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CHITOSAN MEMBRANES: A REVIEW ON ITS PROPERTIES AND APPLICATIONS

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Abstract:

Chitin on deacetylation using alkali results in the formation of chitosan. A variety of industrial, biotechnological, dietary, and commercial applications are made possible by the unique set of beneficial biological and physio-chemical properties that chitin and its main derivative chitosan offer. As a cationic biopolymer and bioactive substance, chitosan derived from shrimp waste has drawn substantial interest in a wide range of possible uses. The effectiveness of chitosan depends highly on its chemical and physical nature. Preparation and studies on various properties of chitosan such as tensile strength, elongation at break, water vapour permeability and oxygen permeability are discussed in this paper.

Key Words: Chitosan, Tensile Strength, Elongation at Break, Permeability

Introduction:

N-acetyl D-glucosamine and D-glucosamine are copolymers that make up chitosan chemically. Chitosan is a natural polysaccharide, extracted from marine sources and has unique characteristics often not found for synthetic polymers. According to Peter (1995), chitosan membranes are more permeable to water and less permeable to oxygen, nitrogen, and carbon dioxide than cellulose acetate membranes. This is combined with superior mechanical strength, great wrapping, packaging, and coating, as well as antibacterial and antifungal qualities. The coating is afforded simply by dipping an article into the chitosan solution. This produces a conserving effect on foodstuffs, there by extending their shelf lives.

Preparation of Chitosan Membrane:

Due to its solubility in acetic or formic acid, chitosan is ideally suited for the preparation of a membrane. Muzzarelli and colleagues described and characterized the chitosan membranes for the first time. There is another method for making chitosan membranes in addition to the simple method that relies on the formic acid being evaporated from a chitosan solution spread on a glass plate. According to reports, the cuttlefish (*Sepia officianalis*) shell has a chitinous membrane. To extract the chitin membrane, the cuttlefish shell was first decalcified and the chitin-protein combination that resulted was deproteinized. It was deacetylated to yield a chitosan membrane (Muzzarelli, 1973).

Artificial chitosan membranes were made by dissolving one gram of chitosan in one hundred milliliters of 65% reagent-grade formic acid. This solution was poured onto a 20 × 20 cm glass plate that was kept perfectly horizontal up on a water bath. A 1mm board of silastic stopped the solution from dripping out of the plate. The glass plate was exposed to cold air after the formic acid had entirely evaporated so that the membrane could be removed from the glass surface with ease. The water-soluble chitosan formate was dipped in to 1N NaOH and rubbed vigorously with gloves, at the same time avoiding folding the membrane. The membrane was then neutralized with distilled water, put out on a clean surface, and dried at 60^0 C (Muzzarelli, 1973).

Properties of Chitosan Membranes:

Tensile Strength:

Depending on the molecular weight of the chitosan and the type of acid utilized, the tensile strength of chitosan films ranged greatly from 7 to 150 Mpa (Park *et al* 2002). For all of the several types of acids utilized, the tensile strength of the films dramatically increased as the chitosan molecular weight rose. According to Muzzarelli *et al*., (1977), the tensile strength of chitosan film grew as the molecular weight of the material did. In chitosan film, chitosan creates hydrogen bonds between hydroxyl and amino groups (Uragami and others 1994). Due to the rise in chitosan concentration, hydrogen bonding in the chitosan films increased when amino and hydroxyl groups were added in greater amounts throughout the film development process.

According to Park *et al*. (2002), the peculiarities of acid solutions, such as ionic strength and the degree of dissociation, have an impact on the intermolecular organization of chitosan in aqueous solution. According to a study by Kienzle-sterzer and colleagues (2003), the kind of acid solvent used affects the mechanical properties of chitosan films. They estimated that topological restrictions and junction density in the film might both be impacted by the acid or chitosan concentration employed in the film preparation. This was due to the different interaction between the chitosan and acid solution. The different interactions were represented by spatial configuration of the chitosan molecule during film formation. Acetic acid produced the toughest films or films with the greatest tensile strength, followed by malic, lactic, and citric acid, correspondingly, according to Park *et al.* (2002). Citric acid was discovered to create films with less strength than other acids. Additionally, Rhim and

coworkers discovered in 1998 that acetic acid produced more durable chitosan films than did malic, lactic, or citric acid. Park and others (1998, 2000) explained the relationship between film properties and organic acid solution properties such as molecular weight and molecular dimension of chitosan measured by light scattering method. Molecular weight of chitosan dissolved in acetic acid was higher than that dissolved in other three acid solutions. In acetic acid solution chitosan forms dimers indicating that the intermolecular interaction is relatively strong which suggests that the chitosan films prepared with acetic acid had tighter structure than those prepared with other acid solutions.

Elongation at Break:

The type of acid and molecular weight of chitosan used also affected the E (a measure of a film's capacity to stretch). Chitosan's mean E values ranged substantially from 4.1 to 117.8%. According to Park *et al*. (2002), citric acid-prepared films were the most resilient while acetic acid-prepared films were the toughest. In general, it is understood that the Tensile Strength and Elongation at break of biopolymer films have an inverse relationship (Rhim *et al*., 2000).

According to Chen and Hwa (1996), the membrane's tensile elongation is influenced by both the membrane's molecular structure and weight. The tensile elongation of the membrane increases with the molecular weight of the chitosan utilized. This was due to the usage of chitosan with a larger molecular weight, which increased the possibility of molecular entanglement forming during film creation. According to Lin (1992), the chain flexibility of chitosan molecules varied depending on the pH of the fluid. Chen and Hwa (1996), reported that the chain flexibility of chitosan molecules in solution was in the range of pH 4.5>pH 2>pH 3. The extremely flexible molecules come together to create coils. Coil-molecule-formed membranes have a higher tensile elongation.

Water Vapour Permeability:

The range of the water vapour permeability of chitosan films made with various organic acids and chitosan molecular weights was 0.26 to 0.69ng.m/m^2.s.Pa. While chitosan films made with lactic acid had slightly lower water vapour barrier values (higher WVP values), those made with acetic acid had slightly higher water vapour barrier values (lower WVP values). With increasing chitosan molecular weight, chitosan films made with citric and lactic acids showed slight increases in WVP values (Park *et al*. 2002). Rhim *et al.* (1998) reported that addition of glycerol during the production of chitosan films led to greater WVP values because the plasticizers' increased segmental mobility.

Oxygen Permeability:

Depending on the type of acid and chitosan molecular weight utilized, the oxygen permeability of chitosan films ranged from 0.4 to 5.89 108cc/m^2.day.atm (Park et al., 2002). These values are in good agreement with the measurements of 7.2 10-8cc/m^2.day.atm made by Muzzaeelli *et al*. in 1974 and the range of 1.2 to 4.5 10-8cc/m^2.day.atm made by Butler *et al*. in 1996.

According to Park *et al*. (2002), there is no clear relationship between the molecular weight of chitosan and the oxygen permeability of chitosan films. The effects of various acid solutions on the oxygen permeability values of chitosan films were studied. Among the acid solutions examined, the chitosan films made with malic acid had the highest oxygen barrier, with (lowest) OP ranging from 0.4 to 1.9 10-8cc/m2.day.atm. Of the films studied, the OP values of chitosan films made with citric acid proved to be the greatest (3.3 to 4.9 10-8cc/m^2.day.atm). Generally OP value of low molecular weight chitosan film was lower than that of chitosan films prepared with high molecular weight chitosan (Park *et.al*., 2002). As indicated by Butler *et al* (1996), OP values of chitosan films are comparable with commercial polyvinylidine chloride (PVDC) or ethylene vinyl alcohol co polymer films. Low oxygen permeability of chitosan can be exploited for food and medical packaging applications.

Permeability of Membrane:

The permeability of membranes made from low Mv chitosan is higher. With running time, the permeability also reduced until, after 30 minutes, it practically reached constant (Chen and Hwa, 1996). The permeability of ultra filtration reduced over time and was typically operated at a 3Kg/cm 2 pressure.

According to Kuo and Cheryan (1983), concentration polarization caused the permeability to initially be high but to decrease over time. However, the flux of distilled water remained constant over time. The amorphous area of the membrane has greater permeability (Kesting, 1971).

According to Tomaszewska (1994), membranes cast from solutions with a higher chitosan concentration displayed less permeability. The amount of gluteraldehyde in the casting fluid increased, which decreased membrane permeability. At increased operation pressure, a higher permeate flux was obtained. Chitosan is an effective biosorbent towards a variety of contaminants due to its -NH_2 and -OH groups enriched structure (Sharififard, Shahraki, Rezvanpanah, & Rad, 2018).

Applications of Chitosan Membranes:

Chitosan and chitin have been widely used in a variety of applications because of their low-cost, abundance and renewability (Hamed *et al*., 2016). Chitosan membranes are made by casting them from a solution, either by themselves or in combination with other reagents and a suitable polymer to offer the desired

properties (Blair *et al*., 1987). By casting solutions containing 2.5% chitosan in acetic acid, 5% polyvinyl alcohol solution, and 5% glutaraldehyde, Uragami *et al*. (1982) created a chitosan membrane that was used to transport different anions. (Kim and Rha, 1989a) examined the efficiency of encapsulation in terms of the growth and production of monoclonal antibodies by encapsulating mammalian cells in a chitosan-alginate bi-polymer membrane. In a chitosan/carboxy methyl biopolymer membrane, protein encapsulated by Shioya and Rha (1989) was discovered to be permeable. Kim and Rha (1989b) examined the parameters affecting permeability when encapsulating protein in a chitosan-alginate bi-poymer membrane. Izume *et al*. (1989) used a chitosan collagen bi-polymer matrix to evaluate the rate of cell proliferation. The chitosan-albumin membrane was created by Chandy and Sharma in 1989 and Claramma *et al*. in 1988 and used for haemodialising.

Drug Delivery Using Chitosan Membrane:

There has been growing interest in grafting of vinyl monomers on chitosan for biomedical and industrial applications. This chemical combination of natural and synthetic polymers yields new materials, which could have desirable properties including biodegradability. Alonso and co-workers (1998) carried out design and evaluation of chitosan/ethyl cellulose muco adhesive bilayered devices for buccal drug delivery. The investigations highlight preparation of devices for buccal drug delivery and devices comprising a drug free backing layer, by two different methods. It was clearly evident that hydrophilic chitosan was easily laminated on to hydrophobic ethyl cellulose and that perfect binding between the mucoadhesive and backing layers was achieved. The double-layered structure design was expected to provide drug delivery in a unidirectional fashion to the mucosa and avoid loss of drug due to wash out with saliva. It was demonstrated that chitosan shows promising potential for use in controlled delivery of drugs to the oral cavity.

Wound Healing using Chitosan Membrane:

Drug distribution involves the usage of chitosan membrane. A number of factors, including (a) compatibility with the gastric environment, (b) stability during the time of drug delivery, (c) adequate mechanical properties, (d) ease of fabrication and cost, and (e) no discernible swelling in water and softening point above 37 0C, dictated the choice of the biomaterials for the carrier film matrix and the barrier films. In order to create carrier films, several polymers were discovered that satisfied all or most of the aforementioned requirements. To give the basic polymer a proper level of flexibility and to promote the diffusion of the drug from the films, excipients and plasticizers were frequently included.

Chitosan films made with acetic acid (chitosan -AA) and lactic acid (chitosan LA) have been tested for their potential as wound healing materials (Khan *et al*., 2000). Mechanical, bioadhesive and biological evaluation of the prepared films were carried out. The results were compared with the commercial preparation Omiderm. Chitosan -LA exhibited a lower tensile strength; however, it was more flexible and bioadhesive than chitosan-AA. Chitosan- LA and Omiderm did not cause any skin allergic reactions.

Other Applications:

Recent publications of chitosan and derivatives have been classified into its various applications in food, pharmaceutical, biotechnology, medical, textile, paper, agriculture and environmental applications. (Bakshi et al., 2020). Research has been carried out on membrane separation process with use of chitosan-based membranes: ultra filtration (Musale et al, 1999); reverse osmosis (Yeom et al, 1998); nanofiltration (Musale and Kumar, 2000); Dialysis (Kubota et al, 1993); Amiji (1996); pervaporation (won et al 2002) and affinity membranes for isolation of biologicals (Ruckenstein and Zeng, 1997; Bayramoglu et al, 2003).

Conclusion:

Chitosan obtained by the de-acetylation of chitin exhibit various physical properties like tensile strength, water vapour permeability, oxygen permeability and so on. It also finds extensive application in medical industry, food, textile industry, agriculture, biotechnology etc.

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