization, benzoylation, bacterial cellulose treatment and graft copolymerization are among the great techniques for surface modification of natural fibers.

Nanofibrillated celluloses show a large surface area in the order of 50–70 m^2/g due to their nano-sized. These nano-sized celluloses indicate the great improvement of the amount of hydroxyl groups on the surface for modification and modify the normal conditions of grafting. Besides, the method of production will generally control the surface chemistry of CNF. Undoubtedly, few techniques have been reported before to reduce the consumption of energy for fibrillation through the surface modification method. For instance, carboxylic acid groups were introduced at the fibrillated cellulose surface through TEMPO-mediated oxidation method (Missoum et al., 2013). The use of carboxymethylation reaction as pre-treatment followed by mechanical defibrillation has successfully modified the surface chemistry of the nanofiber to produce carboxymethylated CNF (Wågberg et al., 2008). Thus, it is important to look precisely into any pre-treatment when studying about the surface medication strategies of CNF.

Silane-coupling agents often enhance the cross-linking level, lead to a perfect bonding in the interface region. Silanes perform hydrolysis and condensation stage before the formation of bond. Through interaction with hydroxyl groups on the fiber surface, silanols can produce polysiloxane structure. Hydrolyzable alkoxy group results in the fabrication of silanols in the presence of moisture condition. The silanol then produce strong covalent bonds to the cell wall that are chemisorbed onto the surface of fiber, through reaction with the hydroxyl groups on the fiber surface. Owing to formation of a cross-linked network through strong covalent bonding between polymer matrix and fiber, the hydrocarbon chains introduced by the use of silane reduce the swelling properties of the fiber (Kalia et al., 2009).

Another common method to fabricate good quality fibers is known as mercerization (Ray et al., 2001). Figure 2.6 represents the possible mechanism of mercerization of cellulose fibers. In general, mercerization results in fibrillation, which leads to cleavage of the bundle of composite fiber into smaller fibers. This technique decreases the diameter of fiber, resulting in improvement of aspect ratio. Improvement in mechanical properties and interfacial adhesion of fiber-polymer matrix are correlated to the formation of rough surface topography as reported by researcher (Joseph et al., 2000). Furthermore, the amount of possible active sites can be improved by mercerization which provides better wetting of fiber. Mercerization has a significant consequence on the polymerization degree and orientation of the cellulose crystallites molecules as well as the chemical component of the flax fibers. This is owing to the removal of cementing substances such as hemicelluloses and lignin in the mercerization technique. Thus, it have been reported that mercerization enhanced the mechanical properties for a long-lasting period, particularly on the stiffness and strength of fiber (Gassan and Bledzki, 1999).

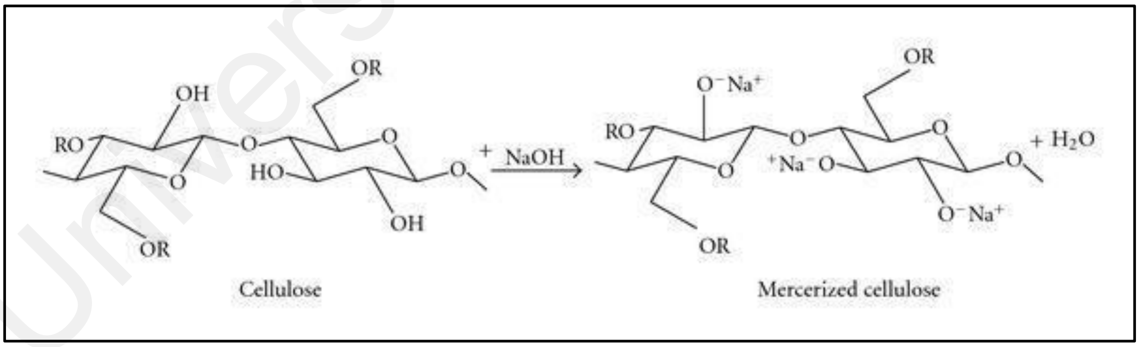

Figure 2.6 : Probable mechanism of mercerization of cellulose fibers. Adapted from ―Cellulose-based bio- and nanocomposites: A review,‖ by Kalia, Dufresne, et al., 2011, *International Journal of Polymer Science*.

Acetylation of cellulose is one of the great methods for improving the performances of cellulose fibers. Acetylation of cellulose fibers to provide plasticization is a common method called esterification. Acetylation is a good technique for wood cellulose to protect the cell walls against moisture in the surrounding, enhance stability of dimensional and prevent environmental degradation. By substituting the hydroxyl groups on the cell wall with acetyl groups through pre-treatment of nanofibers with acetic anhydride, has modified these polymers to turn hydrophobic. It is possible by utilizing acetic anhydride moieties in acetic acid for homogeneous and heterogeneous acetylations of CNFs of bacterial nanocelluloses. For the homogeneous acetylation, once the partially acetylated molecules were soluble enough, they will be transferred into the medium for acetylation process. Meanwhile for heterogeneous acetylation, the cellulose acetate was insoluble and the crystalline region of unreacted chains of cellulose was surrounded. It has also been reported for the simultaneous situation of acetylation and cellulose hydrolysis of hydroxyl groups. A possible one-pot reaction methodology includes the simultaneous occurrence of cellulose chains hydrolysis on amorphous phase and Fischer esterification of hydroxyl groups that allows separation of acetylated CNFs in a single-step reaction (Braun and Dorgan, 2008).

One of the great methods that have increased the interests of researchers is peroxide technique of cellulose fiber due to its low difficulty to process and significant enhancement in mechanical properties. The free radicals are easily produced through the decomposition of organic peroxides. The free radicals obtained are then able to react with the hydroxyl groups of the cellulose fibers and matrix. Figure 2.7 illustrates the peroxide treatment technique on cellulose fibers (Sreekala et al., 2000).

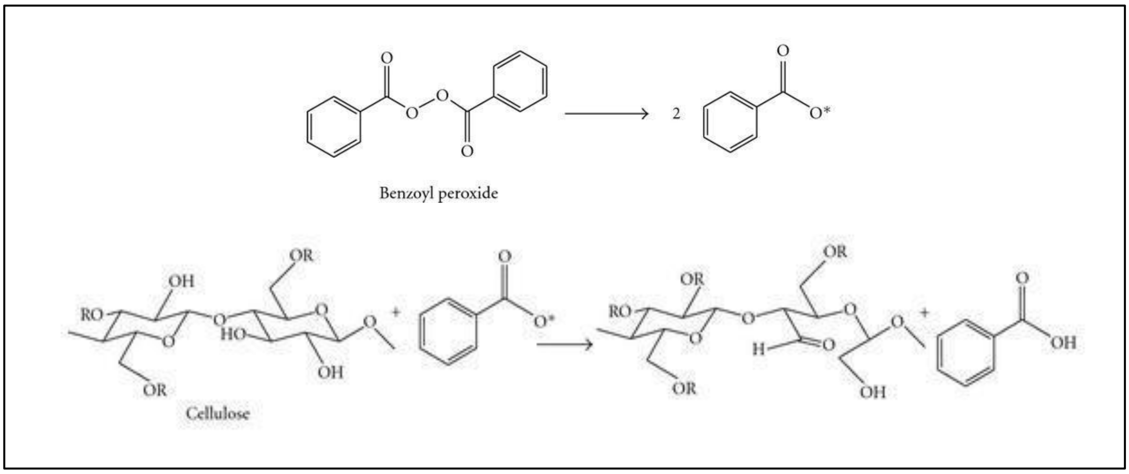

Figure 2.7 : Peroxide treatment technique on cellulose fibers. Adapted from ―Cellulose-based bio- and nanocomposites: A review,‖ by Kalia et al., 2011, *International Journal of Polymer Science.*

The chemical that most often used in benzoylation treatment is benzoyl chloride. In this pre-treatment, the reduced hydrophilic properties of the treated fiber depends on the introduction of benzoyl groups ($C_6H_5C=O$) in the fiber (Joseph et al., 2000). 35 g of washed fibers were soaked in 18% NaOH solution for half an hour and then filtration and washing with water. The treated fiber was immersed in 10% NaOH solution and mixed with 50 mL benzoyl chloride to introduce the benzoyl groups into the fiber. Figure 2.8 illustrates the reaction between the hydroxyl group of sisal cellulose fiber and benzoyl chloride.

Surface chemical modification can be done through covalent binding of small molecules or polymers to cellulose nanoparticles. The major purpose of this modification is to improve the apolar properties of the nanoparticles, which leads to a higher compatibility with hydrophobic polymer matrix. There are two main methods for polymer grafting on the CNFs surface called the ―grafting-onto‖ and ―grafting-from‖. ―Grafting-onto‖ was usually used for the fibers or the particles of cellulose nanocrystals (CNCs) but not for the CNFs.

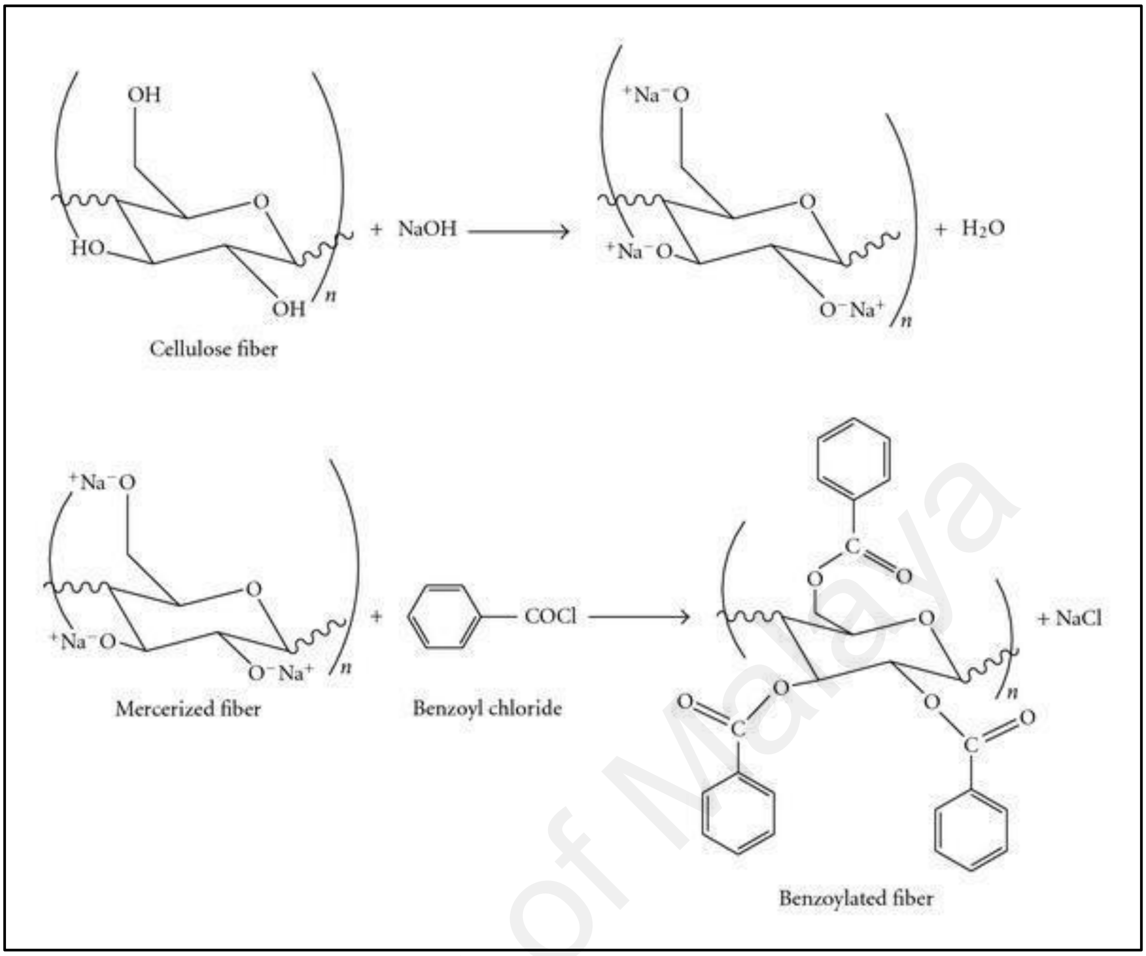

Figure 2.8 : Reaction between hydroxyl groups of sisal cellulose fiber and benzoyl chloride. Adapted from —Effect of benzoylation and graft copolymerization on morphology, thermal stability, and crytallinity of sisal fibers,‖ by Kalia et al., 2011, *Journal of Natural Fibers*, 8(1), p. 27-38.

There are two main techniques for —grafting-onto‖ approach. First is the mixing of the nanoparticles of cellulose with a polymer followed by adding a coupling agent to bind the polymer to the surface of nanoparticle. Second is the grafting of one onto the other one after activating the polymer or the cellulose substrates. This approach gave low grafting densities due to the steric hindrance caused by the chains of polymer. Besides, the high viscosity of reaction medium is probably due to the presence of macromolecular chains. The major advantage of this approach is that the characteristics of the products obtained are well modified since the molecular weight of bound polymer can be identified before grafting.

The ―grafting from‖ approach is about the mixing of nanoparticles of cellulose or the activated nanoparticles of cellulose with a monomer followed by adding an initiator agent to generate polymerization of the monomer from the surface of nanoparticle. This approach seems to be an extremely effective method to provide higher grafting densities due to less steric hindrance and reduced viscosity of reaction medium. In contrast to ―grafting-onto‖ approach, it is harder to control their properties since the molecular weight of the grafted polymer are difficult to identify precisely, as this is the limiting factor for low degree of polymerization. The amount of non-grafted homopolymer is hard to identify. The preparation of polycaprolactone (PCL)-grafted cellulose nanoparticles by the ―grafting from‖ approach has been reported. PCL is classically prepared through the ring-opening polymerization of cyclic ε-caprolactone monomer in the presence of $Sn(Oct)_2$ as catalyst. This approach was also utilized to produce PCL-grafted ramie (Habibi et al., 2008) and native linter (Lin et al., 2009) CNCs.

Through the coating of bacterial cellulose onto cellulose fibers, the interaction between the fibers and polymer matrix can be easily manipulated. Bacterial cellulose coated fibers induce homogeneous dispersion of bacterial cellulose within the polymer matrix and enhance the interfacial adhesion between fibers and polymer matrix through the reaction of mechanical interlocking (Pommet et al., 2008). Coating of cellulose fibers using bacterial cellulose is considered as one of the eco-friendly methods for surface modification of fibers. The use of bacterial cellulose for surface modification has received increased attention for further research due to its significant characteristics such as biodegradability, water absorption, moldability, excellent biological affinity, porosity and mechanical behaviours in both dry and wet states (Shoda and Sugano, 2005). Because of those characteristics, bacterial cellulose could provide a broad range of potential applications.

Furthermore, a variety of eco-friendly approaches have been identified such as bacteria, fungi and enzymatic treatments. The compatibility of natural fibers with hydrophobic polymer matrix can be improved through all these approaches. Kalia and Sheoran (2011) have reported the bio-polishing of ramie fibers assisted by cellulase enzyme using bacteria *Streptomyces albaduncus*. The biopolishing of ramie fibers was investigated for 5 days, at the pH 7.4 and 2.0 g glucose. As a result, this method has improved the brightness since the gum materials and small fibrils protruding from the fiber surface have been removed. However, this treatment shows only little consequence on crystalline structure and thermal stability of ramie fibers.

2.6.1 TEMPO-Mediated Oxidized Cellulose Nanofibers (TOCNs)

Nowadays, the more regularly used surface modification method is TEMPO-mediated oxidation. TEMPO-mediated oxidation is a prominent technique for selectively modifying the surface of cellulose under mild and aqueous conditions (Missoum et al., 2013). Figure 2.9 shows that the primary hydroxyl groups at C6 position of cellulose are expected to be oxidized to carboxylate groups by TEMPO/NaBr/NaOCl oxidation method in water at pH 10. It was proved that the carboxylate groups are formed at C6 position in the presence of oxidized TEMPO and NaOCl in the TEMPO/NaBr/NaOCl system at pH 10 (Isogai et al., 2010). In general, CNFs can be produced by TEMPO-mediated oxidation of cellulose fibers and then mild mechanical homogenization of the oxidized celluloses slurry (Fujisawa et al., 2011). TEMPO-mediated oxidized cellulose nanofibers (TOCNs) shows uniform widths of 3-4 nm, high aspect ratios (>50) and high crystallinity as compared to the nanocelluloses produced from other methods. Moreover, due to the effective electrostatic repulsion present on the anionically charged on the TOCNs surfaces, the individualized oxidized cellulose nanofibers can be well distributed in water (Fujisawa et al., 2011). This individualization of microfibril cellulose (MCC) from cellulose fiber is almost impossible without severe destruction and yield loss owing to the existence of intermolecular hydrogen bonding between MCC in cellulose fibers.

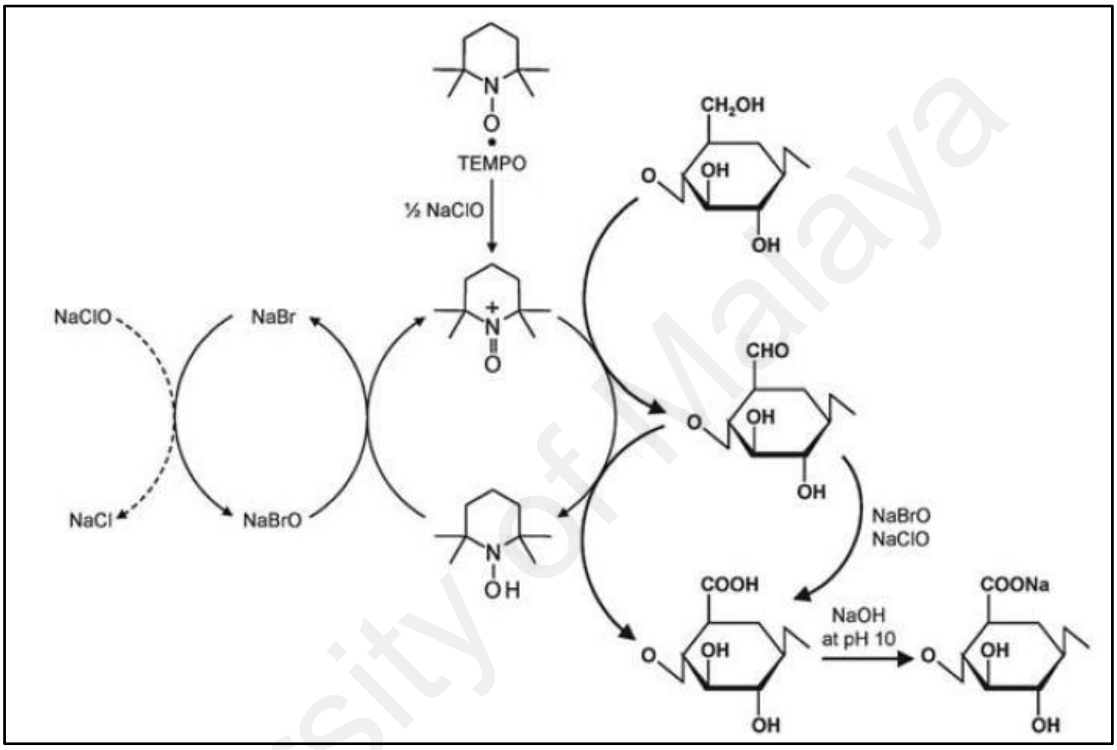

Figure 2.9: Regioselective oxidation of primary hydroxyls at C6 position of cellulose to carboxylate groups by TEMPO/NaBr/NaClO oxidation in water at pH 10. Adapted from ―TEMPO-oxidized cellulose nanofibers,‖ by Isogai et al., 2011, *Nanoscale*, 3(1), p. 71-85.

An alternative of TEMPO oxidation has been suggested for the use of TEMPO/NaOCl/$NaClO_2$ oxidation methods in organic solvents, where TEMPO and NaOCl with known amounts are mixed with $NaClO_2$ as the primary oxidant (Zhao et al., 1999). Figure 2.10 shows the mechanism scheme of TEMPO/NaOCl/$NaClO_2$ oxidation system applied to commercial cellulose immersed in a buffer at pH 4.8 to 6.8. Numerous TEMPO-mediated oxidation systems and conditions have been tested on curdlan, chitin, cellulose and other mono- and polysaccharides based on regioselectivity of the primary hydroxyl groups at C6 position, elimination of depolymerisation or residual reactions, usage of non-chlorine based primary oxidants and efficiency of oxidation system (Isogai et al., 2011).

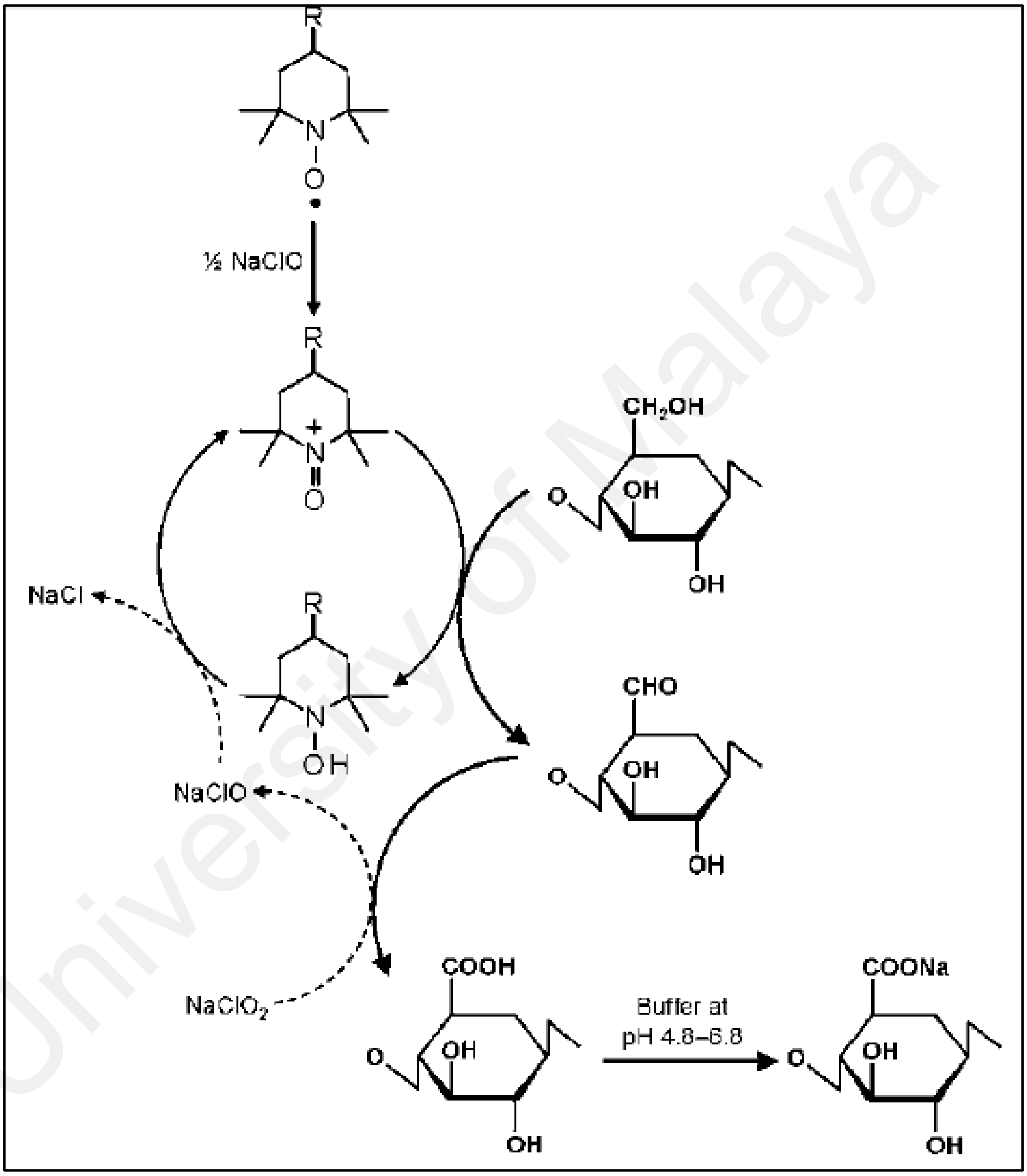

Figure 2.10: Selective oxidation of primary hydroxyl groups at C6 position of cellulose to carboxylate groups by TEMPO/NaOCl/NaClO$_2$ system in water at pH 4.8 to 6.8. Adapted from ―TEMPO-oxidized cellulose nanofibers,‖ by Isogai et al., 2011, *Nanoscale*, 3(1), p. 71-85.

Researcher has reported the use of TEMPO-oxidized nanocellulose in various fields. One of the applications is to produce bio-nanocomposite films. For example, TEMPO-mediated oxidized bacterial cellulose as a reinforcing phase, is mixed with CS to produce films with different ratios (Lai et al., 2014). As a result, the films obtained could have potential application in the biomedical field such as topical delivery lidocaine, wound dressings, ventral hernia patches and contact lenses. Another usage of TEMPO-oxidized nanocellulose is the cross-linking agent in which the cross-linked alginate/cellulose sponges are designed through the preparation of TEMPO-oxidized nanocellulose (Lin et al., 2012). It is reported that these cross-linked sponges showed enhanced mechanical properties, promising enhanced water absorption, porosity and structural stability. Hence, these sponges could show their potential applications as reinforcing platforms, thermal and acoustic insulating materials, kinetic energy absorbers, scaffolds for nanocomposites and etc (Lin et al., 2012).

Besbes et al. (2011) used various fiber sources such as eucalyptus, pine and alfa with 5-20 nm in diameter. To improve the content of carboxyl groups, a TEMPO-mediated oxidation method at neutral pH was done on the fibers to enhance the fibrillarion process during the homogenization technique using high pressure. Syverud et al. (2011) did a comparison study between pinus radiata and eucalyptus pulp fibers, as natural sources for fabricating nanofibers. The CNFs were formed by mechanical treatment and also by the combination of chemical and mechanical treatments. The fibers obtained were then subjected to a TEMPO-mediated oxidation before the mechanical homogenization. The production of nanofibers using eucalyptus pulp fiber as natural source was more favourable as compared to the pinus radiate pulp fiber due the amounts of carboxylic acids after the pre-treatment.

Due to the high hydrophilic surface of nanofiber, it has limited the potential applications of CNFs because of strong water absorption ability (Hubbe et al., 2008). In summary, numerous surface modifications on CNFs can significantly enhanced their miscibility within the hydrophobic polymer matrices. There are:

(a) esterifications involving the hydroxyl groups (Mohanty et al., 2001);

(b) modification of cellulose fibers by acylation with fatty acids (Freire et al., 2008);

(c) addition of surfactant (de Souza Lima and Borsali, 2004; Ljungberg et al., 2005);

(d) usage of cross-linking agents to induce grafting between hydrophilic nanofibers and hydrophobic polymer matrix (Mokoena et al., 2004).

2.7 Biopolymer Composite

All over the last few decades, the benefits and applications of polymer composite material has been extensively studied. Each part of components is always obtained from renewable natural resources such as cellulose, starch and chitosan (CS). In general, there are two types of polymers which are synthetic polymer and biopolymer. Synthetic polymers primarily derived from sources of petroleum while biopolymers mainly derived from renewable natural sources. The huge advantages of biopolymer have attracted much more attention from the researchers in the field of polymer. Numerous sources of biopolymer developed and classified based on its origin.

However, biopolymers are generally very sensitive to various environmental conditions. Although the biopolymers displayed their own potential, it is important to improve some of their properties to an acceptable level that can compete with the petroleum-derived polymers, especially their poor mechanical, barrier, processing and thermal properties, which are the desired properties for packaging applications (Kanmani and Rhim, 2014; Rhim and Ng, 2007; Rodríguez-González et al., 2012).

Many studies have reported for the fabrication of biodegradable polymer composite through the blending of biopolymer and petroleum-derived polymer. There are a lot of possible methods in fabricating biopolymer composite using various types of sources. Numerous researches have been done to produce new composite materials by the blending of two or more natural biopolymers such as chitosan (CS), starch, etc. and synthetic polymers such as polyvinyl alcohol (PVA), polycaprolactone (PCL), polylactic acid (PLA), low density polyethylene (LDPE), etc. (Alix et al., 2013; Bonilla et al., 2013; Kanatt et al., 2012; Tripathi et al., 2009; van den Broek et al., 2015). For example, PVA has been blended with starch and LDPE to produce composite films as packaging materials for intermediate moisture foods (Holton et al., 1994). Blending approaches are a very promising way to produce novel eco-friendly biomaterials with desired thermal, mechanical, optical and barrier properties. (Avella et al., 2005; Chen et al., 2003; Mensitieri et al., 2011; Rhim et al., 2013; Rhim and Ng, 2007). Blending of natural and synthetic polymers may improve the cost effectiveness of the composite films because most synthetic polymers can be easily obtained and have a relatively low production cost (Bahrami et al., 2003). In addition, the most important criteria is the sustainability and renewability of materials supplied for the production (Tan et al., 2015). The bio-composites derived from natural fibres and bio-based plastic materials which are likely to be environmental-friendly are classified as green composite (John and Thomas, 2008).

Extensive researches have also been done on the applications of bio-composites in construction and building industry owing to their characteristics includes lower weight and costs of manufacturing (Christian and Billington, 2009). The potential applications of bio-composites for various types of products such as fencing, decking and etc. have gained much more attentions from the house owners. Based on the applications of bio-composites in building sector, in can be divided into two major groups such as structural and non-structural forms (Rowell, 1995). Bio-composite in structural form can be explained as one that is required to bear the weight in handling. The examples of structural bio-composites are load-bearing walls, stairs, building industry, subflooring and roof systems. In contrast, the bio-composite that do not have to bear the load in use is known as non-structural bio-composite. Examples of these kind of bio-composite materials are wood particles, textiles and thermoplastics. The products of bio-composites in non-structural form are furniture, doors, ceiling tiles and windows.

Since PVA/CS composite blend shows good compatibility, it is a promising strategy to blend PVA and CS to obtain the combined properties of both polymers. It has been reported to be an effective technique by blending PVA and CS using solution casting method to produce films with desired characteristics such as good antimicrobial properties, tensile strength, barrier properties and formability (Bonilla et al., 2014; Tripathi et al., 2009). However, their poor elongation at break and thermal properties are still the main limiting factors for medical and packaging application as reported by researchers (Lewandowska, 2009; Srinivasa et al., 2003; Vidyalakshmi et al., 2004). Unfortunately, the poor performance of most biopolymer composites, especially their low cost effective ratio, material processing problems and barrier properties, has limited their potential application as packaging materials.

Several studies have been done on the properties of PVA/CS composites in biomedical applications (Costa-Júnior et al., 2009; Sundaramurthi et al., 2012). The non-toxicity and biocompatibility of genipin cross-linked PVA/CS composite cross was reported after in vitro examination (Bispo et al., 2010). PVA/CS composite blend is usually utilized for biomedical applications in drug delivery system for gene therapy sue to the biocompatibility of PVA and CS in the matrix. In biomedical engineering areas, the medical treatment of damaged tissue is known as tissue engineering. The formation of PVA/CS composites was done to analyze the crystallinity, chemical structure, mechanical and thermal properties in order to produce the membrane for controlled tissue regeneration (Zhuang et al., 2012). The biomedical applications of PVA/CS blend have been listed in Table 2.2.

Table 2.2 : Biomedical-pharmaceutical applications of PVA/CS blends.

Adapted from ―Chitosan functionalized poly(vinyl alcohol) for prospects biomedical and industrial applications: A review,‖ by Rafique et al., 2016, *International Journal of Biological Macromolecules*, 87, p. 141-154.

Types of Blends	**Applications**
PVA/CS blend nano-fibers	Drug delivery, Wound dressing
PVA/CS derivative blends	Wound healing
PVA/CS hydrogels	Contact lens
PVA/CS composite films	Burner dressing
PVA/CS composite blends	Medicine and oral delivery of enzymes
PVA/CS films	Tissue engineering

In summary, there are much more environmental concerns on the production of polymer composite by the engineers and scientists. The polymer composites must not be harmful to the environment at each step of their life cycle. Therefore, the environmental issues can be clarified using the natural fibers and polymers derived from renewable natural resources. Green bio-composites such as cellulose-, starch and soybean-derived plastics as well as polyhydroxyalkanoates (PHA) which are bacterial polyesters can be fabricated by reinforcing biopolymers derived from natural resources with natural fibers and could be used in the future.

2.8 Nano-Reinforcement of Cellulose Nanofibers in Biopolymer Composites

In general, nanocomposite can be defined as one of the reinforced materials had less than 100 nm in at least one dimension. There are two main approaches for the fabrication of nanocomposite. For examples, formation of nano-sized polymer materials or introduction of nano-sized materials into polymer to fabricate nanocomposite (Gacitua et al., 2005). Nanocomposites may obtain desired properties such as barrier properties, optical transparency, mechanical properties and thermal stability based on the nature and geometry of nanofillers (Lu et al., 2006). In food packaging application, nanofillers have been reinforced into the polymer composites to develop thin film that able to enhance the gas barrier properties, moisture absorption, temperature control and flexibility. Researchers have proved that the utilization of nanofillers in composite films could provide a crucial alternative to the conventional plastics.

In the range of nanoscale, polymer composites may have various electronic properties, which resulting in changes of optical, catalytic and other characteristics (Boccuni et al., 2008). Besides the improvement on the properties as proved by researcher, the use of nanotechnology on the composite polymers may also enhance the cost performance ratio (Sorrentino et al., 2007). However, most reinforcing phases of nanofillers pose weak interactions within the continuous polymer matrix. Macroscopic reinforcing materials in macroscopic size always have defects, which become less crucial with the reduced particles size of the reinforcing materials (Luduena et al., 2007).

In general, there are two types of reinforcement using nanocellulose which are cellulose nanowhiskers (CNWs) and cellulose nanofibers (CNFs) (Azizi Samir et al., 2005). The characteristics of cellulose fiber-based nanocomposite have been stated to be correlated to the aspect ratio and dimensions of the fibers, as well as the effects of mechanical percolation and geometry (Hubbe et al., 2008). By the way, the sources of the cellulose and conditions used in preparation of nanowhiskers may affect the aspect ratios of fibers. Different aspect ratios of CNWs extracted from pea hull fibers were prepared before reinforced into the starch matrix derived from pea to produce bio-nanocomposites. The CNWs with the highest aspect ratio showed the highest tensile properties and transparency as reported by researcher (Chen et al., 2009).

Nano-reinforcements using cellulose have been proved to have a synergetic impact in enhancing the Young’s modulus of polymer matrices (Bhatnagar and Sain, 2005). For example, it has been reported that a poly(styrene-co-butyl acrylate) latex film containing 30 wt% of straw CNWs exhibited a modulus more than a thousand times higher as compared to the bulk matrix (Helbert et al., 1996). In addition, the elongation at break (%E) of polymer composites has been reported to remain significantly unchanged (Iwatake et al., 2008) or improve by the addition of CNFs (Petersson and Oksman, 2006). It is found that the %E of polyurethane was enhanced by the incorporation of CNFs while was reduced when the addition of conventional microcrystalline cellulose (MCC) (Wu et al., 2007). CNFs are recognized as being more effective than their micro-sized counterparts to reinforce polymers due to the interaction between the nano-sized elements and polymer matrix that form a percolated network through hydrogen bonding, assumed there is a good dispersion of the nanofibers in the matrix (Angles and Dufresne, 2000; Nakagaito et al., 2009).

Besides that, the incorporation of CNWs to starch matrixes improves their thermal and mechanical properties, biodegradability behaviour and decreases water sensitivity (de Souza Lima and Borsali, 2004). The reinforcing effects are strongly related to the establishment of a network of CNFs within the polymer matrix due to the development of intermolecular hydrogen bonds interaction during the evaporation stage (Angles and Dufresne, 2001). The improved thermal behaviour of polymers with the incorporation of CNFs has also been reported. As distinguished with those bulk polymers, the increased thermal stability of CNWs reinforced nanocomposites has been reported (Helbert et al., 1996).

Both the degree of dispersion of nanofiller within the polymer matrix and the interfacial adhesion between both phases are strongly related to the degree of compatibility between the nanofiller and the polymer matrix (Hubbe et al., 2008). Due to the hydrophilicity of CNFs surface, it often forms strong interaction with the hydrophilic polymers (Bondeson and Oksman, 2007). Thus, it is crucial to obtain good interaction between nanofiller and polymer matrix, resulting in desired properties of the composites. However, it is observed that the interaction of CNWs with hydrophilic polymer matrix often lead to the weak interactions between nanofiller and polymer matrix (Hubbe et al., 2008). This weak interaction may be due to the aggregation of nanofiber by intermolecular bonding, resulting in low moisture barrier properties and weak interfacial compatibility with the polymer matrices.

To develop biodegradable polymer composites with modified properties, more efforts have been given using different sources of lignin-based cellulose materials especially in the form of nano-sized. Reinforcement using nano-sized materials is one of the crucial and nearly uncommon areas. The types of materials cover a wide range of sources such as inorganic or organic and from origin of natural or synthetic form. As for the natural source from plants, one of the highly potential nano-materials that can be indicated is CNF.

Biodegradable nanocomposites can be synthesized by a natural biopolymer reinforced with CNF. There are some other examples of nano-particles used for reinforcement such as CNFs, chitin and chitosan (CS) nanoparticles, nanosilica, carbon nanotubes, starch nanocrystals, clays and silicates and etc into the composite polymers (Ching et al., 2015; Yee et al., 2016). CNFs have been gaining much more attentions in recent years because they can be used as natural nanofillers to produce bio-nanocomposites due to their renewability, low cost, low density and non-abrasive nature (John and Thomas, 2008). The nanofillers (discontinuous phase) can be easily dispersed in a polymer matrix (continuous phase) to produce bio-nanocomposite films. Some of their properties can be greatly improved by the use of reinforcing nanofillers even though by the incorporation of only a small amount due to their high specific surface area. The well dispersion of incorporated nanoparticles in the inter-phase region could leads to formation of percolating inter-phase network in the bio-composite and improves the characteristics of nanocomposites (Qiao and Brinson, 2009).

Currently, bio-nanocomposite was prepared through the reinforcement of CNFs extracted from wheat straw into thermoplastic starch from modified potato starch using solution casting technique (Alemdar and Sain, 2008b). The characterization of the composites was done in terms of thermal and mechanical properties. The tensile strength (TS) and Young's modulus of the bio-nanocomposite films were significantly improved as compared to the pure thermoplastic starch, which could be correlated to the degree of dispersion of CNFs in the polymer matrix. Besides, the glass transition temperature (T_g) of the bio-nanocomposite films was increased to higher T_g as compared to the pure thermoplastic starch. CNFs-based thermoplastic starch bio-nanocomposites with the incorporation of glyceryl monostearate (GMS) have been fabricated by solution casting technique (Mondragón et al., 2008). The TS and Young's modulus of thermoplastic strarch composites were improved with the reinforcement of CNFs extracted from corncobs and husks. This is because of the strong interactions between the high aspect ratio of CNFs and the starch matrix. The mechanical properties were further enhanced with the addition of GMS as surfactant. Thus, the synergetic effects of nanoreinforcements using CNFs would be greatly useful for many technological and industrial applications in the future (Whitesides, 2005).

2.9 Advanced Functional Materials based on Cellulose Nanofiber Reinforced Bio-nanocomposite

Based on earlier studies, cellulose nanofibers (CNFs) are generally used for the reinforcement of composite materials. The reinforcement is not only focusing on hard composite but also in the formation of thin film. Therefore, CNFs could act as reinforcing phase for potential applications in automotives, construction, food packaging and etc (Khalil et al., 2012). In the initial stage of composite studies, the non-renewable polymer derived from petroleum was blended with the renewable natural bio-based polymer to produce environmental-friendly polymer composite with biodegradable characteristic. The natural fiber is also blended with polymer derived from petroleum to develop different kinds of composites. As the petroleum sources are depleted, the researchers are looking for the alternative by combining natural bio-based polymer with natural fiber in order to have synergetic effect from the composite. It is now known as green composite because it is fully constructed with natural materials. By incorporating natural material into the polymer derived from petroleum source, it can enhance the biodegradability of the petroleum-based polymer. As time going on, greater amounts of advance functional materials are developed based on the reinforcement of natural fiber in nano-sized. Thus, continuous development in novel material has been granted through the research studies on composite material. Nowadays, natural bio-nanocomposite is considered as part of the developing green technologies (Akpan Emmanuel, 2012). This composite also increases the interest of research in academic and industry areas.

In the wood industry, adhesive bonding is a conventional processing stage. Improvement of properties of adhesives depends strongly on the knowledge of polymer chemistry. However, there is still not much attention given on the function of the nanofiller in wood adhesives. The incorporation of fibrous filler into epoxy, an adhesive usually not utilized in the manufacturing of wood, generally enhances the mechanical strength of the bonding of an adhesive (Kinloch et al., 2003; Stewart et al., 2007). The low-priced UF resins are the common grade of wood adhesives. These wood adhesives are pronounced with their limiting mechanical properties due to the brittleness and ability to form micro-cracks. Recently, the reinforcement of CNFs on urea-formaldehyde (UF) resins has been extensively studied by a team of researcher led by Josef Keckes and Wolfgang Gindl. It is found that the mechanical properties of wood adhesives were significantly enhanced after the addition of CNFs. As a result, this improvement could expand the application for UF in other potential fields.

Recently, much more attention has also been gained for the production of nanoscale devices. This technology is very challenging potentially important especially for the applications in biomedical devices and sensors. Cellulose nanowhisker (CNW) is one of the most abundant, cheaper and chemically versatile nanoparticles applicable for production of nanoscale device. The CNWs were produced by acid hydrolysis followed by TEMPO-mediated oxidation method to form carboxylate group at C6 position. DNA grafted CNWs (DNA-g-nanowhiskers) were produced through the reaction of the amino group on the oligomer of modified DNA with the C6 carboxylate groups of CNFs via 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide (EDC)-assisted amide (Lloyd and Burns, 1979). More investigations are required to clearly understand the properties of hybridized DNA-g-nanowhiskers. Nevertheless, this primary study could help in broaden up the application of DNA especially as tissue scaffold in the field of tissue engineering.

CNFs from natural resources have been utilized for many composite applications. Renewable polymers reinforced with simple natural fiber has difficulty to attain the characteristics of commercial composite materials include polypropylene (PP) and glass fiber. Novel renewable bacterial CNFs formed by bacteria belonging to the genera *Alcaligenes, Rhizobium, Acertobacter* or *Agrrobacterium* may give promising effects for applications of composite. The modulus of bacterial CNF is significantly equal or even more than that of glass fibers. Bacterial CNF is light in weight, biodegradable, non-toxic and renewable in conjunction with its interesting mechanical characteristic. For example, the interfacial adhesion between natural fibers and polylactic acid (PLA) and cellulose acetate butyrate (CAB) was improved due to the ―hairy‖ behaviour of the bacterial CNF coated hemp and sisal fibers (Baltazar-y-Jimenez et al., 2008). Besides that, processing problems such as self-filtration, increased melt viscosity and aggregation of anisotropic nanofillers can be avoided through the reinforcement of these ―hairy‖ nanofibers into the polymer matrices. The enhanced thermal and mechanical properties of bio-nanocomposite were due to the strong interfacial adhesion which improved the efficiency of stress transfer between the nanofibers and polymer matrix. The TS and flexibility of the short fiber composites were greater than conventional PP materials utilized in the interior part of automotive, revealing its high potential in automotive application. Thus, it can be summarized that the eco-friendly nanocomposites reinforced with natural fiber are also a very promising materials to reduce or replace the conventional non-renewable plastics since the mechanical properties of some short fiber composites were higher than the commercial PP.

Bio-foams based in CNFs extracted from wood pulp and potato starch rich in amylopectin were prepared as reported by researcher (Svagan et al., 2007). Well-dispersed CNFs were blended with dissolved starch in a water suspension. The water content was removed from the frozen mixtures by sublimation in the dry stage. The structure of developed bio-foams was bio-inspired where the cell walls consist of biopolymer matrix and CNF network, as in cell walls of plant. The compositions of cell wall demonstrated great increment in absorption of energy when loading by compression. As compared to the neat amylopectin, the amount of energy absorption was doubled, with 40 wt% of CNFs. The novel material of biofoams derived from cellulose nanocomposite show its strong potential application in biomedical and packaging industry.

TEMPO-oxidized cellulose nanofibers (TOCNs) were incorporated into a CS polymer matrix using an eco-friendly solution casting technique to develop bio-nanocomposite films. A bio-nanocomposite film of lower oxygen and water barrier properties can be produced due to the crystallinity of TOCNs and the dense structure of the composite films. The resulting bio-nanocomposite films had higher mechanical properties, transparency and thermal stability as compared to pure CS films. The high degree of dispersion of TOCNs within the CS matrix has been proved through images of scanning electon microscopy (SEM) and atomic force microscopy (AFM). Thus, the results clearly revealed that the formation of TOCNs/CS bio-nanocomposite film was a green, feasible and efficient approach for application in food packaging industry due to its transparency and biodegradability (Soni et al., 2016). Furthermore, the cellulose nanocrystals (CNCs)/ZnO reinforced PVA/CS composites were prepared and their properties and structure were characterized to study the potential of bi-functional nanofillers. A strong interaction of nanofiller-matrix was due to the high degree of dispersion of CNCs/ZnO in the composite polymer matrix was indicated through their optical, thermal, morphological and mechanical properties. These bio-composites were reported to possess promising usage as UV-protecting, packaging, and medical materials (Azizi et al., 2014).

Cellulose nanowhiskers (CNWs) were incorporated into PVA/CS composite to produce a ternary bio-nanocomposite system according to intermolecular interaction such as the hydrogen bonding and electrostatic interaction. After CNWs was reinforced into the composite, an improved antimicrobial property was achieved through inhibition zone technique. It is also found that the CS relatively improved the oxygen barrier property of the bio-nanocomposites. Due to the aggregations of CNWs and CS caused by electrostatic interactions, the mechanical properties of the bio-nanocomposites were enhanced. Owing to the excellent properties, PVA/CS/CNWs bio-nanocomposite films were proved for their potential applications in food packaging industry (Li et al., 2015). In summary, nanocellulose reinforced PVA/CS composites provide a wide range of potential in biomedical applications such as biomaterial, drug delivery vehicles and skin tissue engineering (Costa-Júnior et al., 2009) as well as food packaging application.

2.10 Summary

In short, it has been proven that the biopolymers play a vital role in maintaining a sustainable environment. In fact, the use of biopolymers derived from renewable natural sources helps to reduce or replace the application of petroleum-derived polymers. Polyvinyl alcohol (PVA) is one of the most promising synthetic water-soluble polymers with excellent physical and chemical properties as well as good film-forming ability. Chitosan (CS) is a natural biopolymer and most important derivative of chitin which has unique properties such as great film-forming, antimicrobial and mechanical properties.

As validated by researchers, the properties of biopolymers could be improved through polymer blending with synthetic polymers to develop a new composite material. Although the properties of composites show improvement, there is still a huge gap to achieve desired properties to be commercialized in the market. In general, it has been suggested that the use of nanofillers in composites could greatly enhance their properties. Due to its unique properties, CNF could be used as nanofiller to develop nanocomposite with excellent properties. In general, CNFs are differentiated by its raw material, pre-treatment and isolation method. Surface modification of CNFs is a great technique to improve the compatibility between nanofiber and polymer matrix. TEMPO-mediated oxidation is one of the most common methods used for the surface modification of CNFs to produce TEMPO-mediated oxidized cellulose nanofiber (TOCN). TEMPO-mediated oxidation is a prominent technique for selectively modifying the surface of cellulose under mild and aqueous conditions (Missoum et al., 2013). As shown in the literature, the use of CNFs as nano-reinforcing phase could be extremely beneficial for potential applications in automotive, construction, food-packaging, and others.

CHAPTER 3 METHODOLOGY OF STUDY

3.1 Materials and Chemicals

Polyvinyl alcohol (PVA) (Kuraray Poval 220S) as part of the polymer matrix was purchased from Kuraray Co. Ltd, Japan. It has molecular weight of 78 kDa, specific gravity of 1.27-1.31, crystallinity of 82%, viscosity of 27-33 mPa.s, hydrolysis degree of 87-89%, melting temperature of 180°C and pH 5-7. Chitosan (CS) (molecular weight of 190-310 kDa and degree of deacetylation of 75-85%, used as part of polymer matrix), microcrystalline cellulose (MCC) (used as reinforcing agent) and TEMPO with 98% assay (used in surface treatment of cellulose microcrystalline) were purchased from Sigma-Aldrich Co. Llc. Chemicals used for the surface treatment of MCC were sodium bromide (NaBr, 99%, AR grade) (R&M Chemicals, Malaysia) and sodium hypochlorite (NaOCl, 10% chloride) (R&M Chemicals, Malaysia), sodium hydroxide (NaOH) and hydrochloric acid (HCl) (Labchem Sdn. Bhd., Malaysia) All of the chemical reagents are used without further purification.

3.2 Preparation of TEMPO-Mediated Oxidized Cellulose Nanofiber (TOCN)

The microcrystalline cellulose (MCC) was suspended in de-ionized water containing TEMPO and NaBr. The pH of the cellulose slurry was adjusted to 10.0 ± 0.2 with 0.5M NaOH using a pH-meter under gentle agitation. The oxidation was started by adding the NaOCl solution (5.0 mmol NaOCl per gram of cellulose) and conducted at room temperature while stirring. During the oxidation process, the pH was maintained at 10.0 ± 0.2 by adding 0.5M NaOH or 0.5M HCl using a pH meter. The reaction was quenched after 90 min by adding ethanol, and pH 7 was adjusted by adding 0.5M HCl.

The TEMPO-mediated oxidized microcrystalline cellulose (TMOCC) suspension was filtered, thoroughly washed with de-ionized water.

0.5% (w/v) slurry of TMOCC suspension was prepared and agitated at 15,000 rpm for 5 min using a mechanical homogenizer. The slurry was then sonicated for 10 min to produce TOCN with separated dispersion using an ultrasonic bath. The disintegrated suspension was centrifuged at 10,000 x g for 12 min to remove a small amount unfibrillated and partially fibrillated fractions from the supernatant containing TOCNs. The amount of TOCNs was obtained by drying three samples of 50 mL each from the supernatant at 105°C. The resulting suspension obtained was stored at 4°C before further preparation of bio-nanocomposite films.

3.3 Preparation of Bio-nanocomposite Films

The biodegradable PVA/CS/TOCNs bio-nanocomposite films were prepared using solution casting method. CS flakes were dissolved in 2.0% (w/w) aqueous acetic acid solution with continuous stirring, at 60°C for 24 hr to obtain a 1.0% (w/w) solution. Meanwhile, PVA was dissolved in water under constant stirring, at 80°C to obtain a 5% (w/w) solution. Both solutions were allowed to cool until ambient temperature was reached. The TOCN solution was ultrasonicated for 20 min before continued with the blending step. The resulting solutions were blended together based on the desired mass ratios under mechanical stirring at 2000 rpm for 1 hr until a homogeneous suspension is formed. The nanofiller and matrix were mixed carefully in order to avoid water bubbles and voids. Subsequently, the solution mixtures were transferred onto glass petri dishes. It was then dried at 60°C until the composite dried evenly. The dried composite films were then peeled off from their dishes, and then stored in a desiccator for future characterization uses. The weight composition of TOCNs reinforced PVA/CS bio-nanocomposites are shown in Table 3.1.

Table 3.1: Weight composition of TOCNs reinforced PVA/CS bio-nanocomposites.

Samples	PVA %(w/w)	CS %(w/w)	TOCNs %(w/w)
PVA/CS = 100/0 (Pure PVA)	100.0	0.0	0.0
PVA/CS = 75/25	75.0	25.0	0.0
PVA/CS = 50/50	50.0	50.0	0.0
PVA/CS = 25/75	25.0	75.0	0.0
PVA/CS = 0/100 (Pure CS)	0.0	100.0	0.0
PVA/CS/TOCN = 100/0/0.5	99.5	0.0	0.5
PVA/CS/TOCN = 75/25/0.5	74.6	24.9	0.5
PVA/CS/TOCN = 50/50/0.5	49.8	49.8	0.5
PVA/CS/TOCN = 25/75/0.5	24.9	74.6	0.5
PVA/CS/TOCN = 0/100/0.5	0.0	99.5	0.5
PVA/CS/TOCN = 100/0/1.0	99.0	0.0	1.0
PVA/CS/TOCN = 75/25/1.0	74.3	24.7	1.0
PVA/CS/TOCN = 50/50/1.0	49.5	49.5	1.0
PVA/CS/TOCN = 25/75/1.0	24.7	74.3	1.0
PVA/CS/TOCN = 0/100/1.0	0.0	99.0	1.0
PVA/CS/TOCN = 100/0/1.5	98.5	0.0	1.5
PVA/CS/TOCN = 75/25/1.5	73.9	24.6	1.5
PVA/CS/TOCN = 50/50/1.5	49.3	49.3	1.5
PVA/CS/TOCN = 25/75/1.5	24.6	73.9	1.5
PVA/CS/TOCN = 0/100/1.5	0.00	98.5	1.5

3.4 Characterization Study

3.4.1 Tensile Properties

The tensile strength (TS) and elongation at break (%E) of the films were measured as per ASTM D882 test methods, using Autograph AGS-X Universal Tester (Shimadzu, Japan). The tensile samples were cut in rectangular shapes with dimensions of 100 mm in length and 10 mm in width. The gauge length was fixed at 50 mm and the speed of the moving clamp was 5 mm min^{-1}. Five samples were tested and the average values were taken as the reported results.

3.4.2 FESEM Analysis

The surface morphology of the sample films was studied using a field emission scanning electron microscopy (FESEM), Hitachi SU8220 (Japan) with an operating voltage of 1.0kV at a magnification of 20,000 x at room temperature. Each sample was put on a holder before being coated with a thin platinum layer to avoid the charging effect.

3.4.3 Fourier Transform Infrared Spectroscopy (FTIR) Analysis

The Fourier transform infrared spectroscopy (FTIR) analysis of the sample films was performed using a FTIR Spectrum 400 (Perkin Elmer, USA). The analysis was carried out in the range from 4000-400 cm^{-1} with a resolution of 4 cm^{-1} and a total of 32 scans. The FTIR spectrum was recorded in the mode of transmittance.

3.4.4 Thermal Properties

The thermogravimetric analysis (TGA) of the films was conducted using a Mettler Toledo TGA/SDTA851 thermogravimeter (Mettler Toledo Coro, Switzerland). The samples size was approximately 10 mg. The samples were heated at the rate of 15°C min^{-1} from 35°C-600°C under flowing of air.

3.4.5 X-Ray Diffraction (XRD) Analysis

The X-ray diffraction (XRD) analysis of the films was carried out using a Rigaku (Japan) X-ray diffractometer. The instrument was operated at 40 kV and 40 mA and the X-ray radiation was nickel-filtered Cu (wavelength=0.1542 nm). The samples were analyzed over a scanning scope of 2θ from 5° to 80° with a step increment of 0.02°second^{-1} at room temperature.

3.5 Safety Aspects

During the laboratory work, personal protective equipments such as lab coat, gloves and eye protection were used. All the chemicals used such as TEMPO, NaBr, NaOCl, NaOH and HCl were handled in care. Good hygiene procedures were followed when handling chemical materials. The chemicals were avoided in contact with eyes and skin. Hands were cleaned after chemicals handling. The chemicals were also prevented from extreme heat, ignition sources or open flame. Moreover, the chemicals were stored in a safety storage cabinet under cool and dry conditions.

CHAPTER 4 RESULTS AND DICUSSION

In preliminary study, TEMPO-mediated oxidized cellulose nanofiber (TOCN) reinforced PVA/CS bio-nanocomposite films with various amounts of nanofiber were prepared and characterized using several methods. Microcrystalline cellulose (MCC) was treated with TEMPO-mediated oxidation followed by mild mechanical disintegration in order to produce strong interfacial adhesion and bonding as well as better degree of distribution of TOCN within PVA/CS composite matrix. The results and discussion of preparation and characterization tests are stated below.

4.1 TEMPO-Mediated Oxidation from Microcrystalline Cellulose

Microcrystalline cellulose (MCC) was used as the starting material in this section. The 0.5% (w/v) slurry of TEMPO-mediated oxidized microcrystalline cellulose (TMOCC) suspension was mechanically agitated under room temperature. The unfibrillated and partially fibrillated fractions present in the obtained dispersion were removed by centrifugation. The nanofibrillation yield was around 80% for TMOCC prepared from MCC.

Fourier Transform Infrared (FTIR) spectrum of the MCC and TEMPO-mediated oxidized cellulose nanofiber (TOCN) are depicted in Figure 4.1. From spectrum of TOCN, the C=O stretching absorption band of sodium carboxyl and free carboxyl groups were appeared as new peaks at 1614 cm^{-1} and 1717 cm^{-1}, respectively as compared to the spectrum of MCC (Fujisawa et al., 2011). These peaks indicate the formation of sodium carboxyl and free carboxyl group from alcohol group in MCC during pH adjustment using sodium hydroxide and hydrochloric acid in the oxidation process. The C=O stretching absorption band at 1717 cm^{-1} is assigned to C=O stretching of carboxyls with hydrogen bonds while the isolated carboxyls without hydrogen bonds show C=O absorption band at 1740 cm^{-1}. Thus, it could be deduced that majority of the carboxyls in the composite films exhibit intra- or inter-molecular hydrogen bonds with hydroxyl groups or other carboxyl groups (Fujisawa et al., 2011). From this analysis, the success of the chemical oxidation of MCC using TEMPO was undoubtedly verified by FTIR. Bio-nanocomposite films were fabricated using PVA/CS as the polymer matrix and the TOCN as nanofillers.

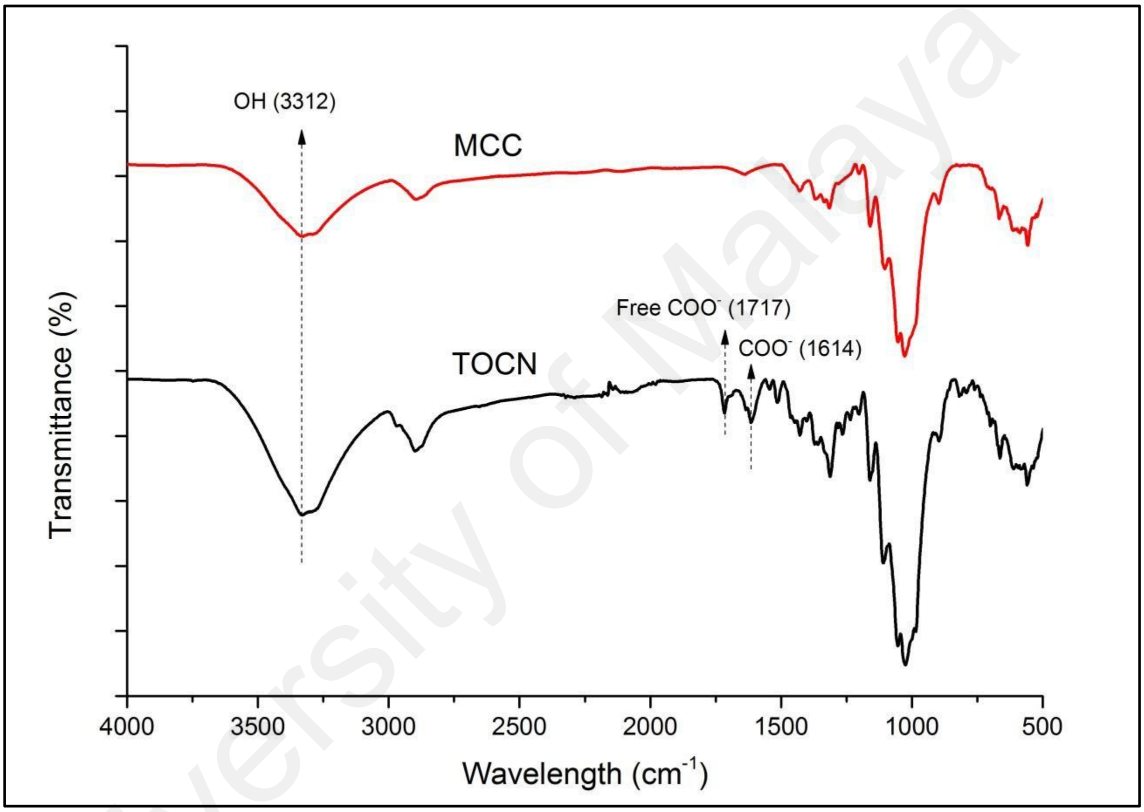

Figure 4.1: FTIR spectra of the MCC and TOCN.

4.2 FESEM Analysis

Morphological test of the composite films was performed using Field Emission Scanning Electron Microscopy (FESEM). Generally, FESEM gives information about the presence of voids, the degree of homogeneity of the composite, the presence of aggregate, the dispersion of the nanoparticles within the continuous polymer matrix, and the possible orientation of nanoparticles (Khan et al., 2012). Figures 4.2 to 4.5 represent

FESEM micrographs of the surface of PVA/CS = 50/50 composite films with TOCNs content of 0, 0.5, 1.0 and 1.5 wt%. It was observed that incorporation of TOCNs changed the microstructure of the film. The smooth surface of the blend film as shown in Figure 4.2 deduced the homogeneous distribution of the continuous polymer matrix. This observation is most likely due to formation of hydrogen bonds between the amino and hydroxyl groups of CS and the hydroxyls group of PVA. It is difficult to observe the individual of filler dispersion in the polymer matrix due to its small nanoparticle size (Li et al., 2009). TOCNs were appeared as white dots as can be seen in Figures 4.3 to 4.5. As can be seen in Figure 4.2, the white dots did not appear in the micrograph. The addition of 0.5 wt% of TOCNs into the composite gave a positive change to the microstructure, showing a good dispersion of TOCN into PVA/CS composite matrix as illustrated in Figure 4.3. In fact, a stronger intermolecular interaction and interfacial adhesion between the polymer matrix and TOCNs were occurred due to the homogeneous dispersion and dense structure which correlated to the improved tensile properties of the bio-nanocomposite films as reported by researcher (Azizi et al., 2014b). However, the surface became rougher when 1.0 wt% of TOCNs was incorporated into the PVA/CS composite and few aggregation of TOCN can be spotted as shown in Figure 4.4. An increased in the concentration of white dots was also observed (Khan et al., 2012). From Figure 4.5, it can be observed that the agglomerate was started to form on the composite matrix. Higher activity of agglomeration was observed in the bio-nanocomposite film with 1.5 wt% TOCNs as shown in Figure 4.5. The agglomeration of nanoparticles was probably due to stronger inter-nanofibers interaction because of the strong hydrophilic nature of TOCNs. In summary, the study of surface morphology has provided the reason behind the enhancement of mechanical and thermal properties of PVA/CS bio-nanocomposite films with the incorporation of TOCNs.

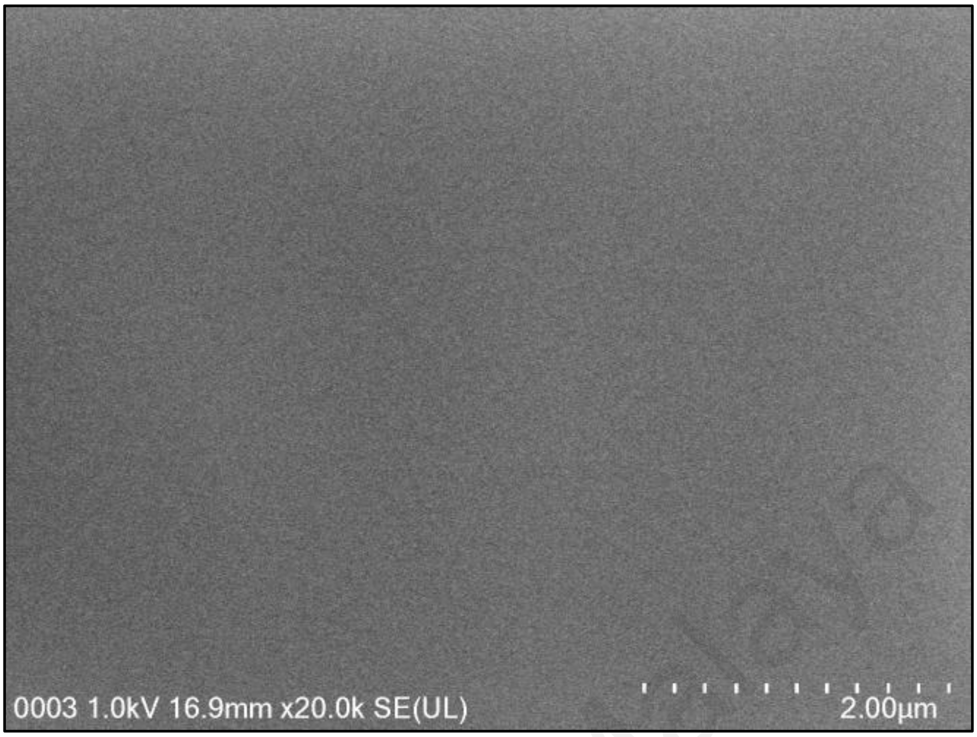

Figure 4.2: FESEM image of the surface of pure PVA/CS = 50/50 composite film.

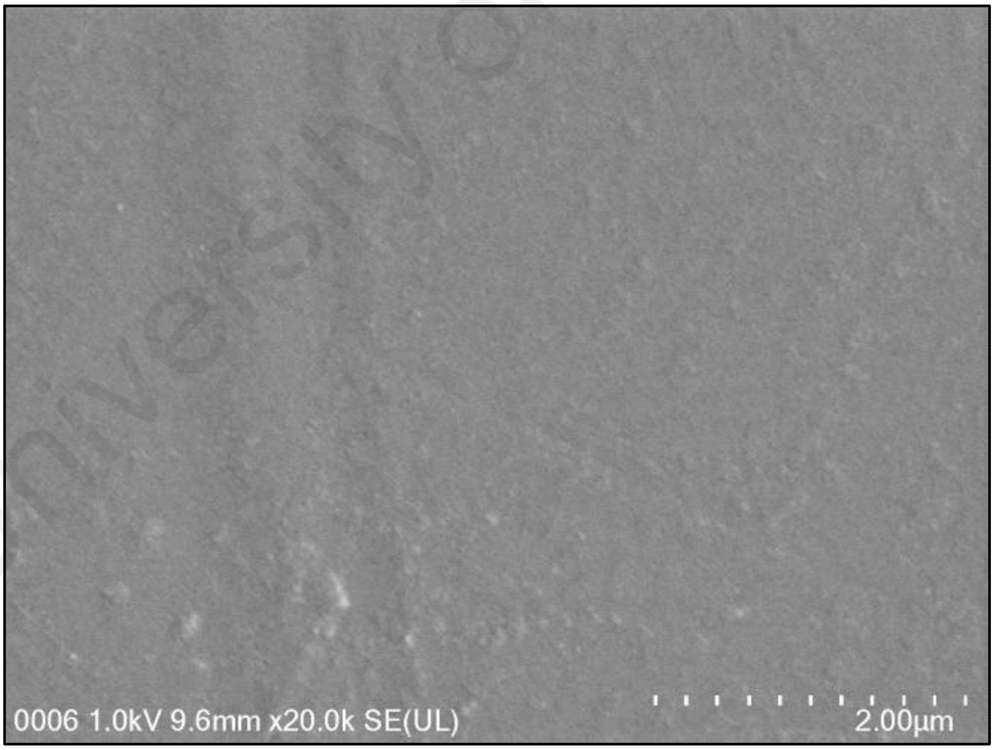

Figure 4.3: FESEM image of the surface of PVA/CS = 50/50 composite film with TOCNs content of 0.5 wt%.

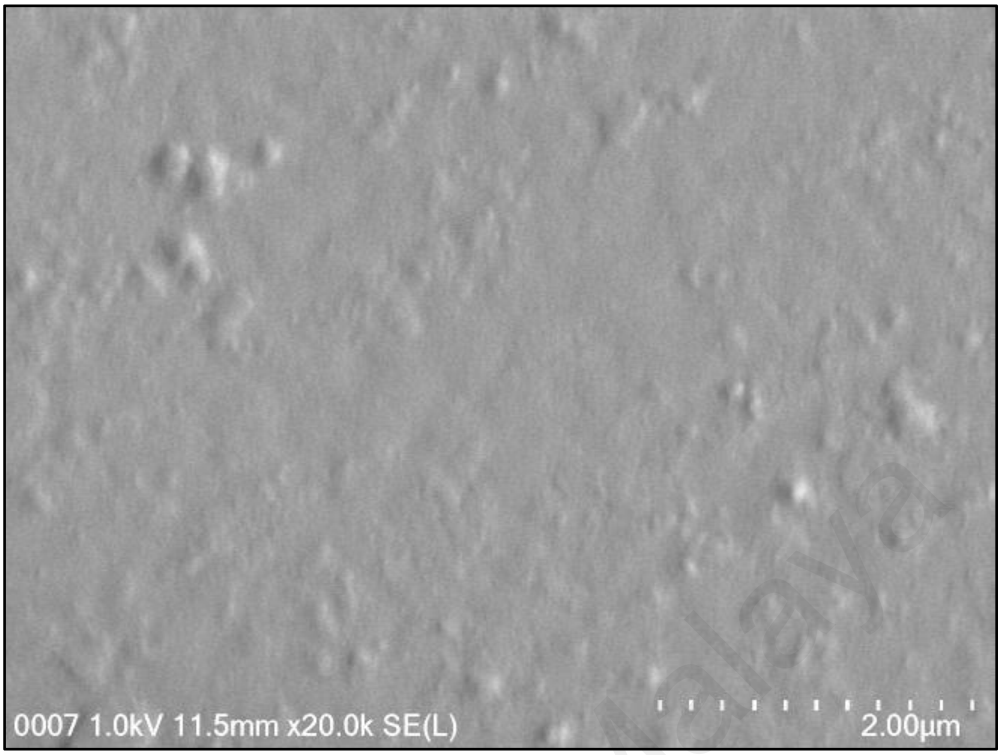

Figure 4.4: FESEM image of the surface of PVA/CS = 50/50 composite film with TOCNs content of 1.0 wt%.

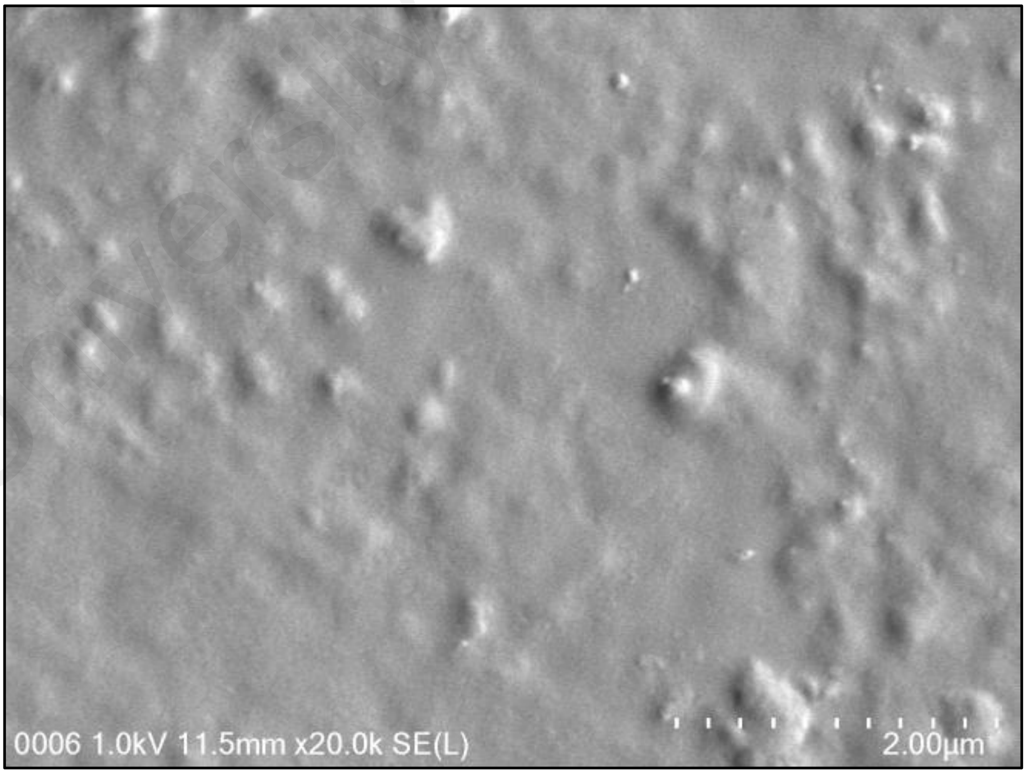

Figure 4.5: FESEM image of the surface of PVA/CS = 50/50 composite film with TOCNs content of 1.5 wt%.

4.3 Tensile Test

Figures 4.6 and 4.7 show the variation of the tensile strength (TS) and elongation at break (%E) of PVA/CS composite films with different weight ratios: (a) PVA/CS = 0/100; (b) PVA/CS = 25/75; (c) PVA/CS = 50/50; (d) PVA/CS = 75/25 and (e)) PVA/CS = 100/0 reinforced with different weight composition of TOCNs content (0, 0.5, 1.0 and 1.5 wt%). For the polymer matrix without the incorporation of TOCNs, the addition of PVA into CS matrix decreased the TS of films by 51.2% as it reached the lowest TS for the pure PVA. On the other hand, the %E of films could be a great increased by 694.4% with the increase of PVA content as it met the highest %E for the pure PVA. This trend was also reported by other researcher (Bonilla et al., 2014). This could be due to high molecular weight and hard backbones of CS compared to PVA. The TS of PVA/CS composites decreased with the increased of PVA content due to more single ordered phase of PVA were formed in the matrix. Eventually, the addition of PVA into CS polymer matrix could largely affects the flexibility of CS polymer meanwhile, it only showed a small reduction in TS (Zhuang et al., 2012).

For the composite films with 0.5 wt% of TOCNs, their TS showed a different trend as illustrated in Figure 4.6. It can be seen that the TS reduced in the initial stage and then increased again for the PVA/CS = 75/25 composite film, which was showed unexpectedly different. It could be likely that the high molecular weight and hard backbones of CS as compared to PVA. When the weight ratio of PVA/CS was less than 50/50, PVA and CS were miscible. Nevertheless, as the content ratio of PVA/CS came to 50/50, PVA and CS started to be a little immiscible and a phase separation happened during the process of drying. When PVA content was increased in the composite films, more single ordered phase of PVA were developed, so the TS of PVA/CS composite films initially reduced and decreased with the addition of more PVA (Costa-Júnior et al., 2009; Jawalkar et al., 2007).

The TS showed the highest value when 0.5 wt% of TOCNs were added into PVA/CS = 25/75, PVA/CS = 50/50 and PVA/CS = 75/25 composite films. There were 11.7%, 42.1% and 43.8% increment in TS when 0.5 wt% of TOCNs were reinforced into PVA/CS = 25/75, PVA/CS = 50/50 and PVA/CS = 75/25 composite films, respectively. It was also observed that PVA/CS = 50/50 composite film with 0.5 wt% of TOCNs content revealed the highest TS as compared to other PVA/CS composite films with 0.5 wt% of TOCNs content. The reason is likely to be the strong hydrogen bonding interaction between filler and polymer blend, which enhances hard portion crystallinity, reduces motion of molecules and thus increases the rigidity. When 1.0 wt% of TOCNs was added into each polymer matrix, the reduction in TS were 4.1%, 23.7% and 23.8% for PVA/CS = 25/75, PVA/CS = 50/50 and PVA/CS = 75/25 composite films, respectively as compared to the PVA/CS composites with 0.5 wt% of TOCNs content. This trend could be due to the aggregation and heterogeneous size distribution of TOCNs in the polymer matrix and thus, the reinforcing effect of filler was inhibited. In fact, phase separation, increased formation of agglomerates and poor particle dispersion within PVA/CS composite matrix were occurred due to excess TOCNs content. The interfacial bonding between the TOCNs and PVA/CS composite matrix became weaker with increased in cellulose nanofiber loading, which led to decreased tensile strength (Azizi et al., 2014b). In addition, an increase of 64.3% in TS was observed with the incorporation of 1.0 wt% of TOCNs to the pure PVA composite where it showed the highest value. This improvement was due to establishment of a more bonded network between PVA and TOCNs via hydrogen bonding. The relative high strength, stiffness and low density of TOCNs could also be the reason for the increment of TS (Li et al., 2015).

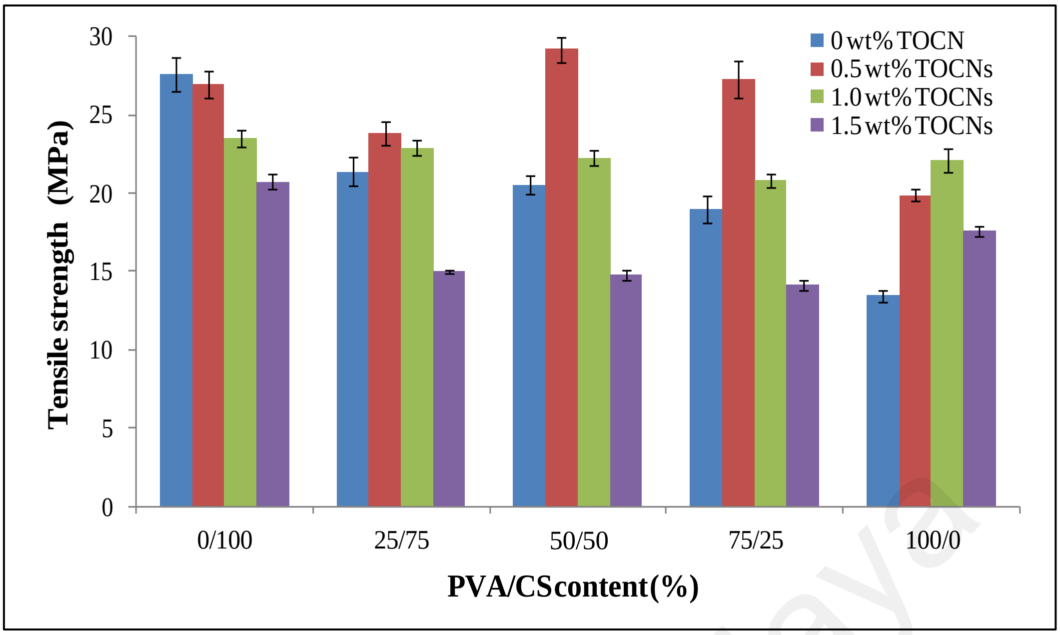

Figure 4.6: Tensile profiles in term of tensile strength of pure PVA, pure CS and PVA/CS composite films reinforced with different weight composition of TOCNs content (0, 0.5, 1.0 and 1.5 wt%).

In contrast, the %E of PVA/CS composite blend matrices showed opposite trend as compared to their TS. There were 1.9%, 7.7%, 62.3%, 50.5% and 31.9% decreases for PVA/CS = 0/100, PVA/CS = 25/75, PVA/CS = 50/50 and PVA/CS = 75/25 and PVA/CS = 100/0 composite films, respectively after the addition of 0.5 wt% of TOCNs. For pure PVA, it showed maximum reduction of %E at TOCNs content of 1.0 wt%. The major reason for the decreased %E as shown by corresponding bio-nanocomposites was higher stiffness of the network structure, which strictly limited the chain mobility of the polymer matrix (Azizi et al., 2014b). Such changes in the %E of composite films were reported by other researchers (Ma and Zhang, 2009; Savadekar and Mhaske, 2012). From the observed trends, it also indicates that the pure CS and PVA/CS composite films were more brittle and less flexible as compared to the pure PVA composite film.

For the composite films with 0.5 wt% of TOCNs, their %E showed a different trend as illustrated in Figure 4.7. The %E is enhanced as the PVA content in the composite films is increased. Although there is a little fluctuation for the %E of

PVA/CS = 50/50 as compared to PVA/CS = 25/75 composite film, their values of %E are much closed. In fact, the highest value of %E occurs with the PVA film (Mangala et al., 2003). A reduction in the %E with respect to pure PVA film was found for all PVA/CS systems. The %E was largely affected by the volume fraction of the added CS into PVA. A researcher has reported that the volume fraction of particle and the interactions between the particles and the matrix could largely alter the flexibility of composite film (Bonilla et al., 2013). These results show that CS did not have much effect when added to PVA matrix as PVA/CS composite films were more fragile than PVA films. Nevertheless, the %E of pure PVA film with 1.0 wt% of TOCNs showed dramatic reduction as compared to the PVA/CS = 75/25 composite film. The reason is likely due to the aggregates of TOCNs formed in the pure PVA film, which largely interrupted the confine network structure of single-ordered phase of PVA.

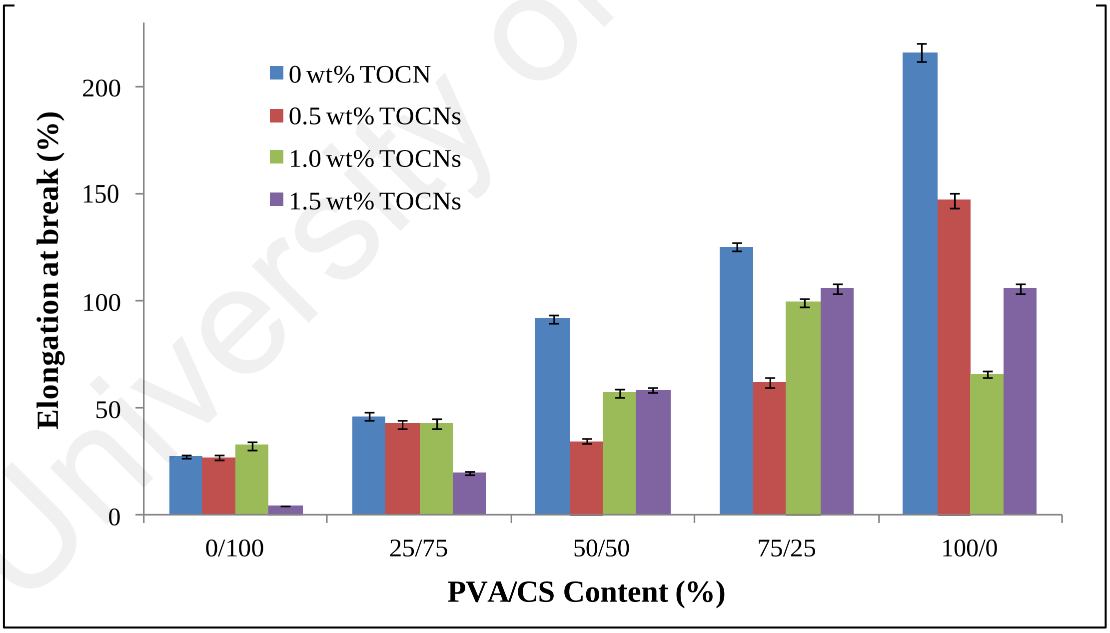

Figure 4.7: Tensile profiles in term of elongation at break of pure PVA, pure CS and PVA/CS composite films reinforced with different weight composition of TOCNs content (0, 0.5, 1.0 and 1.5 wt%).

4.4 Thermal Properties

Figures 4.8 and 4.9 show the TGA and DTG curves of PVA/CS composite films with different weight compositions: PVA/CS = 0/100; PVA/CS = 25/75; PVA/CS = 50/50; PVA/CS = 75/25 and PVA/CS = 100/0. Table 4.1 gives the summary for Figures 4.8 and 4.9 in thermal parameters including T_{onset} and T_{max}. It was investigated that the first weight loss appeared at 100°C due to the evaporation of absorbed water moisture and residual acetic acid. A major weight loss in all the composite films was occurred at about 200-300°C which is attributed to rapid decomposition of polymer segments of PVA and CS due to the thermal scission of the polymer backbone (Bonilla et al., 2014; Khan et al., 2012). The third weight loss was happened at 380-500°C which caused by the degradation of the by-products generated by PVA during the reaction of thermal degradation (Bonilla et al., 2014). Generally, assuming there is no interaction exists between two different polymers with their own different T_{onset}, the thermogram of the blends would show its thermal degradation in two stages. However, from Figures 4.8 and 4.9, it can be observed that all composite films show only one T_{onset} for each blend. Therefore, this indicates the presence of hydrogen bonding interactions between PVA and CS in the composites (Wu et al., 2008). The formation of stronger hydrogen bonds can be verified through the FTIR spectrum illustrated in Figure 4.13. In addition, it can be noted that T_{onset} and T_{max} of the composites slightly change with the different weight composition. It was observed that the T_{onset} and T_{max} of the composites lie between pure CS and pure PVA. Thus, these results deduced that these two polymers are homogenously mixed together to form bio-nanocomposite films (Wu et al., 2008).

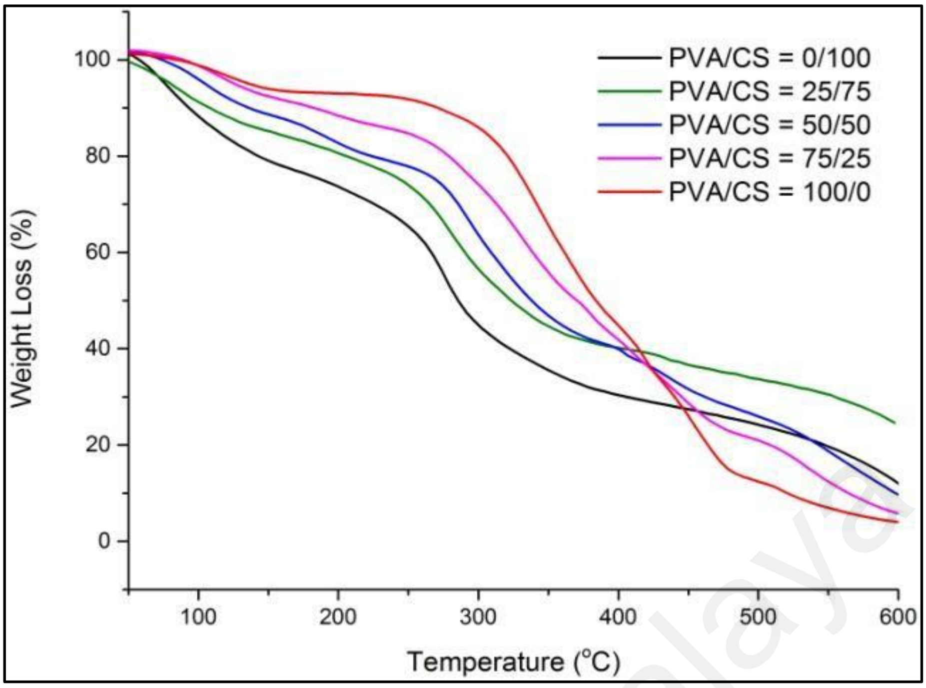

Figure 4.8: TGA thermograms of the PVA/CS composite films with different weight ratios: PVA/CS = 0/100; PVA/CS = 25/75; PVA/CS = 50/50; PVA/CS = 75/25 and PVA/CS = 100/0.

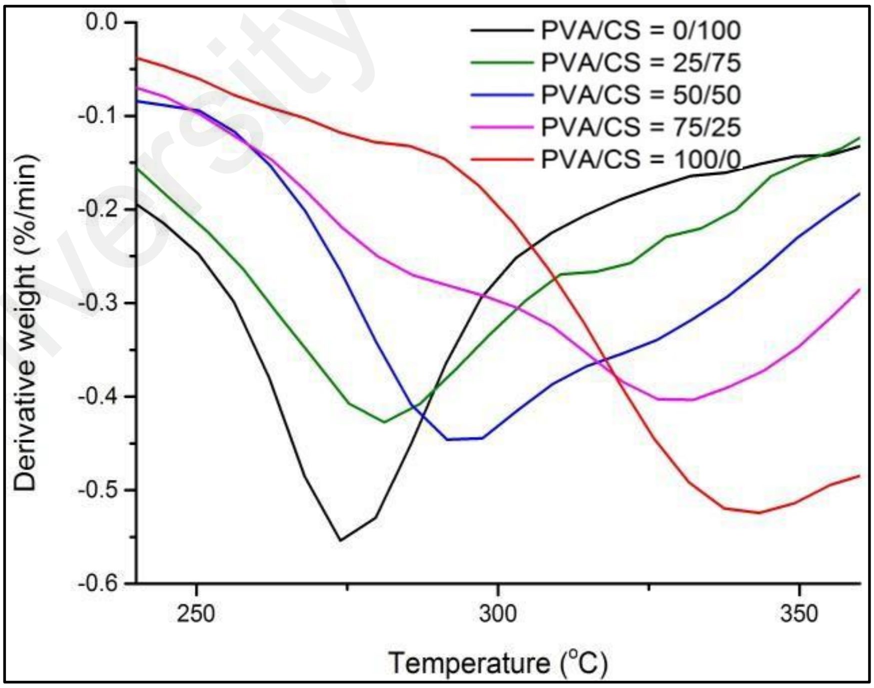

Figure 4.9: DTG thermograms of the PVA/CS composite films with different weight ratios: PVA/CS = 0/100; PVA/CS = 25/75; PVA/CS = 50/50; PVA/CS = 75/25 and PVA/CS = 100/0.

Table 4.1: Summary of TGA and DTG thermograms of the PVA/CS composite films with different weight ratios: PVA/CS = 0/100; PVA/CS = 25/75; PVA/CS = 50/50; PVA/CS = 75/25 and PVA/CS = 100/0 in terms of onset temperature, T_{onset} and maximum point of the degradation, T_{max}.

Sample	Second step	
	T_{onset} (±5°C)	T_{max} (±5°C)
PVA/CS = 0/100	261	274
PVA/CS = 25/75	267	281
PVA/CS = 50/50	272	293
PVA/CS = 75/25	278	329
PVA/CS = 100/0	287	340

Figures 4.10 and 4.11 represent the TGA and DTG curves of PVA/CS = 50/50 composite films with 0, 0.5, 1.0 and 1.5 wt% of TOCNs content. Table 4.2 gives the summary for Figures 4.10 and 4.11 in thermal parameters of onset temperature, T_{onset} and maximum point of the degradation, T_{max}. From Table 4.2, it was observed that T_{onset} of the pure PVA/CS composite film was 272°C. After that, T_{onset} of the composite film enhanced with the increased of TOCNs content until it reached the maximum of 276°C at 1.0 wt% of TOCNs. It was noted that the difference in the T_{max} of PVA/CS composite films with 0 wt% and 1.0 wt% of TOCNs content is only 6°C. Thus, it can be deduced that the TOCNs content have no significant effects on the thermal stability of the films. The high thermal stability of these PVA/CS composite films could be due to the presence of crystalline structure and great compactness between the TOCNs and PVA/CS matrix. Thus, it can be revealed that the conversion of functional groups to carboxylate groups on the TOCNs surface can significantly affect the thermal stability of the PVA/CS based composites (Soni et al., 2016). The highest value of T_{onset} and T_{max} of PVA/CS composite film with 1.0 wt% of TOCNs indicates the great

improvement in the thermal stability with the addition of TOCNs. This could be due to the formation of hydrogen bonding between the –OH groups of TOCNs and –OH and –NH groups of PVA/CS films, which causes a restriction in the motion of polymer matrix at the interfaces between PVA/CS and TOCNs surface. In turn, the existence of hydrogen bonds should improve the value of thermal degradation due to the formation of a compact structure in the bio-nanocomposite films (Azizi et al., 2014b; El Miri et al., 2015). When 1.5 wt% of TOCNs is added, the T_{onset} and T_{max} of PVA/CS composite films were then decreased to 260°C and 284°C, respectively. It suggested that the formation of hydrogen bonding between the PVA/CS composite matrix and nanofiller was reduced due to the agglomeration of TOCNs in the matrix. In short, the thermal degradation value of the composite film was decreased due to the fabrication of a loose structure in the nanocomposites (Kuo, 2008).

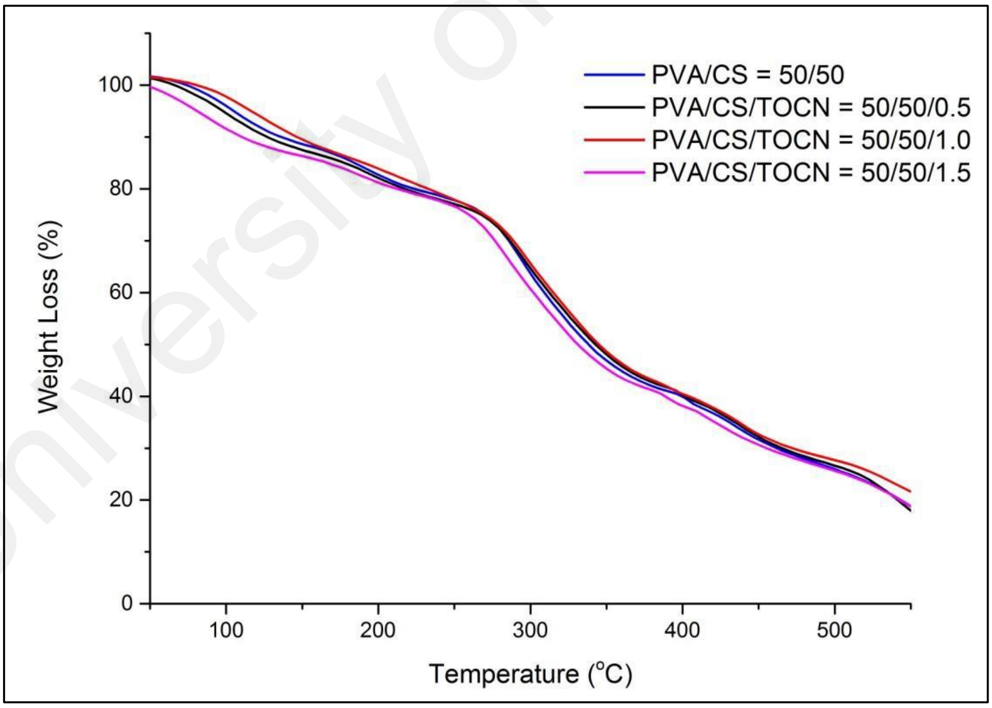

Figure 4.10: TGA thermograms of PVA/CS = 50/50 composite films with TOCNs content of 0, 0.5, 1.0 and 1.5 wt%.

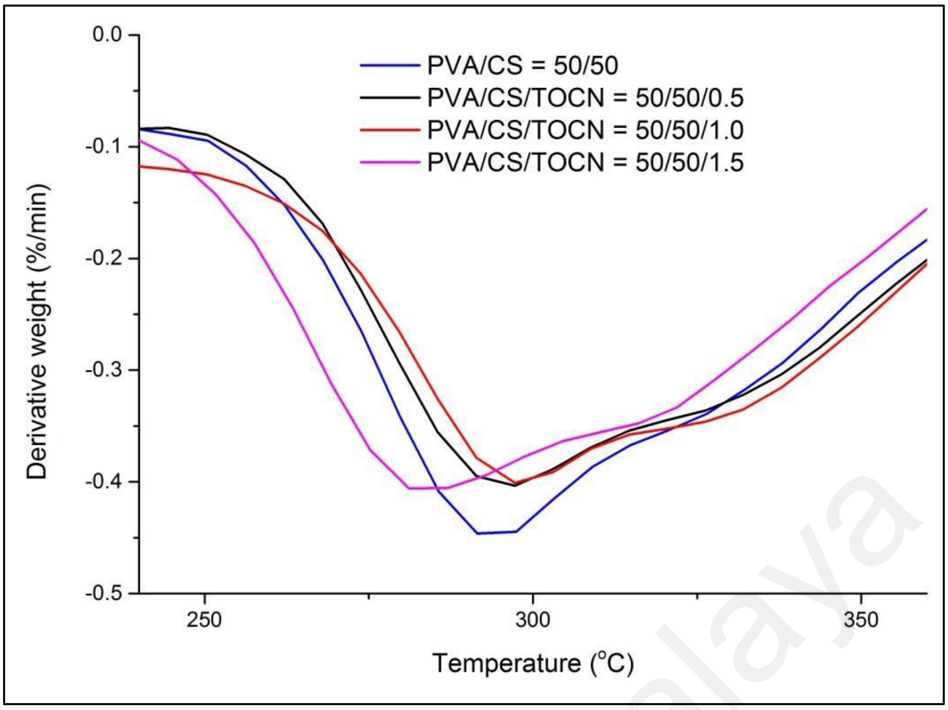

Figure 4.11: DTG thermograms of PVA/CS = 50/50 composite films with TOCNs content of 0, 0.5, 1.0 and 1.5 wt%.

Table 4.2: Summary of TGA and DTG thermograms of PVA/CS = 50/50 composite films with TOCNs content of 0 wt%, 0.5 wt%, 1.0 wt% and 1.5 wt% in terms of onset temperature, T_{onset} and maximum point of the degradation, T_{max}.

Sample	**TOCNs (wt%)**	**Second step**	
		T_{onset} (±5°C)	**T_{max} (±5°C)**
PVA/CS = 50/50	0	272	293
PVA/CS/TOCNs = 50/50/0.5	0.5	273	296
PVA/CS/TOCNs = 50/50/0.5	1.0	276	299
PVA/CS/TOCNs = 50/50/0.5	1.5	260	284

4.5 FTIR

Figure 4.12 highlights the FTIR spectra of PVA/CS composite films with various weight compositions: (a) PVA/CS = 0/100; (b) PVA/CS = 25/75; (c) PVA/CS = 50/50; (d) PVA/CS = 75/25 and (e) PVA/CS = 100/0. From the CS spectrum, the absorption band from 3450-3200 cm^{-1} is assigned to O-H and N-H stretching vibrations. The band at 2925 cm^{-1} is associated to C-H stretching. The band at 1633 cm^{-1} is attributed to C-O stretching of acetyl group (amide I). The band at 1539 cm^{-1} is assigned to N-H bending and stretching (amide II) (Li et al., 2009). A weaker amino characteristic peak at 1255 cm^{-1} is associated with O-H bending vibration and the peak at 1066 cm^{-1} is assigned to C-O stretching. The absorption band at 1152 cm^{-1} and 897 cm^{-1} is assigned to saccharine structure (Naveen Kumar et al., 2010).

For pure PVA, the band at 3301 cm^{-1} is attributed to –OH stretching vibration; the peak at 1425 cm^{-1} is assigned to -OH bending vibration of hydroxyl group. The vibrational band at 2925 cm^{-1} is corresponded to asymmetric CH_2 group stretching vibration. The peak at about 1733-1561 cm^{-1} is attributed to C=C stretching vibration of PVA. The peak corresponding to C-O stretching is occurred at approximately 1089 cm^{-1} while the band at 842 cm^{-1} is attributed to C-C stretching vibration (Bonilla et al., 2014; El Miri et al., 2015).

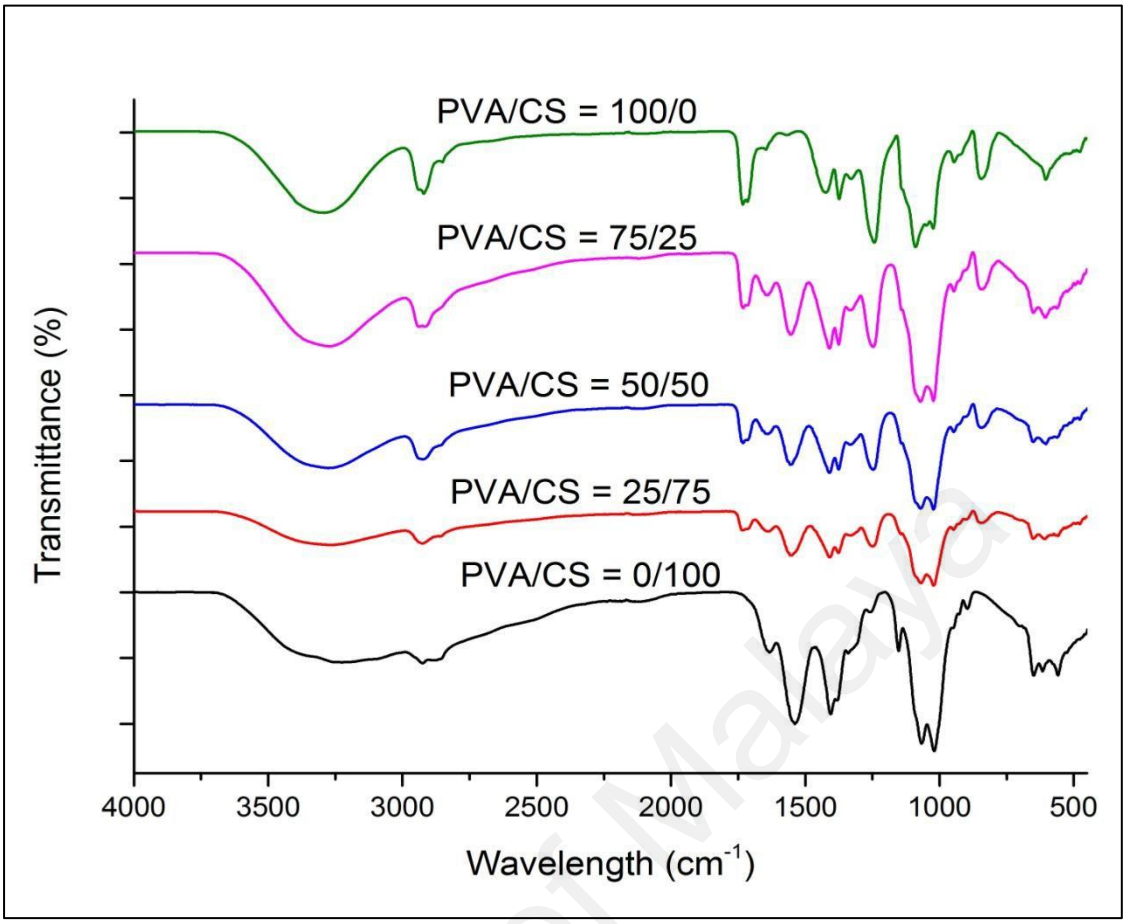

Figure 4.12: FTIR spectra of the PVA/CS composite films with different weight ratios: (a) PVA/CS = 0/100; (b) PVA/CS = 25/75; (c) PVA/CS = 50/50; (d) PVA/CS = 75/25 and (e) PVA/CS = 100/0.

From Figure 4.12, it was observed that a reduction in the intensity of the band at about 3301 cm^{-1} with the increase in CS content in the composites. This could be due to –OH stretching vibration of PVA with secondary –NH groups of CS (Bonilla et al., 2014). The increase in the PVA content in the composites also caused a reduction in the intensity of band corresponding to N-H bending (amide II) at 1539 cm^{-1} of pure CS film. The peak disappeared in the spectrum of the pure PVA film due to absence of –NH functional group. In addition, it was investigated that an increase in the intensity of the absorption band corresponding to C-H stretching vibration at approximately 2925 cm^{-1} with the increased of PVA content. The absorption peak of composite film at around 1245 cm^{-1} disappeared as compared to the spectrum of pure CS film (Naveen Kumar et al., 2010). Besides that, the band observed at 1066 cm^{-1} associated with C-O stretching vibration in the spectrum of pure CS film, shifted to higher wavelength as the PVA content increased in the blend. Moreover, the intensity of absorption band at 842 cm^{-1} corresponding to C-C stretching decreased with the increased of CS content in the composites and finally, the peak disappeared at the spectrum of pure CS film.

In fact, when two or more polymers are mixed together, the occurrence of physical blends and chemical interactions could have caused some changes in the characteristic peaks of the spectra. From the observation and deduction of Figure 4.12, it can be revealed the presence of good miscibility between PVA and CS in the composite. Therefore, the most likely reason was the formation of interfacial adhesion and intermolecular hydrogen bonding between the -OH and -NH groups in CS and the –OH groups in PVA (El-Hefian et al., 2010).

Figure 4.13 shows the FTIR spectra of the PVA/CS = 50/50 composite films with TOCNs content of 0, 0.5, 1.0 and 1.5 wt%. For the spectrum of PVA/CS = 50/50 composite film, the band observed at 3312 cm^{-1} attributed to –OH stretching vibration in the TOCN spectrum, shifted to approximately 3270 cm^{-1} after the addition of TOCNs into the polymer matrix. This indicated that strong interfacial adhesion and hydrogen bonding interaction between the functional group of filler and continuous polymer matrix as reported by other researcher (El Miri et al., 2015). However, only minor changes are observed from the spectra of PVA/CS composite films with the incorporation of TOCNs as compared to the pure composite films. This could be due to the addition of significantly lower weight ratio of TOCN for the fabrication of bio-nanocomposite films.

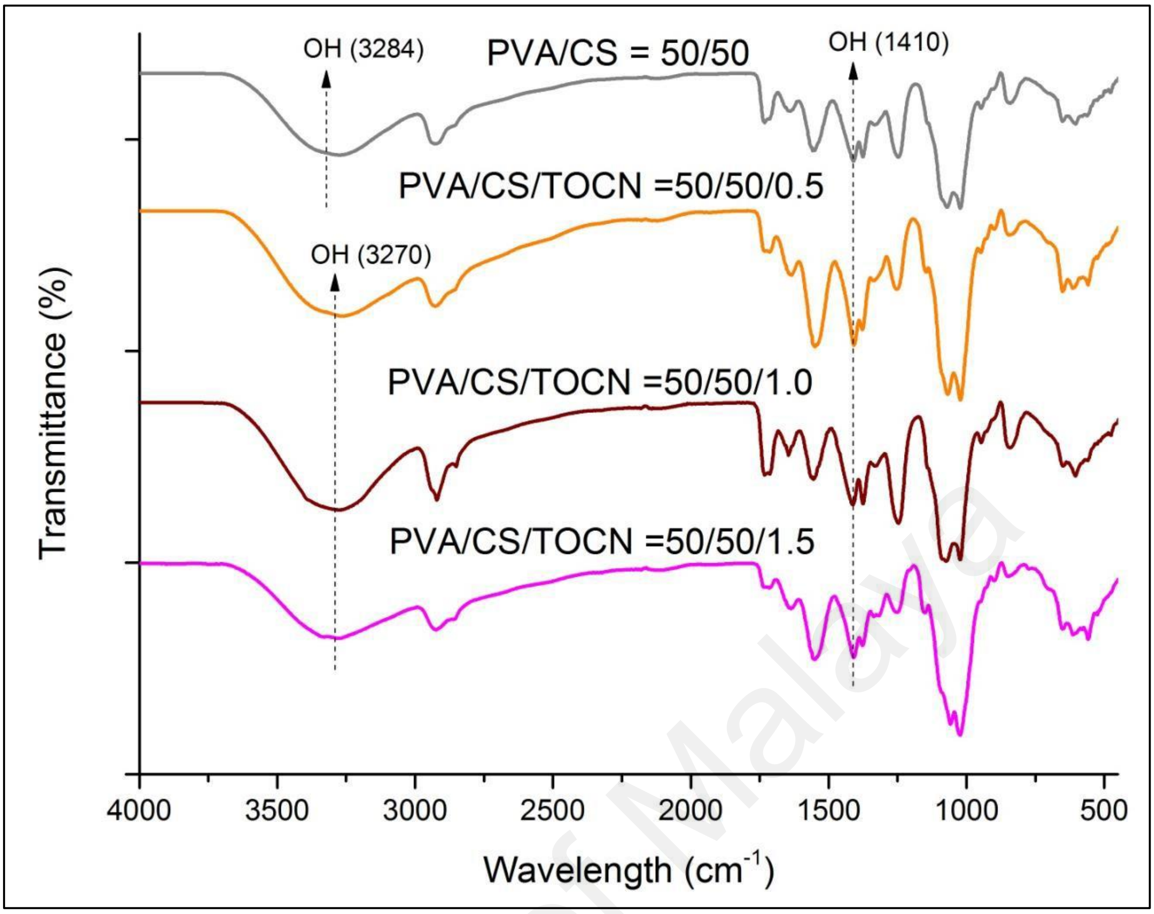

Figure 4.13: FTIR spectra of the PVA/CS = 50/50 composite films with TOCNs content of 0, 0.5, 1.0 and 1.5 wt%.

4.6 XRD

Figure 4.14 shows the XRD patterns of the pure CS, pure PVA, pure PVA/CS and PVA/CS = 50/50 composite films with 0.5 wt% and 1.0 wt% of the TOCNs content. For pure CS film, the diffractogram showed three typical peaks with lower intensity at around $2\theta = 11.1°$, $2\theta = 15.1°$ and another broad peak centered at $2\theta = 21.5°$. The peak at $2\theta = 11.1°$ attributed to a hydrated crystalline structure and predominant amorphous structure of CS respectively. Thus, the high amorphous nature of CS film can be deduced through the broadening of the peaks (Abou-Zeid et al., 2015). For pure PVA film, there were two peaks around $2\theta = 11.0°$ with lower intensity and $2\theta = 19.5°$. In general, if there is no interaction between two polymer components, each component would have its own crystal region in the composite. Thus, it can be deduced that the

XRD patterns would be expressed as simply mixed patterns of different components in case those for mechanical blending (Zheng et al., 2001). For the pure PVA/CS composite film, it showed three characteristic peaks which are the crystalline phase at 2θ = 11.3° and the amorphous state with the main halo centered at 2θ = 19.4° and the second peak with lower intensity at 2θ = 22.8° (Azizi et al., 2014a). The diffraction peak of CS at 2θ = 15.1° disappeared in the PVA/CS = 50/50 composite films. For PVA/CS = 50/50 composite film reinforced with 0.5 wt% of TOCNs, it indicated the three typical peaks which are the crystalline phase at 2θ = 11.3° and also the amorphous phase with the main halo of the typical peak centered at 2θ = 19.5° and another with lower intensity at 2θ = 23.0°. Meanwhile for PVA/CS = 50/50-1.0 composite, the diffractogram also showed the similar trend as PVA/CS = 50/50-0.5 composite with the three characteristic peaks at 2θ = 11.3°, 2θ = 19.6° and 2θ = 22.7°. As the TOCNs content were increased from 0 to 1.0 wt%, the peak at 2θ = 19.4° slightly increased to 2θ =19.6°. Thus, these diffractograms suggested that TOCNs reinforced PVA/CS composite films composed of a combination of crystalline and amorphous peaks (Bodin et al., 2007). These results also indicate that the addition of TOCNs does not affect the uniformity in the structure of the composite polymer matrix, but rather enhance molecular ordering in the amorphous phase of polymer matrix (Azizi et al., 2014b). However, as the content of TOCNs was too low, only minor changes in wavelength or intensity are observed with the increase of TOCNs content in the composite films.

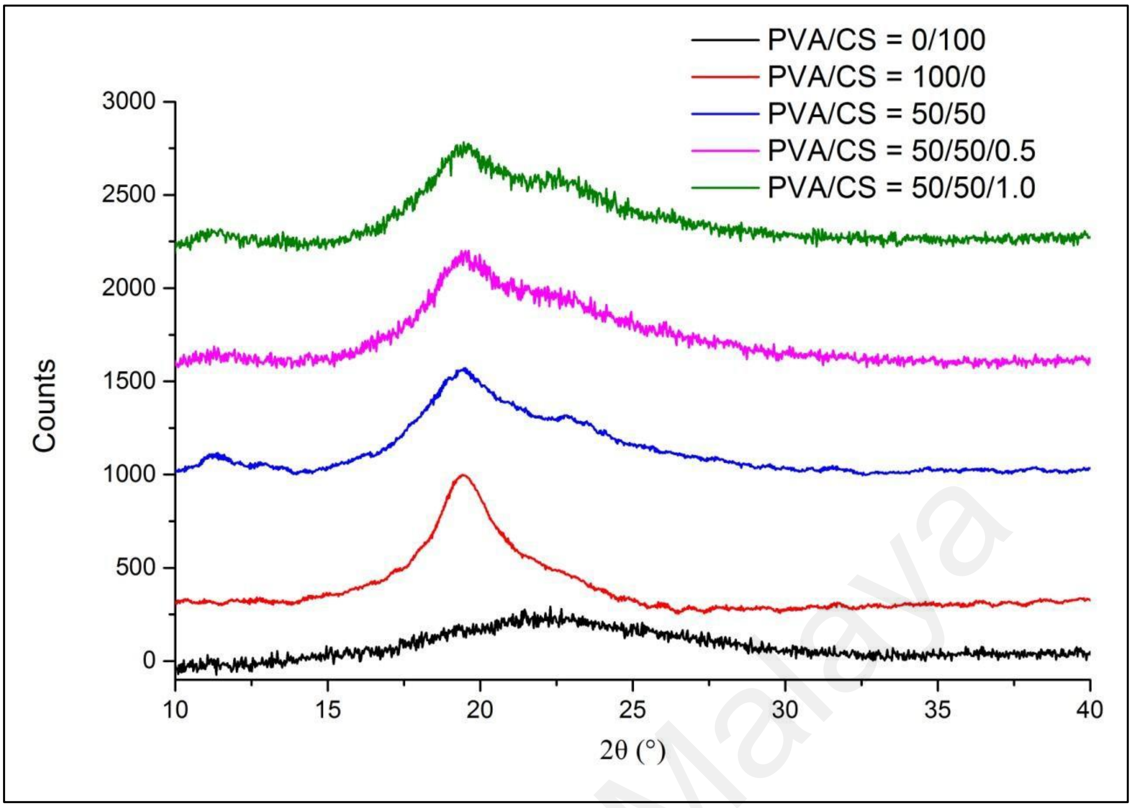

Figure 4.14: XRD data for pure PVA, pure CS, pure PVA/CS = 50/50 and PVA/CS = 50/50 composite films with TOCNs content of 0.5 and 1.0 wt%.

CHAPTER 5 CONCLUSION AND RECOMMENDATION FOR FUTURE WORK

5.1 Conclusion

In conclusion, cellulose nanofiber (CNF) was isolated from microcrystalline cellulose (MCC) using TEMPO-mediated oxidation method. Functional groups on the surface of MCC were successfully oxidized to give carboxyl groups, which indicate the successful isolation of CNF from MCC as proven using Fourier Transform Infrared (FTIR) analysis. As a result, this surface modification method enhanced the adhesion and bonding of nanofiller and polymer matrix.

TEMPO-mediated oxidized cellulose nanofiber (TOCN) reinforced polyvinyl alcohol (PVA)/chitosan (CS) bio-nanocomposite films were fabricated by solution casting method. The characterizations of PVA/CS/TOCN bio-nanocomposite films were performed in terms of field emission scanning electron microscopy (FESEM), tensile tests, thermogravimetric analysis (TGA), FTIR, and X-ray diffraction (XRD). FESEM images indicated that the homogeneous dispersion of TOCNs up to incorporation of 1.0 wt% into the composite. From tensile profile of the bio-nanocomposite, optimum tensile strength (TS) and elongation at break (%E) have been achieved in composite of PVA/CS/TOCNs = 75/25/0.5. There was improvement of 43.8% in TS although the %E was reduced by 50.5% with the introduction of 0.5 wt% of TOCNs into the composite. The thermal study by TGA indicated that there was improvement of 4°C and 6°C in onset temperature and maximum degradation temperature, respectively when 1.0 wt% of TOCNs was added into the PVA/CS = 50/50 composite film. FTIR analysis confirmed that the strong hydrogen bonds have been introduced in between the functional groups of TOCNs and PVA/CS composite. From the crystallinity study by

XRD, the addition of TOCN has successfully enhanced the molecular ordering in the amorphous phase of the composite. The addition of TOCN has no significant effect on the crystallinity as only small amount (up to 1.5 wt% of TOCNs) was added into the composite. The current knowledge will provide a useful insight of developing renewable, biodegradable and environmental-friendly green nanocomposite films for potential applications.

5.2 Recommendation for Future Work

For future study, chemical modifications on the TEMPO-mediated oxidized cellulose nanofiber (TOCN) are possible to be carried out to improve the compatibility of TOCNs and PVA/CS composite matrix, resulting in better mechanical properties. The distribution of chemically treated TOCNs in PVA/CS composites might also be different since it will have less hydrophilic behaviour. Besides, natural cross-linking agents such as ferulic acid can also be introduced into the bio-nanocomposites to study their effect on the intermolecular bonding between the nano-filler and polymer matrix, resulting in modified mechanical and thermal properties. Characterizations such as differential scanning calorimetry (DSC), biodegradability, swelling and barrier tests would be interesting to provide better understanding of the composites affected by incorporation of TOCNs.

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LIST OF PUBLICATION AND PAPER PRESENTED

List of Publications

Ching, Y. C., Ali, M. E., Abdullah, L. C., Choo, K. W., Kuan, Y. C., Julaihi, S. J., Chuah C. H., & Liou, N. S. (2016). Rheological properties of cellulose nanocrystal-embedded polymer composites: a review. *Cellulose*, *23*(2), 1011-1030.

Choo, K., Ching, Y. C., Chuah, C. H., Julai, S., & Liou, N. S. (2016). Preparation and characterization of polyvinyl alcohol-chitosan composite films reinforced with cellulose nanofiber. *Materials*, *9*(8), 644.

Conference Proceeding

Choo, K., Ching, Y. C., Chuah, C. H., Julai, S., & Liou, N. S. (2016). Preparation and characterization of polyvinyl alcohol-chitosan composite films reinforced with cellulose nanofiber. Paper presented at the 10th International Materials Technology Conference & Exhibition, Kuala Lumpur, Malaysia.