Nanocellulose Based Polymer Nanocomposites: Isolation, Characterization and Applications

H.P.S. Abdul Khalil a,b, Y. Davoudpour a, N. A. Sri Aprilia a, Asniza Mustapha, Md. Nazrul Islam a,c, and Rudi Dungani d

Contact information: a: School of Industrial Technology, Universiti Sains Malaysia, 11800, Penang, Malaysia; b: Department of BioComposite Technology, Institute of Tropical Forestry and Forest Products (INTROP), Universiti Putra Malaysia, 43400 UPM Serdang, Selangor, Malaysia; c: Life Science School, Khulna University, Khulna – 9208, Bangladesh; d: School of Life Sciences and Technology, Institut Teknologi Bandung, West Java-Indonesia

*Corresponding author: akhalilhps@gmail.com, Phone: +604 653 2200, Fax: +604 657 3678

ABSTRACT

New and advanced properties and functions, including uniformity, durability, biodegradability and sustainability, are required for the next generation of cellulose based products and their engineering applications. Nanosize cellulosic materials, a good candidate for the preparation of polymer nanocomposites, have been gained a lot of attentions due to their low cost, biodegradability, abundance, high strength, renewability and some other excellent properties. Advantages in the use of nanosize cellulosic materials are related not only to these properties, in fact, its dimensions, in the nanometer scale, open a wide range of possible properties to be discovered. Nanosize cellulosic materials can be isolated from a variety of cellulosic sources, including plants, animals (tunicates), bacteria and algae and in principle could be extracted from almost any cellulosic material by using different procedures. However, main challenges in the field are related to an efficient separation of nanosize cellulosic materials from the natural resources. The noncompatible nature of nanocellulose with most of the polymers is also a crucial issue for its application in composites. In addition, drying process of nanocellulose for application in polymer composite is another challenge. Last but not least point is related to find a process for obtaining higher yield in nanocellulose isolation. All these challenges and drawbacks become the strong driving forces for discovering more efficient processes and technologies to produce nanocellulosates for application in nanocomposites, and for inventing new applications as well. This book chapter will concentrate on the isolation of nanocellulose from various sources and its utilization for fabrication methods, its characterization, drying processes and modification. We will also concentrate our discussion on application of nanoscale cellulosic materials in polymer nanocomposites.

1. Introduction

Nanotechnology is now recognized as one of the most promising areas for technological development in the 21st century. In line with development of nanotechnology and recent concern about environmental issues (Ekebafe et al., 2010) more attention have been paid to utilize biobased material. In this regard, natural fibers have been gained much more consideration because of their promising characteristics such as biodegradable nature, renewability and cheap price (Zhang and Luo, 2011). Among these natural fibers, cellulose as the most plentiful biopolymer which exist in wide variety of natural fibers such as kenaf (Jonoobi et al., 2010), cotton (Morais et al., 2013), banana (Abraham et al., 2011), wood (Nyström et al., 2010), flax (Liu et al., 2010), oil plam (Fahma et al., 2010), bamboo (Visakh et
animal species like tunicate (Zhang et al., 2013) and etc have been the subject of many researches in nanotechnology. Cellulose is a linear biopolymer with β-D-glucopyranose repeating unit (Figueiredo et al., 2010) and also include both crystalline and amorphous region (Lynd et al., 2002). In the case of application of cellulose in nanotechnology, two general types of nanocellulose are recognized, namely cellulose nanocrystall and cellulose nanofiber. These two nanocelluloses can be distinguished by their different production processes and structures. Cellulose nanofiber as a high aspect ratio fiber including both amorphous and crystalline regions can be produce using some techniques such as electrospinning, refining (Antczak et al., 2012), homogenization, grinding, cryocrushing (Siro´ and Plackett, 2010), ultrasonication (Chen et al., 2013) and steam explosion (Deepa et al., 2011). While cellulose nanocrystall is the whisker form of nanocellulose which it’s amorphous part completely removed by acid hydrolysis with H_{2}SO_{4} or HCL (Siqueira et al., 2010).

These nanocelluloses structures have attracted attention as a potential material to reinforced nanocomposites. By inserting these nanoscale compounds into polymers even in small quantities, the properties of polymers improve and hence depend upon the type of nanocellulose it can be used for various applications (Ioelovich 2012). In order to utilize nanocellulose as reinforcement in nanocomposites, the strong hydrogen bonds between nanocellulose which make it hydrophilic must be break down in order to well disperse in the polymers with hydrophobic nature. Surface modification is most common way to make the surface of nanocellulose hydrophobic and to incorporate it homogenously in different polymers including grafting, silylation, acetylation and etc (Missoum et al., 2013). Spite from the modification processes, drying of nanocellulose is another important issue which should be consider for incorporation of nanocellulose in polymers. This is due to changing the size of these materials after drying which may affect their unique properties.

In this chapter, first we will argue about the cellulose and nanocellulose structures. Then the isolation methods and characterization of cellulose nanofiber and nanocrystall will be address. In the next section, drying points of nanocellulose will be presented. After that modification of nanocellulose will be highlighted. At the end, some points regarding nanocomposites production from nanocellulose with thermoplastic and thermoset polymers will be discuss.

2. Cellulose and nanocellulose

Cellulose is the most abundant renewable natural biopolymer on earth, and is present in a wide variety of living species including plants, animals, and some bacteria (de Souza Lima & Borsali, 2004).

As the skeletal component in all plants, cellulose is organized in a cellular hierarchical structure. The cell walls of plants are divided by a middle lamella from each other, followed by the primary cell wall layer. Cellulose is predominantly located in the secondary wall and consists of roughly 6000 glucose units in the primary cell wall (Diotallevi & Mulder, 2007; Klemm, Heublein, Fink & Bohn, 2005; O'Sullivan, 1997). Figure 1 represents the microstructure of wood fiber cell wall, which containing primary cell wall layer, S1, S2 and S3 are the inner, middle and outer layers of the secondary wall, respectively.
This linear polymer is composed of repeated β-1, 4 linked anhydroglucopyranose units that are covalently linked through acetal functions between the equatorial OH group of C4 and the C1 carbon atom forming bundles of fibrils, also called microfibrillar aggregates, which allow the creation of highly ordered regions (i.e., crystalline phases) alternate with disordered domains (i.e., amorphous phases) (Azizi Samir, Alloin & Dufresne, 2005; Sjostrom, 1993).

Cellulose nanofibers are divided into two main families differs from their size and crystallinity, which are cellulose nanocrystal (CNC) and nanofibrillated cellulose (NFC). CNC, also known as nanowhiskers (De Rodriguez, Thielemans & Dufresne, 2006; John & Thomas, 2008; Oksman, Mathew, Bondeson & Kvien, 2006; Petersson, Kvien & Oksman, 2007; Peterssson & Oksman, 2006), nanorods (Azizi Samir, Alloin & Dufresne, 2005; Dujardin, Blaseby & Mann, 2003) and rod-like cellulose crystals (Iwamoto, Nakagaito & Yano, 2007) are usually isolated from cellulose fibers through acid hydrolysis (Bhatnagar & Sain, 2005; Cranston & Gray, 2006). Possess a relatively low aspect ratio, it has typical diameter of 2-20nm and wide length distribution from 100 to 600 nm (Favier, Chanzy & Cavaille, 1995; George, Ramana & Bawa, 2011; Hubbe, Rojas, Lucia & Sain, 2008). On the other hand, nanofibrillar cellulose (Ahola, Österberg & Laine, 2008; Stenstad, Andresen, Tanem & Stenius, 2008), cellulose nanofiber (Abe, Iwamoto & Yano, 2007; Bhatnagar & Sain, 2005), cellulose nanofibril (Ahola, Österberg & Laine, 2008; Henriksson, Berglund, Isaksson, Lindström & Nishino, 2008) are the terms used for microfibrillated cellulose in the literature. Being the smallest structural units of plant fiber, NFC consist of a bundle of stretched cellulose chain molecules (Sakurada, Nukushima & Ito, 1962) with long, flexible and entangled cellulose nanofibers at approximately 1-100nm size (Chakraborty, Sain & Kortschot, 2006). Figure 2 shows the morphology of CNC and NFC. As can be seen in this figure compare to rod-like crystalline structure of CNC, NFC has long and fibrillar structure.
3. Isolation of nanocellulose

Nanocellulose in the form of NFC or CNC can be extracted by various methods. Here we briefly describe about these processes for producing of nanocellulose, their advantages and disadvantages as well as some important issues regarding that method.

3.1. Ultrasonication

High intensity ultrasonication can be considered as a mechanical method for producing cellulose nanofibers with hydrodynamic forces (Cheng et al., 2009). In this process, ultrasonic waves create strong mechanical stress because of cavitations and therefore cause to disaggregation of cellulosic fiber to nanofibers (Frone et al., 2011). Several attempts have been done to isolate cellulose nanofiber by ultrasonication from various cellulose sources such as microcrystalline cellulose, regenerated and pure cellulose fibers (Cheng et al., 2009), kraft pulp (Johnson et al., 2009), flax, wood, wheat straw and bamboo (Chen et al., 2011) (figure 3) para rubberwood sawdust (Kamphunthong et al., 2012), poplar wood powders (Chen et al., 2013) and etc.
Fig 3- Field emission scanning electron microscopoy (FESEM) images of NFC isolated from (a) wood (b) bamboo (c) wheat straw (d) flax (Chen et al., 2011)

The well-individualized, web like structure and long entangled filaments of NFC from wood (Fig 3a), bamboo (Fig 3b) and wheat straw (Fig 3c) with diameter around 10-20nm, 10-40nm and 15-35nm respectively can be easily distinguished. While because of high cellulose content in flax fiber which leads to strong H-bond and difficulty in fibrillation process, not uniform NFC and with 15 to 100nm width is produced (Fig 3d). The schematic of ultrasonic setup can be seen in figure 4 (Johnson et al., 2009).

![Fig 4- Schematic of ultrasonic setup, (1) Power (2)Piezoelectric converter (3) Ultrasonic probe (4) Sample suspension (5) Double walled glass beaker (6) Ice water inlet (7) outlet (Johnson et al., 2009)](image)

The efficiency of defibrillation in ultrasonic process is depend on power, concentration, temperature, size of fibers, time and distance from probe tip to collector (Wang and Cheng 2009). In some cases researchers have been use combination of ultrasonic with other methods to increase fibrillation of nanoscale cellulose. For example, Li et el., (2011) prepared nanocrystalline cellulose by ultrasonication and acid hydrolysis with H$_2$SO$_4$ from bleached softwood pulp. They found that ultrasonication leads to folding and erosion of cellulose surface and thus provide more reactive site to penetrate acid and prepare high crystalline and small size nanocellulose. Furthermore Wang and Chen (2009) reported that combination of ultrasonic and homogenization boost uniformity and fibrillation of cellulose nanofiber in comparison to ultrasonic solely. In addition, compare to mechanical blender, ultrasonic bath and ultrasonic probe, Mishra et al., (2012) concluded that TEMPO-oxidized fibers treatment with ultrasonic probe is more efficient for nanocellulose production than other two methods.

3.2. Electrospinning

Electrospinning is a versatile and simple process for formation of nanofibers from various sources such as cellulosic fibers by electrical force. In 1930, Formhal patented this method (Frenot et al., 2007). The basic parts for electrospinning instrument are high voltage supply, syringe to carry polymer solution and a target to collect nanofibers (Schiffman et al., 2008) (Fig 5). In this process, nanofibers form from polymer solution between two electrodes with
opposite polarity, one electrode connected to syring and the other one to collector (Huang et al., 2003). At a critical voltage a conical shape droplet known as “Taylor cone” is held at capillary tip due to surface tension (Samatham and Kim 2006; Kriegel et al., 2008). When electric force which is created at the surface of polymer solution conquer surface tension of solution, electrically charged jet emerge and electrospinning occurs (Kowalewski et al., 2005; Henriques et al., 2008). When the jet moves in whipping motion between needle and collector, the solvent of polymer solution evaporate and dry nanofiber in the form of nonwoven mat forms on the collector (Abdelmegeid et al., 2010; Nurwaha et al., 2013).

The parameters impacting electrospinning process can be categorized into solution parameters (surface tension, concentration, viscosity and conductivity), processing conditions (voltage, distance from needle to collector, type of collector, flow rate) and ambient conditions (humidity, pressure and temperature) (Cui et al., 2006; Biber et al., 2010). Based on interaction of all these factors, the morphology and size of resultant nanofibers can be changed.

As stated above, for electrospinning process first a polymer solution should be prepare. However, processing of cellulose via electrospinning is a big challenge because of its limited solubility in common solvents as well as its tendency to agglomeration (Vallejos et al., 2012). Nevertheless, several direct solvent systems including N-methylmorpholine oxide/water (NMMO/ H₂O) (Kulpinski 2005; Yeoh et al., 2009; Uppal and Ramaswamy 2011), lithium chloride/ dimethyl acetamide (LiCl/ DMAc) (Yun et al., 2008; Lee et al., 2009; Costa et al., 2012), ionic liquids (ILs) (Meli et al., 2010; Ha¨rdelin et al., 2012; Ahn et al., 2012) and trifluoroacetic acid (TFA) (Kousaku et al., 2009; Montano-Leyva et al., 2011) have been established. However, removing solvent between needle to collector from three solvent systems including NMMO/ H₂O, LiCl/ DMAc and ILs is difficult (Frey 2008). So, one of the solution to tackle this problem is applying cellulose derivatives, such as cellulose acetate (Liu and Tang 2007; Zhou et al., 2011; Konwarh et al., 2013), ethyl cellulose (Park et al., 2007; Jeun et al., 2007; Yu et al., 2013) and other derivatives.

It is worth noting that new type of materials known as composite or hybrid nanofiber using electrospinning of CNC and different polymers such as polyethylene oxide (PEO) (Park et al., 2007), polyvinyl alcohol (PVA) (Peresin et al., 2010), polymethyl methacrylate (PMMA) (Dong et al., 2012) and etc have been fabricated.
Uniform, smooth and continuous nonwoven mat with controllable diameter at all CNC loading were formed (Fig 6). The author stated that using 17% CNC content, the storage modulus of composite nanofiber increased 17%. The diameter of the PMMA nanofibers was 459nm (Fig 6a). The width of PMMA-CNC nanofibers with 5% CNC (474nm), 9% CNC (450nm), 17% CNC (431nm), 23% CNC (280nm), 33% CNC (269nm) and 41% CNC (182nm) decreased with increasing CNC content (Fig 6b-6g). The key point for incorporation of CNC with various polymers for electrospinning is to improve mechanical properties of materials and to give new functionality to these kinds of electrospun nanofibers (Liu et al., 2012).

3.3. Acid hydrolysis

The main chemical process to produce nanocrystalline cellulose is acid hydrolysis by either sulphuric acid ($H_2SO_4$) (Siqueira et al., 2010), hydrochloric acid (HCL) (Braun et al., 2008) or combination of these two acid (Zhang et al., 2007) and with various acid concentrations. In the case of CNC from $H_2SO_4$ hydrolysis the surface of material become negatively charged with sulfonate ester groups and causing to easily dispersion of CNC in aqueous solvents whereas those produced using HCL have weaker charge density and show higher tendency to flocculation in organic solvents (Eichhorn 2011). Native cellulose consists of crystalline and amorphous regions and when cellulose fibers were subjected to insensitive acid treatment, the amorphous parts break up and just the individual crystallites remain. So, the characterization of CNC is depended on various parameters, such as reaction time, cellulose sources, type of acid and reaction temperature (Peng et al., 2011). In figure 7, pathway of acid hydrolysis with $H_2SO_4$ on cotton linter can be seen.
In 1951, for first time R’anby introduced such process to degraded cellulosic fibers with H$_2$SO$_4$. Since that time a series of attempts to prepare CNC from various cellulosic fibers such as curaua fibers (Corre’a et al., 2010), coconut husk (Rosa et al., 2010), cotton and tunicate (Rusli et al., 2011), Sugarcane bagasse (Teixeira et al., 2011), wood (Morelli et al., 2012) and etc have been done. In acid hydrolysis process, first a suspension with specific acid concentration for particulate time and at defined temperature based on various sources of fibers is mechanically stirred. Then the reaction is quenched with cold water. Subsequently washing process using centrifuge is done and in each steps acidic supernatant remove and again water added to suspension. After some centrifuge steps the suspension dialyzes against distilled water to obtain constant PH. Finally the ultrasonic can be done in order to disperse CNC. The dimensions of CNC are depended on hydrolysis condition and the source of cellulose fibers (Habibi et al., 2010a). For example the optimum acid concentration, temperature and hydrolysis time for H$_2$SO$_4$ hydrolysis of kenaf bast fibers reported 65%, 45°C and 40min (Fig 8a) (Kargarzadeh et al., 2012) whereas for oil palm empty fruit bunch fibers (OPEFB) were 64% , 45°C and 1 hour (Fig 8b) (Fahma et al., 2010). Furthermore, in HCL hydrolysis based on the raw material various conditions have been employed. For instance, CNC from MCC produced by 2.5N HCL, 45minute (Habibi et al., 2006) and from Whatmann filter paper using 1.5N HCL, 4 hours, at 100°C (Rojas et al., 2009).
3.4. Steam explosion

Steam explosion is a thermo-mechanical process. At high pressure, steam penetrates to cellulose fiber through diffusion and when the pressure suddenly releases, creates shear force, hydrolysis the glycosidic and hydrogen bonds and leads to formation of nanofibers (Giri and Adhikari 2013). In 1927, Mason introduced the steam explosion method to defibrillate wood to fiber for board production (Vignon et al., 1995). Effective parameters in this process are pressure, temperature and time of being material in autoclave. Steam explosion process can be used solely or in combination with other processes. For instance cellulose nanofibers from banana at 20 lb pressure, 110-120°C, for 1 hour (Deepa et al., 2011) and from pineapple at 20 lb pressure (Cherian et al., 2010) produced just using steam explosion.

TEM and AFM images of figure 9 confirm individualization of NFC from cell wall using steam explosion process. Only little association happened between adjacent NFC. The author estimated the aspect ratio of 50 through TEM and diameter of around 5 to 60nm through AFM for NFC. In another research, banana, jute and pineapple leaf nanofibers extracted with steam explosion along with mild chemical treatment (Abraham et al., 2011). Also, steam explosion accompany with homogenization to increase defibrillation of nanofiber from wheat straw has been reported (Kaushik and Singh 2011).

4. Characterization of nanocellulose

Basically, characterization of cellulosic materials in nanoscale is crucial issue in order to explore their physical, chemical, thermal and morphological properties at various treatment stages. Regarding this point, here we discuss about some of these properties and their evaluation techniques.

4.1. Physical properties
Physical characterizations of nanocellulose are including particle size analysis, surface charge, contact angle and etc. Particle size analysis of nanocellulose can be done using dynamic light scattering (DLS) and surface charge can be measured by zeta-potential (Zhou et al., 2012). They defined that zeta potential can be estimated by following the moving rate of charged particle (negative or positive charged) across an electric field. Generally a value smaller than \(-15\) mV shows starting of agglomeration, whereas higher than \(-30\) mV represents enough bilateral repulsion and colloidal stability. As the author mentioned the zeta potential values of the nanocellulose suspensions was \(-38.2\) mV for nanocellulose using acid hydrolysis (because of sulfonate groups), \(-46.5\) mV for TEMPO oxidized nanocellulose (due to carboxyl groups) and \(-23.1\) mV for ultrasonicated nanocellulose (as a result of its natural hydroxyl groups).

![Fig 10: Measurement of average particle size of nanocellulose from (a) acid hydrolysis (b) TEMPO-oxidized (c) ultrasonication using DLS (Zhou et al., 2012)](image)

Based on the figure 10, the mean particle size of nanocellulose from acid hydrolysis, TEMPO-oxidized and ultrasonication was calculated 115, 210 and 623 nm, respectively. The contact angle measurement provides information about the degree of hydrophilicity or hydrophobicity of nanocellulose surface. In order to measure the contact angle of nanocellulose using sessile drop method, first a dry network of nanocellulose should be prepared, then a droplet of water is deposited on the network and contact angle is measured (Jonoobi et al., 2012). The contact angle higher than 90° means that the surface is non-wetting (hydrophobic) and lower than 90° represents wetting characteristic (hydrophilic) of the surface (Abdul Khalil and Suraya, 2011). For example, the contact angle of kenaf fiber, acetylated fiber, NFC and acetylated NFC after 60s was 0, 113±2, 0 and 114±2° whereas for acetylated NFC (Jonoobi et al., 2010).
4.2. Thermal properties

Thermal decomposition properties of nanocellulose are determined by thermo-gravimetric analysis (TGA). In general, around 5 mg of sample is placed in platinum pan and heated with rate of 10 °C/min from 20 to 600 °C (Cao et al., 2012). Figure 11a shows the TGA curves of CNC from jute fiber (Cao et al., 2012). As the author mentioned the degradation of untreated jute fiber, alkali treated fiber and TEMPO-oxidized CNC start at 270, 270 and 200 °C. They described that TEMPO oxidation cause to reduce thermal degradation due to generation of sodium carboxylate groups. Also figure 14b illustrates the TGA curves of carboxymethylated (c) NFC from refined bleached beech pulp (RBP) (RBP-c), mechanical disintegrated one (RBP-m) and combination of these two methods with various sequences including RBP-mc and RBP-cm (Eyholzer et al., 2010). They stated that carboxymethylation leads to drop of cellulose degradation temperature from 300 to 200 °C.

Differential scanning calorimetry (DSC) can be considered as another thermal test method to measure the glass transition temperature (T_g) of nanocellulose samples. In this context, nanocellulose samples are heated from room temperature to 600 °C, under nitrogen flow and with rate of 10 °C/min (Chan et al., 2013). Figure 15 illustrates DSC curve of bleached kenaf core, unsulfated and sulphated CNC (Chan et al., 2013). They found that the loss of water which shows by first endothermic peak is around 32°C to 130°C for bleached kenaf and 32°C to 140°C for unsulfated and sulfated CNC. Also, they stated that second endothermic peak which represents degradation temperature was 350°C, 298°C and 200°C for bleached kenaf, unsulfated CNC and sulfated CNC, respectively. The author attributed the low degradation temperature of sulfated CNC to remain sulfate groups at the surface of CNC which play flame retardant role and lead to decrease degradation temperature.
4.3. Morphological properties

The atomic force microscopic (AFM) test is a good analysis to evaluate the surface characteristic of nanocellulose. Normally, after preparation of nanocellulose suspension, a drop of this suspension is deposited onto cleaved mica, dried and image is recorded at room temperature and in tapping mode (Satyamurthy and Vigneshwaran 2013). Figure 13 shows the AFM image of NFC from softwood and CNC from MCC.

AFM image (Fig 13a) exhibits a network structure, interconnected, entangled and in coiled form with width of 20 to 30 nm. As AFM picture of CNC (Fig 13b) displays very low agglomeration occurred and the diameter of CNC was lower than 10nm.

The dimension and structure of the nanocellulose can be studied using transmission electron microscopy (TEM). Generally, a drop of diluted nanocellulose suspension is deposited on carbon-coated grid and is dried at room temperature. Size measurements can be done by image
analyzer program (Jonoobi et al., 2010). Figure 14 illustrates the CNC from tunicate using H$_2$SO$_4$ acid hydrolysis (Peng et al., 2011) and NFC from potato pulp (Dufresne et al., 2000). The diameter of CNC is 10-20nm and its length is few microns, whereas NFC diameter is around 5nm with much higher length.

![Fig 14- TEM image of (a) CNC from tunicate (b) NFC from potato pulp](image)

Surface morphology of nanocellulose films can be studied by scanning electron microscopy (SEM) analysis. In this case to avoid increase of electrostatic charge, samples are sputter coated with gold and then are analyzed in the instruments (Qua et al., 2011). Figure 15 shows the FESEM images of NFC from dissolved pulp fiber after 15 passing times through grinder (Fig 15a) (Iwamoto et al., 2007) and CNC from MCC which produced from 60% H$_2$SO$_4$ hydrolysis for 2h and at 40°C combine with HPH (Fig 18b) (Pan et al., 2013). The diameter, length and aspect ratio of CNC were 11nm, 199nm and 18, respectively with uniform orientation while NFC had 20 to 50 nm width and more than 1µm length with aggregate structure.

![Fig 15- FESEM image of (a) NFC from dissolved pulp (b) CNC from MCC](image)

5. Drying of nanocellulose

One of the most important challenges related to application of nanocellulose, either NFC or CNC, is their drying process because nanocellulose is hydrophilic and tend to agglomerate. Why the drying process of nanocellulose is considerable issue in this field? To answer this
question, Peng et al. (2012) stated two main reasons, to maintain nano size of material for application and to reduce transportation cost of nanocellulose in aqueous form. Due to hydrophilic nature of cellulose materials, during drying of nanocellulose hydrogen bonds can be generated and lead to irreversible agglomeration known as hornification (Eyholzer et al., 2010, Kalia et al., 2011) which can change the size of nanocellulosic materials as well as their unique characteristics. To tackle this drawback, a wide variety of drying methods have been employed and compared together by researchers. For instance, solvent exchange of CNC from water to nonaqueous solvent with lower surface tension such as acetone has been done by Ayuk et al. (2009). Sanchez-Garcia and Lagaron (2010) compared freeze drying and solvent exchange of CNC and concluded that freeze-dried CNC show better dispersion, transparency and morphology than solvent exchanged counterparts. Also, producing CNC with ionic charge using H2SO4 hydrolysis can be consider as another solution which leads to relatively easy dispersion of this material after drying in aqueous media (Abitbol et al., 2011). In the case of NFC, Abe et al. (2007) applied un-dried fibers to produce NFC and to reduce their agglomeration. Figure 16 displays four various drying process steps.

The particular feature of crystallization at temperatures lower than the freezing temperature of water is increasing the rate of freezing and thus preventing from aggregation (Voronova et al., 2012). Flow rate of suspension and temperature of hot air are some of key factors in this context (Quievy et al., 2010). In addition parameters such as concentration and feed rate of
liquid as well as gas flow rate have effect on this process (Peng et al., 2012). Oven drying, freeze drying and atomization process (Quievy et al., 2010), spray drying and supercritical drying (Peng et al., 2012) have been utilized by researchers to evaluated their effect on properties of resultant NFC.

6. Modifications of nanocellulose

Modification of NFC has received a significant interest from the scientific community. It is envisaged to improve the hydrophilic nature of cellulose in polar and non-polar environments, thus will increase compatibility with a wider variety of matrices. Numbers of reactions have been performed to modify the surface properties of the cellulose (John & Anandjiwala, 2008; John, Francis, Varughese & Thomas, 2008), including corona or plasma discharges (Bataille, Ricard & Sapieha, 1989), surface derivatization (Hafrén, Zou & Córdova, 2006), graft copolymerization (Gruber & Granzow, 1996) or application of surfactant (Bonini, Heux, Cavaillé, Lindner, Dewhurst & Terech, 2002; Heux, Chauve & Bonini, 2000). Some approaches aiming to hydrophobize nanocellulosic materials are briefly discussed in the following.

6.1. Acetylation

Kim, Nishiyama and Kuga (2002) reported that cellulose was partially acetylated to modify its physical properties while preserving the microfibrillar morphology which material properties are crucial influenced by the degree of acetyl substitution (Henriksson, Berglund, Isaksson, Lindström & Nishino, 2008). In research by Ifuku, Nogi, Abe, Handa, Nakatsubo and Yano (2007), transparency and hygroscopicity of cellulose/acrylic resin composite materials are improved and reduced by acetylation, respectively, though the composites exhibited an optimum degree of substitution and reduced in properties with excessive acetylation. Study by Nogi, Abe, Handa, Nakatsubo, Ifuku and Yano (2006) found that acetylation improved the thermal degradation resistance of cellulotic fibers. The effect of biological exposure upon the properties of acetylated and surface treated plant fiber based polyester composites was studied by Abdul Khalil and Ismail (2000), where it was found acetylation exhibited superior bio-resistance followed by silane, as well as cast resin and glass fiber composites in soil tests up to 12 months exposure.
6.2. Silylation

Isopropyl dimethylchlorosilane is used by Goussé, Chanzy, Cerrada and Fleury (2004) 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 non-flocculating manner into organic solvents. Andresen, Johansson, Tanem and Stenius (2006) reported that hydrophobizing of MFC via partial surface silylation using the same silylation agent resulted in partial solubilization of MFC and loss of nanostructure when silylation conditions were too harsh. 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. Moreover, study by Andresen and Stenius (2007) showed that hydrophobized MFC could be used for stabilization of water-in-oil type emulsions. Figure 20 compares the morphology of MFC samples silylated with four and six equivalents of chlorodimethyl isopropylsilane (CDMIPS) per glucose unit.
Fig 18 - TEM of MFC silylated with six equivalents (A); four equivalents (B) of CDMIPS per cellulose glucose unit; severely decomposed microfibril bundle (C) and compact aggregates of degraded microfibrils and fibre fragments (D) (Andresen, M., Johansson, L.-S., Tanem, B. S., & Stenius, P., 2006)

6.3. Application of coupling agents

The adhesion between microfibrils and epoxy resin polymer matrix is successfully enhanced by applying three different coupling agents, which are 3-aminopropyltriethoxysilane, 3-glycidoxypropyltrimethoxysilane, and a titanate coupling agent, Lica 38. The surface modification changed the character of MFC from hydrophilic to hydrophobic while the crystalline structure of the cellulose microfibrils remained intact. Lica 38 gave the most hydrophobic surface among the tested coupling agents, possibly due to the lower polarity of the titanate modifier alkyl chain. Unlike silane coupling, titanate coupling is thought to occur via alcoholysis, surface chelation or coordination exchange. The monoalkoxy- and neoalkoxy-type titanium-derived coupling agents react with the hydroxyl groups present on the surface of the substrate to form a monomolecular layer (Lu, Askeland & Drzal, 2008). Nair and partners (2003) used phenyl isocyanates and alkenyl succinic anhydride to improve the quality of the interface between natural rubber and chitin whiskers with present of 3-isopropenyl-R, R¢-dimethylbenzyl isocyanate. The expected chemical reactions that occur in the alternative chemical modifications are seen in Scheme 1.
Fig 19- Chemical reactions that occur in the alternative chemical modifications of chitin whiskers with phenyl isocyanate, alkenyl succinic anhydride and 3-isopropenyl-R,R¢-dimethylbenzyl isocyanate (Gopalan Nair, Dufresne, Gandini and Belgacem, 2003)

6.4. Grafting

There are three methods reported by Stenstad, Andresen, Tanem and Stenius (2008) for modification of MFC by heterogeneous reactions in both water and organic solvents to produce cellulose nanofibers with a surface layer of moderate hydrophobicity. Epoxy functionality was introduced onto the MFC surface by oxidation with cerium (IV) followed by grafting with glycidyl methacrylate. Reactive epoxy groups served as a starting point for further functionalization with ligands, which typically unreacted with the surface hydroxyls present in native MFC. As the reaction is conducted in aqueous media, the use of organic solvents and laborious solvent exchange procedures can be avoided, giving this as the major advantage of this technique. In the same research conducted by these authors, grafting of hexamethylene disocyanate followed by reaction with amines yield a far more hydrophobic MFC surface. Succinic and maleic acid groups can be introduced directly onto the MFC surface as a monolayer by a reaction between the corresponding anhydrides and the surface hydroxyl groups of the MFC. Also, noctadecyl isocyanate (C\textsubscript{18}H\textsubscript{37}NCO) has been applied as the grafting agent in order to improve MFC compatibility with polycaprolactone (Siqueira, Bras & Dufresne, 2008).

Apart from this, five different chemicals: ethylene acrylic acid, styrene maleic anhydride, guanidine hydrochloride, and Kelcoloids HVF and LVF stabilizers (propylene glycol alginate) were used to prepare bio-nanocomposites from PLA and PHB as matrices by Wang and Sain (2007) in order to explore the potential use of chemically coated hemp nanofibers as reinforcing agents for biocomposites. Nanofibers were only partially dispersed in the polymers and therefore resulted in low mechanical properties compared to those predicted by theoretical calculations. Morphological analyses of sisal whiskers by Siqueira and co-workers (2008) by using N-Octadecyl isocyanate (C\textsubscript{18}H\textsubscript{37}NCO) as the grafting agent show the homogeneity and nanometric dimensions of sisal whiskers (Figure 20).
Besides enhancing compatibility of nanocellulose with non-polar polymers and improve mechanical properties, the purpose of chemical modification is too add extra functionality to nanocellulosic materials. For instance, Thomas, Heine, Wollseifen, Cimpeanu and Möller (2005) reported that positively charged amine-functionalized MFC is said to be antimicrobially active in biomedical applications. Andresen and Stenius (2007) also added extra functionality to MFC film by covalently grafting the cellulose with octadecyldimethyl (3-trimethoxysilylpropyl) ammonium chloride (ODDMAC). When the atomic concentration of ODDMAC nitrogen on the film surface was 0.14% or higher, the surface-modified MFC films showed antibacterial activity against both Gram-positive and Gram-negative bacteria, even at very low concentrations of antimicrobial agent on the surface, killing more than 99% of E. coli and S. aureus. The chronological order of events for various modification of nanocellulose can be seen in table1.
Table 1. Chronological order of modification of nanocellulose

<table>
<thead>
<tr>
<th>Year</th>
<th>Progress</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>2000</td>
<td>Stable dispersion of cellulose microcrystals in nonpolar solvents by using surfactants as stabilizing agents</td>
<td>Heux, Chauve and Bonini (2000)</td>
</tr>
<tr>
<td>2003</td>
<td>Chitin whiskers surface modification by using three different chemical coupling agents</td>
<td>Gopalan Nair, Dufresne, Gandini and Belgacem (2003)</td>
</tr>
<tr>
<td>2005</td>
<td>Nanofibers from natural and inorganic polymers via electrospinning</td>
<td>Thomas, Heine, Wollseifen, Cimpeanu and Möller (2005)</td>
</tr>
<tr>
<td>2007</td>
<td>Surface modification of bacterial cellulose nanofibers by dependence on acetyl-group DS</td>
<td>Ifuku, Nogi, Abe, Handa, Nakatsubo and Yano (2007)</td>
</tr>
<tr>
<td>2008</td>
<td>Sisal-oil palm fibers treated with varying concentrations of sodium hydroxide solution and different silane coupling agents</td>
<td>Heßler and Klemm (2009)</td>
</tr>
<tr>
<td>2009</td>
<td>Alteration of bacterial nanocellulose structure by in situ modification using polyethylene glycol and carbohydrate additives</td>
<td>Jonoobi, Harun, Mathew, Hussein and Oksman (2010)</td>
</tr>
<tr>
<td>2010</td>
<td>Modification of acetylated cellulose nanofibers from kenaf using acetic anhydride</td>
<td>Uschanov, Johansson, Maunu and Laine (2011)</td>
</tr>
<tr>
<td>2011</td>
<td>Heterogeneous modification of various cellulosic with fatty acids by an esterification reaction</td>
<td>Yang and Ye (2012)</td>
</tr>
<tr>
<td>2012</td>
<td>Liquid crystal of nanocellulose whiskers’ grafted with acrylamide</td>
<td></td>
</tr>
<tr>
<td>2013</td>
<td>Modification of native cellulose nanofibers by functionalized few-walled carbon nanotubes for hybrid nanofiber/nanotube aerogels</td>
<td>Wang et al. (2013)</td>
</tr>
</tbody>
</table>

7. Nanocellulose-based polymer nanocomposites

The development of polymer nanocomposites is rapidly emerging as a multidisciplinary research activity whose results could broaden the applications of polymers to the great benefit of many industry. Polymer nanocomposites filled with nanocellulose represent a new class of material alternative to conventional filled polymers and possess some extremely interesting properties such as high strength and stiffness combined with low weight, biodegradability and renewability (Siro´ and Plackett, 2010).
During the last two decades micro and nanocellulose reinforced composites have been the subject of intensive research and a number of review papers have appeared covering this work (Azizi Samir et al., 2005; Dufresne, 2010; Siqueira et al., 2010; Siro´ and Plackett, 2010; Abdul Khalil et al., 2012; Harfiz Salehudin et al., 2012; Missoum et al., 2013). Nanocellulose either in CNC or NFC form will result in varying reinforcement of nanocomposites. Also, different types of nanocellulose can be used in various forms of reinforcement, including distributed reinforcements, planar reinforcements, or continuous networked structures. Beside the above advantages of nanocellulose as reinforcement in nanocomposites, they present some disadvantages, for instance, high moisture absorption, poor wetability, incompatibility with most of polymeric matrices and limitation of processing temperature. Indeed lignocellulosic materials start to degrade near 220 °C and this character restricts the type of matrix which can be used with natural fillers (Siqueira et al., 2010). To fully utilize the potential of nanocellulose as reinforcement in composite materials, the hydrophilic nature of cellulose should be altered to make it more compatible with organic solvents and nonpolar polymer matrices. This changing improves both the incorporation of cellulose into the composite materials, which results in more homogeneous composites, and the interfacial adhesion between nanocellulose and matrix in the final composite. In this section we focus on thermoplastic and thermoset polymer nanocomposite based on nanocellulose, their production processes, characterization and application.

7.1. Thermoplastic polymer-nanocellulose nanocomposites

Many thermoplastic polymers have been used as matrix with nanocellulose as reinforcement such as poly(vinyl alcohol) (PVA) (Lee et al., 2009; Cho and Park, 2011; Zhou et al., 2012), polyurethane (Wu et al., 2007; Auad et al., 2008), polypyrrolle (Nystrom, 2012), polypropylene (Yang et al., 2012), poly(lactic acid) (PLA) (Bulota and Hughes, 2012), hydroxypropylcellulose (HPC) (Johnson et al., 2009), chitosan (Azeredo et al., 2010), polyacrylamide (Zhou et al., 2011) and etc. Figure 21 and 22 are example for thermoplastics reinforce by nanocellulose.

Fig 21- Photographs of neat film and nanocomposite film (LDPE) based on ramie CNC (de Menezes et al., 2009)
PVA as one of the thermoplastic polymers is a water soluble synthetic polymer, has excellent film forming and emulsifying properties (Cho and Park, 2011), hydophilic, easy to process, has good physical and chemical properties (Peresin et al., 2010) and inexpensive (Yang et al., 2009). It also has high tensile strength and flexibility (Zhou et al., 2012). Because of these interesting properties PVA has been the subject of many researches in this field. For example, Cho and Park (2011) investigated the mechanical and thermal properties of PVA-based nanocomposites reinforced with CNC isolated from MCC. They were casted nanocellulose suspension-PVA on a Teflon coated petri dish. Their results exhibited that the tensile modulus decreases at 1 wt% CNC loading, and then increases with an increase in the CNC content up to 5 wt%, followed by leveling off at higher CNC content (Figure 2).

Fig 2- Photographs of MFC paper (a) and a MFC- polypyrrolle composite (b) (Nystrom, 2012)

Bulota et al., (2011) prepared nanocomposites film from NFC-PVA at various NFC loading. They stated that the highest modulus obtains at a solution concentration of 4 up to 5% (w/w) of NFC. As they stated reinforcement effects and increase in the dispersion viscosity is obvious at 5% NFC loading, implying that the percolation phenomenon takes place at this loading. Furthermore, many other thermoplastic polymers have been used with CNC to produce nanocomposite. The functionalized CNC from ramie which grafted by organic acid chlorides reinforced low density polyethylene (LDPE) nanocomposites studied by Junior de Menezes et al., (2009).

Native and surface trimethylsilylated CNC were employed as the particulate phase in nanocomposites with a cellulose acetate butyrate matrix to improve the mechanical properties of polymers and to enhanced adhesion between the particulate and matrix phase in composites (Grunert and Winter, 2002). Poly(oxyethylene) based polymer electrolytes should be used above their melting temperature to display appropriate conductivity. Unfortunately, at this temperature the mechanical properties are very poor. In this regard Azizi Samir et al., (2004) evaluated the effect of CNC extracted from tunicate to improve the mechanical properties of poly (oxyethylene) (PEO) based nanocomposite electrolytes above its melting temperature. SEM fracture surface of CNC-PEO composite illustrated in Figure 24. As their SEM images shows some holes can be seen which attributed to entrapped air within the film during the water evaporation step despite degassing of the suspension.

Fig 23- Tensile modulus and tensile strength of PVA nanocomposites as function of CNC content (Cho and Park, 2010)
In addition, NFC can be utilized to reinforce thermoplastic polymers. For instance, Nystro¨m et al., (2010) produced a nanocomposite from NFC isolated from wood and polypyrrole. They demonstrated that it is possible to coat the individual NFC with polypyrrole using in situ chemical polymerization to obtain an electrically conducting continuous high-surface-area nanocomposite. Johnson et al., (2009) studied about a new bio-based nanocomposite using TEMPO-oxidized NFC through high intensity ultrasonication in hydroxypropylcellulose (HPC) matrix. In bionanocomposites, the polymer matrix also should be biodegradable. In this context, Poly(ε-caprolactone) (PCL) as semicrystalline biopolymer with a glass transition temperature around -60 °C and a melting temperature around 60 °C can be consider to manufacture bionanocomposite. So, NFC covalently grafted with PCL via ring-opening polymerization of ε-caprolactone introduced by Lonnberg et al., (2011). They evaluated the effect of PCL graft length and ring-opening polymerization to different molecular weights of the grafts on the mechanical properties of the bionanocomposite. Qu et al., (2010) added poly(ethylene glycol-1000) (PEG) as a compatibilizer to PLA in order to improve the interfacial interaction between the hydrophobic PLA and the hydrophilic NFC. Their result illustrated that when the PEG is added to the blend of PLA and NFC, the composites show significant improvements in tensile strength and elongations.

7.2. Thermoset polymer-nanocellulose nanocomposites
Thermosetting composites can be cured with low or no heat which can be advantageous for limited thermal stability of nanocellulose. Thermosetting plastics are polymer materials that irreversibly cure. The curing maybe done through heating, radiation or a chemical reaction (e.g. a two part epoxy). Once the curing is complete, the thermoset cannot be melted into a liquid form. Several of thermosets, including epoxy, formaldehyde, polyester and etc have been investigated to use with nanocellulose in nanocomposites. A high-strength elastomeric nanocomposite has successfully been prepared by dispersing microcrystalline cellulose in a polyurethane matrix (Wu et al., 2007 and Auad et al., 2008). The SEM and TEM image the use of CNC with water bond polyurethane as a matrix in figure 25 and 26.
Epoxy-based nanocellulose composites have the potential for wide application due to their high mechanical properties. Epoxy is a thermosetting copolymer, also known as polyepoxide, formed from reaction of an epoxide resin with polyamine hardener. Masoodi et al., (2011) compared traditional epoxy and bio-based epoxy reinforced with NFC. The wet layup process was employed to manufacture the double cantilever beam specimens. They found that the biobased epoxy has similar performance characteristics for fracture toughness compared to the standard epoxy and also it does not show reductions at the room temperature test conditions. Lu et al., (2008), reported surface treatments of NFC with three different coupling agents including 3-aminopropyltriethoxysilane(APS), 3-glycidoxypropyl trimethoxysilane, and a titanate coupling agent reinforced epoxy resin using acetone solvent. The effect of silanetreated NFC in unsaturated polyester and epoxy resin matrices was studied by Abdelmouleh et al., (2005). They found that large loss of mechanical properties is related to insufficient silane treatment to prevent NFC from water absorption. Beside epoxy and polyester manufacturing of nanocomposite film from TEMPO oxidized NFC and water-soluble phenol formaldehyde was the subject of research by Qing et al., (2012). SEM micrographs of the film clearly presented the lamellar structure of NFC in cross-section of the neat film as well as the composite. The mechanical properties of NFC reinforce themoset polymer matrices in Table 2.

### Table 2- Mechanical properties of thermoset polymer matrices filled NFC

<table>
<thead>
<tr>
<th>Resin</th>
<th>Nano-cellulose form</th>
<th>Strength (Mpa)</th>
<th>Elastic modulus (Gpa)</th>
<th>Strain to failure (%)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Epoxy</td>
<td>NFC film (0-5% fiber content)</td>
<td>-</td>
<td>1.5-2.9</td>
<td>-</td>
<td>Masoodi R., et al., 2011</td>
</tr>
<tr>
<td>Phenol formaldehyde</td>
<td>MFC film (5-20% wt. Fibers)</td>
<td>201-216</td>
<td>4.16 – 4.48</td>
<td>12.6 – 14.7</td>
<td>Qing Y., et al., 2012</td>
</tr>
<tr>
<td>Melamin formaldehyde</td>
<td>NFC (13% wt fiber)</td>
<td>142</td>
<td>16.6</td>
<td>0.81</td>
<td>Henriksson and Berglund, 2007</td>
</tr>
</tbody>
</table>

Nanocelluloses have been mixed or dispersed in various resins using a wide variety of processing techniques. Gong et al., (2012) prepared composite from both NFC and CNC in
polyvinyl acetate using a master batch followed by melt extrusion. Yang et al., (2011) used three general processes, viz. melt blending, grinding, and injection molding to produce CNC-polypropylene nanocomposites. Agarwal et al., (2012) prepared the nanocomposite from polypropylene reinforced with CNC by extrusion method.

While techniques for preparation of nanocellulose reinforced nanocomposite are different in complexity, they typically involve physically mixing and dispersing the nanocellulose and resin in a solvent system. In many cases, solvent exchange techniques are used, often along with surface modification of nanocellulose to make it compatible with organic solvents and/or the resin system. In this context, nanocomposite films from nanocellulose generally are prepared through three various techniques as below:

(i) by casting on Teflon or propylene dishes followed by water evaporation at moderate temperatures,
(ii) by freeze-drying and hot-pressing, or
(iii) by freeze-drying, extruding, and hot-pressing the mixture.

Here we mention some examples of nanocomposites films production processes. Sehaqui et al., (2011) reported manufacturing of NFC reinforced hydroxyethylcellulose (HEC) film in a polystyrene Petri dish under air atmosphere at room temperature with thickness of 65–80 mm. Preparing process of the nanocomposites film are illustrated in figure 27.

![Fig 27- Preparation scheme for NFC nanopaper (arrow to the left) and NFC/HEC biocomposites](image)

Gray (2008) has mentioned about transcry crystallization of polypropylene at CNC surface. There is a resurgence of interest in composite materials incorporating cellulose as fibrous reinforcement in semicrystalline melt-processed polymers. Potential natural cellulose sources range from flax and ramie fibres down to whiskers and nanocrystals isolated from bacteria (Figure 28).
7.3. Application of Nanocomposites Based on Nanocellulose

Green technology has been boosted by utilization of this renewable materials as natural fibers to non-wood biomass based products in various application (such as light construction, furniture, food packaging, automotive components, etc). In generally, non-wood biomass was made as composite for almost all utilization, and some of those still used as traditional application (solid biomass).

Cho and Park, (2011) casted nanocellulose suspension-PVA on Teflon coated Petri dish. Their results exhibited that the tensile modulus decreases at 1 wt% CNC loading, and then increases with an increase in the CNC content up to 5 wt%, followed by leveling off at higher CNC content. Azizi Samir, (2004) produced nanocomposite film from CNC in poly (oxyethylene) with thickness around 200 mm by casting on teflon plates and water evaporation at 40 °C for one week. SEM images of fracture surface of the film showed some holes which attributed to entrapped air within the film during the water evaporation step despite degassing of the suspension.

Processing techniques have an important incidence on the final properties of the nanocomposites based on nanocellulose. So that, the achievement of superior strength properties of nanocomposite based on nanocellulose can be used for many application. However, the use of nanocellulose as a reinforcement is in its infancy, and the full reinforcing potential of nanocomposites has yet to be realized partly because of issues related to scaling manufacturing processes.

Nanocellulose becomes very important because incorporation of nano-reinforcement has been related to improvement in overall performance of nanocomposites. Over decades, this particular field of study becomes more interesting that lead to the advancement of nanocellulose characteristic. This is solely because many research found that properties of nanocellulose plays important role in nanocomposite. Better understanding of organic and polymer chemistries makes the current researcher to look deeply on interaction between polymer matrix and nanocellulose hence lead to the advancement of nanocellulose values so that it could be used universally into various nanocomposites.

Applications of all above nanocellulose reinforced nanocomposites with thermoplastic and thermoset polymers are mainly considered to be in paper and packaging products, construction, automotive, furniture, electronics, pharmacy, and cosmetics. Figure 29 show drawing the application biocomposite from processing of nanocellulose.
8. Conclusion

Cellulose fibers are being used as potential reinforcing materials because of so many advantages such as abundantly available, low weight, biodegradable, cheaper, renewable, low abrasive nature, interesting specific properties, since these are waste biomass and exhibit good mechanical properties. Cellulose fibers also have some disadvantages such as moisture absorption, quality variations, low thermal stability and poor compatibility with the hydrophobic.

Applications of nanocellulose are mainly considered to be in paper and packaging products, although construction, automotive, furniture, electronics, pharmacy and cosmetics are also being considered. For companies producing electroacoustic devices, nanocellulose is used as a membrane for high quality sound. Additionally, nanocellulose is applied in membrane for combustible cells (hydrogen), additives for high quality electronic paper (e-paper), ultra-filtrating membranes (water purification) and membranes used to retrieve mineral and oils.

There are two basic approaches for creating nanostructures - bottom-up and top-down. The bottom-up method involves construction on a molecular scale from scratch using atoms, molecules and nanoparticles as building blocks. This method uses chemistry- and physics derived technologies which are based on chemical synthesis or strictly controlled mineral growth. The top-down method in producing nanofiber involves the disintegration of macroscopic material to a nano-scale by the following methods: mechanical (e.g. grinding), chemical (e.g., partial hydrolysis with acids or bases), enzymatic (e.g., treatment with enzymes hydrolysing cellulose, hemicellulose, pectin and lignin) and physical (e.g. techniques using focused ion beams or high-power lasers).

Acknowledgement

The author H. P. S. Abdul Khalil highly acknowledge and pay gratitude to the School of Life Sciences and Technology, Institut Teknologi Bandung, Jln Ganesha 10 Bandung, Indonesia for providing technical support and facilities during his short visit as a visiting professor.

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