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Alginate Based Sustainable Films and Composites for Packaging: A Review

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Alginate is an abundantly hydrophilic polysaccharide as much as 40 % of dry weight and commonly available in the cell wall of brown seaweed. The thickening, gel-forming and stabilizing properties of alginate makes it widely used biopolymer with a broader range of application including packaging. The superior valuable feature of alginate is the capability to yield a stable gel and insoluble polymer when they react through their carboxylate group with polyvalent metal cation especially Ca^{2+}. Despite a wide range of applications, alginate has some drawbacks on the water resistivity due to hydrophilic nature, so its modifications with synthetic and natural polymers are carried out. This review article presents a different type of additives or polymer and their impact on the functional properties of alginate based composite films with special emphasis on packaging application.

1. Introduction

The world's plastics manufacturing today is more than 320,000 kg /y in a various application such as packaging, medical devices, agriculture and construction which 40 % of them is used as disposable packaging material to generate plastic waste (PlasticEurope, 2019). In recent times, environmental concerns have motivated the development of biopolymers or biopolymer composites since the increasing consumer's concern on environmental problems ensuing from the use of synthetic or petroleum-based packaging materials (Le and Opaprakasit, 2020). Biopolymers from natural resources such as seaweed, cellulose, lignin, protein and starch are being used in packaging applications due to their biodegradability, non-toxicity, availability, affordability and can degrade as being exposed to the bioactive environment such as soil and compost (Abdul Khalil et al., 2018). However, the major drawbacks of usage of biopolymers in packaging applications are their relatively poor mechanical and barrier properties and to overcome this drawback, one of the most frequently used methods is to fabricate composite films by mixing one polymer with another polymer or hydrophobic component or nanoparticles. This method enables one to utilize the distinct functional characteristic of every component of the composite film, resulting in the improvement of mechanical and barrier properties over neat polymeric film (Abdul Khalil et al., 2017).

Seaweed is a biopolymer that has received widespread attention in the past few years since they offer a new market for low-cost and biodegradable packaging products. Seaweed is known as multicellular marine macro-algae and has potential as biomass resources for the full or partial substitution and displacement of terrestrial biomass to generate valuable biochemical products (Point Reyer National Seashore Association, 2020). Seaweeds are green, abundantly available, biodegradability, biocompatibility, hypoallergenic nature, able to grow in a wide range environment, cost-effective and easy to cultivate in a natural environment (Abdul Khalil et al., 2017). Seaweeds have a large amount of cell wall polysaccharides, storage polysaccharides and mycopolysaccharides. Seaweed polysaccharides are gaining interest due to their sustainability and availability in large amounts which can be derived from brown seaweed such as alginates, red seaweed such as carrageenans and green seaweed such as ulvans (Zia et al., 2017).

Alginate is the most abundant polysaccharide as much as 40 % of dry weight and commonly available in the cell wall of brown seaweed. It can form a viscous gum with water and having the capacity to absorb water around 200-300 times of its weight (Abdul Khalil et al., 2017). Alginate is a hydrophilic colloidal carbohydrate

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extracted using a dilute alkaline solution (Yang et al., 2016), which allows the formation of an insoluble gel through gelation with calcium cation (Venkatesan et al., 2015). The thickening, gel-forming and stabilizing properties of alginate makes its widely used biopolymer with a broader range of application including packaging, tissue engineering, drug delivery and wound healing.
The objective of this review is to discuss a different type of additives or polymer used and their impact on the functional properties of alginate based composite films with special emphasis on packaging application since a comprehensive review on alginate on packaging application is lacking. Due to this, there is a need to provide insight into these current trends and prospects.

1.1 Sources, structure and properties of alginate

Alginate is the structural polysaccharide extracted from brown seaweed that naturally includes a carboxylic group in every constituent residue. Alginate composed of a monomeric unit of (1,4)-linked β-D-mannuronic acid (M) and α-L-guluronic acid (G) residues (Figure 1) that form a region of M-blocks, G-blocks and alternating sequences of MG-blocks where relative proportions of these sequential organizations depend on the sources of alginate in term of age, species or part of brown seaweed (Yang et al., 2016).
Alginate is commonly used as a thickening, stabilizing, film-forming, gel-producing and emulsion stabilizing agent (Abdul Khalil et al., 2017). Alginate is a transparent biopolymer that has low toxicity, relatively low cost, excellent film characteristics, good biocompatibility, biodegradability and osteoconductivity biopolymer but it has poor water resistivity due to the hydrophilic nature (Venkatesan et al., 2015).

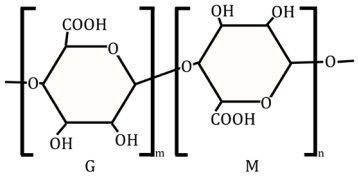

Figure 1: Chemical structure of alginate

1.2 Crosslinking of alginate

Alginate is a polysaccharide which abundant in brown seaweed is made of M blocks and G blocks. The G blocks of the adjacent alginate polymer chains can be efficiently crosslinked through the ionic bonding by the multivalent cation. The crosslinking capacity of alginate is closely associated with the length and content of G blocks where high a proportion of the G block produces the increase in strength and its low content leads to elastic properties (Kim et al.,2018). The ionic crosslinked of the alginate very fast and influenced by many experimental factors such as polymer concentration, cation concentration, crosslinking time, temperature and humidity (Su and Chen, 2018). Alginate becomes insoluble in water when G blocks of alginate chains are ionically crosslinked by cation (Dodero et al., 2019). The crosslinking process is conventionally described in the terms of the “egg-box” model (Figure 2), which results in strong and specific interactions between the cation and the carboxyl group of the guluronic moieties. Different steps are occurring for the “egg-box” formation, relying first on the interaction between the cation and the G block monomer, secondly the formation of the egg-box dimers and at last in the association of dimers resulting in multimers. The tendency to bind with cation occurs in G blocks. Some factors like the G sequences, G percentage and alginate molecular weight are very relevant to determine how the dimer and multimer will associate and influence the strength of the produced structure (Costa et al., 2018). Giz et al. (2020) stated that at 0 % of glycerol and 30 % of glycerol with increasing the crosslinking from 0 % to 0.5 % of $CaCl_2$ had increased the tensile strength of the film up to 134.8 MPa and 146.5 MPa. The low $CaCl_2$ crosslinking had a great effect, increasing the stiffness and strength of the film by ionically bonding the alginate chain.

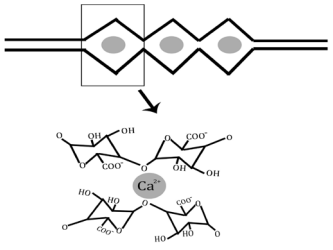

Figure 2: Alginate crosslinking with Ca^{2+} and “egg-box” formation

The glycerol concentration did not have any effect on the thermogravimetric profile but the addition of the 2 % of $CaCl_2$ the degradation peak is broader appears indicating that the crosslinking structure is shifting the alginate degradation to a relatively higher temperature that resulting in the enhancement of thermal stability. For the water vapour permeability (WVP) properties, they have suggested that as crosslinking increased, the chain entanglement increased and the water diffusion through the films become difficult and WVP decreased as $CaCl_2$ crosslinking was increased.

Dodero et al. (2019) found that the Ba^{2+}-crosslinked hydrogel has a high crosslinking density that displayed a low water uptake due to the high number of constraints between the polymer chains that result in a low initial swelling degree of the hydrogel. The Ba^{2+}-crosslinked hydrogel also had a greater compressive modulus as compared to Ca^{2+} and Sr^{2+}-crosslinked hydrogel and this may probably due to the major affinity of barium ions towards alginate. There were no significant changes in the thermogravimetric analysis thermograms of samples crosslinked with different ions and under different crosslinking conditions which types of crosslinking agents and effective crosslinking degrees do not strongly influence the thermal behavior of alginate-based hydrogels.

Costa et al. (2018) stated that the moisture content of the high G content film decreased as $CaCl_2$ concentration increases where the Ca^{2+} ions mostly react with G block in series in the chain. Regarding water solubility, high G content film has high solubility values since it has higher molecular weight and consequently has a longer chain that can lead to stronger films and cause low solubility values. Conversely, the water solubility and WVP are decreasing with increasing the concentration of $CaCl_2$ indicates that there are still free G blocks available in the matrix. The tensile strength and Young's modulus values of the high G content film increased for a higher concentration of $CaCl_2$ while the elongation at break decreased where this increment indicates an increase of the film resistance and stiffness, which explained the reaction of the Ca^{2+} ion with alginate.

2. Alginate-based synthetic polymer composites for packaging application

Yang et al. (2020) stated that incorporation of 5 % of melanin into the sodium alginate/polyvinyl alcohol (SA/PVA) matrix, the WVP value had decreased by 25.7 % while incorporated of 3 % of melanin, the water content of the film also decreases by 26.7 %. This may attribute to the hydrogen band interactions among SA, PVA and melanin which decreased the active sites for binding additional water molecules. After incorporation of the melanin, tensile strength and elongation at break of SA/PVA/melanin films were significantly higher than SA/PVA film and the thermal stability of the film was enhanced since the onset of the thermal decomposition temperature and weight loss of alginate had increased.

Llorens-Gamez et al. (2020) observed that there a significant decrease of water sorption even a minimum amount of carbon nanofibers (CNF) incorporated into the alginate and this is attributed to the swelling restriction produced by the simultaneous crosslinking of CNF and alginate chains with divalent cations of calcium. All the film that incorporated CNF had enhanced the dynamic-mechanical modulus but at 0.5 % of CNF lead to the highest dynamic-mechanical modulus. The tensile strength and modulus of the SA/CNF film increased with increasing the percentage of incorporated CNF due to the strong H-bonding between CNF and SA and also the crosslinking between SA and $CaCl_2$ that produce a continuous crosslinking network. The incorporation of 0.1 % CNF possesses transparency very close to the neat alginate but the opacity of the film increases as the incorporation of more than 0.1 % of CNF.

Biao et al. (2019) have reported that the alginate/polyphenol composite films were flexible and free-standing with a homogeneous yellow-brown appearance. The incorporation of the tea polyphenol, the moisture content decreased to 14.5 % and the solid content and WVP increased to 85.5 % and 4-fold. Also, the incorporation of tea polyphenol had little impact on the ability of the oil to penetrate through the films. The optimum tensile strength and elongation at break value for the edible films occurred at 1 % of tea polyphenol concentration where the impact of the polyphenol on the structural organization and interaction of the alginate chains that make up the gel network. There was a significant increase in both the DPPH and ABTS radical scavenging activities of the films as the polyphenol content increased. Dou et al (2018) evaluated that the addition of 2.0 % of the tea polyphenols (TP) have increased the tensile strength up to 72.05 MPa which was 84.08 % greater than gelatin-sodium alginate (GSA) film while the incorporation of the 1.2 % of TP had decreased the elongation at break to 22.65 %. The crosslinking degree of the GSA-TP films had increased to 35.7 % with the incorporation of 2.0 % of TP content. The WVP of the GSA film with TP had significantly decreased from 0.228 to 0.138 $g.mm/m^2.h.kPa$ since the TP could insert into the network structure of GSA to form a more dense system which led to a reduction of WVP value.

3. Alginate-based natural polymer composites for green packaging

3.1 Alginate/cellulose composites

Deepa et al. (2020) stated that the addition of TEMPO-oxidized cellulose nanocrystals (TOCNC) with ultrasonication treatment into the SA matrix, the diffraction peak is more prominent in the XRD pattern. This may due to the presence of a more homogeneous dispersion and partially oriented nanocrystal particles within the nanocomposite film. Additionally, ultrasonicated TOCNC particles are more homogeneously dispersed in the SA matrix since the surface roughness of the sample decreased which results in a lower tendency for agglomeration of the TOCNC and higher hydrogen bonding capacity which could promote strong interfacial interactions between TOCNC filler and SA matrix. The addition of 10 % of TOCNC exhibited higher glass transition temperature which was 25.88°C that resulting in the TOCNC interact with alginate components forming a crosslink complex in which TOCNC are more homogeneously dispersed. The storage modulus of the 10 % of ultrasonicated TOCNC is higher than pure SA which was 4.499 GPa since the formation of the 3D network of interconnecting layers in the polymer matrix which is formed a strong intermolecular hydrogen bonding between TOCNC and SA.
Ma et al. (2017) were observed that the XRD peak of the cellulose nanocrystal (CNC) disappear in most composite fibres which indicated good dispersion of the CNC in the alginate composites. With increasing the CNC content, the tensile strength and elongation at break of the CNC-alginate fibre composite increase initially and reaching a maximum at 0.5 wt% loading. The water absorbency of the composite fibres increases initially as the CNC content increases and reaching a maximum of 1,333 % at 1.0 wt% of CNC. The addition of a small amount of CNC can break an H-bonding between alginate and improving the fibre's water absorbency.
Abdollahi et al. (2013) observed that the water solubility of the alginate/CNC composite showed the decrement from 99.55 % of neat alginate to the 77.49 % which related to the strong hydrogen bond formation between the hydroxyl group of biopolymer and nanofiller. This interaction improves the cohesiveness of the biopolymer matrix and decreases the water sensibility because water molecules are not able to break these strong bonds sufficiently. The addition of CNC into the alginate matrix had decreased by about 18 % of WVP. This improvement in the barrier may due to the tortuous path caused by the impermeable layered of crystalline parts of CNC distributed in the matrix. The tensile strength and Young's modulus of the alginate/CNC had improved due to their similar polysaccharide structures, homogeneously dispersed high-performance CNC fillers in the biopolymer matrix could properly make interfacial hydrogen and ionic interaction with functional group of alginate molecule.

3.2 Alginate/oil composites

Mahcene et al. (2020) reported that glass transition temperature (T_g) and melting temperature (T_m) values of the SA films incorporated with essential oil (EO) were slightly decreased while the enthalpy of heating (ΔH_m) values were higher for all samples with EO as compared to neat SA film. The film samples with EO had a significant decreased in the moisture content, WVP and oxygen permeability due to the change in hydrophilicity of the films. The tensile strength of the SA films incorporated with EO had decreased significantly from 2.14 MPa to 0.71 MPa which EO has weakened the intermolecular forces between adjacent macromolecule chains and increased the free volume that resulting in reducing the strength of the film. The antimicrobial and antioxidant activity tests showed that the SA films with EO had a considerably high antibacterial effect against foodborne pathogenic bacteria and a strong DPPH radical scavenging ability. Abdel Aziz et al. (2018) stated that when castor oil (CO) was added to SA, the temperature of the maximum decomposition rate was shifted to a higher temperature and the percentage of mass loss was decreased were indicated that the thermal stability was enhanced after incorporation of CO. The tensile strength was significantly increased upon the incorporation of up to 1 % of CO due to increasing the interaction resulting from the formation of hydrogen bonds and electrostatic attraction between SA and CO. The elongation at break was increased with increasing CO which acts as a plasticizing agent and facilitating the chain mobility. The WVP of the SA was found to decrease significantly with incorporation and increasing the CO content where this behaviour might result from the hydrophobicity of CO and the increased the crosslinking density which hinders the water mobility across the films.

3.3 Alginate/chitosan composites

Li et al. (2019) had prepared a chitosan-alginate (CTS-SA) films through a layer-by-layer (LBL) assembly combined with ferulic acid (FA) crosslinking. They stated that the tensile strength of the LBL-CTS-FA-SA film increases up to 38.2 % as compared to CTS-SA film. The LBL-CTS-FA-SA film exhibited an increase of 189.26 % in opacity where LBL assembly and FA crosslinking enhanced the interaction between molecules and make film structure more compact, leading to increases opacity. The water vapor transmission and water solubility were lower than CTS-SA film, by 70.7 % and 68.8 %, the LBL assembly and FA crosslinking

methods can enhance the water resistance property of the film and the water vapor molecule is better hindered by the outside or required a longer time to penetrate the film. Wang et al. (2019) reported that the addition of carboxymethyl chitosan-ZnO nanoparticles (CMCS/ZnO) into the chitosan/SA film, the surface became rougher because of the embedded and well dispersed CMCS-ZnO particles in the matrix and thickness of the film had little bit increment. With the increase of CMCS-ZnO, the tensile strength of the chitosan/SA film has increased significantly due to the increased internal fiction in the matrix while elongation at break of films reduced to 25.32 % due to the weakening of the hydrogen bonding between chitosan and SA and formation of new hydrogen bonds between CMCS-ZnO and matrix molecules which result in a decrease elongation at break. The water solubility of the chitosan/SA film decreased to 39.84 % with the introduction of CMCS-ZnO and this could attribute to the interaction between matrix and nanoparticles which restricted the movement of the SA chains. The WVP of the films decreased obviously as CMCS-ZnO content increases because the water resistance of the CMCS-ZnO was better than the matrix and well dispersed of the CMCS-ZnO probably introduced a few tortuous paths for a water molecule to pass through. The films incorporated with the CMCS-ZnO had higher antibacterial ratios than chitosan/SA film with a higher amount of the CMCS-ZnO have significantly increased the bactericidal effect.

3.4 Alginate/cotton composites

Oliveira Filho et al. (2019) reported that the incorporation of the cottonseed protein hydrolysates (PH) increased the film thickness by 10 μm, 50 μm and 110 μm in the film with 0.15 %, 0.30 % and 0.60 % of PH due to an increased in the solids content after PH incorporation. But, the moisture content of the film was not affected by the incorporation of PH into the SA film. The incorporation of the PH in the SA films did not significantly affect the biodegradability of the film and produced value between 95.75 % and 98.01 % which suggests that PH is capable of the rapid action of microorganism and the biodegradation process. The WVP of the film significantly increased by 74.2 % for the film with 0.60 % of PH where incorporating PH may lead to the increase in the plasticizer effect that resulting in an increase in the free volume of the film matrix and the network became less dense and more permeable. The water solubility of the film after incorporation of PH was higher than 98 % due to the hydrophilic nature of the SA and PH.

4. Conclusions

Nowadays, seaweed polysaccharides are gaining interest due to their sustainability and availability in a large amount. However, alginate is the most frequently used in research polymer among all seaweed polysaccharides as a packaging material due to its ability to react with multivalent cation via ionic bonding which resulting in enhanced its properties. Alginate can be blend with other synthetic polymers (PVA, polyphenol or gelatin) and nanofiller (melanin, CNF, ZnO or SiO_2) to improve their tensile, water barrier and thermal properties depend on the types of packaging that is used. Other than that, alginate also can be reacted with a natural biopolymer to produce a green packaging film that 100 % biodegradable. Alginate reacts with cellulose, chitosan and oil have shown the improvement in tensile, water barrier and grease properties. The antimicrobial properties of the alginate also can be improved with the addition of essential oil which is an important parameter to be considered as food packaging. Recent advances in the field of alginate-based composites enable their usage in food and industrial packaging.

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