TIMBER TECHNOLOGY BULLETIN
NO. 68, 2016
ISSN: 139-258

MINISTRY OF NATURAL RESOURCES AND ENVIRONMENT, MALAYSIA

SURFACE FUNCTIONALIZATION OF NANOCELLULOSE AND ITS POTENTIAL APPLICATION

J Latifah

Introduction

Nanocellulose is a material with nanoscale (10^{-9} of a meter) structure that can be produced from natural renewable materials such as woody biomass, algae, sea animal and bacteria. Nanocellulose has gained a growing interest because of the following advantages: high stiffness, high surface area, biodegradable, non-toxic, renewable and interesting optical properties that make it a versatile material for many applications. Figure 1 shows nanocellulose produced from wood pulp at FRIM.

In 2015, the global demand value for nanocellulose market was estimated at USD 65 million, and is expected to reach USD 530 million in 2021, recording a growth of about 30% between 2016 and 2021 (Marketresearchstore 2016). This trend shows the increasing importance and awareness of this material for various products from multiple industry players worldwide. In terms of its usage, nanocellulose is currently being tested across various application fields (packaging, automotive, biomedical etc.) due to its exceptional properties. However, new nanocellulose-based products such as paper and packaging products are almost approaching the market in the next few years to come (Cowie et al. 2014).

Figure 1 Nanocellulose produced from acacia wood pulp in the form of powder and suspension

Nanocellulose is hydrophilic (water loving) in nature therefore its use is limited to water-based processes or products. Hence, modification on nanocellulose is needed to expand the applicability of nanocellulose. The surface modification on nanocellulose is carried out in order to impart specific functionalization to nanocellulose such as hydrophobicity, fluorophoricity (coloured material) or ionic moieties (charged material) for use in nanocomposite, biomedical and many other research fields.

In the early years of nanocellulose research, modification of nanocellulose has been limited to application in polymer nanocomposite due to the dispersion issue (owing to their hydrophilic nature). Nanocellulose can only be used in water-based polymeric system which limits its application. Therefore, most of the surface functionalization conducted has been mainly focused to improve compatibility and dispersibility between nanocellulose and non-polar matrices/solvents in nanocomposite field. Hence, to widen the scope of incorporating nanocellulose into a wide range of non-polar polymer matrices system, nanocellulose needs to be surface modified into hydrophobic form in order to obtain nanocrystal/polymer nanocomposite with exceptional mechanical reinforcement properties. Moving away from nanocomposite area, surface functionalization has also been conducted on nanocrystals to introduce charged groups that is either cationic (positively charged) or anionic (negatively charged) groups on the nanocrystalline cellulose. The ionic nanocellulose can be used as a material in drug delivery system and prepared as smart hydrogel in pharmaceutical research. Some potential applications of functionalised nanocellulose in various fields based on the work reported in the literature are shown in Figure 2.

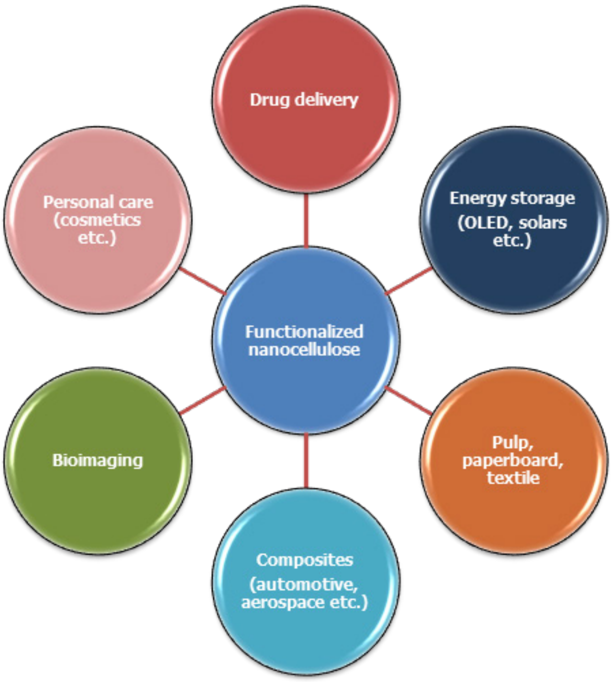

Figure 2 Potential applications of functionalised nanocellulose

Native cellulose modification has been widely studied and some modified celluloses have long been available in the market (Klemm et al. 1998 & 2005). The typical chemical reaction routes for cellulose modification are esterification, etherification and oxidation. These types of modifications are carried out because of the need to introduce different functional groups on the cellulose such as nitrate, acetate etc. From this reaction, the most common commercially modified cellulose products include cellulose acetate, cellulose nitrate, ethyl cellulose, hydroxypropyl cellulose and carboxymethyl cellulose. These versatile cellulose-based products are used in a host of applications from pharmaceuticals, textile, personal care, industrial, paints and coatings to food industries.

In the case of nanocellulose, several chemical modifications similar to native cellulose have also been studied i.e esterification, oxidation, etherification and silylation (Figure 3).

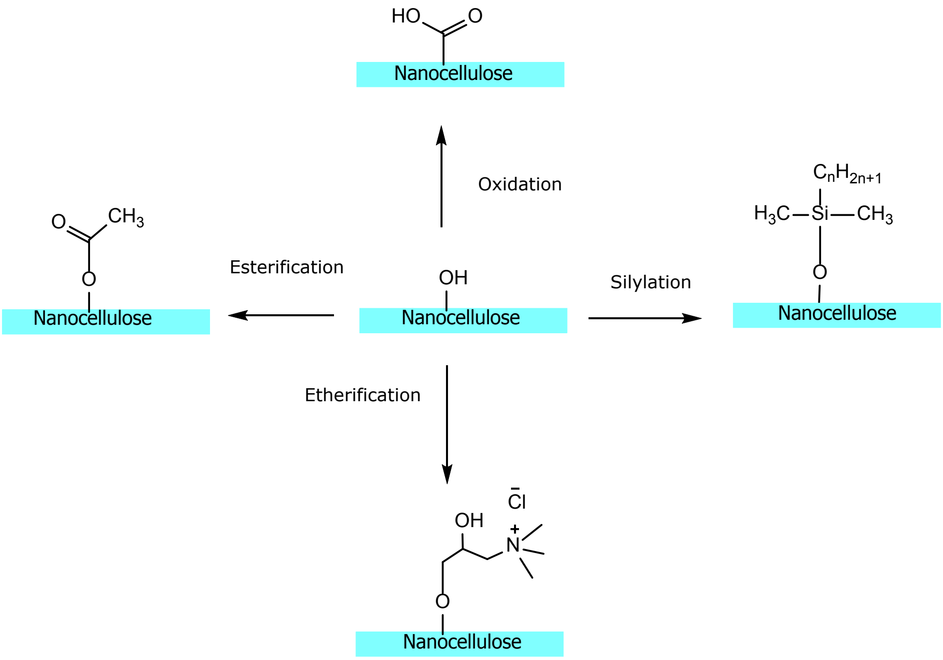

Figure 3 Common functionalization of nanocellulose through chemical reaction routes

These modifications are feasible due to the presence of a large number of hydroxyl groups at their surface which can be functionalised to impart and tailor desired properties to the nanocellulose for many general and specific applications. It is interesting to note that most of the chemical modifications performed on nanocellulose are generally an extension of what has been done previously on native cellulose. For nanocellulose however, the challenges of heterogeneous cellulose modification remains, i.e. to have a good extent of modification while preserving the structural integrity in order to take advantage of their intrinsic properties especially toward development of new highly engineered smart materials. In other words, the modification needs to be carried out under controlled condition so much so that its crystallinity will not be affected.

Functionalization of nanocellulose and its potential application

Hydrophobic nanocellulose

Early work on modification of nanocellulose has been mainly involved around making the surface hydrophobic and to improve nanocellulose dispersibility in various solvents. Hydrophobization is the process of making material water repellent or resistant. This is important for any process or product that could not use water or function in the presence of water. Hydrophobization of cellulose usually takes place through chemical route i.e esterification as shown in Figure 3. By doing so, modification of nanocellulose is achieved by the attachment of hydrophobic molecules. To act as good nanofiller in polymer matrices, nanocellulose needs to have good dispersibility not only in a water-soluble polymeric system but also to be applicable in non-polar polymer systems. Modifications are thus performed on the nanocellulose to improve their dispersibility and broaden their application in those non-aqueous (non-water) nanocomposite applications. Cellulose acetate, for instance, is the most common cellulose derivative in the market used as apparel, absorbent etc. Hydrophobic nanocellulose can be used in polymer matrices system such as polypropylene and polyethylene that can be further developed into finished products such as body and interior components for automotive industry.

Besides nanocomposites area, hydrophobic nanocellulose could find further applications in packaging industry in which moisture is the important parameter to consider. Controlling the moisture penetration could be materialized by attaching hydrophobic molecules on the nanocellulose. As a results, making the paperboard hydrophobic could make the food packaging particularly last longer. In the coating field, whilst adding unmodified nanocellulose could enhance the durability of coating from UV exposure, using hydrophobic nanocellulose could further improve the function of nanocellulose as being anti-corrosion, self-cleaning, anti-microbial, anti-stain and many others. These multitude benefits can be applied into various industrial products uses such as self-cleaning or anti-fogging glass, anti-stain textile, anti-finger print displays etc.

Another potential product that can be produced from nanocellulose is aerogel (sponge-like material). Aerogel is a highly porous and light-weight material that can act as absorbent. Making the aerogel hydrophobic can expand its applicability to absorb oil, such that it has the potential to be made into a product for separation and filtration for environmental cleanliness.

Ionic (charged) nanocellulose

Nanocellulose has also been modified on the surface with an aim to impart cationic (positive) charges on the surface. Cationized cellulose has long been used in industries such as papermaking, textiles and the dyeing industries to improve the process effectiveness. In the case of papermaking, this is achieved through the use of cationic cellulose that aids to improve the dispersion of dyes and fillers. This in turn would increase the mechanical properties of paper product. Similarly in textile industry, cationic cellulose improves the retention of dye in the dyeing process, hence reducing the use of electrolytes. Due to its binding affinity for negatively charged compound, cationic modified cellulose has also been studied for applications in cosmetics, pharmaceuticals and drug delivery (Hasani 2009). For instance, a study has been performed to prepare smart hydrogel that could have huge potential in biomedical, pharmaceutical fields. Smart hydrogels, also known as stimuli-responsive gels, are capable to change their properties in response to environmental stimuli (pH, temperature or chemicals) (Xia et al. 2013). In one study, the smart hydrogel can respond to change in media of various pH and ionic strength (Rodriguez 2003). Furthermore, charged cellulose can also be used as protein carrier; a subject matter that has attracted high interest due to the therapeutic merits of proteins over chemical drugs (Song et al. 2009).

Besides positively charged cellulose, nanocellulose can also be made into negatively charged material. This type of nanocellulose is usually obtained by performing oxidation process using oxidizing agent. The resulting cellulose or also known as oxidized cellulose has been investigated for its use as wet strength additive in papermaking process. Paper products such as tissue paper or kitchen towel rely on this important mechanical strength when in contact with wet surface. In other words, these types of paper need to hold its shape when wet. Oxidized cellulose can also be used as a precursor for subsequent hydophobization of cellulose. It has been successfully substituted by non-polar groups such as amine-functionalised molecules to produce hydrophobic nanocellulose.

Oxidized cellulose has also been used as a substrate in the adsorption of cationic surfactants and some organic compounds. These charged solid substrates could find many application potentials such as in chemical sensors, membranes, cosmetic, soil remediation. Oxidized cellulose used as a component have been patented in numerous application preparation such as cosmetic, papermaking, gel, thickener and oxygen barrier (Johnson 2010).

In FRIM, we have embarked on surface modification study by preparing oxidized nanocellulose from acacia, mahang and kenaf. Our early findings confirmed the presence of carbonyl group at 1731 cm^{-1} on nanocellulose via Fourier Transform Infrared Spectroscopy (FTIR) as shown in Figure 4, thus confirming the production of oxidized nanocellulose. The oxidized cellulose is being further evaluated for adsorbent application potential.

Fluorescent (coloured) nanocellulose

Fluorescent labeling on nanocellulose has been done to attach fluorophore that can be used in nanomedicine. Labelling of nanocellulose has been carried out with fluorescent dye as indicator in medical imaging (Dong & Roman 2007). This coloured nanocellulose has the potential to be used in biomedical as imaging tool, biosensor and so on.

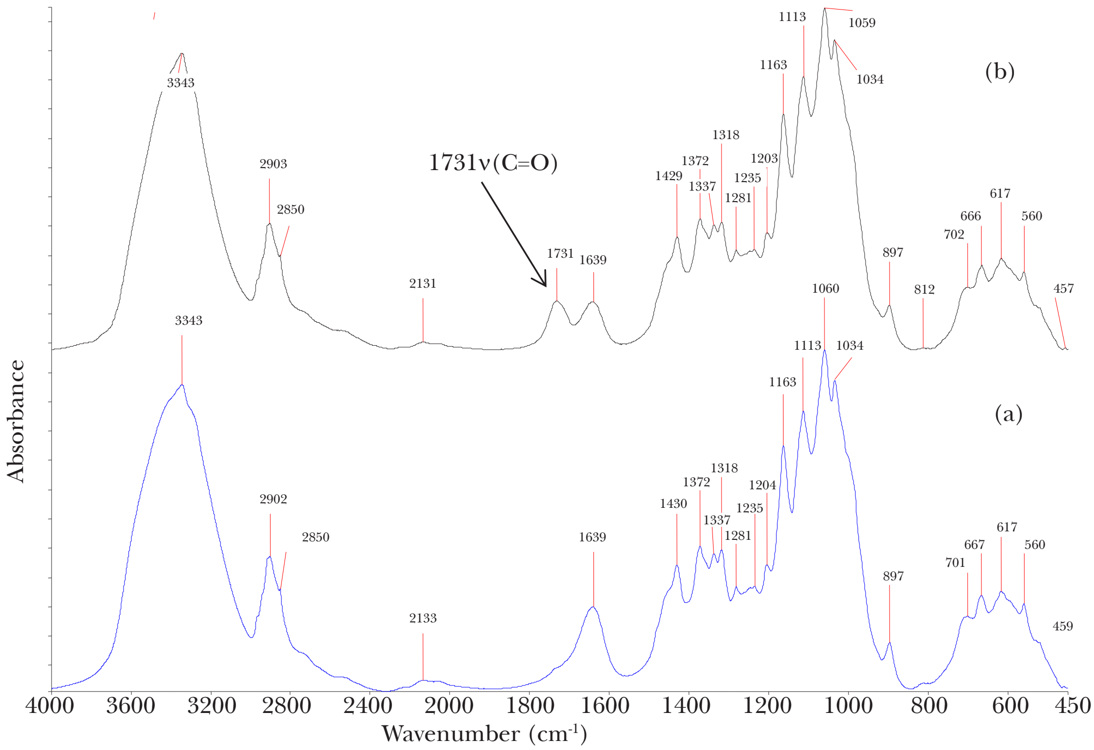

Figure 4 FTIR spectra of unmodified (a) and oxidized nanocellulose (b) from acacia

Summary

Functional nanocellulose offers a myriad of industrial applications ranging from composites, biomedical, textiles, cosmetics to packaging. Functionalised nanocellulose is an extra feature with added functionality from the original nanocellulose that related industries should take advantage to suit their application needs.

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Printed by Publications Branch, Forest Research Institute Malaysia
52109 Kepong, Selangor