

CAFEi2012-142

CELLULOSE NANOFIBER ISOLATION AND ITS FABRICATION INTO BIO-POLYMER -A REVIEW

Mohd Harfiz Salehudin¹ Dr Eraricar Saleh² & Prof. Madya Dr. Ida Idayu Muhamad³
Siti Nurhana Bte Mamat⁴

^{1,2,3,4} Universiti Teknologi Malaysia, 81310 Skudai, Johor Malaysia
Email: mharfizutm@gmail.com¹; eraricar@cheme.utm.my²

ABSTRACT

Green technology recently drags major attention that makes the development of natural and renewable based products are on the rise. Native biopolymers matrices such as starch, natural resin, chitosan, bacterial cellulose and others are generally have low performance in term of strength, oxygen barriers and water absorption. Many attempts were conducted to enhance the performance of biopolymers. Focusing on green material development, reinforcement material from natural fiber was studied. Natural cellulose nanofiber possessed valuable characteristics such as a renewable and biodegradable with satisfactory mechanical and barrier properties when applied into a polymer or synthetic polymer. As depletion of the synthetic polymer source becomes critical, an alternative such cellulose nanofiber as biopolymer strengthener is found to be promising. Even nanocellulose has a great potential, however its natural behavior gives a drawback in certain ways. Cellulose fiber is sponge-like structure that could absorb water, when chemically, it contains highly hydrophilic surface that binds water. Therefore, several pretreatment and isolation process has been invented to enhance cellulose properties that later could be incorporated properly into polymer. In this study, we will discuss about the morphology and structure of nanofibers, nanofiber isolations, the importance and effect of pretreatment process, and application of nanofiber in biocomposites. Finally, the aim of this review is to study the current trend and exploration of cellulose based nanocomposite.

Keywords: *Biodegradable, Biopolymer, Green Technology, Nanocomposite, Nanofiber*

INTRODUCTION

Nanotechnology is found to be a potential technology that emerged in wider areas such as medicine, electronics and food technology by manipulating the nanoparticles for various purposes. A nanoparticles is defined as a discrete entity that has at least one of its dimension is 100nm or less [1]. Nanomaterials may include any of the following nano forms: nanoparticles, nanotubes, fullerenes, nanoclays, nanocor, nanofibres, nanowhiskers and nanosheets. The application of nanomaterial is broad. Some of them were used as nano-sensor in smart food packaging technology [2]. It also could provide an antimicrobial mechanism by introducing nano-bullet in active packaging. The most popular purpose of this nanomaterial is wide. It has been used as nanoreinforcement in composite polymer in fact, many studies on nanoreinforcement were reported. Nano-reinforcement that's been studied are such as clay and silicates [3-14] cellulose-based nanoreinforcement [15-27] carbon nanotubes [28-39] starch nanocrystal [40-41], and chitin/Chitosan nanoparticles [42-45]. However, cellulose nanofiber that also known as nano cellulose, is such an emerging source of material such intense term nowadays. Generally, this particular nanofiber is used as filler or fabricator for material reinforcement and toughness. In addition, futuristic mind of the researcher with nanotechnology background has found that highly crystalline nanofiber invention is interesting as it has unique properties and sizes different from synthetic nanofibers[46]. Cellulose nanofibers have a high potential to be used as reinforcing material in many different areas. Differs from other nanofiller such as nanoclays, the usage of cellulose nanofiber becomes such serious deal because it is natural and the source is readily available yet abundant. Furthermore, this green cellulose nanofiber is not only renewable but also a multifunctional raw material and is expected to be able to replace many non-renewable materials.[47]. Natural cellulose nanofibers come from different sources and category. Natural fibers which also known as lignocellulosic fibers are subdivided based on their origins, which are plants, animal or minerals [48]. In general, natural fiber which origin of the plant is usually

referred as cellulosic fiber since the fibers usually often also contain a natural polyphenolic polymer, lignin, in their structure [49]. A general classification of natural fiber is represented in fig. 1.

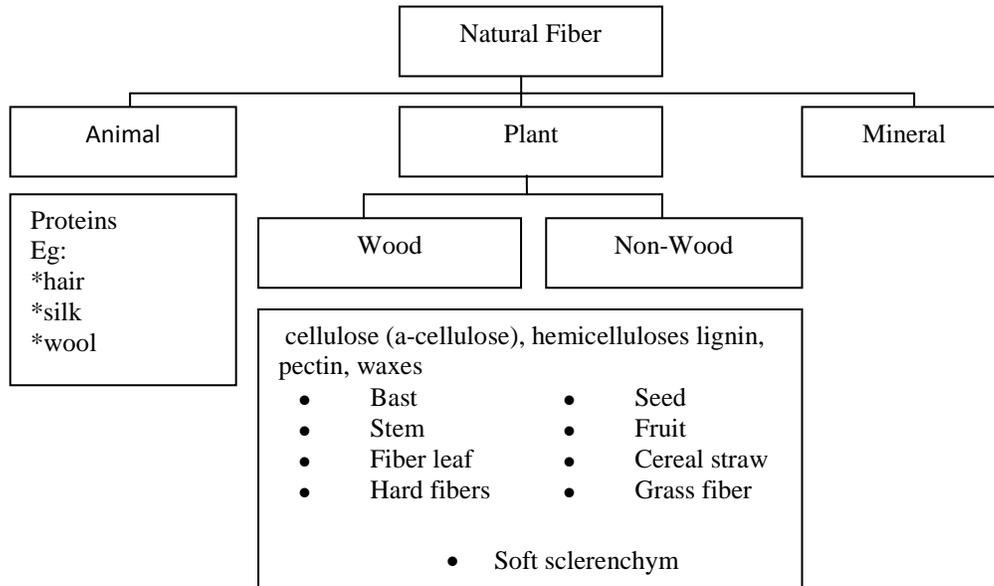


Fig. 1: general classification of natural fiber

The utilization and manipulation of natural fiber source is not new. In history, different class of natural fiber was used as source in making paper, silk, cupboard and others. This natural polymer serves humankind for over centuries before low cost petroleum-based synthetic takes place. This synthetic material well establishes and its applications are varied because of their high specific strength and modulus with longer durability [50]. As times goes by, massive production of synthetic polymer was established to supply wide sectors. However, the use of great amount of this synthetic polymer led to ugly consequences as it gives problem on material disposal and depletion of non-renewable source. At early 90's natural polymer was resurfaced as it gives better prospect [50]. There are reasons that leading to this situation. Today's humankind is aware of eco-friendliness that led to growing attention in reducing environmental impact cause by polymers and composites. Another point is, limited petroleum source force people to find another alternative to decrease pressure on petroleum-based product. Thus, the potential of maximizing the use of renewable material suddenly become interesting. Other than that, sudden increase in research study on this particular field which mean cellulose based material makes data on the properties and morphologies of natural fiber generously available thus gives better understanding in the structure and correlation of bio-polymer properties. Such achievements are possible to reach through modern instrument that assist in better understanding of natural biocomposite hence assist the development of new materials.

Natural fibers are naturally-occurring composite consisting mainly of cellulose fibrils embedded in lignin matrix [48]. Cellulose in the other hand is the abundant organic compound that is a structural component of the cell walls of many plants. It is present mainly in the forest with wood as the most important source. In addition, cellulose fiber has unique pecking order. It comprised of nanofibers assemblies with diameter that range from 2 – 20 nm and a length of more than few micrometers [46]. Other cellulose-containing materials include agriculture residues (fruit bunch, leaves, trunk,), grasses and vegetable (jute). Other than cellulose, plant cell wall contains hemicelluloses, lignin, and small amount of extractives. From recent studies, cellulose is found to be the most common organic polymer and considered as an almost infinite source of raw material for the increasing demand for environment-friendly and biocompatible products. It represents about 1.5 billion tons of the total annual biomass production [51]. As lignocellulosic fiber becomes vital, many possible plants were tested. Natural fiber not only can be harvested from cotton, wool and other ancient source, but it covers different variety and different source all over the world. Available natural fiber that has been conducted in previous research are such as wood [55,56,57], cotton [58,59], jute fiber [60,61], potato tuber cells [62] wheat straw and soy hulls [63], pineapple fiber [64], sisal [65] oil palm empty fruit bunch [66], coconut husk [67], banana fiber [68], lemons and maize [69], hemp [70], sugar beet

[71,72], peas hull [22], cladodes and spines from opuntia ficus-indica [73] prickly pear fruits of Opuntia ficus-indica [74], and rice husk [74].

In fact, scientists now are looking at the various possibilities by combining biofibres such as sisal, flax, hemp, jute, banana, wood and various grasses with polymer matrices from non-renewable and renewable resources to form composite materials to keep biocomposite revolves to achieve better values [52]. The combination of those fibers with natural or synthetic polymer is expected to produce material with great properties.. Previously, the fiber is composted to make cupboard, disposable plate and all, but with the help of nano-technology, the fiber could be grinded chemically, biologically, and mechanically into nanosize. The application of nano-technology in the polymer field somehow upgrade its standard to advanced level. Obviously, nano-size fiber is more suitable to be incorporated into a finer product such as thin film to strengthen it. It is even crucial to develop such filler for reinforcement purpose as the natural based-polymer for an examples starch-based polymer has weak mechanical strength. Previous report shows that the nano-sized fiber exhibits unique characteristics that could give getter reinforcement to the film. Hence, there are many research has been conducted in making nano-size fiber. According to previous method, suspension of cellulose microcrystal from pea hull fiber [22], filter papers [53], and pulp wood [55] was prepared by sulfuric acid hydrolysis. However there are several extraction method that been developed and integrates such as chemical and mechanical pulping, enzymatic hydrolysis, high pressure homogenization, and high intensity sonication, where each method has disadvantages and a drawback in term of the composition and properties of the final product.

Lignocellulosic fiber and cellulose nanofiber

Over decades, a number of researchers have been involved in investigating the exploitation of natural fibers as load bearing constituents in composite materials. The use of such materials in composites has increased due to many advantages and the fact that they can compete well in terms of strength per weight of material [48]. Basically, lignocelluloses contents that exist in natural fibers are cellulose, hemicelluloses, lignin, and other extractives such as waxes, ashes and others. The standard contents of the constituent have been studied by researchers found that the amount of each content is varied according to its fiber sources [52]. The cellulose fibrils are aligned along the length of the fibre, that provides rigidity to plant. The reinforcing capabilities of natural fiber is related to the nature of cellulose and its crystallinity. The primary occurrence of cellulose exists as lignocellulosic materials in the forest and as well as the agricultural residues, water plants and grasses. Previously, a study has been done in a vessel of vascular bundles of wheat straw that reveals more findings about the morphology and orientation of cellulose [76]. Cellulose acts as a framework in the vascular bundles and with high chain orientation. As the major constituent of cell wall, cellulose is mostly located in the secondary wall of the biofiber. Fig. 2 [77] shows the structural constitution of a natural fiber cell.

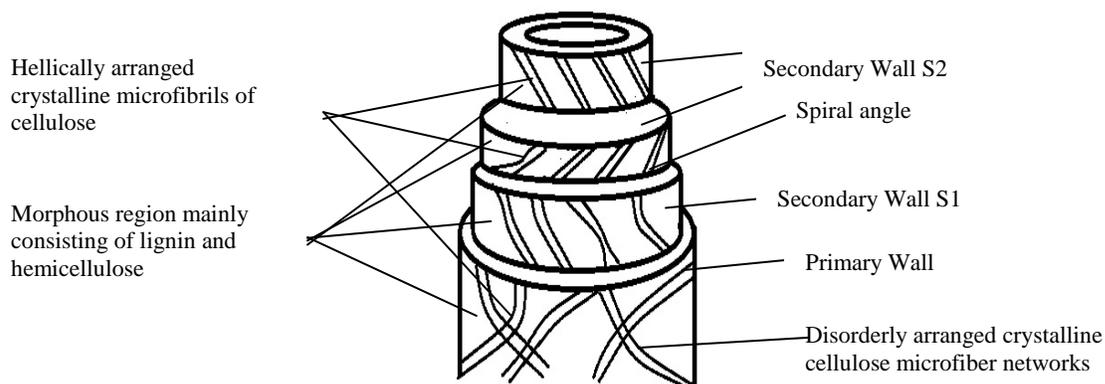


Fig. 2 : Structure and contents of biofiber [77].

As mentioned before, there are three major constituents in the lignocellulosic fiber that are cellulose, hemicelluloses and lignin . Cellulose could be defined as purified plant tissues. It also has been called as “cellulose” for what is nowadays called pulp [78]. Other researchers continued to use the term “cellulose” as in Payen’s

original definition [79]. Table 1 shows the characteristic and properties of the major constituent in lignocelluloses fiber.

Table 1: Characteristic and properties of the major constituent in lignocelluloses fiber [46, 47 ,79, 80, 81,82]

Lignocellulosic material /characteristic	Cellulose	Hemicellulose	Lignin
Shape and physical structure	Slender rod like crystalline microfibrils made of solid cellulose High Order: Crystalline Low order: Amorphous	Random, amorphous structure	Random, Amorphous structure
Chemical structure	D-anhydroglucose (C ₆ H ₁₁ O ₅) repeating units joined by 1,4-β-D-glycosidic linkages at C1 and C4 position. Each repeating unit contains three hydroxyl groups	A group of polysaccharides composed of a of both 5- and 6-carbon ring sugars	Complex hydrocarbon polymer with both aliphatic and aromatic constituents. Contain five hydroxyl and five methoxyl groups per building unit
Thermoset/thermoplastic	Thermoset	Thermoplastic	Thermoplastic
Degree of Polymerization	10,000	50–300.	NA
Hydrophobicity	Hydrophilic	Very hydrophilic	Hydrophobic
Solubility in alkali	Resistant to strong alkali (17.5 wt%)	Soluble in alkali	Soluble in hot alkali
Solubility in acid	Easily hydrolyzed by acid to water-soluble sugars	Easily hydrolyzed in acids.	Not hydrolyzed in acid
Glass transition state	N/A	N/A	90°C
Melting temperature	N/A	N/A	170°C
Oxidizing agent Resistance	Resistant	Not resistant	Not resistant

Biofiber is composites of hollow cellulose fibrils held together by a lignin and hemicelluloses matrix [83]. The cell wall in fiber is not a homogenous membrane. Each fibril has a complex, layered structure consisting of thin primary wall that is the first layer deposited during cell growth encircling a secondary wall. The secondary wall is made up of three layers and the thick middle layer determines the mechanical properties of the fibre. In the primary cell wall, cellulose consists of roughly 6000 glucose units. In vessel thickening, cellulose exists in the form of cellulose crystalline lamellae instead of microfibrillated form. Cellulose fibers however, exhibit a unique structural hierarchy derived from their biological origin. Depends on its origin, they are composed of nanofiber assemblies with a diameter that range from 2 to 20 nm, and a length of more than a few micrometers [14,16,45]. For a record, each microfibril is formed by aggregation of elementary fibrils, which are made up of crystalline and amorphous parts. The crystalline parts, that can be isolated by several treatments, are the whiskers, also known as nanocrystals, nanorods, or rodlike cellulose microcrystals, or cellulose crystal that could be further exploited as reinforcement [84,85].

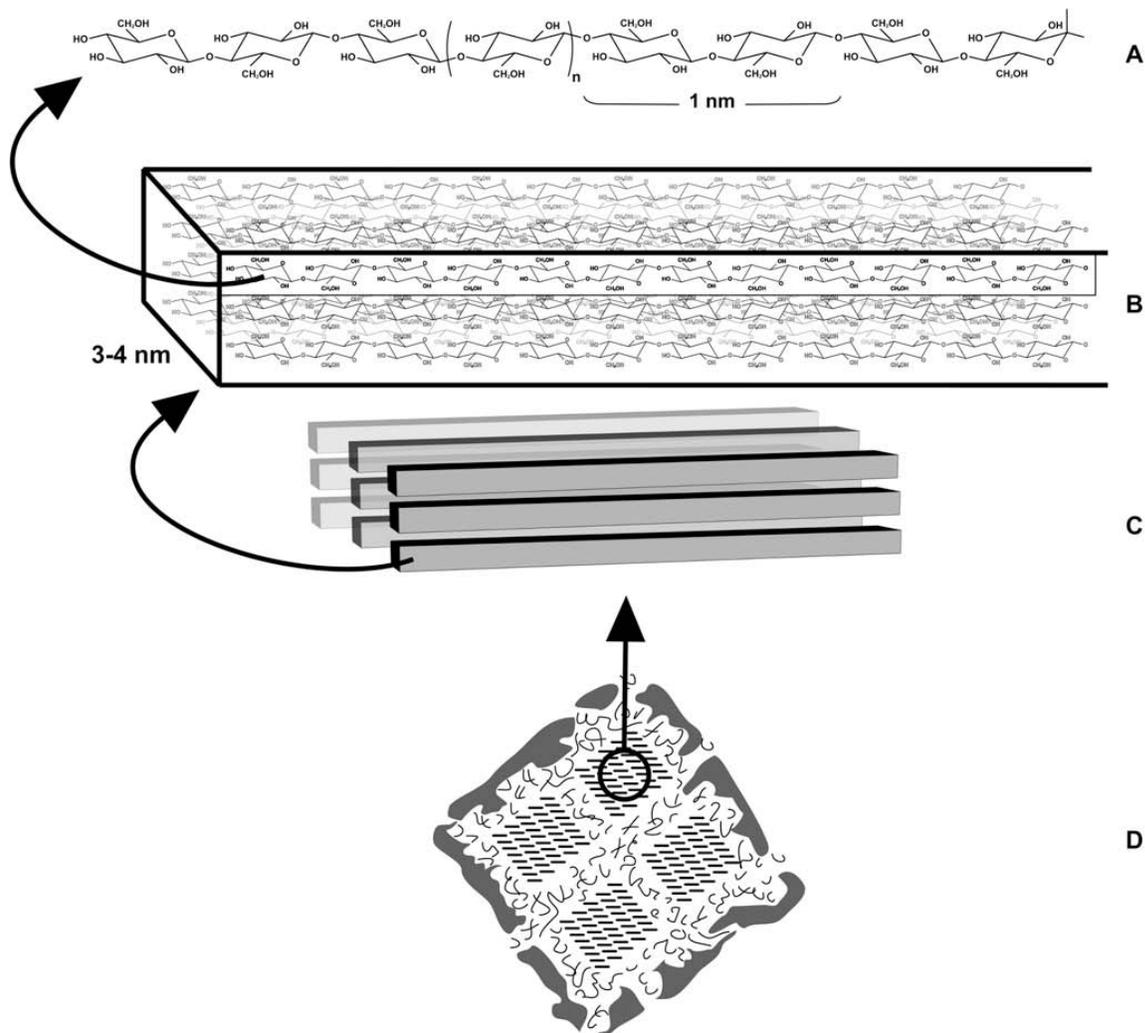


Fig. 3 : (A) four microfibrils held together by hemicellulose and lignin Internal structure of a cellulose microfibril; (B) parallel elementary fibrils; (C) an elementary fibril containing bundles of cellulose chains; (D) a cellulose chain; (Adapted from Ramos, 2003) [86].

The exploitation of lignocelluloses source can be possibly done by breaking down the hierarchical structure of the plant into individualized nanofibers. Breaking down the pecking structure by hydrolyzing process able to produce the cellulose with high crystallinity, and at the same time reducing the amount of amorphous material. The schematic model of the structure of a microfibril are shown in fig. 3 and explain about the hierarchy of the structure as well. Plant fibers is basically fibrous in nature. Through yielding the fibrous material (nanowhiskers, nanofibrils), it provides excellent aspect ratio (length/diameter) that make it reinforcement in composite material.

CELLULOSE NANOFIBER ISOLATION

Nanofiber material are vary in types that distinguish its isolation method, raw material and pre-treatment. However, the most important is, the product is mostly influence by disintegration process itself. Combination of mechanical and chemical process could improve the isolation process by means increasing the yield of cellulose production. In general, the mechanical processes included disintegration, refining, cryo crushing, and high-pressure homogenization [87]. A schematic diagram of the overall isolation process of nanofibers is shown in fig. 4. In

extend, there are several extraction methods that commonly used in order to extract nanofiber that will be discussed in this paper.

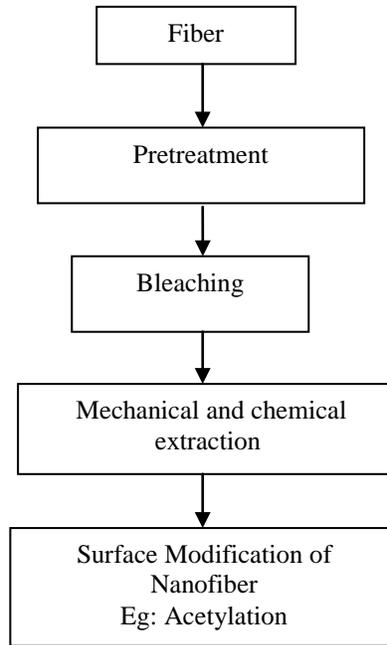


Fig. 4 : Schematic diagram of nanofiber isolation process

Pre-treatment process

Before isolation process, a series of process is designed, called as pre-treatment. Major purposes of pre-treatments are to remove unwanted particles before the fiber is further processed into nanofiber. Pre treatment and washing able to remove ashes, waxes and non-cellulosic compound that is crucial to produce a pure and high quality cellulosic product. Pre treatment could improve mechanical properties of the composite [88]. During the pretreatment process, lignin contents in the cellulose fiber able to be removed. The removal of lignin is crucial because it is believed to give some drawback in composite features. The general concept of pretreatment is illustrated in figure 5 [89]. During the pretreatment process, lignin will be broken and crystalline structure of cellulose will be disrupted that made lignin removal possible [89]. There are several pre-treatment that's available that's been developed by years of study. However, alkali/base treatment is frequently used method.

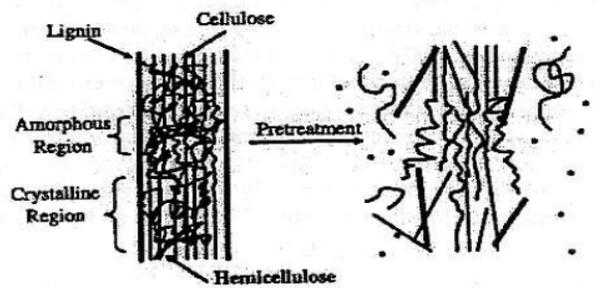


Fig. 5 : Disruption process of lignocelluloses material by pre-treatment method. ⁸⁹

Alkaline pretreatments can be divided into two major groups: i) Pretreatments that use sodium, potassium, or calcium hydroxide; and ii) Pretreatments that use ammonia [90]. Alkaline treatments are more effective in lignin solubilization exhibiting only minor cellulose and hemicellulose solubilization, excepting ammonia recycling percolation treatment, which yield biomass solids mostly containing cellulose [91,92,93]. During alkali treatment, fibers were dipped in 5% sodium hydroxide solution for about 48 h. Based on Wyman et al., 2005,94 high concentration of sodium hydroxide in pretreatment process will give good results due to the ability of lignin removal and hemicelluloses removal at the end of the process [95]. Previous findings show that 2.5 M of NaOH is the suitable ratio to give good results in fiber final products and economical value [94] Moreover, certain findings states that the pretreatment process reaction could be accelerated by introducing the heat in the yielding process. Previous reports show that the range of temperature during the reaction are usually kept at 75°C [88] and 80°C [94]. After base treatment, the fiber suspension was filtrated using vacuum filtration. It was further washed with water containing a few drops of acetic acid. At the final step, the filter cake was washed again with fresh distilled water until pH 7. The fiber will let to dry at temperature 50 °C. Various pretreatment methods that available are tabulated in table 2 below.

Table 2 : Pretreatment and its purpose

Method	Purpose	Reference
Fibers were dipped in 2.5M sodium hydroxide (NaOH) solution, 48 hours, temperature at 80°C. Fibers were filtrated and washed with distilled water + few drop of acetic acid Fibers were washed again with distilled water until ph 7 Fibers were dried at 50 °C	Lignin removal and hemicelluloses removal.	Wyman et al., (2005)[93]
After drying the fiber, it then cut and sieved.	To get uniform size and remove ashes.	Carvalho et al., (2008) [90]
Fibers were soaked with hot distilled water at temperature around 65°C- 80°C, 12 hours	Eliminate impurities and large particles.	Sun et al., (2004) [96]
Fibers were soaked in 10%-30%(w/v) NaOH maintained in water bath at temperature 75°C, speed 40rpm about 3hr	To remove lignin content	
Fibers were washed with distilled for a few time		
Fibers were treated with distilled water containing 2% H ₂ O ₂ in water bath at temperature 45°C, speed 40 rpm for 8 hour.	To remove NaOH	
Fibers were washed with distilled water	To remove more lignin content and active the OH group of the cellulose.	
Then, it was treated with 10% (v/v) acetic acid (at room temperature) for 30min. present in treated fiber residue.	To remove excess H ₂ O ₂	
The fibers were washed repeatedly using distilled water	To neutralize the excess NaOH	
The washings were repeated until cellulose residue is free from acid.	Remove acid residue from fiber	
Treated fiber was dried in an oven at 70°C for overnight		
Fibers were soaked into acidified sodium chlorite solution (ph 4-5) at 75 °C for an hour. This process is then repeated five times until the product became white.	To remove lignin	Abe & Yano (2010) [105]
The fibers were treated in 3 wt% potassium hydroxide at 80 °C for 2 hr, ¹⁰⁵ or 6wt% potassium hydroxide at 20°C for 24 hr. ⁶⁶	To leach hemicellulose, residual starch, and pectin.	Fahma et al., (2010) [66]
Fibers are filtered and rinsed with distilled water.	Neutralize the sample.	

Bleaching

Pulp can be bleached, to obtain a whiter product with lower amounts of impurities and improved ageing resistance (yellowing and brittleness resistance). These effects are mainly connected to lignin in chemical pulp. In several stages, different chemicals are used for bleaching, e.g. hydrogen peroxide (H_2O_2), chlorine dioxide (ClO_2), ozone (O_3) or peracetic acid [97,98]. Sulfite pulps are more readily bleached and are obtained in higher yields [99]. Other bleaching agent that been used is potassium hydroxide (KOH) that reported can remove hemicelluloses [66].

Extraction method

Isolation of nanofiber is complex that it must through tedious processing step including of purification, bleaching, fibrillation, hydrolysis and the low yield of the final dispersion of cellulose whiskers [17]. Through the years, different methods for isolation of cellulose nanofibers from cell wall were developed for instance mechanical, chemical, chemo-mechanical, and enzymatic isolation processes [87]. Previous study reported that the novel isolation process of cellulose nanofiber is achieved through high-pressure homogenization [100,101]. The developments of technology lead researchers to enhance and invent new processing technique in order to obtain fine and purer nanocellulose. Extraction process and method that available today are such mechanical treatments, e.g. cryocrushing grinding [102-106] ; high pressure homogenizing [100,101,107-110]; chemical treatments, e.g. acid hydrolysis [111-113] ; biological treatments, e.g. enzyme-assisted hydrolysis [114-116] ; TEMPO-mediated oxidation on the surface of microfibrils and a subsequent mild mechanical treatment [117-120] ; synthetic and electrospinning methods [121-123], and ultrasonic technique [123-127]. In fact, numerous of studies investigated isolation of nanocellulose from various raw materials, mainly of plant origin, using different techniques.

Mechanical process

This process is applicable for pulp consists cellulose fiber that mainly acquire from wood. In industrial level, this process is called as pulping process. In mechanical process, ground wood pulp will be produced by pressing round wood logs against a rotating cylinder. Rotating cylinder that made of sandstone will then scraping the fibers off (figure 6 a). Another type of mechanical pulp is a refiner pulp as shown in figure 6b. It is obtained by supply wood chips into the center of rotating, refiner discs in the presence of water spray. The groovy structure of the disc make the finer pulp as the wood material gets closer to the edge of the disk [97]. Apart from fibers released from the wood matrix, mechanical pulp also contains a constituents that so called fines. These are tiny particles, such as broken fibers, giving the mechanical-produced pulp a specific optical characteristics [97,98].

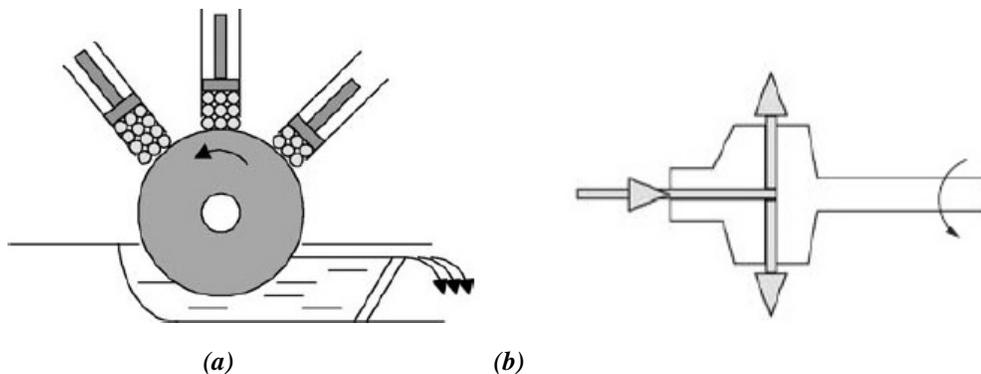


Figure 6 : a) Schematic figure of stone grinder. b)Pulp refiner

Homogenization

In the homogenization process, dilute slurries of cellulose fibers is first treated by the refining process. Next step, it will be pumped at high pressure and fed through a spring high pressure loaded valve assembly. This valve opens and closes rapidly make the fibers subjected to a large pressure drop with shearing and impact forces that promotes high degree of microfibrillation of the cellulose fibers. 100 The refining process is carried out prior to

homogenization due to the fact that refining produces external fibrillation of fibers by gradually peeling off the external cell wall layers (P and S1 layers) and exposing the S2 layer and also causes internal fibrillation that loosens the fiber wall, preparing the pulp fibers for subsequent homogenization treatment [129]. Others researchers also have studied how the degree of fibrillation of pulp fibers affects the mechanical properties of cellulose composites [109]. For instance some finding shows that if the fiber passes through the refiner treatment between [16] and [30] passes or cycle, the pulp fibers underwent a degree of fibrillation that resulted in gradual increment of mechanical properties, particularly in bending strength [109].

Chemical pulping

Chemical pulping is used to isolate fibers from the wood and mainly to remove the matrix substance lignin. The removal of lignin or so called the delignification process is done by degrading the lignin molecules, bringing them into solution then finally removing them by washing. However, there are no chemicals being entirely selective toward lignin. Therefore, also a certain amount of the carbohydrates (cellulose and hemicellulose) is lost in this process. In addition, complete removal of lignin is not possible without severely damaging the carbohydrates. After delignification, some lignin is therefore remaining in the pulp and this amount is determined by the pulps kappa number. Of all pulp produced worldwide, almost three quarters are chemical pulp, of which the major part is produced by the kraft process [97,98]. The kraft process (or sulphate process) is the dominant chemical pulping method worldwide. However, more recently, the pulping technique is developing. It uses organic solvents as ethanol, methanol and peracetic acid ($\text{CH}_3\text{CO}_3\text{H}$) as pulping agent [97,98].

Acid hydrolysis

In chemical method, nanocrystalline cellulose is prepared by acid hydrolysis. Hydrolysis is usually carried out by introducing sulphuric acid in the fiber with constant stirring. The cellulose is easily hydrolyzed by acid into water-soluble sugar. The cellulose should be degraded gently to form finer fiber and because of that reason, the process should be control to prevent excessive degradation of cellulose. At certain time, after the cellulose degraded to finer and favorable size, the process should be stop immediately by adding water. It then should be diluted 10 times with deionized water to stop the reaction. The suspension centrifuges at 6000 RPM for 10 min to concentrate the cellulose and to remove excess aqueous acid. The resultant precipitate should be rinsed, recentrifuged, and dialyzed against water for 5 days until constant neutral pH [130]. Other method reported that the cellulose fiber is hydrolyzed with sulphuric acid (96 wt%) under strong agitation.66 The time of reaction is varied from 15-90 minutes and the reaction terminated by adding cold water. Then the diluted suspensions were centrifuged at 11,000 rpm for 10minutes to obtain precipitate. Using strong agitation, the precipitate is re-suspended in water and centrifuged repeatedly until the pH reached 5.

Steam explosion

Steam explosion treatment is currently still being extensively studied as a promising treatment method. Lignocellulosic biomass materials can be fractionated by steam explosion technique. Treating various biomass resources by steam explosion has been studied by many researchers [131, 132, 133,134,135]. The steam explosion techniques allows lignocellulosic matter undergo a high pressure of steam, for short periods of time, followed by sudden decompression (explosion). The process represents a simple treatment for biomass that achieves fiberization by combination of chemical and mechanical action [46]. During the steam explosion process, the raw material is exposed to pressurized steam followed by rapid reduction in pressure resulting in substantial break down of the lignocellulosic structure, hydrolysis of the hemicellulose fraction, depolymerization of the lignin components and defibrillization [136,137,138]. Some mentions that the steam explosion is an auto hydrolysis process [139]. Steam explosion could give significant effect on biomass which leads to the cleavage of some accessible glycosidic links, β -ether linkages of lignin, lignin-carbohydrate complex bonds and minor chemical modification of lignin and carbohydrates. In extensive studies, it found that aspect ratio and percentage yield of nanocellulose obtained by this technique has been found to be very high as compared to other conventional methods.

High-intensity ultrasonication

This process requires the combination of chemical pretreatment and high-intensity ultrasonication. In the chemical pretreatment stage, the wood fibers are being purified to prepare the cellulose fibers according to general

methods.^{104,105} To avoid generating strong hydrogen bonding among nanofibers after matrix removal, the samples are kept in a water-swollen state during the whole chemical process. After chemical pretreatment, the purified cellulose fibers are soaked in distilled water (concentration: ~0.5% in mass). About 120 ml of solution containing chemical-purified cellulose fibers are then placed in a common ultrasonic generator of 20–25 kHz in frequency equipped with a cylindrical titanium alloy probe tip of 1.5 cm in diameter. The subsequent ultrasonication is conducted for 30 min to isolate the nanofibers.

Surface modification of cellulose nanofiber

The contact angle measurements showed that the surface characteristics of nanofibers were changed from hydrophilic to more hydrophobic when acetylated [87]. The acetylation process generally provide better surface characteristic of the nanofiber. Due to the hydrophilic nature of cellulose, it cannot be uniformly dispersed in most non-polar polymer media [46]. Hence, cellulose modifications become main interest in order to improve compatibility with a wider variety of matrices. Several methods have been proposed for cellulose surface modification, corona or plasma discharges [140], surface derivatization [141], graft copolymerization [142] and application of surfactant [143,144]. Reports on surface modification of microfibrillated cellulose nanofiber (MFC) is however are limited [145,146]. Surface modification of nanocellulose fiber basically adapted from previous studies on surface fiber modification. Table 4 shows the effect of surface treatment to fiber properties where the effect of that particular treatment to nanocellulose fiber also could be predicted. Those information could give general idea how the treatment going to take effects on micro fibrillated cellulose nanofiber thus preliminary study could be conducted.

Table 4 : Effect of surface treatments on properties of OPF (Oil Palm Fiber) [150,211-216]

Treatment	Effect on EFB
Mercerization	Amorphous waxy cuticle layer leaches out.
Latex coating	Partially masks the pores on the fiber surface.
γ irradiation	Partially eliminates the porous structure of the fiber and causes microlevel disintegration. It degrades mechanical properties considerably.
Silane treatment	Imparts a coating on fiber surface
Toluene diisocyanate (TDI) treatment	Makes fiber surface irregular as particles are adhered to surface.
Acetylation	Removes waxy layer from the surface and makes the fiber hydrophobic.
Peroxide treatment	Fibrillation is observed due to leaching out of waxes, gums and pectic substances.
Permanganate treatment	Changes the colour and makes fibers soft. Porous structure is observed after treatment.
Acrylation	Imparts a coating on fiber surface and removes pits containing silica bodies and keeps surface irregular. It improves mechanical properties of fibers.
Silane treatment	Keeps the fiber surface undulating and improves mechanical properties
Titanate treatment	Smoothens fiber surface.
Benzoylation	Imparts a rough surface to the fibers and makes pores prominent, which helps improving the mechanical interlocking with matrix resin.
Oil extraction	Imparts bright colour to the fiber. Removal of oil layer exposes surface pits and makes surface coarse.
Alkali treatment	Makes the surface pores wider and fiber become thinner due to dissolution of natural and artificial impurities.

Acetylation

In previous research that conducted, cellulose was partially acetylated to modify its physical properties while preserving the microfibrillar morphology [147]. In this case, the degree of acetyl substitution had a crucial influence on material properties. Other finding recorded that acetylation improved the transparency and reduced the hygroscopicity of cellulose/acrylic resin composite materials [148]. However, the composites had an optimum degree of substitution (DS) and excessive acetylation reduced their properties. Acetylation has also been reported to improve the thermal degradation resistance of cellulosic fibers [149]. However, no report about acetylation of MFC surfaces have been published so far.

Silylation/Silane Treatment

Silane is a coupling agent. It has chemical structure (fig. 6) that allows it to react with water to form a silanol and an alcohol. Fibers were dipped in 1% silane solution (tri-ethoxy vinylsilane) in water-ethanol mixture (40 : 60) for about 3 h. During the reaction, the pH of the solution was maintained to 3.5–4. Fibers were washed and then dried before further use.

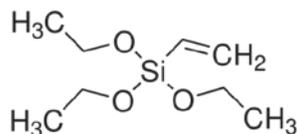
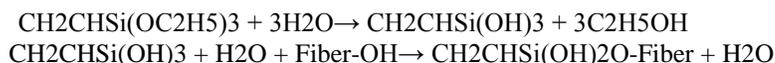


Fig. 6: tri-ethoxy vinylsilane.¹⁵⁰



Equation 1: tri-ethoxy vinylsilane reaction with water to produce silanol and followed by silanol reacts with the cellulosic hydroxyl group [150].

The reaction occur with silane molecule absorb chemically onto the fiber. The reaction and absorption of chemical depends on free OH group available on the surface of the fiber. On the other hand, with presence of moisture, silanol will reacts with cellulosic hydroxyl group in the fiber to form stable covalent bonds to the cell wall. The purpose of silylation is to increase hydrophobicity of the fibers. It is possible because it will remove the site for moisture absorption. The hydrophobic coupling agent forms a protective monolayer on the proton-bearing. Such modification is most effective in surface regions. However, as the concentration and time of the treatment increases, the treatment effect may penetrate into the fiber. Same with other reaction principles, there will be a saturation point which no further reaction takes place [152].

Isopropyl utilized dimethylchlorosilane for surface silylation of cellulose microfibrils resulting from the homogenization of parenchymal cell walls. These authors claimed that microfibrils retained their morphology under mild silylation conditions and could be dispersed in a nonfloculating manner into organic solvents. Other method hydrophobized MFC via partial surface silylation using the same silylation agent and reported that when silylation conditions were too harsh, partial solubilization of MFC and loss of nanostructure could occur [152]. Films prepared from the modified cellulose by solution casting showed a very high water contact angle (117–146°). It is probable that in addition to decreased surface energy, higher surface roughness as a result of modification could contribute to increased hydrophobicity. It has also been reported that hydrophobized MFC could be used for the stabilization of water-in-oil type emulsions [153]

BIOCOMPOSITE AND NANO-BIOCOMPOSITE

Throughout decades, a new branch of polymer composite material has been widely investigated. Bionanocomposite for instance, is composite material based on incorporation of natural nanosized fiber or filler into matrix phase. Each fractional component is usually derived from renewable resources such as starch, cellulose and

protein [154]. Polymer could be categorized into two general types according to its source which are synthetic polymer and bio-polymer. Synthetic polymer mainly originates from petroleum source whether bio/natural polymer come from a renewable source which both of them play an important role in the polymer industry.

However, development of this advantageous biopolymer has really attracted major attention which that more research is focusing on this type of polymer. In general, biopolymers can be classified into four different types which are shown in fig. 7. Consequently, various source of bio polymer are invented and classified according to its source. Some of the biopolymer is blended with petrochemical-based polymer to produce a biodegradable polymer composite. There are many possible ways in making bio-nanocomposite with all these kind of source. In fact, many attempts have been carried on in order to prepare biodegradable composite using other various interpretations of lignocellulosic materials for instance in nano-form. Nanosize reinforcement is one of the important and almost unfamiliar fields. It exploit sources either organic or inorganic and synthetic or from natural origin. As in natural origin, one of potential materials that can be revealed is cellulose nanofibers.

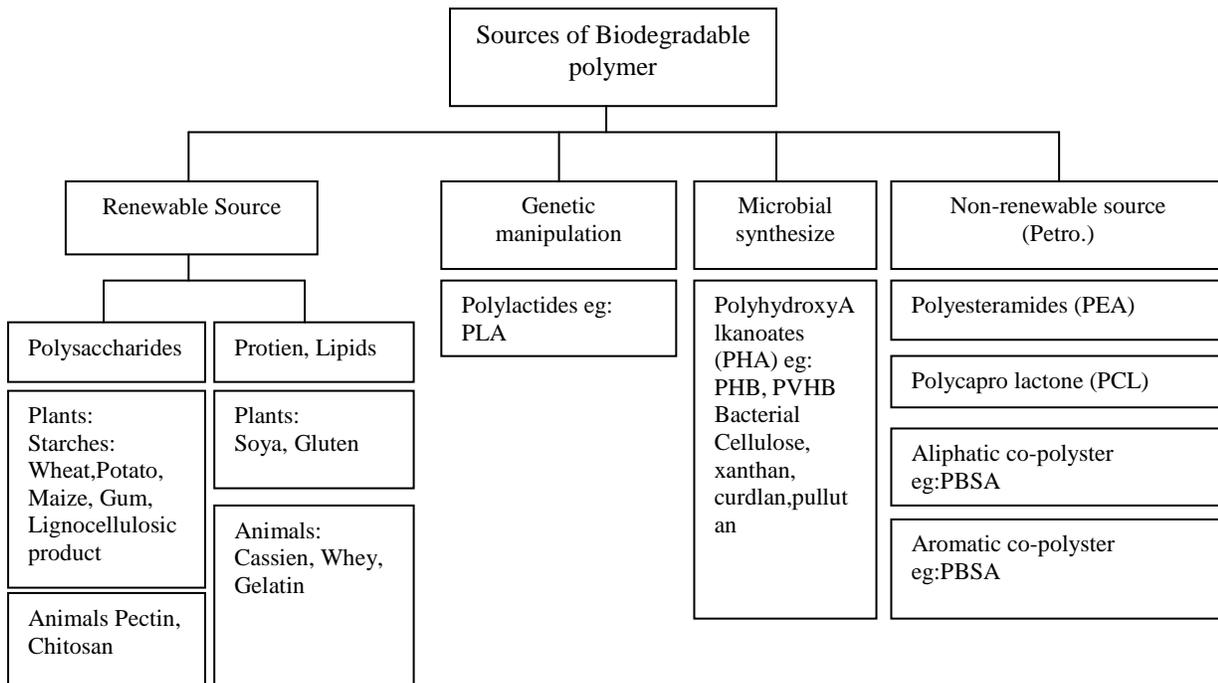


Fig. 7 : Classification of potential biopolymers in composite fabrication.

Cellulose nanofiber reinforced a natural biopolymer that finally results in fully biodegradable nanocomposites. There are other nano-reinforcement particles are available. Recent report shown that starch-based nanocomposites have been prepared with various nano-sized fillers such as cellulose nanofibers, chitin and chitosan nanoparticles and nanoclays. However, nano cellulosic fiber attracts more attention due to its good reputation and has provided many advantages than other filler [48]. Broadly defined, biocomposites are composite materials made from natural/bio fibre and petroleum derived non-biodegradable polymers (Poly propylene, polyethylene) or biodegradable polymers (PLA, PHA). The latter category i.e. biocomposites derived from plant derived fibre (natural/biofibre) and crop/bioderive plastic(biopolymer/bioplastic) are likely to be more eco-friendly and such composites are termed as green composite [48].

The relation between composite, nano composite and green composite is shown in diagram 7. Basically, composite is considered as nanocomposite if one of the materials that incorporated reached size of below 100nm. There are two major approaches of producing polymer nanomaterials/nanocomposite. It's either produce nano-scale polymer material or otherwise introduce nanomaterial into polymer to produce nanocomposite [155]. Depending on the geometry and the nature of the nanofillers, nanocomposites may exhibit new and/or substantially

improved properties (e.g. mechanical performance, barrier properties, thermal stability and transparency [156]. In thin film food packaging aspect, FMC(food packaging materials) have been developed with the inclusion of nano size filler that able to improved flexibility, gas barrier properties, temperature control and moisture stability. It eventually could reinforce the polymer matrix. In general, researchers approve that the use of nanoscale fillers in composite films represents a radical, promising alternative to conventional polymer composites [10,156,157].

APPLICATION OF NANOFIBER IN COMPOSITE

From previous research, applications of cellulose nanofibers are generally for composite reinforcement. The reinforcement using nanofiber is only focusing on hard composite but in thin film too. Consequently, its application could be applied in material reinforcement for construction, automotives, food packaging and many more. It is possible to be achieved by composing the nanofiber into different source of polymer or biopolymer that available (figure 8). At the very beginning of the composite development era, the petroleum based polymer was combined with natural bio-derived polymer to create biodegradable polymer composite. Next, the natural fiber is then mixed with petroleum based polymer to create other types of composite. As the petroleum sources become depleted, the researcher find other alternative by combining natural bio derived polymer with natural biofiber that hope could give synergy effects. It is called as green composite because it fully constructed with green materials. The purpose of introducing bio-based material into the petroleum based polymer is to enhance biodegradability. As time goes by, more advance material is created by disintegration of natural fiber into nano-size fiber that finally fabricates into polymer matrix to create nanocomposite. Composite material studies keep evolving and there are so many possible inventions in new material has been found and studied. Fully green nano-composite is then emerging as green technology became serious business and the researches about this particular field is to be studied.

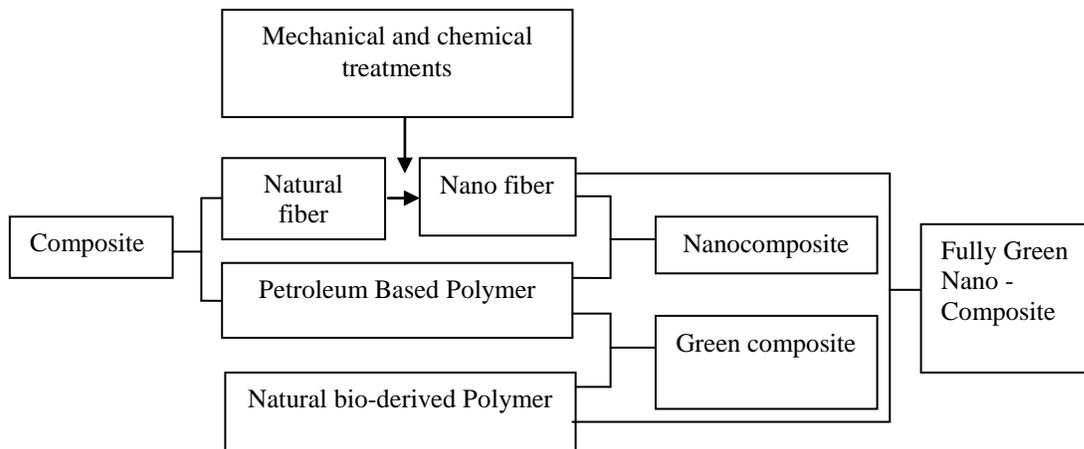


Fig. 8 : The connection between composite, green composite

Starch-based nano-biocomposites

Starch based nano-biocomposites is a new class of composite composed of nano-sized filler (nanofiller) incorporated into a bio-based matrix [159]. Such an association between natural biopolymers and nano-objects, with the aim to obtain synergic effects, is one of the most innovating routes to enhance the properties of these bio-matrices [11]. Starch is originated from variety of crops such as potato, wheat, rice and corn. The source is abundant, and readily available at low cost [160]. Previously, starch already been used to produce biodegradable films in aiming to partially or entirely replace plastic polymers due to its ideal feature that is low cost, abundant and renewable with satisfactory mechanical properties [161]. Starch is a biopolymer that contains major components of amylose and amylopectin that role as binder and barriers in packaging materials. At the beginning, water and glycols are commonly used as plasticizer in bioplastic making that make the starch behave like thermoplastic instead of thermoset [162,163].

However, native starch based film properties suffers from poor mechanical properties and high water uptakes [163, 164]. This limitation has led to the development of the improved properties of starch based films by modifying starch properties and/or incorporating other materials [165]. Blending starch with different proteins could decrease the water vapor permeability of the films and increase tensile strength. In fact, there are many attempts has been done to enhance starch base plastic by incorporation with other binder or filler. Previous studies have shown that starch based composites were fabricated with different type of filler from different sources such as polyhydroxybutyrate PHB [166,167], Polylactides PLA [168,169,170], Polycapro lactone PCL [122,172,173], Chitosan [174,175,161] Clays [176,177,178,179] natural fiber [180,181,182,183] cellulose whisker [184,185] microcrystalline cellulose [163,186,187] and microfibrillated cellulose MFC and biofiber composite BFC [188,189,190].

However, these films still not perform well compared to synthetic polymer based films. Thus, innovative researchers took a step by incorporating the native starch based plastic with nanofiber. It is expected to bring starch based nano composite film to a new level that hopefully could catch up with synthetic polymer based film. New bio-based nanofillers coming from starch [191], cellulose [192], or chitin [193] have been intensely studied since the last decade. The distinguished advantages of the starch that are renewable, available anywhere, cheap, have low density, biodegradable and easily destroyed when incinerate at the end of life makes the starch based biopolymer more developed.

Poly lactic acid (PLA) based nanocellulose composite

Derivation of natural and renewable sources such as corn can produce polylactide or poly (lactic acid), one of the biodegradable thermoplastic polyester. PLA is manufactured by biotechnological process. PLA possessed a low value in nature like other bioplastic. Thus, it makes reinforcement of this particular bioplastic is crucial. Reinforcement of polylactic acid (PLA) is achieved by incorporating microfibrillated cellulose (MFC, mechanically fibrillated pulp, mostly consisting nanofiber) [25]. The study was carried out to study the potential of reinforcement by a nanofiber network, with the goal of making sustainable 'Green composite' [25].

The fabrication of the PLA-based nanocomposite is by direct mixing. A procedure is introduced in order to attain uniform dispersion of MFC in a PLA. Both components will be premixed and kneaded using solvent then the film will cast using hot pressed method before mechanical and thermo-mechanical properties of the film were studied [46]. There are numbers of studies supporting that the nanocellulose incorporation into PLA composite could give reinforcement as the young modulus and tensile strength of PLA composites could be increased

Poly-Hydroxy butyrate (PHA) composite

PHAs are polyesters produced naturally by bacteria from renewable sugars or fats, to store carbon and energy in their cells [194]. Since the 1970s, a number of companies have pursued industrial processes to optimize fermentation conditions for polymer growth within the microorganism. It's a polymer that first discovered and was initially described as lipid inclusion in the bacterium *Bacillus megaterium* [195]. PHA has the simplest family form of biopolymer which is poly-R-3-Hydroxybutyrate (PHB). A few years after, PHB was demonstrated as high molecular weight polymer utilized in carbon and energy storage by variety of microorganism [196]. Emerging potential of PHAs brings out large number of study that bound on microstructure, thermal and mechanical properties through to studies on biodegradation [197].

Furthermore, PHA's are renewable source and its physical properties are similar to conventional plastic that extends lead more research on this topic [198,199]. Nanocrystal is prepared through acid hydrolysis of cellulose microfibril [200]. On the other hand, composites were made by dispersing either native or silylated crystals in cellulose acetate butyrate matrixes and solution casting of the dispersions. As a results, PLA composite exhibit better reinforcement characteristics. However, there is one restriction on the use of cellulose crystals as reinforcement is their incompatibility with a typically more hydrophobic thermoplastic matrix. To overcome this problem, cellulose nanocrystals from bacterial cellulose were topochemically trimethylsilylated [46].

Hydroxypropylmethylcellulose (HPMC) reinforced with cellulose nano-particles

Hydroxypropyl methylcellulose (HPMC) is one of the cellulose ethers (derivation of plant source), the most commonly used biopolymer. It is approved for food uses by the FDA (21 CFR 172.874) and the EU (EC, 1995). It also been used in the food industry as an emulsifier, protective colloid, stabilizer, suspending agent, thickener, or film-forming agent [201]. The films obtained from HPMC are resistant to oils and fats, flexible, transparent, odorless, and tasteless but tend to have moderate strength [202]. Similar to other biopolymer, the HPMC based biopolymer exhibit limited performance related to brittleness and moisture barrier [201].

The application of nanotechnology by developing polymer nanocomposite films with the addition of fillers in the nano-form may open new possibilities for improving mechanical and barrier properties. This particular feature provides nanocomposites a unique and outstanding property that never found in conventional composites. From previous research, reinforcing effect of the cellulose particles is observed when whiskers is used as the filling material; an increase of 22% in tensile strength and 55% in Young's modulus were achieved while the elongation at break of the films was preserved. Addition of whiskers also improved the water barrier properties of the composite films. This effect was attributed to the lower water affinity of the composite films, as compared with the HPMC films, since the water diffusivity values were not affected by the addition of whiskers.

Furthermore, the whiskers only decreased 3–6% the transparency of the HPMC films showing 86–89% visible light transmission values, allowing application as edible barrier and transparent film. It can be concludes that the composite produced by using whiskers as filling material were transparent, flexible and homogeneous; the nanocomposite films exhibited better water barrier and mechanical properties than HPMC films while decreasing only slightly the transparency of the films. These results indicate the great potential of HPMC/cellulose whiskers composite films that give synergy effect for sustainable packaging applications.

Nanocomposite films based on sodium caseinate and nanocellulose fibers

Different from HPMC, Sodium caseinate is the biochemical name for casein, a type of protein that found in a milk of all mammals. Casein, Latin term for "cheese," is a major component of commercial cheese and its principle source of protein. Caseinate containing protein (the rest being lactose, lipids, attached moisture, and ashes) [203]. In general, films made from sodium caseinate and nanocellulose were prepared by dispersing the fibrils into film forming solutions, casting and drying. Sodium caseinate aqueous solutions with adequate amount of protein were prepared by dissolving the sodium caseinate powder in distilled water and stirring at room temperature. After the addition of plasticizer agent, the nanocellulose fibers that dispersed in distilled water by ultrasonication is then mixed with the film forming solutions to prepare composites. Films were prepared according to the usual casting method for instance by casting it onto Teflon Petri dishes and let to dry in convection oven in room temperature.

After the excess of water is evaporated, obtained film is peeled off from the plates and kept in a closed reservoir at 50% relative humidity (RH) and constant temperature. As a result, composite films were less transparent and have more hydrophilic surface than native and pure sodium caseinate. Furthermore, the overall moisture uptake is almost not affected by filler concentration. Addition of nanocellulose to the neat sodium caseinate films produced an initial increase in the barrier properties to water vapor, and then, it decreases as filler content increased. This was explained in terms of additional detrimental changes (cracks and bubble formation) induced in the morphological structure of the film by the reinforcement. The tensile modulus and strength of composite films increased significantly with increasing cellulose concentrations, while the values of elongation decreased. In the same way it was found that the storage modulus increases considerably with the filler addition in the low temperature range (<60 °C), though the effect of temperature on the film performance is even more dramatic, that as expected in protein-based materials.

EXPLORATION AND DEVELOPMENT OF CELLULOSE NANOCOMPOSITE

As sustainable development becomes a huge tagline, many research intensely studied in the particular field especially development in biopolymer composites. Effects of global warming, increment non-biodegradable waste, and depletion of petroleum reserved has triggered intense study of cellulose source material. Cellulose nanofiber becomes so important because incorporation of nanoreinforcement has been related to improvement in overall

performance of biopolymers. Many findings validates that the addition of nanofiber could enhance mechanical, thermal and barrier properties of biopolymer that have many drawbacks.

Over decades, this particular field of study becomes more interesting that lead to the advancement of nanofiber filler values. It's because many research revealed that the properties of filler is actually plays important role in polymer reinforcement. Thus, better understanding of organic and polymer chemistries makes the researcher look deeply at the interaction between polymer matrix and filler (nanofiber) hence lead to the advancement of nanofiber values. Hence, many process steps, cellulose nanofiber modification and study on application of cellulose and its compatibility with various polymers has been studied. In recent studies, it is shown that by applying other nanoparticles into the nanocomposite has an important role to improve the feasibility of use of biopolymer for several applications including food packaging. For an example, chitosan flakes could be derived into nanoparticles to be incorporated into bioplastic packaging that act as antimicrobial bullets. The same thing goes on other particles such as nanosilver and others. Recent exploration and development on nano-scale cellulose and its related applications is shown in table 5.

Table 5: Exploration and development of cellulose nanocomposite.

Year	Progress
2009	Bionanocomposites of thermoplastic starch reinforced with bacterial cellulose nanofibers. Effect of enzymatic treatment on mechanical properties [204].
2009	Nanocomposites for food packaging applications.205
2009	Progress in nano-biocomposites based on polysaccharides and nanoclays [154].
2009	Fabrication and characterisation of chitosan nanoparticles/plasticised-starch composites [206].
2009	Nanoscale particles for polymer degradation and stabilization—Trends and future perspectives [207].
2010	Starch-based composites reinforced with novel chitin nanoparticles [160]
2010	Isolation, preparation, and characterization of nanofibers from oil palm empty-fruit-bunch (OPEFB) [66].
2011	Structure and properties of nanocomposite films based on sodium caseinate and nanocellulose fibers [203].
2011	Characteristics of cellulose nanofibers isolated from rubberwood and empty fruit bunches of oil palm using chemo-mechanical process [208].
2012	Reinforcing potential of micro- and nano-sized fibers in the starch-based biocomposites [209].
2012	Synthesis of nano cellulose fibers and effect on thermoplastics starch based films [210].

CONCLUSIONS

The future of bio based material becomes brighter not only because the source is infinite, but it could compete and may replace synthetic material that's available today. All these are possible since there are numerous exploration about cellulose material has been conducted. Available information from previous research could clarify and make present researcher understand more about characteristic and the morphology of cellulose nanofiber. Hence, modification of cellulose nanofiber is possible to achieve chemically or physically. In order to extract nanofibers, various methods have been reviewed. The source of nanofiber is varied either from animal or plant sources. However, every extraction method gave different results in term of quality and yields. Disruption of cellulose may occur during treatment and extraction, hence an effort in order to reduce is to be explored. An

effective production should be achieved or else it will be worthless. Effective production should require a low amount of energy with high yield of nanofiber. In an effort to fulfill this, mixture of chemical, enzymatic and physical method might be combined in the extraction process. In fact, researchers found that by adding pre-treatment into process integration, it could significantly reduce energy consumption. Different biopolymer may exhibits different effect after the incorporation of cellulose nanofiber that due to its chemical structure of the biopolymer itself Next, excellent interaction between polymer matrix and nanofiber is important since it can effect on the composite strength. Some might require chemical modification of cellulose nanofiber. However, there are various polymer matrixes available that ready to be incorporated with nanocellulose. In general, bio-based polymer is hydrophilic where the incorporation of cellulose nanofiber into it would not be a problem. In contrary, nanocellulose need to be modified before incorporation into hydrophobic synthetic polymer that mostly based on petroleum. Consequently, further exploration regarding modification of cellulose with minimum environmental impact, and understanding the chemical and physical interaction occurred between polymer matrix and nanofiber is necessary.

REFERENCES

- [1] Soma C., Bergesb M., Chaudhryc Q., Dusinskad M., Fernandese T.F., Olsenf S.I., Nowacka B., (2010). The importance of life cycle concepts for the development of safe nanoproducts., *Toxicology* 269 160–169.
- [2] Duncan, TV. (2011). Applications of nanotechnology in food packaging and food safety: Barrier materials, antimicrobials and sensors. *Journal of colloid and interface science*. 363(1) 1-24
- [3] Collister, J. (2002). Commercialisation of polymer nanocomposites. In R. Krishnamoorti & R. A. Vaia (Eds.), *Polymer nanocomposites: Synthesis, characterisation and modelling*. Washington: American Chemical Society.
- [4] Ray, S., Easteal, A., Quek, S. Y., & Chen, X. D. (2006). The potential use of polymer– clay nanocomposites in food packaging. *International Journal of Food Engineering*, 2(4). art. 5.
- [5] Bharadwaj, R. K., Mehrabi, A. R., Hamilton, C., Trujillo, C., Murga, M., Fan, R., Chavira, A., et al. (2002). Structure-property relationships in cross-linked polyester–clay nanocomposites. *Polymer*, 43(13), 3699–3705.
- [6] Mirzadeh, A., & Kokabi, M. (2007). The effect of composition and draw-down ratio on morphology and oxygen permeability of polypropylene nanocomposite blown films. *European Polymer Journal*, 43(9), 3757–3765.
- [7] Alexandre, B., Langevin, D., Mederic, P., Aubry, T., Couderc, H., Nguyen, Q. T., et al. (2009). Water barrier properties of polyamide 12/montmorillonite nanocomposite membranes: structure and volume fraction effects. *Journal of Membrane Science*, 328(1–2), 186–204.
- [8] Luduena, L. N., Alvarez, V. A., & Vasquez, A. (2007). Processing and microstructure of PCL/clay nanocomposites. *Materials Science and Engineering: A*, 121–129.
- [9] Weiss, J., Takhistov, P., & McClements, D. J. (2006). Functional materials in food nanotechnology. *Journal of Food Science*, 71(9), R107–R116.
- [10] Adame, D., & Beall, G. W. (2009). Direct measurement of the constrained polymer region in polyamide/clay nanocomposites and the implications for gas diffusion. *Applied Clay Science*, 42, 545–552
- [11] Alexandre, M., & Dubois, P. (2000). Polymer-layered silicate nanocomposites: Preparation, properties and uses of a new class of materials. *Materials Science and Engineering R-reports*, 28(1), 1–63.
- [12] Osman, M. A., Ploetze, M., & Suter, U. W. (2003). Surface treatment of clay minerals – thermal stability, basal-plane spacing and surface coverage. *Journal of Materials Science*, 13, 2359–2366.
- [13] Paul, M. A., Alexandre, M., Degee, P., Henrist, C., Rulmont, A., & Dubois, P. (2003). New nanocomposite materials based on plasticized poly(L-lactide) and organomodified montmorillonites: thermal and morphological study. *Polymer*, 44(2), 443–450.
- [14] Dean, K., Yu, L., & Wu, D. Y. (2007). Preparation and characterization of meltextruded thermoplastic starch/clay nanocomposites. *Composites Science and Technology*, 67, 413–421.
- [15] Azizi Samir, M. A. S., Alloin, F., & Dufresne, A. (2005). Review of recent research into cellulosic whiskers, their properties and their application in nanocomposite field. *Biomacromolecules*, 6, 612–626.

- [16] Wang, B., & Sain, M. (2007). Isolation of nanofibers from soybean source and their reinforcing capability on synthetic polymers. *Composites Science and Technology*, 67(11–12), 2521–2527.
- [17] Oksman, K., Mathew, A. P., Bondeson, D., & Kvien, I. (2006). Manufacturing process of cellulose whiskers/poly(lactic acid) nanocomposites. *Composites Science and Technology*, 66(15), 2776–2784.
- [18] Helbert, W., Cavaille, C. Y., & Dufresne, A. (1996). Thermoplastic nanocomposites filled with wheat straw cellulose whiskers. Part I: processing and mechanical behaviour. *Polymer Composites*, 17(4), 604–611.
- [19] Petersson, L., & Oksman, K. (2006a). Biopolymer based nanocomposites: comparing layered silicates and microcrystalline cellulose as nanoreinforcement. *Composites Science and Technology*, 66, 2187–2196.
- [20] Hubbe, M. A., Rojas, O. J., Lucia, L. A., & Sain, M. (2008). Cellulosic nanocomposites: a review. *Bioresources*, 3(3), 929–980.
- [21] Dogan, N., & McHugh, T. H. (2007). Effects of microcrystalline cellulose on functional properties of hydroxyl propyl methyl cellulose microcomposite films. *Journal of Food Science*, 72(1), E16–E22
- [22] Chen, Y., Liu, C., Chang, P. R., Cao, X., & Anderson, D. P. (2009). Bionanocomposites based on pea starch and cellulose nanowhiskers hydrolyzed from pea hull fibre: effect of hydrolysis time. *Carbohydrate Polymers*, 76(4), 607–615.
- [23] Lu, Y., Weng, L., & Cao, X. (2005). Biocomposites of plasticizers starch reinforced with cellulose crystallites from cottonseed linter. *Macromolecular Bioscience*, 5, 1101–1107
- [24] Tang, C., & Liu, H. (2008). Cellulose nanofiber reinforced poly(vinyl alcohol) composite film with high visible light transmittance. *Composites Part A: Applied Science and Manufacturing* 39(10), 1638–1643.
- [25] Iwatake, A., Nogi, M. & Yano, H. (2008). Cellulose nanofiber-reinforced poly(lactic acid). *Composites Science and Technology*, 68, 2103–2106.
- [26] Wu, Q., Henriksson, M., Liu, X., & Berglund, L. A. (2007). A high strength nanocomposite based on microcrystalline cellulose and polyurethane. *Biomacromolecules*, 8, 3687–3692
- [27] Sanchez-Garcia, M. D., Gimenez, E., & Lagaron, J. M. (2008). Morphology and barrier properties of solvent cast composites of thermoplastic biopolymers and purified cellulose fibers. *Carbohydrate Polymers*, 71, 235–244.
- [28] Zhou, X., Shin, E., Wang, K. W., & Bakis, C. E. (2004). Interfacial damping characteristics of carbon nanotube-based composites. *Composites Science and Technology*, 64(15), 2425–2437.
- [29] Lau, K. T., & Hui, D. (2002). The revolutionary creation of new advanced Materials –carbon nanotube composites. *Composites Part B*, 33(4), 263–277.
- [30] Kim, J. Y., Han, S., II, & Hong, S. (2008). Effect of modified carbon nanotube on the properties of aromatic polyester nanocomposites. *Polymer*, 49, 3335–3345.
- [31] Chen, W., Tao, X., Xue, P., & Cheng, X. (2005). Enhanced mechanical properties and morphological characterizations of poly(vinyl alcohol)–carbon nanotube composite films. *Applied Surface Science*, 252, 1404–1409.
- [32] Lopez Manchado, M. A., Valentini, L., Biagotti, J., & Kenny, J. M. (2005). Thermal and mechanical properties of single-walled carbon nanotubes–polypropylene composites prepared by melt processing. *Carbon*, 43, 1499–1505.
- [33] Zeng, H., Gao, C., Wang, Y., Watts, P. C. P., Kong, H., Cui, X., et al. (2006). In situ polymerization approach to multiwalled carbon nanotubes-reinforced nylon 1010 composites: mechanical properties and crystallization behavior. *Polymer*, 47, 113–122.
- [34] Wu, C.L.;Zhang, M.Q.;Rong, M.Z.;Friedrich, K. (2002). Tensile performance improvement of low nanoparticles filled-polypropylene composites. *Composites Science and Technology*, Volume 62, Issue 10-11, August 2002, Pages 1327-1340
- [35] Xiong, H. G., Tang, S. W., Tang, H. L., & Zou, P. (2008). The structure and properties of a starch-based biodegradable film. *Carbohydrate Polymers*, 71, 263–268.
- [36] Vladimirov, V., Betchev, C., Vassiliou, A., Papageorgiou, G., & Bikiaris, D. (2006). Dynamic mechanical and morphological studies of isotactic polypropylene/ fumed silica nanocomposites with enhanced gas barrier properties. *Composites Science and Technology*, 66, 2935–2944.
- [37] Jia, X., Li, Y., Cheng, Q., Zhang, S., & Zhang, B. (2007). Preparation and properties of poly(vinyl alcohol)/silica nanocomposites derived from copolymerization of vinyl silica nanoparticles and vinyl acetate. *European Polymer Journal*, 43, 1123–1131.
- [38] Sun, D. P., Zhou, L. L., Wu, Q. H., & Yang, S. L. (2007). Preliminary research on structure and properties of nano-cellulose. *Journal of Wuhan University of Technology – Materials Science Edition*, 22(4), 677–680.

- [39] Xu, Y., Ren, X., & Hanna, M. A. (2006). Chitosan/clay nanocomposite film preparation and characterization. *Journal of Applied Polymer Science*, 99(4), 1684–1691.
- [40] Kristo, E., & Biliaderis, C. G. (2007). Physical properties of starch nanocrystal-reinforced pullulan films. *Carbohydrate Polymers*, 68, 146–158.
- [41] Chen, Y., Cao, X., Chang, P. R., & Huneault, M. A. (2008). Comparative study on the films of poly(vinyl alcohol)/pea starch nanocrystals and poly(vinyl alcohol)/ native pea starch. *Carbohydrate Polymers*, 73, 8–17.
- [42] Lu, Y., Weng, L., & Zhang, L. (2004). Morphology and properties of soy protein isolate thermoplastics reinforced with chitin whiskers. *Biomacromolecules*, 5, 1046–1051.
- [43] Sriupayo, J., Supaphol, P., Blackwell, J., & Rujiravanit, R. (2005). Preparation and characterization of a-chitin whisker-reinforced chitosan nanocomposite films with or without heat treatment. *Carbohydrate Polymers*, 62, 130–136.
- [44] Lopez-Leon, T., Carvalho, E. L. S., Seijo, B., Ortega-Vinuesa, J. L., & Bastos-Gonzalez, D. (2005). Physicochemical characterization of chitosan nanoparticles: electrokinetic and stability behavior. *Journal of Colloid Interface Science*, 283, 344–351.
- [45] De Moura, M. R., Aouada, F. A., Avena-Bustillos, R. J., McHugh, T. H., Krochta, J. M., & Mattoso, L. H. C. (2009). Improved barrier and mechanical properties of novel hydroxypropyl methylcellulose edible films with chitosan/tripolyphosphate nanoparticles. *Journal of Food Engineering*, 92, 448–453.
- [46] H.P.S. Abdul Khalil, A.H. Bhat, A.F. Ireana Yusra. (2012) Green composites from sustainable cellulose nanofibrils: A review. *Carbohydrate Polymers* 87 963– 979
- [47] Wegner, T.H.; Jones, P.E. *Cellulose* 2006, 13, 115
- [48] John M. J., & Thomas S. (2008). Biofibres and biocomposites. *Carbohydrate Polymers* 71 343–364
- [49] Phiriyawirut, M., & Maniaw, P., (2012). Cellulose Microfibril from Banana Peels as a Nanoreinforcing Fillers for Zein Films. *Open Journal of Polymer Chemistry*, 2, 56–62
- [50] Satyanarayana, K. G., Arizaga, G. G. C., & Wypych, F. (2009). Biodegradable composites based on lignocellulosic fibres – An overview. *Progress in Polymer Science*, 34, 982–1021.
- [51] Klemm, D., Heublein, B., Fink, H.-P. & Bohn, A. (2005). Cellulose: Fascinating biopolymer and sustainable raw material. *Angewandte Chemie International Edition*, 44, 3358–3393.
- [52] Mohanty, A. K., Misra, M. & Drzal, L. T. (2002). Sustainable bio-composites from renewable resources: Opportunities and challenges in the green materials world. *Journal of Polymers and the Environment*, 10(1/2), 19–26.
- [53] Dong, X.M.; Revol, J.F.; Gray, D. Effect of microcrystallite preparation conditions on the formation of colloid crystals of cellulose. *Cellulose* 1998, 5, 19–32.
- [54] Beck-Candanedo S, Roman M, Gray DG (2005) Effect of reaction conditions on the properties and behavior of wood cellulose nanocrystal suspension. *Biomacromol* 6:1048–1054
- [55] Abe K, Iwamoto S, Yano H (2007) Obtaining cellulose nanofibers with a uniform width of 15 nm from wood. *Biomacromolecules* 8:3276–3278
- [56] Chen, W., Yu, H., Liu, Y., Chen, P., Zhang, M. & Yunfei, H. (2011). Individualization of cellulose nanofibers from wood using high-intensity ultrasonication combined with chemical pretreatments. *Carbohydrate Polymers*, 83, 1804–1811.
- [57] Rowell RM, Petterson R, Han JS, Rowell JS, Tshabalala MA (2005) Cell wall chemistry. In: Rowell RM (ed) *Handbook of wood chemistry and wood composites*. CRC Press, Florida, p 37
- [58] Adebajo MO, Frost RL, Kloprogge JTK, Kokot S (2006) Raman spectroscopic investigation of acetylation of raw cotton. *Spectrochim Acta Part A Mol Biomol Spectrosc* 64(2):448–453
- [59] de Morais Teixeira, E., Correa, A., Manzoli, A., de Lima Leite, F., de Oliveira, C. & Mattoso, L. (2010). Cellulose nanofibers from white and naturally colored cotton fibers. *Cellulose*, 17(3), 595–606.
- [60] Soykeabkaew, N., Supaphol, P., Rujiravanit, R., (2004). Preparation and characterization of jute- and flax-reinforced starch-based composite foams. *Carbohydrate Polymers* 58 53–63
- [61] Bledzki AK, Reihmane S, Gassan J. 1996. Properties and modification methods for vegetable fibres for natural fibre composites. *Journal of Applied Polymer Science* 29:1329–1336.
- [62] Dufresne, A., Dupuyre, D. & Vignon, M. R. (2000). Cellulose microfibrils from potato tuber cells: Processing and characterization of starch-cellulose microfibril composites. *Journal of Applied Polymer Science*, 76(14), 2080–2092.
- [63] Alemdar A, Sain M (2007) Isolation and characterization of nanofibers from agricultural residues–wheat straw and soy hulls. *Bioresour Technol* 99(6):1664–1671

- [64] Cherian, B. M., Leao, A. L., de Souza, S. F., Thomas, S., Pothan, L. A. & Kottaisamy, M. (2010). Isolation of nanocellulose from pineapple leaf fibres by steam explosion. *Carbohydrate Polymers*, 81(3), 720–725
- [65] Moran, J., Alvarez, V., Cyras, V. & Vazquez, A. (2008). Extraction of cellulose and preparation of nanocellulose from sisal fibers. *Cellulose*, 15(1), 149–159.
- [66] Fahma F, Iwamoto S., Hori N, Iwata T, Takemura A., (2010). Isolation, preparation, and characterization of nanofibers from oil palm empty-fruit-bunch (OPEFB). *Cellulose* 17:977–985
- [67] Rosa, M. F., Medeiros, E. S., Malmonge, J. A., Gregorski, K. S., Wood, D. F. & Mattoso, L. H. C. (2010). Cellulose nanowhiskers from coconut husk fibers: Effect of preparation conditions on their thermal and morphological behavior. *Carbohydrate Polymers*, 81(1), 83–92.
- [68] Zuluaga, R., Putaux, J. L., Cruz, J., Velez, J., Mondragon, I. & Ganan, P. (2009). Cellulose microfibrils from banana rachis: Effect of alkaline treatments on structural and morphological features. *Carbohydrate Polymers*, 76(1), 51–59.
- [69] Rondeau-Mouro, C., Bouchet, B., Pontoire, B., Robert, P., Mazoyer, J. & Buleon, A. (2003). Structural features and potential texturising properties of lemon and maize cellulose microfibrils. *Carbohydrate Polymers*, 53(3), 241–252.
- [70] Wang, B. & Sain, M. (2007). The effect of chemically coated nanofiber reinforcement on biopolymer based nanocomposites. *Bioresources*, 2, 371–388.
- [71] Dinand, E., Chanzy, H. & Vignon, R. M. (1999). Suspensions of cellulose microfibrils from sugar beet pulp. *Food Hydrocolloids*, 13(3), 275–283.
- [72] Dufresne A, Cavaille JY, Vignon MR (1997). Mechanical behavior of sheets prepared from sugar beet cellulose microfibrils. *J Appl Polym Sci* 64:1185–1194
- [73] Malainine, M. E., Dufresne, A., Dupeyre, D., Mahrouz, M., Vuong, R. & Vignon, M. R. (2003). Structure and morphology of cladodes and spines of *Opuntia ficus-indica*. Cellulose extraction and characterisation. *Carbohydrate Polymers*, 51(1), 77–83.
- [74] Habibi, Y., Heux, L., Mahrouz, M. & Vignon, M. R. (2008). Morphological and structural study of seed pericarp of *Opuntia ficus-indica* prickly pear fruits. *Carbohydrate Polymers*, 72(1), 102–112.
- [75] Arayaprane, W., Na-Ranong, N., Rempel, G. L., (2005). Application of Rice Husk Ash as Fillers in the Natural Rubber Industry. *Journal of Applied Polymer Science*, Vol. 98, 34–41
- [76] Yu, H., Liu, R., Shen, D., Jiang, Y., Huang, Y., (2005). Study on morphology and orientation of cellulose in the vascular bundle of wheat straw. *Polymer* 46 5689–5694
- [77] M. Z. Rong, M. Q. Zhang, Y. Liu, G. C. Yang, and H. M. Zeng, “The effect of fiber treatment on the mechanical properties of unidirectional sisal-reinforced epoxy composites,” *Composites Science and Technology*, vol. 61, Article ID 10.1016/S0266-3538(01)00046-X, pp. 1437–1447, 2001.
- [78] Zugenmaier, P. (2008). Crystalline cellulose and derivatives: Characterization and structures springer series in wood science. In P. Zugenmaier (Ed.), *Crystalline cellulose and derivatives, characterization and structures* (pp. 7–8). Berlin Heidelberg: Springer-Verlag.
- [79] Purves, C. B. (Ed.). (1946). *Chemical nature of cellulose and its derivatives*. New York: Interscience.
- [80] Nevell, T. P., & Zeronian, S. H. (1985). *Cellulose chemistry and its applications*. New York: Wiley.
- [81] Olesen, P. O., & Plackett, D. V. (1999). Perspectives on the performance of natural plant fibres presented at natural fibres performance forum, Copenhagen, May 27–28. <<http://www.ienica.net/fibreseminar/olesen.pdf>>.
- [82] Bismarck, A., Mishra, S., & Lampke, T. (2005). In A. K. Mohanty, M. Misra, & L. T. Drzal (Eds.), *Natural fibres, biopolymers and biocomposites* (pp. 37). CRC Press.
- [83] Jayaraman, K. (2003). Manufacturing sisal-polypropylene composites with minimum fibre degradation. *Composites Science and Technology*, 63, 367–374.
- [84] Azizi Samir, M. A. S., Alloin, F., Paillet, M. & Dufresne, A. (2004). Tangling effect in fibrillated cellulose reinforced nanocomposites. *Macromolecules*, 37, 4313–4316.
- [85] Dujardin, E., Blaseby, M., & Mann, S. (2003). Synthesis of mesoporous silica by sol–gel mineralisation of cellulose nanorod nematic suspensions. *Journal of Materials Chemistry*, 13(4), 696–699.
- [86] Ramos, L. P. (2003). The chemistry involved in the steam treatment of lignocellulosic materials. *Química Nova*, 26(6), 863–871.
- [87] Jonoobi, M., Harun, J., Mathew, A. P., Hussein M. Z., & Oksman, K. (2010). Preparation of cellulose nanofibers with hydrophobic surface characteristics. *Cellulose*, 17, 299–307
- [88] S. S. Suradi., R. M. Yunus, M. D. H. Beg and Z. A. M. Yusof (2009). Influence pre-treatment on the properties of lignocellulose based biocomposite. *National Conference on Postgraduate Research (NCON-*

- PGR) 2009 1st October 2009, UMP Conference Hall, Malaysia © Centre for Graduate Studies, Universiti Malaysia Pahang
- [89] Mosier, N., Wyrnan, C., Dale, B., Elander, R., Lee, Y. Y., Hol Eapple M., & Ladisch, M. (2005). Feature of promising technologies for pre-treatment lignocelluloses Biomass. *Bioresource Technology*, 97, 673-686.
- [90] Carvalho, F., Duarte, L. C., and Gírio, F. M., (2008) Hemicellulose biorefineries: a review on biomass pretreatments. *Journal of Scientific & Industrial Research* Vol. 67, November 2008, pp.849-864
- [91] Hamelinck C N, van Hooijdonk G & Faaij A. P. C., (2005). Ethanol from lignocellulosic biomass: techno-economic performance in short-, middle- and long-term, *Biomass Bioenergy*, Vol. 28, 384-410.
- [92] Sun Y & Cheng J., (2002). Hydrolysis of lignocellulosic materials for ethanol production: a review, *Biores Technol*, 83 (2002) 1-11.
- [93] Wyman C. E., Dale B. E., Elander R. T., Holtzapple M., Ladisch M. R., & Lee Y. Y., (2005). Comparative sugar recovery data from laboratory scale application of leading pretreatment technologies to corn stover, *Biores Technol*, Vol. 96, 2026- 2032.
- [94] Hamzah, F., Idris, A., Shuan, T. K., (2011). Preliminary study on enzymatic hydrolysis of treated oil palm (Elaeis) empty fruit bunches fibre (EFB) by using combination of cellulase and b 1-4 glucosidase. *Biomass and bioenergy* 35 1055-1059
- [95] Tay, G.S., Zaim, J. M., & Rozman, H. D., (2010). Mechanical Properties of Polypropylene Composite Reinforced with Oil Palm Empty Fruit Bunch Pulp. *Journal of Applied Polymer Science*, Vol. 116, 1867–1872
- [96] Sun, J.X., Sun, R. C., Sun, X.F. and Su, Y.Q. 2004. Fractional and physico-chemical characterization of hemicelluloses from ultrasonic irradiated sugarcane bagasse. *Carbohydrate Research*, 339 : 291–300.
- [97] Ek, M., Gellerstedt, G. & Henriksson, G. (2009). *Pulp and paper chemistry and technology Volume 2, Pulping chemistry and technology* Berlin: Walter de Gruyter GmbH & Co. School of Chemical Science and Engineering. Royal Institute of Technology 10044 Stockholm Sweden. pg 6.
- [98] Sjostrom, E. (1993). *Wood chemistry: Fundamentals and applications* (2nd ed.). San Diego, CA: Academic Press, Inc.
- [99] Young, R. A. (1994). Comparison of the properties of chemical cellulose pulp. *Cellulose*, 1(2), 107–130.
- [100] Herrick FW, Casebier RL, Hamilton JK, Sandberg KR (1983) Microfibrillated cellulose: morphology and accessibility. *J Appl Polym Sci: Appl Polym Symp* 37:797–813
- [101] Turbak AF, Snyder FW, Sandberg KR (1983) Microfibrillated cellulose, a new cellulose product: properties, uses, and commercial potential. *J Appl Polym Sci: Appl Polym Symp* 37:815–827
- [102] Chakraborty, A., Sain, M. & Kortschot, M. (2006). Reinforcing potential of wood pulp derived microfibrils in a PVA matrix. *Holzforschung*, 60(1), 53–58.
- [103] Abe K, Iwamoto S, Yano H (2007) Obtaining cellulose nanofibers with a uniform width of 15 nm from wood. *Biomacromolecules* 8:3276–3278
- [104] Abe, K. & Yano, H. (2009). Comparison of the characteristics of cellulose microfibril aggregates of wood, rice straw and potato tuber. *Cellulose*, 16(6), 1017–1023.
- [105] Abe, K. & Yano, H. (2010). Comparison of the characteristics of cellulose microfibril aggregates isolated from fiber and parenchyma cells of Moso bamboo (*Phyllostachys pubescens*). *Cellulose*, 17(2), 271–277.
- [106] Nogi, M., Iwamoto, S., Nakagaito, A. N. & Yano, H. (2009). Optically transparent nanofiber paper. *Advanced Materials*, 21(16), 1595–1598.
- [107] Nakagaito AN, Fujimura A, Sakai T, Hama Y, Yano H. (2009). Production of microfibrillated cellulose (MFC)-reinforced polylactic acid (PLA) nanocomposites from sheets obtained by a papermaking-like process. *Compos Sci Technol* 69:1293–7.
- [108] Nakagaito, A. & Yano, H. (2008). Toughness enhancement of cellulose nanocomposites by alkali treatment of the reinforcing cellulose nanofibers. *Cellulose*, 15(2), 323–331.
- [109] Nakagaito, A. N. & Yano, H. (2004). The effect of morphological changes from pulp fiber towards nano-scale fibrillated cellulose on the mechanical properties of high-strength plant fiber based composites. *Applied Physics A: Materials Science & Processing*, 78(4), 547–552.
- [110] Nakagaito, A. N. & Yano, H. (2005). Novel high-strength biocomposites based on microfibrillated cellulose having nano-order-unit web-like network structure. *Applied Physics A: Materials Science & Processing*, 80(1), 155–159.
- [111] Araki, J., Wada, M., Kuga, S. & Okano, T. (2000). Birefringent glassy phase of a cellulose microcrystal suspension. *Langmuir*, 16(6), 2413–2415.

- [112] Elazzouzi-Hafraoui, S., Nishiyama, Y., Putaux, J.-L., Heux, L., Dubreuil, F. & Rochas, C. (2007). The shape and size distribution of crystalline nanoparticles prepared by acid hydrolysis of native cellulose. *Biomacromolecules*, 9(1), 57–65.
- [113] Liu, H., Liu, D., Yao, F. & Wu, Q. (2010). Fabrication and properties of transparent polymethylmethacrylate/ cellulose nanocrystals composites. *Bioresource Technology*, 101(14), 5685–5692.
- [114] Hayashi, N., Kondo, T. & Ishihara, M. (2005). Enzymatically produced nano-ordered short elements containing cellulose I crystalline domains. *Carbohydrate Polymers*, 61(2), 191–197.
- [115] Henriksson, M., Henriksson, G., Berglund, L. A. & Lindstrom, T. (2007). An environmentally friendly method for enzyme-assisted preparation of microfibrillated cellulose (MFC) nanofibers. *European Polymer Journal*, 43, 3434–3441.
- [116] Paakko, M., Ankerfors, M., Kosonen, H., Nykanen, A., Ahola, S. & Osterberg, M. (2007). Enzymatic hydrolysis combined with mechanical shearing and high-pressure homogenization for nanoscale cellulose fibrils and strong gels. *Biomacromolecules*, 8(6), 1934–1941.
- [117] Iwamoto, S., Kai, W., Isogai, T., Saito, T., Isogai, A. & Iwata, T. (2010). Comparison study of TEMPO-analogous compounds on oxidation efficiency of woodcellulose for preparation of cellulose nanofibrils. *Polymer Degradation and Stability*, 95(8), 1394–1398.
- [118] Saito, T., Hirota, M., Tamura, N., Kimura, S., Fukuzumi, H. & Heux, L. (2009). Individualization of nano-sized plant cellulose fibrils by direct surface carboxylation using TEMPO catalyst under neutral conditions. *Biomacromolecules*, 10(7), 1992–1996
- [119] Saito, T., Kimura, S., Nishiyama, Y. & Isogai, A. (2007). Cellulose nanofibers prepared by TEMPO-mediated oxidation of native cellulose. *Biomacromolecules*, 8(8), 2485–2491.
- [120] Saito, T., Nishiyama, Y., Putaux, J. L., Vignon, M. & Isogai, A. (2006). Homogeneous suspensions of individualized microfibrils from TEMPO-catalyzed oxidation of native cellulose. *Biomacromolecules*, 7(6), 1687–1691.
- [121] Frenot, A., Henriksson, M. W. & Walkenstrom, P. (2007). Electrospinning of cellulosebased nanofibers. *Journal of Applied Polymer Science*, 103(3), 1473–1482.
- [122] Kim, E. G., Kim, B. S. & Kim, D. S. (2007). Physical properties and morphology of polycaprolactone/starch/pine-leaf composites. *Journal of Applied Polymer Science*, 103, 928–934.
- [123] Ma, Z., Kotaki, M. & Ramakrishna, S. (2005). Electrospun cellulose nanofiber as affinity membrane. *Journal of Membrane Science*, 265(1/2), 115–123.
- [124] Cheng, Q., Wang, S. & Han, Q. (2010). Novel process for isolating fibrils from cellulose fibers by high-intensity ultrasonication. II. Fibril characterization. *Journal of Applied Polymer Science*, 115(5), 2756–2762.
- [125] Cheng, Q., Wang, S., Rials, T. & Lee, S. (2007). Physical and mechanical properties of polyvinyl alcohol and polypropylene composite materials reinforced with fibril aggregates isolated from regenerated cellulose fibers. *Cellulose*, 14(6), 593–602.
- [126] Cheng, Q., Wang, S. & Rials, T. G. (2009). Poly(vinyl alcohol) nanocomposites reinforced with cellulose fibrils isolated by high intensity ultrasonication. *Composites Part A: Applied Science and Manufacturing*, 40(2), 218–224.
- [127] Wang, S. & Cheng, Q. (2009). A novel process to isolate fibrils from cellulose fibers by high-intensity ultrasonication. Part 1. Process optimization. *Journal of Applied Polymer Science*, 113(2), 1270–1275.
- [128] Zhao HP, Feng XQ, Gao H (2007) Ultrasonic technique for extracting nanofibers from nature materials. *Appl Phys Lett* 90:073112
- [129] Wagberg, L. (2005). Wood material science. Finnish–Swedish research programme, year book.
- [130] Cranston, E. D. & Gray, D. G. (2006). Morphological and optical characterization of polyelectrolyte multilayers incorporating nanocrystalline cellulose. *Biomacromolecules*, 7, 2522–2530.
- [131] Chornet, E. & Overend, P. R. (1989). A unified treatment for liquefaction. In A. Bridgwater, & J. Kuester (Eds.), *Research on thermochemical biomass conversion* (pp. 411–428). Amsterdam, The Netherlands: Elsevier Appl. Sci. Inc.
- [132] Donaldson, L. A., Wong, K. K. Y. & Mackie, K. L. (1988). Ultrastructure of steam exploded wood. *Wood Science and Technology*, 22, 103–114.
- [133] Excoffier, G., Toussaint, B. & Vignon, M. R. (1991). Saccharification of steam exploded poplar wood. *Biotechnology and Bioengineering*, 38, 1308–1317.
- [134] Tanahashi, M. (1990). Characterization and degradation mechanisms of wood components by steam explosion and utilization of exploded wood. *Wood Research*, 77, 49–117.

- [135] Tanahashi, M., Takada, S., Aoki, T., Goto, T., Higuchi, T. & Hanai, S. (1982). Characterisation of explosion wood I. Structure and physical properties. *Wood Research*, 69, 36–51.
- [136] Cristobal, C., Encarnacion, R., Ignacio, B., Maria, J. N. & Eulogio, C. (2006). Enhanced enzymatic hydrolysis of olive tree wood by steam explosion and alkaline peroxide delignification. *Process Biochemistry*, 41, 423–429.
- [137] Cristobal, C., Encarnacion, R., Mercedes, B., Paloma, M., Jose, M. N. & Eulogio, C. (2008). Production of fuel ethanol from steam-explosion pretreated olive tree pruning. *Fuel*, 87, 692–700.
- [138] Deep, B., Abraham, E., Cherian, B. M., Bismarck, A., Blaker, J. J., Pothen, L. A., et al. (2011). Structure, morphology and thermal characteristics of banana nano fibers obtained by steam explosion. *Bioresource Technology*, 102, 1988–1997.
- [139] Marchessault, R. H. (1991). Steam explosion: A refining process for lignocellulosics. In B. Vol Focher, V. Marzetti, & V. Crescenci (Eds.), *Steam explosion techniques: Fundamentals and industrial applications* (pp. 1–19). Philadelphia: Gordon and Breach Science Publishers
- [140] Bataille, P., Ricard, L. & Sapieha, S. (1989). Effects of cellulose fibers in polypropylene composites. *Polymer Composites*, 10, 103–108.
- [141] Hafren, J., Zou, W. B. & Cordova, A. (2006). Heterogeneous ‘organoclick’ derivatization of polysaccharides. *Macromolecular Rapid Communications*, 27, 1362–1366.
- [142] Gruber, E. & Granzow, C. (1996). Preparing cationic pulp by graft copolymerisation. 1. Synthesis and characterization. *Papier*, 50, 293.
- [143] Bonini, C., Heux, L., Cavaille, J. Y., Lindner, P., Dewhurst, C. & Terech, P. (2002). Rodlike cellulose whiskers coated with surfactant: A small-angle neutron scattering characterization. *Langmuir*, 18, 3311–3314.
- [144] Heux, L., Chauve, G. & Bonini, C. (2000). Nonflocculating and chiral-nematic selfordering of cellulose microcrystals suspensions in nonpolar solvents. *Langmuir*, 16, 8210–8212.
- [145] John, M. J. & Anandjiwala, R. D. (2008). Recent developments in chemical modification and characterization of natural fiber-reinforced composites. *Polymer Composites*, 29, 187–207.
- [146] John, M. J., Francis, B., Varughese, K. T. & Thomas, S. (2008). Effect of chemical modification on properties of hybrid fiber biocomposites. *Composite Part A-Applied Science and Manufacturing*, 39, 352–363.
- [147] Kim, D. Y., Nishiyama, Y. & Kuga, S. (2002). Surface acetylation of bacterial cellulose. *Cellulose*, 9, 361–367.
- [148] Ifuku, S., Nogi, M., Abe, K., Handa, K., Nakatsubo, F. & Yano, H. (2007). Surface modification of bacterial cellulose nanofibers for property enhancement of optically transparent composites: Dependence on acetyl-group DS. *Biomacromolecules*, 8, 1973–1978.
- [149] Nogi, M., Abe, K., Handa, K., Nakatsubo, F., Ifuku, S. & Yano, H. (2006). Property enhancement of optically transparent bionanofiber composites by acetylation. *Applied Physics Letters*, 89(23), 1–3.
- [150] Sreekala, M. S., Kumaran, M. G., Thomas, S., (1997.) Oil palm fibers: morphology, chemical composition, surface modification, and mechanical properties. *Journal of Applied Polymer Science*, Vol. 66, 821–835
- [151] Gousse C, Chanzy H, Cerradab ML, Fleury E (2004) Surface silylation of cellulose microfibrils: preparation and rheological properties. *Polymer* 45(5):1569–1575
- [152] Andresen, M., Johansson, L. S., Tanem, B. S. & Stenius, P. (2006). Properties and characterization of hydrophobized microfibrillated cellulose. *Cellulose*, 13, 665–677
- [153] Andresen, M. & Stenius, P. (2007). Water-in-oil emulsions stabilized by hydrophobized microfibrillated cellulose. *Journal of Dispersion Science and Technology*, 28, 837–844.
- [154] Chivrac F, Pollet E, Averous L. (2009). Progress in nano-biocomposites based on polysaccharides and nanoclays. *Mater Sci Eng R* 67:1–17.
- [155] Gacitua E. W., Ballerini A. A., Zhang, J., (2005). Polymer nanocomposites: synthetic and natural fillers a review. *Ciencia y tecnología* 7(3): 159-178
- [156] Lu Y, Weng L, Cao X. (2006). Morphological, thermal and mechanical properties of ramie crystallites—reinforced plasticized starch biocomposites. *Carbohydr Polym* 63:198–204.
- [157] Giannelis, E.P. (1996). Polymer Layered Silicate Nanocomposites. *Advanced Materials*, 8, 29-35
- [158] Sinha-Ray, S.; Yamada, K.; Okamoto, M. & Ueda, K. (2002). Polylactide-Layered Silicate Nanocomposite: A Novel Biodegradable Material. *Nano Letters*, 2, 1093-1096
- [159] Sinha Ray, S., & Okamoto, M. (2003). Polymer/layered silicate nanocomposites: A review from preparation to processing. *Progress in Polymer Science*, 28(11), 1539–1641.

- [160] Chang, P.R., Jian, R., Yu, J. & Ma X., (2010). Starch-based composites reinforced with novel chitin nanoparticles. *Carbohydrate Polymers* 80, 420–425
- [161] Xu, Y. X., Kim, K. M., Hanna, M. A. & Nag, D. (2005). Chitosan-starch composite film: Preparation and characterization. *Industrial Crops and Products*, 21, 185–192.
- [162] Huang, M. F., Yu, J. G. & Ma, X. F. (2004). Studies on the properties of Montmorillonite reinforced thermoplastic starch composites. *Polymer*, 45, 7017–7023.
- [163] Ma, X. F., Chang, P. R. & Yu, J. G. (2008). Properties of biodegradable thermoplastic pea starch/carboxymethyl cellulose and pea starch/microcrystalline cellulose composites. *Carbohydrate Polymers*, 72, 369–375.
- [164] Averous, L. (2004). Biodegradable multiphase systems based on plasticized starch: A review. *Journal of Macromolecular Science-Polymer Reviews-C*, 44, 231–274.
- [165] Jagannath JH, Nanjappa C, Das Gupta DK, Bawa AS. 2003. Mechanical and barrier properties of edible starch-based films. *J Appl Polym Sci* 88: 64-71
- [166] Lai, S. M., Don, T. M. & Huang, Y. C. (2006). Preparation and properties of biodegradable thermoplastic starch/poly(hydroxyl butyrate) blends. *Journal of Applied Polymer Science*, 100, 2371–2379.
- [167] Thire, R. M. S. M., Ribeiro, T. A. A. & Andrade, C. T. (2006). Effect of starch addition on compression-molded poly(3-hydroxybutyrate)/starch blends. *Journal of Applied Polymer Science*, 100, 4338–4347.
- [168] Hao, A. Y., Geng, Y. Y., Xu, Q., Lu, Z. Y. & Yu, L. (2008). Study of different effects on foaming process of biodegradable PLA/starch composites in supercritical/compressed carbon dioxide. *Journal of Applied Polymer Science*, 109, 2679–2688
- [169] Jang, W. Y., Shin, B. Y., Lee, T. X. & Narayan, R. (2007). Thermal properties and morphology of biodegradable PLA/starch compatibilized blends. *Journal of Industrial and Engineering Chemistry*, 13, 457–464.
- [170] Ning, W., Jiugao, Y. & Xiaofei, M. (2008). Preparation and characterization of compatible thermoplastic dry starch/poly(lactic acid). *Polymer Composites*, 29, 551–559.
- [171] Rosa, D. D., Volponi, J. E. & Guedes, C. D. F. (2006). Biodegradation and the dynamic mechanical properties of starch gelatinization in poly(epsilon-caprolactone)/corn starch blends. *Journal of Applied Polymer Science*, 102, 825–832
- [172] Sarazin, P., Li, G., Orts, W. J. & Favis, B. D. (2008). Binary and ternary blends of polylactide, polycaprolactone and thermoplastic starch. *Polymer*, 49, 599–609.
- [173] Wang, Y. M., Rodriguez-Perez, M. A., Reis, R. L. & Mano, J. F. (2005). Thermal and thermomechanical behaviour of polycaprolactone and starch/polycaprolactone blends for biomedical applications. *Macromolecular Materials and Engineering*, 290, 792–801.
- [174] Durango, A. M., Soares, N. F. F., Benevides, S., Teixeira, J., Carvalho, M., Wobeto, C., et al. (2006). Development and evaluation of an edible antimicrobial film based on yam starch and chitosan. *Packaging Technology and Science*, 19, 55–59.
- [175] Nakamatsu, J., Torres, F. G., Troncoso, O. P., Yuan, M. L. & Boccaccini, A. R. (2006). Processing and characterization of porous structures from chitosan and starch for tissue engineering scaffolds. *Biomacromolecules*, 7, 3345–3355.
- [176] Cyras, V. P., Manfredi, L. B., Ton-That, M. T. & Vazquez, A. (2008). Physical and mechanical properties of thermoplastic starch/montmorillonite nanocomposite films. *Carbohydrate Polymers*, 73, 55–63.
- [177] Lee, S. Y., Xu, Y. X. & Hanna, M. A. (2007). Tapioca starch-poly (lactic acid)-based nanocomposite foams as affected by type of nanoclay. *International Polymer Processing*, 22, 429–435.
- [178] Lee, J. M., Heitmann, J. A. & Pawlak, J. J. (2007). Local morphological and dimensional changes of enzyme-degraded cellulose materials measured by atomic force microscopy. *Cellulose*, 14, 643–653.
- [179] Yoon, S. Y. & Deng, Y. L. (2006). Clay-starch composites and their application in papermaking. *Journal of Applied Polymer Science*, 100, 1032–1038.
- [180] Alvarez, V. A., Terenzi, A., Kenny, J. M. & Vařquez, A. (2004). Melt rheological behavior of starch-based matrix composites reinforced with short sisal fibers. *Polymer Engineering and Science*, 44, 1907–1914.
- [181] Duanmu, J., Gamstedt, E. K. & Rosling, A. (2007). Hygromechanical properties of composites of crosslinked allylglycidyl-ether modified starch reinforced by wood fibres. *Composite Science and Technology*, 67, 3090–3097.
- [182] Ma, X. F., Yu, J. G. & Kennedy, J. F. (2005). Studies on the properties of natural fibers reinforced thermoplastic starch composites. *Carbohydrate Polymers*, 62, 19–24.

- [183] Romhany, G., Karger-Kocsis, J. & Czigany, T. (2003). Tensile fracture and failure behavior of thermoplastic starch with unidirectional and cross-ply flax fiber reinforcements. *Macromolecular Materials and Engineering*, 288, 699–707.
- [184] Cao, X., Chen, Y., Chang, P. R., Muir, A. D. & Falk, G. (2008). Starchbased nanocomposites reinforced with flax cellulose nanocrystals. *Express Polymer Letters*, 2, 502–510.
- [185] Mathew, A. P., Thielemans, W. & Dufresne, A. (2008). Mechanical properties of nanocomposites from sorbitol plasticized starch and tunicin whiskers. *Journal of Applied Polymer Science*, 109, 4065–4074.
- [186] Kadokawa, J., Murakami, M., Takegawa, A. & Kaneko, Y. (2009). Preparation of cellulose-starch composite gel and fibrous material from a mixture of the polysaccharides in ionic liquid. *Carbohydrate Polymers*, 75, 180–183.
- [187] Kumar, A. P. & Singh, R. P. (2008). Biocomposites of cellulose reinforced starch: Improvement of properties by photoinduced crosslinking. *Bioresource Technology*, 99, 8803–8809.
- [188] Grande, C. J., Torres, F. G., Gomez, C. M., Troncoso, O. P., Canet-Ferrer, J. & Martinez- Pastor, J. (2008). Morphological characterization of bacterial cellulose-starch nanocomposites. *Polymer Composites*, 16, 181–185.
- [189] Mondragon, M., Arroyo, K. & Romero-Garcia, J. (2008). Biocomposites of thermoplastic starch with surfactant. *Carbohydrate Polymers*, 74, 201–208.
- [190] Sreekala, M. S., Goda, K. & Devi, P. V. (2008). Sorption characteristics of water, oil and diesel in cellulose nanofiber reinforced corn starch resin/ramie fabric composites. *Composite Interfaces*, 15, 281–299.
- [191] Le Corre D, Bras J, Dufresne A. (2010). Starch nanoparticles: a review. *Biomacromolecules*. 11(5):1139-53.
- [192] Eichhorn SJ, Dufresne A, Aranguren M, Marcovich NE, Capadona JR, Rowan SJ, 2010. Review: current international research into cellulose nanofibres and nanocomposites. *J Mater Sci* 45: 1–33.
- [193] Lifeng Qi, Zirong Xu, Xia Jiang, Caihong Hu and Xiangfei Zou. 2004. Preparation and antibacterial activity of chitosan nanoparticles. *Carbohydrate Research* 339 :2693– 2700
- [194] Randall W. Powell, Elton, C., Prestidge, R., & Belanger, H., (2011). *Biobased Chemicals and Polymers. Plant Biomass Conversion, First Edition.*
- [195] Gilmore, D. F., Fuller, R. C. & Lenz, R. (1990). Biodegradation of poly (betahydroxyalkanoates). In S. A. Barenberg, J. I. Brash, R. Narayan, & A. E. Redpath (Eds.), *Degradable materials: Perspectives, issues and opportunities*. Boca Raton: CRC Press.
- [196] Luzier, W. D. (1992). Materials derived from biomass/biodegradable materials. *Proceedings of National Academy of Science of the United States of America*, 89(3), 839–842.
- [197] Hankermeyer, C. R. & Tjeerdema, R. S. (1999). Polyhydroxybutyrate: Plastic made from and degraded by microorganisms. *Reviews of Environmental Contamination and Toxicology*, 159, 1–24.
- [198] Evans, J. D. & Sikdar, S. K. (1990). Biodegradable plastics: An idea whose time has come? *Chemical Technology*, 20, 38–42.
- [199] Williams, S. F. & Peoples, O. P. (1996). Biodegradable plastics from plants. *Chemtech*, 38, 38–44.
- [200] Grunert, M. & Winter, W. T. (2002). Nanocomposites of cellulose acetate butyrate reinforced with cellulose nanocrystals. *Journal of Polymers and the Environment*, 10(1/2), 27–30.
- [201] Sainza, C. B., , Brasb, J., Williams, T., Sénechalb, Tangi., & Ortsa, W., (2011). HPMC reinforced with different cellulose nano-particles. *Carbohydrate Polymers* 86, 1549– 1557
- [202] Krochta, J. M., & Mulder-Johnston, C. (1997). Edible and biodegradable polymer films: Challenges and opportunities. *Food Technology*, 51(2), 61–75.
- [203] Pereda, M., Amica, G., Rácz, I., & Marcovich, N. E., (2011). Structure and properties of nanocomposite films based on sodium caseinate and nanocellulose fibers. *Journal of Food Engineering* 103 (2011) 76–83
- [204] Woehl M.A, Canestraro C.D, Mikowski A, Sierakowski M.R., Ramos L.P., Wypych F., (2009). Bionanocomposites of thermoplastic starch reinforced with bacterial cellulose nanofibres: Effect of enzymatic treatment on mechanical properties. *Carbohydrate Polymers* 80 (2010) 866–873
- [205] Henriette M.C. de Azeredo(2009). Nanocomposites for food packaging applications. *Food Research International* 42 (2009) 1240–1253
- [206] Chang, P. R., Jian R., Yu, J., Ma, X., (2010). Fabrication and characterisation of chitosan nanoparticles/plasticised-starch Composites. *Food Chemistry* 120 , 736–740
- [207] Kumar A.P., Depan D., Tomer N.S., Singh R.P., (2009). Nanoscale particles for polymer degradation and stabilization—Trends and future perspectives. *Progress in Polymer Science* 34 (2009) 479–515

- [208] Jonoobi A. Khazaeian A, Tahir P.M, Azry S.S., Oksman K, (2011). Characteristics of cellulose nanofibers isolated from rubberwood and empty fruit bunches of oil palm using chemo-mechanical process. *Cellulose* 18:1085–1095
- [209] Soykeabkaew, N., Laosat, N., Ngaokla, A., Yodsuwan N., & Tunkasiri, T., (2012). Reinforcing potential of micro- and nano-sized fibers in the starch-based biocomposites *Composites Science and Technology* 72, 845–852
- [210] N.R. Savadekar, S.T. Mhaske (2012). Synthesis of nano cellulose fibers and effect on thermoplastics starch based films, 89, 146–151
- [211] Hill, C.A.S., Khalil, H.P.S.A., 2000b. Effect of fiber treatments on mechanical properties of coir or oil palm fiber reinforced polyester composites. *J. Appl. Polym. Sci.* 78, 1685–1697.
- [212] Sreekala, M.S., Kumaran, M.G., Joseph, S., Jacob, M., Thomas, S., 2000. Oil palm fibre reinforced phenol formaldehyde composites: influence of fibre surface modifications on the mechanical performance. *Appl. Compos. Mater.* 7, 295–329.
- [213] Rozman, H.D., Tay, G.S., Kumar, R.N., Abusamah, A., Ismail, H., Ishak, Z.A.M., (2001). The effect of oil extraction of the oil palm empty fruit bunch on the mechanical properties of polypropylene–oil palm empty fruit bunch–glass fibre hybrid composites. *Polym. Plast. Technol. Eng.* 40, 103–115.
- [214] Zakaria, S., Poh, L.K., 2002. Polystyrene-benzoylated EFB reinforced composites. *Polym. Plast. Technol. Eng.* 41, 951–962.
- [215] Agarwal, R., Saxena, N.S., Sharma, K.B., Thomas, S., Sreekala, M.S., 2003. Temperature dependence of effective thermal conductivity and thermal diffusivity of treated and untreated polymer composites. *J. Appl. Polym. Sci.* 89, 1708–1714.
- [216] AbuBakar, A., Hassan, A., Yusof, A.F.M., 2006. The effect of oil extraction of the oil palm empty fruit bunch on the processability, impact, and flexural properties of PVC-U composites. *Int. J. Polym. Mater.* 55, 627–641.