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Abstract

Polysaccharide-based composite materials have been the recent research focus in the field of material science and engineering because of their biocompatibility, renewability, and sustainability. In this chapter, the authors attempt to review and discuss recent works in developing polysaccharide-based composites in applications of tissue engineering, drug delivery, and biopolymer-based film packaging. This chapter focuses on carrageenan, alginate, chitosan, starch, and cellulose composites. Introduction on these types of polysaccharides used as biomaterials is briefly discussed.

Keywords: polysaccharide, biomaterials, composites, renewable, biocomposites

1. Introduction

Biomaterials are defined as materials that are used in therapeutic or diagnostic procedure by interactions with components of living systems [1]. Over the years, synthetic polymers, ceramics, and metals were preferred for these types of applications due to their reproducibility and better performance. However, the growing concern on environment and health side-effects have promoted researches to look for naturally derived polymers. Biomaterials are designed to be inert and not to interact in biological systems and not to cause any harmful changes to the body. Polysaccharides are natural polymers found in plant and organism. The abundance of polysaccharide as a renewable resource promised its sustainability and economic value for biomaterials. Their production cost is less than any synthetic polymers and is easily processable.
Polysaccharides are polymeric carbohydrate molecules consisting of long chains of monosaccharide units bound by glycosidic linkages. The fact that these polymers are extracted from natural resources has led to the impression of good biocompatibility and biodegradability. Chemically, nearly all materials from plants are carbohydrate in nature and composed of repeating unit of monosaccharides. Thus, they are nontoxic. Its biocompatible nature is also attributed to the structural similarity of glycosaminoglycans (GAGs), which is a vital component of extracellular matrix in tissue. There is an emerging interest in reducing the amount of undisposable plastic waste that often leads to serious environmental problem. Polysaccharides are potential alternative for replacing conventional petroleum-based plastics which are able to biodegrade naturally in soil. Polysaccharides are famous for their used in the food and dairy industries. However, its unique structure and versatile modification can be explored for other important fields.

Polysaccharide can be categorized into structural and storage polysaccharides. Examples of structural polysaccharides are cellulose in plant and chitin in the shells of crustacean, while storage polysaccharides include starch and glycogen. Polysaccharides are present in most living organisms. In fact, polysaccharides comprise about 70% of the dry weight of the total biomass [2]. Although polysaccharide is advantageous as biomaterials as they are more ecofriendly than petro-polymers, there are still critical drawbacks that need special attention to make it an ideal choice. Polysaccharide exhibits poorer mechanical properties than the conventional plastics. Some polysaccharides also have strong hydrophilic behavior that may cause early rupture. Thus, polysaccharide composites have been extensively studied in regard to counter this problem and obtain additional properties for specific application.

2. Types of polysaccharide

Several types of polysaccharide were widely studied over the past decades due to their potential in numerous research areas. Some of the polysaccharides being explored as biomaterials are carrageenan, alginate, chitosan, starch, and cellulose.

2.1. Carrageenan

Carrageenan is a sulfated polysaccharide extracted from red algae. Marine organisms from Rhodophyceae family like Hypnea, Euchema, Chondrus, Crispus, and Gigartina are the main type of red seaweeds manufactured for carrageenan sources. Different types of red seaweed is used to extract different carrageenan, namely, kappa (κ), iota (ι), lambda (λ), nu (ν), mu (μ), ksi (ξ), and theta (θ). The structures of the three most prevalent and commercialized carrageenans are shown in Figure 1. Examples of some different sources of carragennans are Euchomadenticulatum (spinorum) for ι-carrageenan, Kappaphycusalsaverezi (cottoni) for κ-carrageenan, and Gigartinaradula and Chondruscrispus for extraction of both ι- and κ-carrageenans [3]. All types of carrageenans are water-soluble.

Carrageenans contain alternate units of D-galactose and 3, 6-anhydro-galactose linked glycosidically. As can be seen in Figure 1, κ-carrageenan has only one sulfate group per
disaccharide chain, two for ı-carrageenan, whereas λ-carrageenan got three. This resulted in anionic polysaccharide that is often neutralized by cations like sodium, potassium, calcium, magnesium, and ammonium. Interesting to note that the structure of λ-carrageenan does not have 3,6-anhydro-bridge like in the κ- and ı-carrageenans. This structure gives κ- and ı-carrageenans gelling ability in response to thermal condition. The location of ester sulfate group affects the solubility and gel strength of carrageenan, while existence of 3,6-anhydro-bridge results in polysaccharide gelation [5]. Besides galactose and sulfate units, other carbohydrate residues that commonly exist in carrageenan are xylose, glucose, and uronic acids [6]. Carrageenans are used in a variety of commercial applications as gelling, thickening, and stabilizing agents, especially in food products and sauces. Aside from these functions, carrageenans are being explored in experimental medicine, pharmaceutical formulations, cosmetics, and industrial applications.

Figure 1. Structure of carrageenan [4].

2.2. Alginate

Alginate, or also called alginic acid, can be derived from both algal and bacterial sources. Current commercial alginates are mostly from the cell walls of brown algae (Phaeophyceae) [7] such as Laminaria hyperborea, Laminaria lessonia, Macrocystis pyrifera, and Ascophyllum nodosum. They are harvested to be converted into raw material commonly known as sodium alginate. On the other hand, alginates that are synthesized by bacterial biosynthesis obtain more defined chemical structures and physical properties than that of seaweed-derived alginates [8]. These bacterial alginates can be produced from Azotobacter and Pseudomonas. Other common forms of alginates are potassium alginate and calcium alginate. Alginate are anionic polysaccharides that can form viscous gum when bound with water. They are composed of linear unbranched copolymers containing blocks of (1,4)-linked β-D-mannuronic acid (M) and α-L-guluronate (G) residues, covalently linked in different sequences or blocks. The blocks can be consecutive MMMMM or GGGGG, or alternating GMGMGM. The amount of G and M blocks and the length depends on the alginate origin. The gel formation of alginate occurs when two G blocks of adjacent chains chelate with cations like Ca2+ with their carboxylic groups [9].

Alginate is also another popular material used in foods as a thickening agent, gelling agent, emulsifier, stabilizer, and texture improver. It can be added to color paste for textile printing.
and act as binder of flux in welding rod production. Alginates are also established as biomaterials in the pharmaceutical industry where they can be compounded into tablets to accelerate disintegration of tablet for faster release of drugs. In cosmetic field, alginate can help to retain the color of lipstick on lip surface by forming gel network.

2.3. Chitosan

Chitosan is a natural aminopolysaccharide produced from partial alkaline deacetylation of chitin. Chitin, the second largest natural polymer after cellulose, is the structural element found in the exoskeleton of crustaceans, insects, and fungi. Just like plants produce cellulose in their cell walls, insects and crustaceans produce chitin in their shells. Chitosan is composed of linear copolymer of β (1-4) linked 2-acetamido-2-deoxy-β-D-glucopyranose and 2-amino-2-deoxy-β-D-glycopyranose. Different factors, such as alkali concentration, incubation time, ratio chitin to alkali, temperature, atmosphere, source of chitin, and particle size, play a role in affecting the properties of chitosan [10]. Chitin possesses poor solubility in aqueous solution and organic solvents mainly because of the highly extended hydrogen bonded semicrystalline structure of chitin, thus limiting its practical application in biomaterials [11]. Chitin has the degree of acetylation (DA) of 0.90 [12]. Whereas chitosan possess primary amino groups with pKa value of 6.3. These amines get protonated and form water-soluble and bioadhesive chitosan which readily bind to negatively charged surfaces [13].

Unlike chitin, chitosan has highly sophisticated functionality and wide range of applications in biomedical and other industrial areas. The advantage of chitosan over other polysaccharides is because of its cationic character and primary amino group [14]. Although they exhibit similar structure, chitosan display different properties from that of cellulose. When the degree of deacetylation of chitin reaches about 50%, it becomes chitosan and soluble in aqueous acidic media [15]. Chitosan has been applied in agriculture, water and waste management, food and beverages, cosmetics and toiletries, and biopharmaceutics.

2.4. Starch

Starch comprises of two main components: (1) amylose (Figure 2a), a nonbranching helical polymer consisting of α-1, 4 linked D-glucose monomers and (2) amyllopectin (Figure 2b), a highly branched polymer consisting of both α-1,4 and α-1,6 linked D-glucose monomers. All starches are biosynthesized as semicrystalline granules with small amount of water [16]. There are amorphous and crystalline growth rings arranged alternately encircling hilum which is the point of initiation of the granule. Starch gelatinization is done by heating native starch in water [17]. After heating, starch granules start to swell and burst. The semicrystalline structure is disrupted and smaller amylose molecules start to leach out of the granules. Gelatinization irreversibly dissolves starch granule in water where water acts as a plasticizer. It forms network that holds water and increase the solution viscosity.

Starch is a resourceful natural polymer where it can be found in many plant roots, crop seeds, stalks, and staple crops. Main sources of native starch are maize (82%), wheat (8%), cassava (5%), and potatoes (5%) [18]. Starch is produced by all green plants as source of stored energy.
They were used in many applications in the form of native and modified starches. Starches are popular in food making including bakery, dairy products, confectionery, and processed foods. Other nonfood industries using starches are papermaking, adhesives, clothing, and cosmetics. Starch also involves in production of antibiotics, vitamins, penicillin, and dialysis solutions.

2.5. Cellulose

Cellulose is a linear chain of ringed glucose molecules and has a flat ribbon-like conformation. It has the formula \( (C_6H_{10}O_5)_n \), where \( n \) depended on the source of cellulose linked by \( \beta(1\rightarrow4) \) glycosidic bonds. Cellulose is an essential structural component of cell walls in higher plants and is the most abundant organic polymer on the Earth. It is relatively stiff and rigid because of the intramolecular hydrogen bonding that can be reflected from its tendency to crystallize, high viscosity, and ability to form fibrillary strands [19]. Cellulose is insoluble in water and indigestible by the human body [20]. The glucose units in cellulose are linked by \( \beta \) glycosidic bonds, different than the \( \alpha \) glycosidic bonds found in glycogen and starch. Cellulose has more hydrogen bonds between adjacent glucose units, both within a chain and between adjacent chains, making it a tougher fiber than glycogen or starch. This is why wood is so tough. Wood, paper, and cotton are the most common forms of cellulose. The purest natural form of cellulose is cotton. Other than these, cellulose can also be produced by certain types of bacteria and they are called bacterial cellulose. While cellulose is a basic structural component in most plants, it is also produced in *Acetobacter, Sarcina ventriculi*, and *Agrobacterium*. Bacterial cellulose contains higher purity and water uptake capability compared to plant cellulose [21]. It has a tensile strength that is almost comparable to the Kevlar and steel and it can achieve stress-strain behavior resembling that of a soft tissue in never dried form [22].
3. Applications of polysaccharide composite biomaterials

Fabrications of polysaccharide-based composites containing different kind of reinforcements were subjected to many applications.

3.1. Tissue engineering

Tissue engineering and regenerative medicine have been important research areas that aim to repair and replace malfunction tissues or organs [23]. Assistive material or system is produced in order to support tissue generation which then can continue growing and functioning like original tissue in the body. Ideal three-dimensional (3D) tissue scaffolds must have certain characters to promote new tissue formation. Polymer-based material for 3D tissue scaffolds needs to possess high porosity, high surface area, suitable biodegradability, and good structural integrity. Human bodies are made up of complex and sensitive biological systems. Therefore, thorough attention needs to be taken in developing materials for tissue regeneration. Polysaccharide-based materials have since been of interest because of their important properties for biomedical application such as biocompatibility, biodegradability, and low cost [24]. They have acceptable response to the host and have ability to promote cell proliferation and adhesion. The emerging technology has investigated and explored many potential new forms of biomaterials for this purpose.

Halloysite nanotubes have been of interest since decades as biomaterials and fillers in composite scaffolds. A study by Liu et al. used this clay in alginate matrix to construct porous tissue engineered scaffolds [25]. They have successfully produced scaffold with 96% porosity. The composite scaffolds showed increased mechanical properties of alginate where higher compressive strength and modulus than pure alginate scaffold were obtained in dry and wet states. Halloysite nanotubes assisted in cell attachment and improved the stability against enzymatic degradation. Another attempt reported that chitosan/alginate/halloysite nanotube undergo amine treatment which later showed better cell growth and adherence than nonamminated composite scaffold [26]. Biomimetic synthetic scaffold was fabricated with inclusion of amorphous silica into alginate hydrogel [27]. They embedded bone cells, osteoblast-related SaOS-2 cells, and osteoclast-like RAW 264.7 cell into the hydrogel beads. The bead encapsulation of bone cells is a useful technique to produce bioactive programmable hydrogels. It is observed that it does not impair the viability of the encapsulated cells. Furthermore, incorporation of nanoceramic may improve the capability of polymeric scaffold for tissue regeneration. A study found that as-fabricated alginate/nano-TiO2 needles nanocomposites by lyophiliza-
A unique honeycomb composite of mollusca shell matrix and calcium alginate was fabricated to carry cells for soft tissue, skin, bone, and cartilage tissue regenerative therapies [29]. The composite was produced by frozen and treated mixture of Anodonta woodiana shell powder and sodium alginate with hydrochloric acid. It was transplanted into rats for 7, 14, 42, and 70 days. The composite displayed honeycomb structure under laser confocal microscope. This composite has significant mechanical properties, good biological safety over 70-day period, and lower degradation rate compared to the calcium carbonate (control). The regeneration of soft tissue requires substitutes that exhibit mechanical properties similar to native tissue. Thin saloplastic membranes from chitosan/alginate polyelectrolyte complexes containing different concentration of sodium chloride were prepared [30]. The membranes are resistant to degradation by lysozyme and stale at different pH. With high salt concentration, the water uptake and tensile moduli were increased, but decreasing the ultimate strength. High proliferation rates and viability of L929 fibroblasts were demonstrated. Structural modification to bacterial cellulose/alginate scaffold was constructed by two procedures, first is producing composite sponge bacterial cellulose/alginate (BCA) by crosslinking and freeze drying, and second is by reversing the previous procedure [31]. These procedures resulted in open and interconnected porous structure and thus lift up the problem of limited in vivo application due to dense outer layer of scaffolds.

3.1.1. Bone tissue engineering

Scaffolds fabrication in bone tissue engineering becomes preferable alternative to autografts and allografts which require surgical transplant of tissue or bone whether from the patient’s own body or from a donor, respectively. These procedures often suffer from limited availability and risks of immunogenicity [32]. The performance of scaffolds for hard tissue critically depends on their mechanical and biological properties. Reinforcement of nanomaterials inside polysaccharide matrix is always proposed to increase the material surface area for enhanced cell adhesion and proliferation.

A blend of alginate and chitosan was added with nanosized bioactive silica (SiO$_2$) particles to provide biomineralization capability and polymer stiffness [33]. The composite scaffolds showed increased protein adsorption, controlled swelling ability, and improved apatite deposition without significant cytotoxicity toward osteolineage cells. Nanoscale fibers have been suggested to be effective reinforcing agents because of their resemblance to the fibrous structures of bone tissue bone extracellular matrix (ECM). A composite was developed by unique combination of wet electrospinning, particulate leaching, and freeze drying of starch/silk fibroin [34]. Silk fibroin has slow degradation rate with high oxygen permeability and thus is suitable for slow regeneration of tissue. Hadisi et al. fabricated the silk fibroin nanofibers by wet spinning directly via wet electrospinning using methanol coagulation bath before incorporating the chopped electrospun nanofibers into the starch matrix, followed by particulate leaching and freeze drying. The silk fibroin-containing starch hydrogel was further coated with calcium phosphates for better compatibility with the surrounding tissues. The
viability of osteoblast-like cells (MG63) exposed to the composites’ extracts was significantly higher than that of the pure starch.

Hydroxyapatite (HAp) is the main inorganic component of natural bone that has been extensively used in many biocomposites to boost osteoconductivity and reinforce the structure of polymer-based bone scaffolds [35, 36]. The formation of bone-like apatite on scaffolds can be seen through the detection of calcium phosphates on the material surfaces. Incorporation of HAp nanoparticles in carrageenan [37], alginate [38, 39], cellulose [40, 41], and chitosan [42] displayed favorable site for bone cell adhesion and tissue regeneration compared to the neat polysaccharide scaffolds. The preparation of HAp-containing composites can be carried out either by using conventional mixing technique or by precipitating HAp crystals on the polymer matrices [36]. Mixture of two or more types of polysaccharides with HA like in Sharma et al. were believed to generate more synergistic effect to better mimic to the bone extracellular matrix, which comprises a variety of components [43].

3.1.2. Skin tissue engineering

Skin is the largest organ of human body. It serves as the first protection to human from environmental and surrounding threat. Fabrication of quaternary composite scaffold using chitosan, alginate, gelatin, and silk fibroin has successfully produced scaffold of 88% porosity with good mechanical stability [44]. L929 fibroblast cell cultured onto this quaternary composite scaffold showed good viability, adhesion, and proliferation, thus indicating the great prospect of the scaffold for skin tissue engineering. Boateng et al. studied two different methods for wound dressing to test their adhesive properties [45]. Solvent cast films and freeze-dried wafers containing polyethylene oxide (polyox) and carrageenan or sodium alginate. Wafers and films produced demonstrated high detachment force indicating strong interactions between polymers and the model wound surface. The adhesive properties were evaluated using attenuated reflectance Fourier transform infrared spectroscopy by monitoring the diffusion of mucin solution. The diffusion of mucin solution as model protein was faster for the wafer form than the film.

Wound dressings with antimicrobial and antiinflammatory properties are favorable besides the general nontoxic requirement. The gel-forming ability of polysaccharide materials helps in dressing application and removal without much pain to the skin. Incorporation of certain fillers to the dressing can provide additional function to the wound dressing to meet patients’ needs. Encapsulation of antimicrobial and antiinflammatory drugs into wound dressing is the most common attempt for this purpose. The previous polyox/carrageenan composite has been loaded with diclorofenac and streptomycin to enhance the healing effect of wound [46]. The dressing showed higher zones of inhibition against three microbes compared to the individual drugs zones of inhibition. The insertion of diclorofenac can prevent inflammation while streptomycin can prevent the wound infections. However, adding multiple drugs into wound dressing without disturbing the healing function of the dressing is quite challenging. Thus, several studies have been done to incorporate other materials as antimicrobial agents, such as essential oil [47] and metal oxide [48], inside wound dressing to support its purpose.
3.1.3. Neural tissue engineering

Central nervous system diseases are usually caused by the death of neurons and progressive loss of its function. Current developments in neural technology have opened up possibilities of nerve tissue regeneration. Two potential natural polymers for nerve tissue engineering were combined with hyaluronic acid and heparan sulfate via freeze-drying technique [49]. The composite scaffolds demonstrated highly homogenous and interconnected pores with porosity above 96%. The presence of hyaluronic acid and heparan sulfate has promoted the adhesion of initial neural stem and progenitor cells. Nanofiber-hydrogel of polycaprolactone (PCL) and sodium alginate composite was prepared by electrospinning [50]. The fibrous form of this scaffold is to provide suitable environment for regeneration of the peripheral nerve injury. This kind of combination of natural and synthetic polymers has long been worked on to utilize the mechanical properties of PCL while preserving alginate hydrophilicity to support cell adhesion. The composite displayed that a good suture pulled out strength and assists the human mesenchymal stem cells (hMSCs) viability, adhesion, proliferation, and neurogenic differentiation in neural induction media.

3.2. Drug delivery

Drug delivery area involves an art of transporting drugs or therapeutic compounds to human body. It is a critical research field where the transported compounds must achieve the optimum therapeutic effect to protect or heal from any kind of disease. The use of polysaccharide materials in drug delivery systems is increasing mainly because of their ability to form hydrogel with stimuli-responsive properties [51, 52]. Besides being mechanically deficient, polysaccharide-based drug carrier normally have initial burst problem in the delivery system. Therefore, controlled delivery systems were proposed by addition of various fillers into polysaccharide matrix. This includes incorporation of Fe$_3$O$_4$ [53], CaCO$_3$ [54], silica nanoparticle [55], graphene oxide [56], gold nanoparticle [57], and montmorillonite [58].

Oral drug administration is one of the preferred routes since it is convenient and has no cross-infection. However, drugs taken through oral route have to pass through different phases of gastrointestinal tract, where pH values vary greatly. The change in pH may lead to loss of mechanical strength and fast degradation. To protect the drugs from the harsh environment in stomach before they can be absorbed in the intestine, pH-sensitive polysaccharide composites were developed. Protein drugs were encapsulated in inorganic carrier [59, 60] and gel beads [61, 62] to prolong their release. Series of pH-sensitive composite hydrogel composites of alginate and chitosan base were prepared with addition of attapulgite [61], bone ash [63], and other polymer-like pectin [64] that clearly showed their release dependence to pH condition. It was found that cross-linking and nanofiller loading can significantly improve the targeted release [65, 66] in the pH-sensitive polysaccharide composites.

Polysaccharides like starch and carrageenan are thermoresponsive polymers. They can be utilized in drug delivery with thermal sensitivity. ?-carrageenans were incorporated with Au [67] and silica [68] nanoparticles. The effect of both nanoparticles on the microstructure and strength of the hydrogel had implications in the mechanism of controlled release as demonstrated by in vitro release studies using a drug model and displayed potential for thermally
controlled drug delivery. Schmitt et al. loaded aqueous drug containing 5-aminosalycylic acid (5-ASA) into halloysite nanotubes and dispersed them well in thermoplastic starch matrix [69]. The swelling of the produced nanocomposite strongly depends on the temperature but not on pH. Furthermore,  𝛾-carrageenans were also studied for a triple-response hydrogel by simultaneous formation of super paramagnetic iron oxide nanoparticles (SPION) and crosslinking of poylacrylyc acid (PAA) [70]. The swelling capacity and drug release of  𝛾-carrageenan-PAA/SPION hydrogel were tested to different temperature, pH, and magnetic field to assess the sensitivity of the hydrogel. They have successfully synthesized biocompatible hydrogel with considerable temperature, pH, and external magnetic field sensitivity using simple and convenient one-pot strategy. Another interesting functional hydrogel of  𝛾-carrageenan was prepared by reinforcing with multiwalled carbon nanotubes (MWCNT) [71]. This hydrogel composite shows increased release of a model drug in vitro conditions due to the near-infrared (NIR) photothermal effect of MWCNTs, thus demonstrating its promising role as carrier for remotely activated drug delivery.

Apart from being too focused on the additional function on drug carrier material, excipients must have the ability to encapsulate and protect the drugs. Some drugs have some specific needs to achieve targeted release. Targeted release is very important to ensure optimum drug effects. Aceclofenac is an orally administered phenyl acetic acid derivative with effects on a variety of inflammatory mediators. Its frequent administration and prolong treatment was associated with various side effects. The use of Boswellia gum resin into chitosan polymer to deliver nonsteroidal antiinflammatory drug has caused significant improvement in drug entrapment efficiency (~40%) of the polymer composites [72]. Highly hydrophobic drug like curcumin frequently has poor solubility in polysaccharide excipients. An attempt to add pluronic F127 into alginate/chitosan matrix found to have increased the encapsulation efficiency of curcumin inside the composite, indicating better dispersion of curcumin inside matrix [73]. Local avascular delivery to treat orthopedic infections caused by Methicillin-resistant Staphylococcus aureus (MRSA) was developed by fabrication of porous chitosan/bioceramic β-tricalcium phosphate (CS/β-TCP) [74]. The composite was then coated with poly(?-caprolactone) (PCL) to retard the release of vancomycin for 6 weeks at levels to inhibit MRSA proliferation. Recently, the potential application of deferoxamine (DFO) in several iron dysregulation diseases has been highlighted. However, DFO presents significant limitations in clinical use due to its poor absorption in the gut and very short plasma half-life. Inclusion of poly(D,L-lactide-co-glycolide) microspheres into preformed chitosan/alginate hydrogel provided strong DFO entrapment in the hydrogel network and slow release [75].

3.3. Packaging films

The disability of conventional plastic material used in packaging to biodegrade has led to serious solid waste problem. Polysaccharide materials are fully recognized as potential alternative for petroleum-based plastics, mainly contributed by its biodegradability and environmental friendly properties. Packaging basically functions as container and external preserver or protector to consumer goods including food. Materials used in packaging need
to possess excellent mechanical properties and barrier properties so they will be able to maintain the condition for the products to extend their shelf-life. Therefore, several reinforcements have been identified to be good fillers for polysaccharide films.

Clay minerals have received extensive study as reinforcing filler in polysaccharide-based packaging film and coating [76]. Nanoclays have been a subject of interest nowadays considering their high aspect ratio and surface area, alongside with biocompatibility feature. The inclusion of clays showed good dispersion in polysaccharide matrix and resulted in superior mechanical and barrier properties. Incorporation of montmorillonite (MMT) nanoclay into alginate film has shown increase in tensile strength of up to 36% [77]. MMT may also enhance the thermal stability, storage modulus, and barrier properties of chitosan [78]. A comparative study of nanobiocomposite of carrageenan/zein and carrageenan/mica found mica clay to be more efficient as an additive to carrageenan for clay has better dispersion in carrageenan composite [79]. Cellulose nanocomposite film containing MMT was investigated as a substitution for synthetic polymer foam trays. The presence of nanoclay caused more uniformity in the structure of the foam, thus resulted in higher compressive strength, Young’s modulus, and density [80]. The use of sepiolite and palygorskite fibrous clays in some polysaccharides of different types was reported [81]. The good compatibility between these fibrous clays with the polymers resulted in improved mechanical properties, barrier to UV light, stability in water, and reduction of water absorption, which make them very attractive bionanocomposite in the food packaging sector. Other fillers included into polysaccharide-based packaging films are nanosilica [82], zinc oxide [83], and copper [84] nanoparticles.

In terms of polysaccharide composites, certain fillers were added to the packaging films not only to improve their mechanical and barrier properties, but special characteristics can also be instilled for the production of active packaging films. Active packaging refers to the packaging systems used for products like foods and pharmaceuticals that have extra function to extend their shelf-life, in addition to the general purpose of providing external protective barrier. Introduction of different kinds of natural and synthetic antimicrobial agents into packaging have been studied against various pathogens such as *Listeria monocytogenes*, *Escherichia coli*, *Clostridium perfringens*, *Staphylococcus aureus*, *Salmonella pullorum*, *Bacillus cereus*, and *Pseudomonas aeruginosa*. The inhibitory effect of the films was determined by measuring the bacterial growth inhibition zones. Preparation of polysaccharide-based packaging films with incorporation of nanometals, organically modified clay minerals, plant essential oils and extracts, and other natural antibacterial agent were tested for their antimicrobial properties.

Clays are organically modified to increase their hydrophobicity since the polysaccharide matrix is already water sensitive and has low water vapor barrier properties. They also exhibit biocompatibility, bioactivity, and can be used as antibacterial materials. The inclusion of modified clay Cloisite 30B in carrageenan/locust bean gum matrix [85] and zeolite-A inside chitosan matrix [86] have demonstrated high antimicrobial efficiency compared to neat polysaccharide. A combination of halloysite nanotube and nisin had been expected synergistic effect in active packaging [87]. Nisin is an antimicrobial agent recognized to fight against
Listeria and spores of Bacilli and Clostridia. However, a study by Lu et al. showed the formation of 3% alginate solution containing nisin-ethylenediaminetetraacetic acid (EDTA) might have limited the release of nisin [88]. Lower concentration of alginate was proposed to see the effect of alginate concentration to nisin performance. Another study included silver (Ag) nanoparticles combined with Cloisite 30B in 7-carrageenan as antimicrobial bionanocomposite films [89]. Ag nanoparticles have attracted considerable attention for packaging application for their antibacterial activities, high thermal stability, and low toxicity. Ag/clay mineral was prepared to overcome the tendency of Ag nanoparticles to agglomerate when used alone. While organically modified nanoclay exhibited strong antibacterial activity against Gram-positive bacteria, Ag nanoparticles exhibited strong antimicrobial activity against Gram-negative bacteria. Thus, the combination of these two antibacterial agents helps in providing polymer packaging with strong antimicrobial properties. Shankar et al. investigated different types of Ag particles incorporated into alginate-based films [90]. They found Ag zeolite and citrate reduced Ag nanoparticles provide better antimicrobial activity than metallic silver and laser-ablated Ag nanoparticles in alginate compared to the neat films.

Strong antimicrobial activities can also be induced inside packaging films by plant extracts and essential oils. Extracts of green and black tea were added into chitosan displayed good antioxidant and antimicrobial capacity [91]. Natural extract from the seeds, pulps, and peel of grapefruit was also put inside carrageenan film to encourage the antibacterial, antifungal, and antioxidant properties [92]. However, addition of plant extracts showed decreased tensile strength and elongation at break of the packaging films. In addition, oregano, thyme, and Satureja hortensis essential oils were used in carrageenan films to overcome the poor water vapor barrier and as possible substitutes for synthetic antioxidant-antimicrobial agents to achieve oxidative and microbial stability [93, 94]. The tensile strength was lowered with increasing essential oil concentration. They suggested it happened because of the replacement of strong polymer-polymer interaction with oil-polymer interaction in the film network.

4. Conclusions

Polysaccharide-based composites are attractive biomaterials because of their chemical structure and ease of manipulation. They are easily processable and abundant in nature, forming a vast potential economical application compared to other synthetic biomaterials. Moreover, they are highly environmental friendly and nontoxic to humans and animals. Preserving the nature while taking advantage of its application leads to promising future for renewable and sustainable materials. Polysaccharide-based composites are mainly to overcome the problem of low mechanical and water barrier properties of common natural polymers. Many studies have been done and successfully associated different reinforcements and fillers to polysaccharides for variety of fabrication purposes. Polysaccharide-based composites are thus a favorable alternative to the commercial petroleum-based polymers and highly recommended for renewable and sustainable composite materials.
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References


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