Reinforced biopolymers from Seaweed using Plant-Based Celluloses – A Review

Joanne Lim Chia Pei[1], Eunice Lua Hanry[1], Rachel Fran Mansa[2], Moh Pak Yan[3,4], Tan Wei Hsiang[4], Noumie Surugau[1,4*]

[1]Seaweed Research Unit, Faculty of Science and Natural Resources, Universiti Malaysia Sabah, Jalan UMS, 88400 Kota Kinabalu, Sabah, Malaysia

[2]Faculty of Engineering, Universiti Malaysia Sabah, Jalan UMS, 88400 Kota Kinabalu, Sabah, Malaysia

[3]Water Research Unit, Faculty of Science and Natural Resources, Universiti Malaysia Sabah, Jalan UMS, 88400 Kota Kinabalu, Sabah, Malaysia

[4]Industrial Chemistry Programme, Faculty of Science and Natural Resources, Universiti Malaysia Sabah, Jalan UMS, 88400 Kota Kinabalu, Sabah, Malaysia

*Corresponding Author: N. Surugau (email: lnoumie@ums.edu.my)

ABSTRACT

Seaweed and cellulose are promising naturally occurring polymers. This article discusses the basic knowledge and recent advances of both seaweed and cellulose biopolymer products and analyses the feasible formation of seaweed/cellulose composite films. Both seaweed and cellulose show intriguing film-forming properties. However, the seaweed has a weak water vapor barrier and mechanical properties due to its hydrophilicity in nature, while cellulose is a strong crystalline structure. The alteration of these hydrocolloids has also been performed to exploit their beneficial properties. To optimize desirable characteristics, the blending of biopolymers is recommended. Besides that, comparisons between two different nanocellulose and their isolation method is being further discussed. From the study, seaweed is well compatible with cellulose, which has outstanding mechanical, water-resistant properties and biodegradable.

Keywords: Seaweed biopolymers, Plant celluloses, Cellulose nanocrystals, Biodegradable plastics

1.0 INTRODUCTION

Scientists first recorded plastic waste in the ocean in the 1970s, yet it has received considerable media interest in recent years and a growing array of scientists spanning from numerous fields, including ecology, environmental engineering, marine biology, polymer science, toxicology, and oceanography. Phenomena such as litters piling on the coastlines, aquatic animals trapped in fishing nets, or found undigested plastics in their stomach, have been jeopardizing the environment, portraying the essence of pollution. (Law, 2017). Many synthetic devices and materials have been produced to meet human needs over the years. Such synthetic products have a potential effect on the environment and life, creating harmful impacts on soil, water, and climate (Geyer *et al.*, 2017; Stafford and Jones, 2019). To create sustainable materials that are easily disposable yet not environmentally damaging, intensive study has also been carried out (Jumaidin *et al.*, 2016).

Nowadays, natural material biopolymer attracts more attention because it is a realistic alternative to the deposition of petroleum-based plastic in the environment. Starch serves as one of the most convincing biopolymer manufacturing materials because it is readily available, low cost, biodegradable, renewable and can portray thermoplastic properties in the presence of plasticizer (Jumaidin *et al.*, 2016). However, the usage of starch was being restricted in the industry and market due to some limitations such as low water barrier properties and low mechanical characteristics (Doh, 2020; Jumaidin *et al.*, 2016).

Recently, seaweed biopolymers, also known as phycocolloids, have become highly common in the field of biodegradable materials and are likely to revolutionize the bio-plastic industry, as these biopolymers come from feedstock that are non-food crops such as algae and their by-products (Freile-Pelegrín & Madera, 2017). In addition, seaweed derivatives such as alginate, carrageenan, and agar are widely used in the food industry as thickening, stabilizing, and suspension agents (Abdul Khalil *et al.*, 2018). According to Shit and Shah, in terms of pharmaceutical applications, alginate is used in the preparations of medications such as (Gaviscon, Bisodol and Asilone). However, the downside is the

hydrophilicity properties of seaweed that caused the films formed to have weak water-resistance properties and mechanical properties. For instance, past researches have shown that the incorporation of two or three biopolymers by using various method could improve the properties of the film and to overcome the poor properties (Ghanbarzadeh *et al.*, 2010).

Cellulose is also one of the polysaccharides that form hydrocolloids and are most abundantly available. This makes cellulose a brilliant material for film-making. Past researches has demonstrated that bioplastics produced from cellulose exhibit high water-resistant properties and microwave heating. Cellulose is also able to blends with other hydrocolloids, which makes its possibility become widen. Based on Sudharsan *et al*, polymer matrix that is being reinforced by cellulose possesses an increase in tensile strength and film's rigidity.

This review paper aims to discuss the compatibility between seaweed and cellulose, the different types of cellulose and method of isolating cellulose from various sources. The properties and future development of biofilm will also be focused on and discussed.

2.0   Seaweed: Biodegradable Polymer Matrices

Alginate, agar, and carrageenan are of the example of naturally occurring polysaccharides derived from various varieties of seaweed (Abdul Khalil *et al.*, 2017) such as brown seaweed and red seaweed. Not only are these products easy to be isolate, but they are also cheap. Seaweeds have recently received a great deal of interest and recognition in

terms of application to food, medical engineering, biosensors, and drug delivery systems (Venkatesan *et al.*, 2016). Based on the studies from

Since strong interactions can be formed by the polysaccharides isolated from the seaweed matrix, they have benefits for use as precursors for film-forming materials. Film-forming biopolymers extracted from seaweeds possess properties such as high rigidity and low deformability. Besides that, it is also non-toxic, degrade easily in the environment, and biocompatible (Doh, 2020). Figure 1 and 2 belows shows the gelling properties of seaweed derivatives that are used as a backbone of biopolymer films.
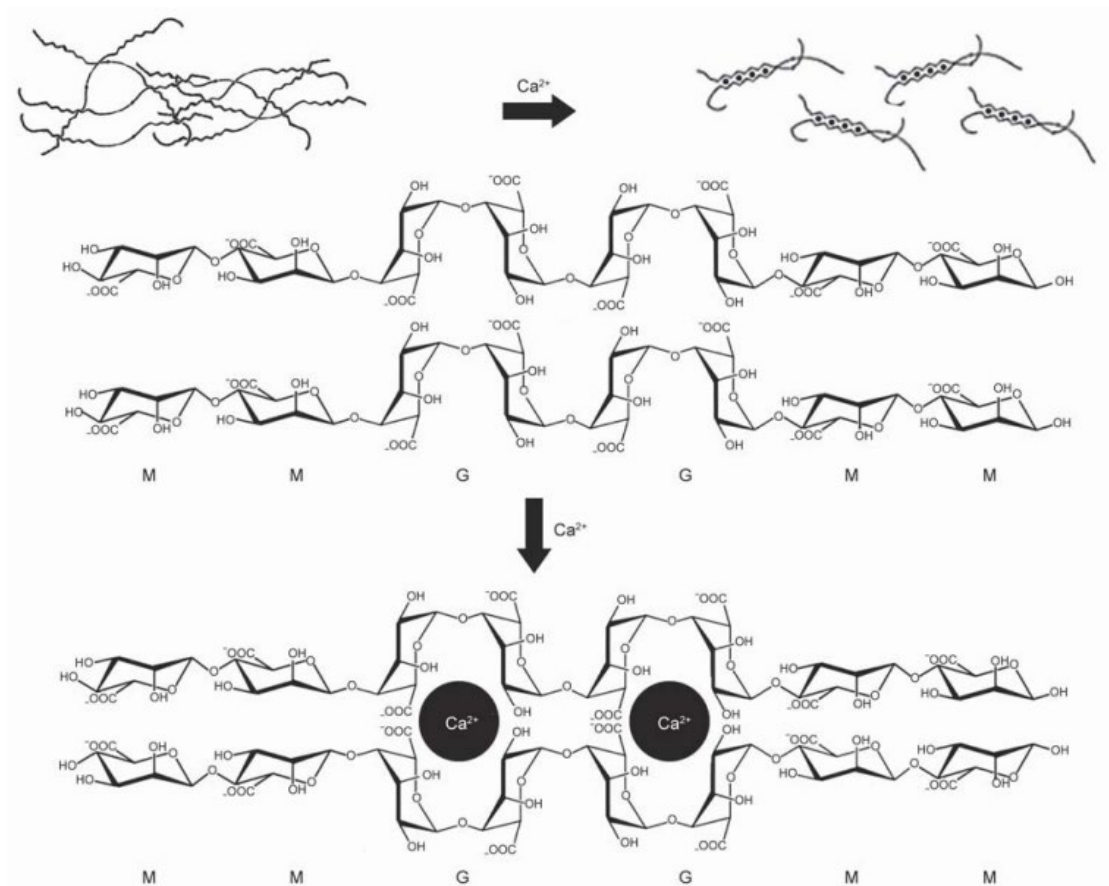
Figure 1: Gelling mechanism of calcium cross-linked alginate (Source: Abdul Khalil *et al.*, 2017; Doh, 2020; Tavassoli-Kafrani *et al.*, 2016).
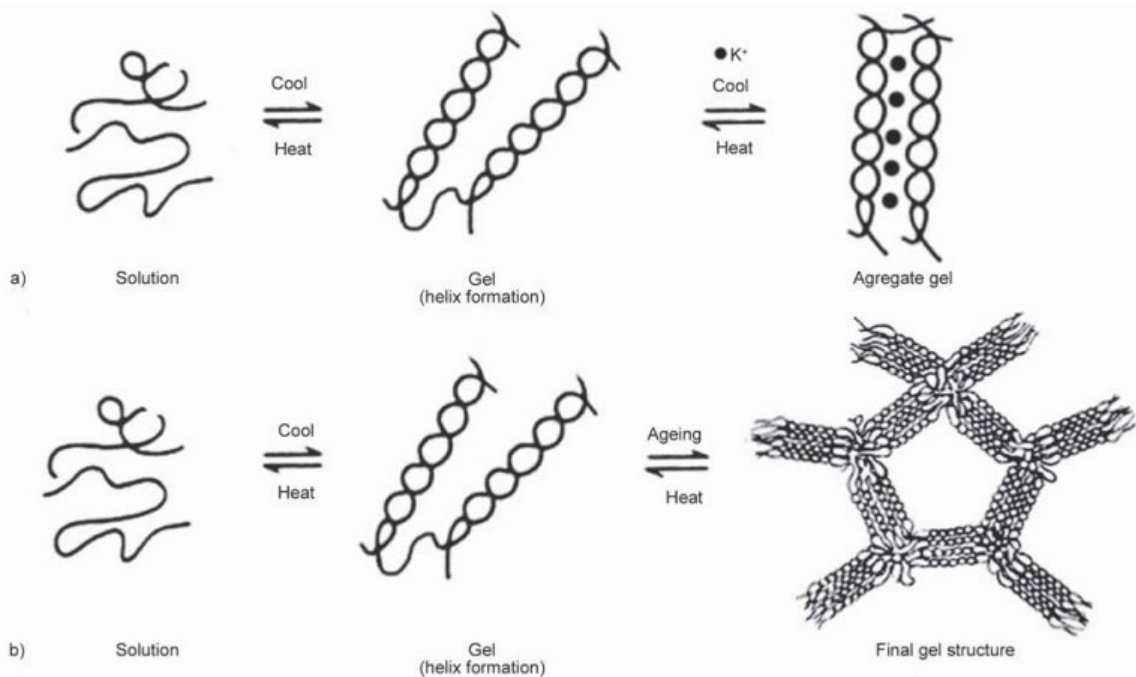
Figure 2: Gelling mechanism of a) carrageenan and b) agars (Source: Abdul Khalil *et al.*, 2017; Doh,2020; Tavassoli-Kafrani *et al.*, 2016).

However, seaweed films are extremely low in water tolerance due to the hydrophilic nature of seaweed extracts (Abdul Khalil *et al.*, 2017; Doh, 2020), in contrast, these are the features that make seaweed films less attractive for applications as food packaging (Freile-Pelegrín and Madera-Santana, 2017). For instance, the studies of incorporation of two polymer components are supported by a few scholars as it can improve the desired functions, harness their beneficial properties and extend their applications (Abdul Khalil *et al.*, 2017). Previous studies suggest that the addition to the alginate matrix of nanoparticles such as clay and silver nanoparticles will increase the mechanical strength and water vapour barrier (Abdul Khalil *et al.*, 2017; Shanker *et al.*, 2016). Moreover, studies have shown higher antibacterial activity in alginate films made with essential oils such as cinnamon bark oil, soybean oil, lemongrass oil, and garlic oil (Abdul Khalil *et al.*, 2017; Zhang *et al.*, 2015). Similarly, for carrageenan, some studies indicate that the addition of nanoparticles like nanoclays, silver nano-particulates, and chitin nanofibrils into the carrageenan matrix can reduce the permeability of the water vapour while increasing the mechanical characteristics of carrageenan film (Abdul khalil *et al.*, 2017; Fouda *et al.*, 2015; Shanker *et al.*, 2015; Shojaee-Aliabadia *et al.*, 2014).

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3.0   Cellulose: Reinforcement Component

Cellulose is a biopolymer that exists naturally abundant on earth. Because of its special properties such as renewability, biodegradability, high tensile strength and hardness, cost-effectiveness, lightweight, and environmental benefits, cellulose is commonly used for various industrial applications (El Achaby *et al.*, 2017). Cellulose is the key component of lignocellulosic biomass and is about 35-50% found in the plant cell wall (Phanthong *et al.*, 2018). The cellulose polymer is a linear homo-polysaccharide composed of β-1,4-glycosidic bonds bound together by D-anhydroglucopyranose units (AGU). With respect to its neighbour, each of the AGU is turned 180° and two AGUs form a cellobios unit, the smallest repeating unit in the polymer, next to each other. The figure 3 below shows the molecular structure of the cellulose polymer (Börjesson and Westman, 2015).
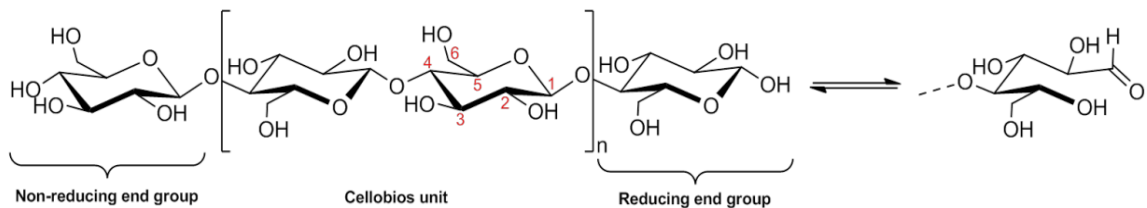
Figure 3: The molecular structure of a cellulose polymer, with cellobios unit and reducing end group that can be either free hemiacetal or an aldehyde (Source: Börjesson and Westman, 2015).

The cellobios unit consists of three hydroxyl groups that form a close hydrogen bond with the adjacent glucose unit in the same chain and the chains are called intramolecular and intermolecular hydrogen-bonding networks. In the crystalline sections of cellulose fibrils, these hydrogen bonding networks are strong and tightly packed, resulting in durable, strong, fibrous, water-insoluble, and high resistance to most organic solvents in plant cell walls (Phanthong *et al.*, 2018). Therefore, with the crystalline parts, cellulose are able to exhibit excellent mechanical properties (Abdul Khalil *et al.*, 2018). This is the main reason for cellulose being the choice of reinforcement components in a polymer matrix. Figure 4 below shows the parallel cellulose chain of intra- and inter-molecular hydrogen bonding of cellulose.
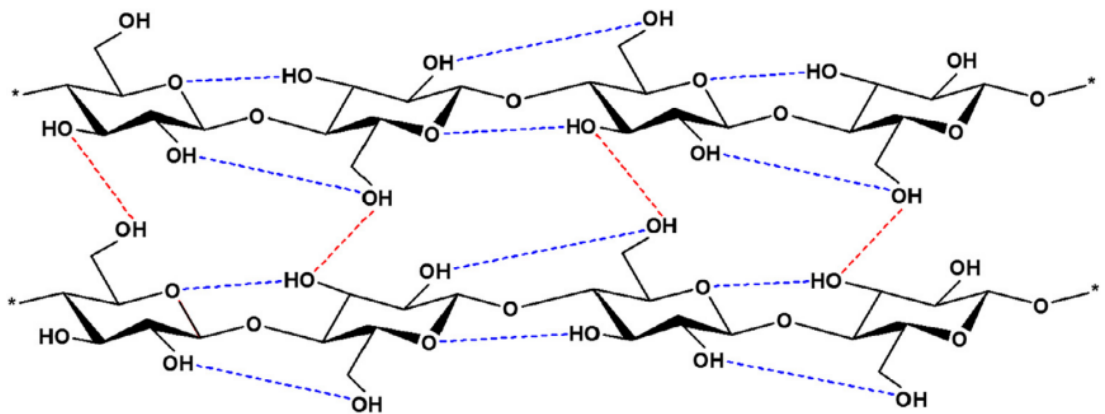
Figure 4: Cellulose chain of intra-(red line) and inter-(blue line) molecular hydrogen bonding (Source: Phanthong *et al.*, 2018).

For some parts in cellulose chains, which cannot be laterally stabilized by hydrogen bonding due to the absence of hydroxyl groups, they will form disordered amorphous fragments of holocellulose, bound to cellulose crystals. The chains for the amorphous regions of microfibrils are lower density and further apart compare to the crystalline regions. Besides that, the chains are more accessible for hydrogen bonding with other molecules such as water (Ng *et al.*, 2015).

3.1.1 Plant-based cellulose

The most abundant renewable polymer resource available today is cellulose from plant fiber, and it is known to be an almost limitless supply of raw material that can satisfy the growing demand for environmentally sustainable and biocompatible goods (Abdul Khalil *et al.*, 2017). We can obtain cellulose by isolating it from lignocellulosic sources such as cogon grass (Kassim *et al.*, 2015), Sugarcane bagasse (Kassab *et al.*, 2018), tara gum (Ma and Wang, 2016), rice husk (Johar and Dufresne, 2012), grapefruit seed (Kanmani and Rhim, 2014), pomelo (Mat Zain, 2014) and etc.

The extracytoplasmic matrices are the plant cell walls of each of the plant cells, which are not a homogeneous membrane but a complex layered structure composed of a thin primary wall that is surrounding the secondary wall (Ng *et al.*, 2015). Figure 5 below shows the morphology of plant cell wall.
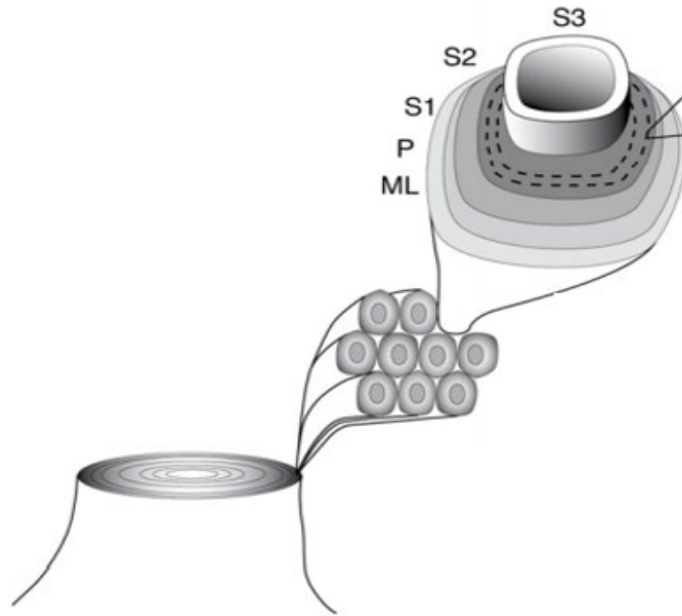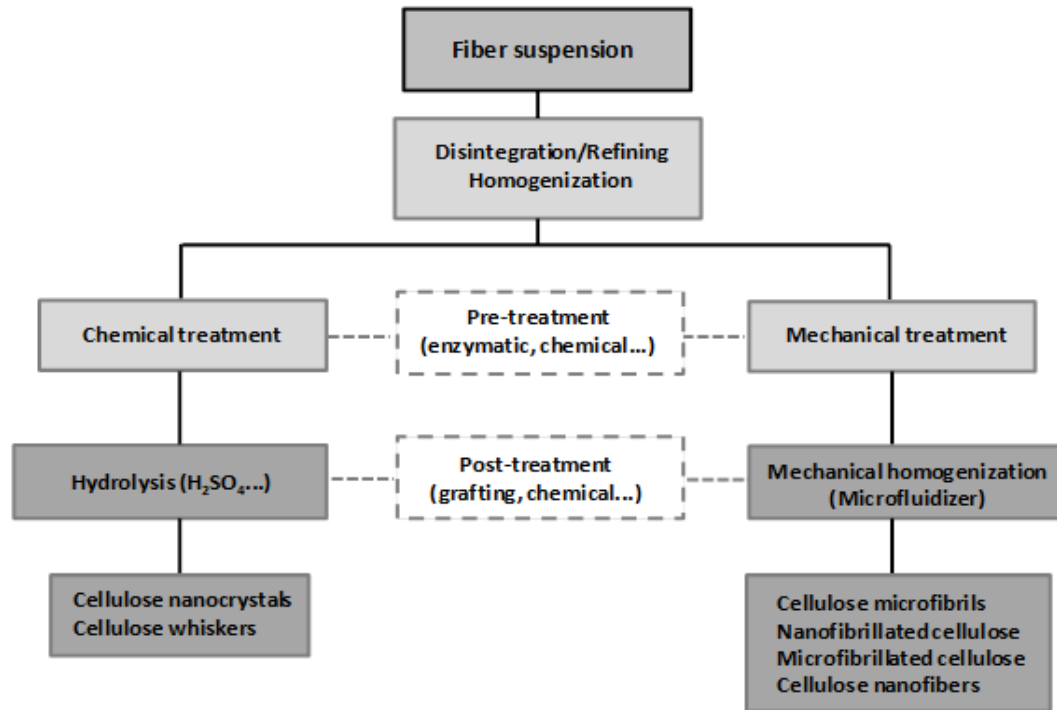
Figure 5: The morphology of plant cell wall, where (S1, S2, and S3) are the secondary layers while S2 is the thick middle layers (Source: (Börjesson and Westman, 2015).

The secondary wall is composed of three layers, while the thick middle layer plays an important role in preserving the structure and rigidity of the plant due to this layer consisting of multiple cellulose fibers as seen in figure 5. Cellulose fibers can essentially be treated as naturally occurring compounds composed of cellulose, lignin, and hemicellulose, though it is often referred to as lignocellulosic natural fibers (Ng *et al.*, 2015).

In general, the cellulose in plant fibers existed as a type of microfibrils and was surrounded by lignin, hemicellulose, and pectin cementing matrix (Abdul Khalil *et al.*, 2017; Ng *et al.*, 2015). Several processes chemically or mechanically can be performed on the plant in order to remove the non-cellulosic material in order to extract pure cellulose content. Figure 6 below shows a schematic diagram of chemical and mechanical treatment to obtained cellulose from fibers.

```mermaid
Fiber suspension
  → Disintegration/Refining Homogenization
      → Chemical treatment
          → Hydrolysis (H₂SO₄...)
              → Cellulose nanocrystals / Cellulose whiskers
      → Mechanical treatment
          → Mechanical homogenization (Microfluidizer)
              → Cellulose microfibrils / Nanofibrillated cellulose / Microfibrillated cellulose / Cellulose nanofibers
  Pre-treatment (enzymatic, chemical...)
  Post-treatment (grafting, chemical...)
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Figure 6: Schematic overview of chemical and mechanical approaches to obtained cellulose from plant fiber (Source: Johansson *et al.*, 2012).

3.1.2 Nanocellulose

Nanocellulose (NC) is referring to cellulose nanocrystals (CNCs) and cellulose nanofibrils (CNFs) (Isogai, 2017; Kargarzadeh *et al.*, 2018; Su *et al.*, 2018). Due to their high availability, strength and stiffness, low weight, and biodegradability, nanoscale cellulose

fibers are a promising candidate for the preparation of bio-nanocomposites. The packaging industry is one field in which nanoscale-enhanced polymer films are of importance, and there are a wide variety of nanocellulose applications. Films produced from nanocellulose can be achieved in competition with unfilled polymeric films with high transparency and better mechanical and barrier properties (Johansson *et al.*, 2012; Su *et al.*, 2018).

Nanocellulose is obtained from sources like wood from the forest resources which include softwood and hardwood, non-wood which consists of agricultural waste or lignocellulose (e.g. kenaf fibers, cotton, rice husk, wheat straw, sugarcane bagasse and etc). (Abdul Khalil *et al.*, 2017; Ng *et al.*, 2015). In addition to wood and plants, cellulose can also be extracted from different bacterial species, seaweed, and sea animal (tunicates) which are composed of proteins and carbohydrates (Börjesson and Westman, 2015). These cellulose in the plant cell wall exhibit a conglomerate structure, therefore a thorough understanding on the plant morphology and physical is very important. Figure 7 below shows a schematic diagram of cellulose fibers with emphasis on microfibrils bundles composed of amorphous and crystalline regions (Ng *et al.*, 2015).

Figure 7: Schematic diagram of cellulose fibers with emphasis on microfibrils bundles composed of amorphous and crystalline regions (Ng *et al.*, 2015).

At figure 7 above, we can see that microfibrils are packaged or assembled together to form macrofibril or better known as microfibrillated cellulose (MFC) (Börjesson and
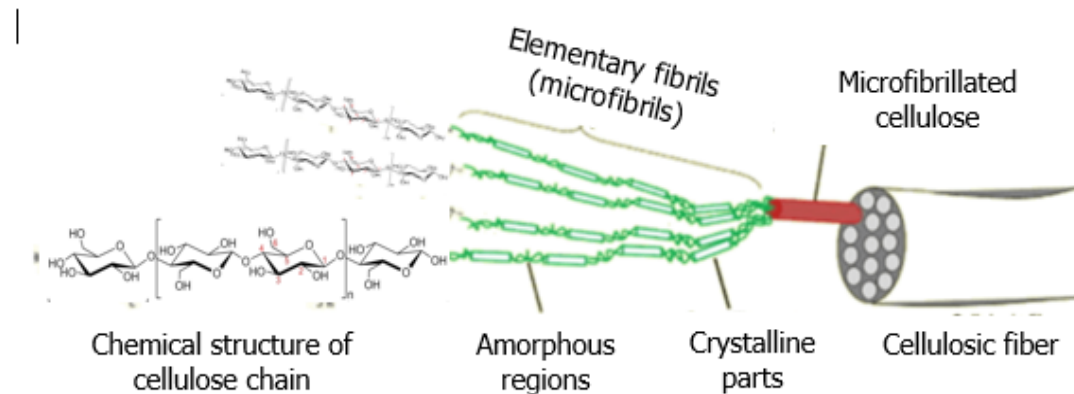
Westman, 2015; Ng *et al.*, 2016). As we all know, microfibrils are not crystalline because the amorphous (or para-crystalline) phases occurred alternatively along the microfibrils

axis in the crystalline domains (or whiskers), whereas such crystalline structure is known to be one of the nanocellulose, cellulose nanocrystal (CNC). Nanofibrillated cellulose (NFC) is another type of nanocelulose, which actually is an isolated microfibril. It exhibits a web-like or network structure under SEM image (Ng *et al.*, 2016).

CNFs is sometimes being referred to as nanofibrillated cellulose (NFC), and sometimes interchanged with microfibrillated cellulose (MFC) (Abdul Khalil *et al.*, 2017; Johansson *et al.*, 2012), because the only distinction between the classification is additional mechanical processes, often complemented by enzymatic and chemical processes, for the case of NFCs (Su *et al.*, 2018). According to Abdul Khalil *et al*, Johansson *et al*, and Su *et al*, a significant level of energy input are needed for the mechanical fibrillation process, and the resulting fibril may suffer the loss of yield and length. Therefore enzymatic pretreatment serves as an alternative solution in resulting finer fibril scale and cost-effective. In addition, CNFs portray characteristics of high aspect ratio, durability, high specific surface area, and abundance of hydroxyl groups (Su *et al.*, 2018).

Cellulose nanocrystals, which are also commonly referred to as nanocrystalline cellulose, crystallites, whiskers, and rod-like (Abdul Khalil *et al.*, 2017; Ferrer *et al.*, 2017). CNCs are often prepared by an acid-hydrolyzed method where the cellulose fibers undergo treatment with hydrochloric acid (HCl) or sulphuric acid (H_2SO4), which then further accompanied by mechanical treatment of sonication. The non-crystalline component of cellulose fibers are being vigorously hydrolyze due to the extreme acidic conditions. (Doh, 2020; Ng *et al.*, 2015; Ferreira *et al.*, 2018; Su *et al.*, 2018). CNCs have outstanding optical characteristics, mechanical features, well-defined dimensions and high aspect ratio. (Dufresne and Castaño 2017; Scaffaro *et al.*, 2017). These properties make possible CNCs as a reinforcement in packaging films (Scaffaro *et al.*, 2017). Due to the highly crystalline nature of CNCs, the oxygen barrier properties of packaging materials can be enhanced by using them as composite filler by increase both crystalline properties and the path for gas diffusions (Su *et al.*, 2018).

Table 1 below shows the summarized of two different types of nanocellulose, (CNF and CNC) (Source: Abdul Khalil *et al.*, 2017; Abdul Khalil *et al.*, 2017; Börjesson and Westman, 2015; Doh, 2020; El Achaby *et al.*, 2018; Ferrer *et al.*, 2018; Kargarzadeh *et al.*, 2018; Li

et al., 2018; Osong et al., 2015; Trache et al., 2016; Zarina and Ahmad, 2015; Zhang et al., 2016).

	CNF	CNC
Source	• Hardwood • Non-wood resources (agricultural crops and their by-product), such as wheat straw, sugarcane bagasse, pineapple leaf fibers, banana leaf, bamboo pulp, • cocoa pod husk, sugar beet pulp and etc.	• Hardwood pulp • Softwood pulp • Microcrystalline cellulose (MCC) • Lignocellulosic material, such as wheat straw, cotton, cogon grass, kenaf fibre, sugarcane bagasse and etc.
Isolating process	• High-pressure homogenizers • Micro-fluidizers • Ultrafine grinders • Other involves either chemical or enzymatic pretreatment combined with mechanical treatment	• High-pressure homogenization • Ultrasonic homogenization • Ball-milling or grinding processes
Structure	Semi-crystalline cellulose	Rod-like shape (rice-like or whiskers like)
Size and length	5 nm to 60 nm with wide range of lengths, typically several micrometers	2 to 30 nm, could be several hundreds of nanometers in length
Crystallinity	51-69%	54-90%
Aspect ratio (length/width)	50-100	10-100
Applications	• Network structure • Antibacterial support coating	• Earphones diaphrams • Drug delivery vehicle

• Packaging products	• Scaffolds in tissue engineering
• Dental application	
• Food coating	• Optical application
• Paper making carrier, binders and coating	• Rheology modifier

3.1.3 Cellulose nanofibrils vs Cellulose nanocrystals

In today advancement, one use of cellulose in composite materials is to improve its engineering polymer structures because of its excellent mechanical properties. Pure cellulose in various types with different mechanical characteristics is commonly available. The distinction between the types of cellulose depends on the shape, size and the particles' degree of crystallinity (Shokri, 2013).

Recent years, there has been much interest in the studies on various enhancing potentials in polymer matrix. Therefore, several methods for the preparation and separation of these fibril materials were suggested. Both MFC and CNF exhibit broad aspect ratios and some comparisons are anticipated as reinforcing materials; however, relative to MFC, extended mechanical fibrillation imparts complex fibril networks and much thinner fibrils to CNFs. It is very interesting to compare various forms of cellulose nanofibers as polymer reinforcing agents in nanocomposites. The performance of CNFs and CNCs as reinforcement materials for nanocomposites are being compare due to the differences between short rigid CNCs and long comparatively tough CNFs in terms of their reinforcement effects and mechanism (Xu *et al.*, 2013).

According to Su *et al*, (2018) CNFs consists of both crystalline and disordered amorphous regions. Consequently, the CNFs have a lower crystallinity and a higher aspect ratio (Abdul Khalil *et al.*, 2017; Börjesson and Westman, 2015; Jonoobi *et al.*, 2015; Ng *et al.*, 2015; Ng *et al.*, 2016). It is this disparity that gives the pure film of CNFs excellent properties in terms of oxygen barrier due to its increasing tortuosity and entanglements. On the other hand, CNCs exhibit high crystallinity that are able to improve the mechanical properties of resultant biocomposites (Abdul Khalil *et al.*, 2017). Primarily, crystalline properties are advantageous in barrier properties, because molecules are less able to reach

the crystalline regions. As a result, the water resistance and water vapour barrier can be improved (Helanto *et al.*, 2019).

Following the studies from Achaby *et al*, (2018), Criado *et al*, (2016), De Mesquita *et al*, (2012), Doh and Whiteside, (2020), Kassab *et al*, (2018) Ma and Wang, (2016), Miranda *et al*, (2015) and Reddy and Rhim (2014), film that are incorporated with CNCs have improvement in terms of mechanical properties. Besides that, Ng *et al*, (2015) stated that CNCs are more favourable as load-bearing constituents due to its excellent ability to enhance strength and stiffness by interfacing interaction between the CNCs with matrix. In addition, the highly versatile fibrils of CNFs are being characterized by being several micrometers long and with a higher aspect ratio than CNCs, to form rigid web-like fibril networks that were supposed to provide greater reinforcement. However, these characteristics would be disadvantageous in CNFs in terms of dispersion in polymer matrix during extrusion compounding, due to coaggregation and strong entanglement between the long nanofibrils through strong hydrogen bonding, and thereby limiting the well-dispersion of fillers. Moreover, due to the amorphous regions in CNFs with imperfect axial orientation that could not be removed by mechanical fibrillation, not only it leading to a lower density compared to nanocrystalline regions, but also not contributable to the mechanical properties of filler and even composites. Thus, Ng *et al*, (2015) and Abdul Khalil *et al*, (2017) suggested that CNCs is of particular interest to apply as reinforcing agent in polymer. However, Ferrer *et al*, (2017) stated that nanocellulose has strong barrier properties, especially in terms of oxygen, it may be attributed to the dense structure of the network that nanofibrils form. The density can be due to the small, uniform particle sizes in the case of nanocrystalline cellulose. In the case of nanofibrillated cellulose, the intrinsic versatility of the wet substrate strengthens the densification. Studies from Deepa *et al*, (2016), Babaee *et al*, (2015), Kaushik *et al*, (2010), Savadekar and Mhaske, (2012), and Prakobna *et al*, (2015) shows that film produced from CNFs improved in terms of air permeability. While film produced by Sirviö *et al*, (2014) exhibit grease barrier properties.

The pores that exists inside the films act as the primary route for permeating oxygen molecules, according to Nair *et al*, (2014). Meanwhile with intrinsic durability, CNFs will be able to create a denser film, locking much of the gaps between the fibrils down to

a molecular size. This is supported by Su *et al*, (2018) saying that the higher aspect ratio along with the high surface area contributes to a denser network of CNFs film with further entanglements. As an outcome, the pathway for gas molecules diffusion increases, and better barrier properties can be seen by the film. Xu *et al*, (2013) concluded that the findings of this comparative analysis are significant for the proper selection of nanocellulose materials as reinforcement agents in polymer composites. Table 2 below shows the incorporation of nanocellulose in different types of polysaccharides film.

Cellulose	Polysaccharides -based film	Loading level	Plasticizers	Film improvement	Ref
CNC from *Sargassum fluitans*	Alginate	0-10wt%	Glycerol	Tensile strength, Young Modulus, water vapor, oxygen, light barrier and thermal stability increased	Doh and Whiteside, 2020
CNC from paper-mulberry (*Broussonetia kazinoki Siebold*)	Agar	1-10wt%	Glycerol	Tensile strength, Elongation at break and water vapor barrier properties improved	Reddy and Rhim, 2014
CNC from sugarcane bagasse	Kappa-carrageenan	1-8wt%	Glycerol	Tensile strength and Young's Modulus improved	Kassab *et al.*, 2018
CNC from CMF	Alginate	1-8wt%	Glycerol	Tensile strength and Young's Modulus improved	Achaby *et al.*, 2018

CNC from gravata fibers	Starch	0.5-3wt%	Glycerol and Lignin	Tensile strength, elongation at break, thermal properties and barrier properties of film is improved	Miranda *et al.*, 2015
CNC from Eucalyptus wood pulp	Chitosan	5-8wt%	Acetic acid	Tensile strength and hydrophobicity of the films are improved	De Mesquita *et al.*, 2012
CNC from microcrystalline cellulose (MCC)	Tara gum	2-8wt%	Glycerol	Tensile strength, elastic modulus , contact angle measurement and oxygen permeability are improved	Ma and Wang, 2016
Freeze-dried CNC	Gellan gum	0-20wt%	Glycerol	Tensile strength and barrier properties are improved	Criado *et al.*, 2016
Commercial CNF	Chitosan	1-32wt%	Acetic acid	Tensile strength and Young's Modulus increased	Wu *et al.*, 2014
CNF from sisal fibers	Alginate	2.5-15wt%	Glycerol	Water-resistance and mechanical properties of the film improved	Deepa *et al.*, 2016
CNF from wheat straw	Starch	5-15%	Glycerol	Tensile modulus and water vapor permeability improved	Kaushik *et al.*, 2010

Commercial CNF	Chitosan	5-20wt%	Acetic acid	Tensile strength, elongation at break, thermal stability, and storage modulus increased	Fernandes *et al.*, 2010
CNF from bleached birch pulp	Alginate	0-50wt%	Calcium	Show improvement in mechanical and grease barrier properties	Sirviö *et al.*, 2014
CNF from short staple cotton	Starch	0.1-1.0wt%	Glycerol/acetic acid	Tensile strength, storage modulus and air permeability improved	Savadekar and Mhaske, 2012
CNF from Softwood floor	Starch	5-20wt%	Sorbitol	Young's modulus, tensile strength and air permeability increased	Hietala *et al.*, 2013
CNF from kenaf bast fibers	Starch	10wt%	Glycerol	Tensile strength, Young's modulus, storage modulus, air permeability and biodegradable	Babaee *et al.*, 2015
CNF from spruce sulphite pulp	Starch	77-85wt%	N.S.	Tensile strength and air permeability increased	Prakobna *et al.*, 2015

4.0   Isolation process of Nanocellulose

Cellulose can be derived from a wide variety of plants, animals, and bacteria. The source is very significant because it may influence the size and properties of the cellulose obtained (Kargarzadeh *et al.*, 2017). The various types of cellulose sources and different pretreatment conditions give rise to a variety of different shapes, surface charge, aspect ratio, and dimensions, which can vary from source to source (Börjesson and Westman, 2015; Joonobi *et al.*, 2015; Ng *et al.*, 2015; Shen *et al.*, 2017). In general, methods that mitigate cellulose degradation are usually favored (e.g. limited morphological changes, degree of crystallinity, and molecular weight) (Johansson *et al.*, 2012), therefore to achieve the requirement, extreme conditions such as high temperature, intense acid hydrolysis and prolonged time during treatment should be prevented (Ng *et al.*, 2016).

In order to extract nanocellulose from cellulose fibers, lignocellulosic biomass needs to undergo a series of treatment. The process consists of four main stages: (1) pretreatment to reduce the size of lignocellulose structure, (2) bleaching or delignification, (3) acid-hydrolysis, and (4) mechanical dispersion (Doh, 2020; Martelli-Tosi *et al.*, 2020; Ng *et al.*, 2015). Acid hydrolysis treatment is used to produce CNCs, while mechanical treatment is used to obtain CNFs (Kargarzadeh *et al.*, 2018).

4.1.1 Cellulose Nanocrystals

Acid hydrolysis is a process that involves the dissociation of cellulose fibers at the amorphous regions while retained the crystalline regions. Moreover, studies from Hernández *et al*, (2018) shows that CNCs can also be prepared using organosolv treatment. The resulting CNCs have higher yield with lesser ash content and has diameter sizes of 45 ±7.8 nm, and length size of 195 ±37.2 nm. However, there are a few parameters that should be taken into accounts for acid hydrolysis process such as the reaction temperature, reaction time, and concentration of acid. Extreme conditions will affect the properties of CNCs in terms of morphology and crystallinity (Börjesson and Westman, 2015; Doh, 2020).

This process is then followed by multiple post-treatment steps, such as centrifugation or dialysis, to remove the excess acid and ultrasound (Shen *et al.*, 2017). In addition to that,

the concentrated acid used in this process is mainly common acids available such as sulphuric acid (H_2SO_4), hydrochloric acid (HCl), oxalic acid, hydrobromic acid (HBr), and nitric acid (HNO_3) (Ng *et al.*, 2015). Sulphuric acid is the commonly used acid for the acid hydrolysis process (Doh, 2020), this is because, during acid hydrolysis, the acidic sulfate groups ($-SO_4^{2-}$) were left on the surface of CNCs, resulting in CNCs yielding negative surface charge, which results from the formation of sulfate half-ester groups Thus, the negative charges serve as a mean for CNCs to form a stable colloidal dispersions with polymer matrix (Doh, 2020; Hubbe *et al.*, 2017; Ng *et al.*, 2015). However, Yu *et al*, (2013) compared the reinforcing effects of two CNCs obtained from different acid mainly sulphuric acid and hydrochloric acid and the result from the studies shows that the film reinforced with CNCs treated with hydrochloric acid shows better performance in terms of mechanical and thermal properties compared to film that reinforced with CNCs treated with sulphuric acid.

4.1.2 Cellulose Nanofibrils

CNFs, unlike CNCs formed by mechanical treatment, which retains the non-crystalline sections and the length of the fibrils. The pulp fibers undergo mechanical treatment that consists of pulp refining, and accompanied by process of high pressure homogenization to extract individualized nanofibrils (Börjesson and Westman, 2015). Before mechanical treatment, all the unwanted material such as lignin, hemicellulose, and pectin that bind to the fibril structure must be removed as these cementing material could possible decrease the performance of cellulose obtained in terms of ratio of crystallinity, and mechanical and thermal stability (Ng *et al.*, 2015). Besides that, another reason for pretreatment is to reduce the energy consumption at the stage of mechanical treatment. The chemical pretreatment include refining and cryochrusching. These process facilitate the later process by unlooses the fiber wall and exposing the cellular wall fragments. The resulting individualized nanofibrils is then takes place in the high-pressure homogenizer (Börjesson and Westman, 2015). In the homogenizer, size reduction is achieved via significant pressure drop, strong shear forces, interparticles collisions and turbulent flow. Combination of high pressure and forces on cellulose fibers will gives high degree of

microfibrillation and thus results in cellulose nanofibrils solution (Börjesson and Westman, 2015; Kargarzadeh *et al.*, 2017).

4.2   Compatibility of Seaweed and Cellulose

A promising polysaccharide that can act individually as a polymer matrix to manufacture edible films and coatings is certainly seaweed and cellulose. However, owing to its hydrophilicity in nature, there are certain restrictions on films made from seaweed and hence the film exhibits low water resistance properties (Abdul Khalil *et al.*, 2017). Therefore, to solve this undesired problem, reinforcement techniques has been carried out such as blending, composites, plasticization, crosslinking, and grafting. The definition of a composite film has been noted with high interest among these strategies, which is described as a reinforcement agent added to the backbone polymer matrix with physicochemical interaction since it leads to the enhancement of general film properties (Miao and Hamad, 2013). Because of the chemical homogeneity of composition, plant cellulose is said to be suitable to promote the mechanical and barrier properties of seaweed film (Abdul Khalil *et al.*, 2017). According to Johansson *et al*, (2012) and Shen *et al*, (2017) hydrophilic biopolymers and hydrophilic nanosized fillers are easily compatible. This can be observed as cellulose consists of three reactive hydroxyl groups, while seaweed has hydrophilic surface groups, which consists of hydroxyl, carboxyl, and sulphate group which make them highly compatible. It can be seen that after the incorporation of seaweed and cellulose, the mechanical and water resistant characteristics have been enhanced. This can be described by the relationship between intermolecular connections and molecular compatibility where a strong 3D continuous hydrogen-bonding network formed between the filler and matrix as a consequence of the crystallinity existence of cellulose derivatives in terms of mechanical properties, which involve tensile strength and even elongation at break (Abdul Khalil *et al.*, 2017; Deepa *et al.*, 2016). Similar mechanical performance had been reported with other biopolymers such as agar and alginate (Doh and Whiteside, 2020; Shankar and Rhim, 2016).

For the water resistance properties, powerful hydrogen bonds formed between the seaweed/cellulose reinforced, where hydroxyl groups from cellulose and hydroxyl,

carboxyl groups from seaweed experience strong interactions through hydrogen bonds that increase the cohesion of the biopolymer matrix and result in a decrease in water permeability (Deepa *et al.*, 2016). Figure 8 below indicates the pattern of the tortuous course of water derived from the addition of CNCs.
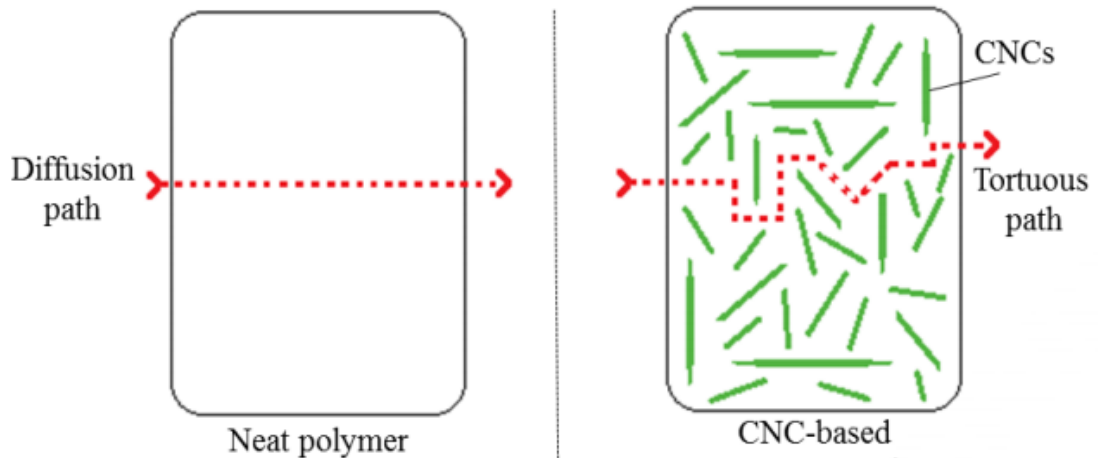
Figure 8: Schematic representation of the tortuous course of water derived from the addition of CNCs (Source: Ferreira *et al.*, 2018).

We can observed clearly that CNCs serve as blocking agents within the polymer matrix, leading to a complicated pathway for water and gas molecules, and even light (Doh,2020). However, research paper of Sirviö *et al*, (2014) reveals that by increasing the volume of cellulose fibers with a decrease in scale shows better results. This is because compared to microscale dimensions, nanosize measurements implied greater surface area and surface atoms (Abdul Khalil *et al.*, 2017). Interactions between nano-elements and the seaweed matrix therefore indicated a much stronger percolated network linked in the interphase region by hydrogen bonds (Ma and Wang, 2016).

5.0   Properties of nanocomposites reinforced with CNCs

5.1.1 Mechanical Properties

Recently, attention among the researchers are focused on biodegradable composite films prepared using a hydrocolloid mixture. This is due to the chemical similarity of hydrocolloids that offers the advantageous associations and thereby improving the films properties, such as mechanical properties (Abdul Khalil *et al.*, 2017). The addition of CNCs to the polymer matrix is critical for achieving the necessary mechanical properties of nanocomposite films (Doh, 2020). Mechanical properties serves as an important properties especially in the food packaging. Tensile strength, elongation at break and Young's modulus are the measures for mechanical properties (Doh and Whiteside, 2020). Tensile strength is being defined as the highest tensile stress that the sample film can withstand during the tension test. Meanwhile, elongation at break is the potential for flexibility and elongation until the films begins to crack. Young modulus is a measure of film's stiffness as the film is vertically extended by tensile stress (Othman *et al.*, 2019).

Previous studies from Doh and Whiteside (2020), who prepared alginate nanocomposites (Alg/CNCs), where the CNCs is being extracted from *Sargassum fluitans* reported an increase in mechanical properties after the addition of CNCs to the film. When the CNCs were added at 1%, 3% and 5 wt%, the tensile strength of the films increased by 13.7%, 21.7% and 35.5%. However, when the addition of CNCs increase to 10%, the tensile strength only increase by 17.7% and indicated that the tensile strength was lower in compare to 3, and 5 wt% in Alg/CNCs films. Besides that, elongation at break showed a trend of gradual decrease as tensile strength increased in the film (Doh and Whiteside, 2020). On the other hand, Ma *et al.* achieved a quite similar outcome, when the CNCs is added at 2%, 4% and 6 wt%, the tensile strength of the films increased from 17.60 MPa to 65.73 MPa at the addition of 6 wt% of CNCs respectively. However, the tensile strength decrease to 40 MPa when CNCs increased to 8 wt%. While in the case of elongation at break, the value reduced with increasing amount of CNCs. Meanwhile, the Young modulus showed a similar trend as tensile strength, the Young modulus of the film increased from 160 MPa to 882.49 MPa when CNCs was added in 6 wt% and decrease to 450.97 MPa when the amount of CNCs increased to 8 wt% (Ma *et al.*, 2016).

The overall mechanical enhancement in film is due to the relatively broad aspect ratio and high elastic modulus of CNCs that could depict the reinforcement effect on the polymer's mechanical properties. The key points required to achieve polymer nanocomposite films with improved final properties are the homogenous dispersion/distribution of CNC along with the desirable interfacial interactions between CNCs and the polymer matrix (El Miri *et al.*, 2015). Besides that, the addition of CNCs to the degree of theoretical threshold will cause to film to achieve homogenous dispersion. However, when too much CNCs was added to the film, the pattern of the film change from a percolated system to a non-percolated system, thus leads to agglomeration (Doh and Whiteside, 2020; Ferreira *et al.*, 2018; Ma *et al.*, 2016; Reddy and Rhim, 2014; Sung *et al.*, 2017; Vaezi *et al.*, 2020). This agglomeration not only causes stress levels within the polymer matrix, but can also reduce the elongation at break by dissipating additional stress by the interaction of particulate-polymer (Doh, 2020; Ferreira *et al.*, 2018). In addition, other factors like extraction methods, CNC surface modifying and nanocomposite film preparation methods can also influence the mechanical properties of the nanocomposite film (Ferreira *et al.*, 2018).

5.1.2 Biodegradability Properties

In recent years, biodegradation properties have been recognized as a crucial condition for the packaging industry. Since biopolymer-based materials can be an excellent option for addressing environmental problems such as global warming and accumulation of non-degradable conventional petrol-based waste to landfill, several research have studied the properties of biodegradation (Doh, 2020). Degradation is an inevitable mechanism leading to a substantial alteration in the composition of a substance, usually marked by a loss of properties (e.g. consistency, molecular weight, structure, or mechanical strength) and fragmentation, according to the American Society for Testing and Materials (ASTM) and the International Organisation for Standardization (ISO). Degradation is caused by environmental factors and continues over a span of one or more phases (Zambrano *et al.*, 2020).

Cellulose fibers stand out as a promising candidate to provide access to bioplastic composites for moisture and microbial enzymes. Studies also proved that the reactions of hydrolysis are no longer restricted to the exterior of a bioplastic phase by having access to enzymes and aqueous media. Cellulosic fibers can swell when moistened and the swelling may create cracks in the bio-polymer as a further contributing mechanism (Hubbe *et al.*, 2021). Figure below shows possible mechanism of hydrophobic polymer matrix being facilitate by cellulosic reinforcements in decomposition.
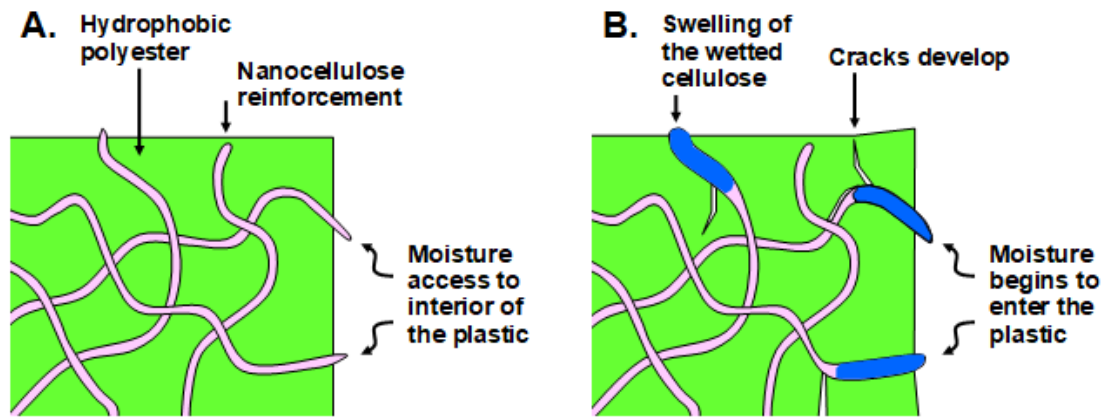
Figure 9: Mechanism of hydrophobic polymer matrix being facilitate by cellulosic reinforcements in decomposition (Hubbe *et al.*, 2021).

Previous studies from Hasan *et al.* reported that seaweed film that incorporated with microcrystalline cellulose (MCC) undergo soil burial test for biodegradability testing. After 7 days, the weight loss of pure seaweed can be seen to shrink and degraded. This is resulting from the hydrophilicity of seaweed in nature. Whereas the weight loss found in seaweed/MCC films was less significant relative to pure seaweed films from 7 to 14 days of burial periods. However, all the films have eventually experienced further shrinkage, cracks and the colour has changed from yellowish to black with a larger loss of weight (Hasan *et al.*, 2020). Besides that, Deepa *et al.* reported a similar result, in alginate film without cellulose nanofibril (CNF), it has shown degradability of up to 90% in soil while retained a 60% of moisture content in 35 days, while alginate nanocomposite films which included 10 wt% of CNF, displayed an average weight loss of approximately 60% with the same time span (Deepa et al., 2016).

Degradability in nanocomposite film manifest a lower degradability relative to pure seaweed film. This is due to the strong interaction of hydrogen bonding between cellulose and the seaweed matrix and also the high crystallinity of cellulose. As crystalline regions are more immune to hydrolysis, the degradation rate of the polymer matrix is influenced by crystallinity and crystal size of cellulose. This is turn improve the rigidity of the manufactured seaweed/cellulose composite films (Deepa *et al.*, 2016; Doh *et al.*, 2020; Ferreira *et al.*, 2018; Hasan *et al.*, 2019). Apart from that, another factors that affect degradation is plasticizer. Plasticizer like glycerol can weaken the attachment of seaweed polymer chains by opening up more void between chains. These indirectly enable water diffusion into the matrix and results in increased degradation by promoting more moisture to penetrate the films (Hermawan *et al.*, 2019).

6.0   Conclusion and Future work

Cellulose is the most plentiful natural polymer on Earth and a nearly inexhaustible supply for the manufacture of environmentally sustainable and biocompatible goods. Cellulose-based products have now been a significant bio-resource in the 21st century. Throughout the review, we can observed that seaweed/cellulose composite film offered advantages in the food industries especially food packaging. The film possess characteristics such as biodegradable, high mechanical and barrier properties which are ideal for packaging applications. The synergistic blends between nanomaterials and polymer matrix are able to portray properties similar to those traditional petroleum-based packaging. Their surface-to-volume ratio is high and it results in excellent stress-transfer and thus improve the mechanical properties within the nanocomposites. However, in order to fully replace traditional petroleum-based polymers, criteria such as environmental, social and economic sustainability should be taken into account, besides there are still many challenges still in question on this field. Their durability, renewability and unique structures pave the way for them to emerging economies.

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