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Review Article

NATURAL POLYMER BASED CLING FILMS FOR FOOD PACKAGING

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ABSTRACT

In the last decades, there has been a marked increase in the use of natural polymer based film materials in packaging, which prevents food from external contamination, retardation of deterioration by extension of its shelf life and maintenance of its quality and safety. Natural polymer based cling films for food packaging can replace the non-biodegradable petroleum-based synthetic polymers at a low cost, thereby producing a positive effect both environmentally and economically. This review aims to obtain a better understanding of use of natural polymers based cling films available for food packaging which include: protein based edible films and films from cellulose and its derivatives. Protein-based edible films offer alternative packaging sources that can be used for versatile food products to reduce loss of moisture from food, can restrict the absorption of oxygen, lessen the migration of lipids, improving mechanical handling properties, and can provide physical protection to food. Cellulose derivatives are a class of natural polymers in which cellulose is swollen to form films with higher tensile strength and improved water vapor properties. However, currently research is focusing on the blending, layering, and filling cellulose derivatives with different biopolymers or synthetic polymers to enhance the mechanical and barrier properties, therefore strengthening their position in competition with other packaging materials available for food packaging. Cling films are synthesized involving biopolymers and the preparation of their modified derivatives to develop a class of natural packaging films which will revolutionize the food packaging industry using various different formulations. The aim in future is to come up with best films for the food industry by increasing their shelf lives and by validating the films according to ASTM standards for food packaging.

Keywords: Food packaging materials, Cling films, Protein films, Cellulose packaging films.

INTRODUCTION

Cling film is also known as plastic wrap, food wrap, or saran wrap, is a thin plastic film used for packaging food items in containers for keeping them fresh over a long period of time. Advances in food packaging play an important role in keeping the food products supply safest in the world. Packaging maintains the benefits of food processing and enables food to travel safely over long distances and reach the consumers in a wholesome form. Hence, packaging technology should balance food protection with environmental pollution and with disposal of solid waste. The synthetic polymers used for packaging of food from decades originate from petroleum resources and are regarded as non-degradable in nature. Petroleum resources being limited in nature will soon get depleted as well as there are serious issues related to the disposal of synthetic polymers for food packaging. The advent of biodegradable packaging material in the market is due to the increase in the prices of crude oil, consumer demand for increased shelf life of food, proliferation of convenience packaging, the need of a cleaner and pollution free environment. Nowadays consumer's demands for products that are non-toxic, economically and environmentally feasible leading to a conclusion that biodegradable packaging of food products will become increasingly popular in a span of time.

Biopolymers are long chain compounds which are made up of long chain molecule subunits. A biopolymer can be an organic polymer. For example starch, proteins, nucleic acids etc. Biopolymers have been around for billions of years longer than synthetic polymers like plastics. Various natural biopolymers such as starch, cellulose, chitosan, PLA, PHB etc. are used for packaging of food. Food packaging also utilizes blends of different biopolymers like starch-PLA blends, starch-PCL blends etc. Household items like bottles, jars, drums, cans, packaging films, food containers, disposable cups are all manufactured using biodegradable packaging.

Origin of biobased polymers

Biobased polymers can be divided into three main categories on their origin and production; biopolymers directly extracted from biomass, those synthesized from monomers, and the ones synthesized by microorganisms. fig.1 illustrates the classification of biobased polymers with examples.

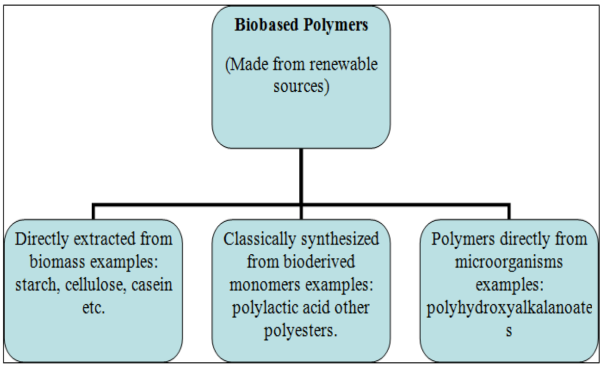

Fig. 1: It shows origin of biobased polymers (Source: Environmental Benefits of Ecofriendly Natural Fiber Reinforced Polymeric Composite Materials) [1]

Background of cling films

Cling film is a thin transparent plastic film adheres to surfaces and to itself, is used for sealing food items. Cling films are high-quality food wrap films, which prevent food from insects and microbial contamination, dust, keep it fresh, and also minimize the risk of wastage of food by increasing its shelf life.

A Dow Chemical lab worker Ralph Wiley in 1933 discovered polyvinylidene chloride or Saran accidently. Saran polyvinylidene chloride and films (PVDC) has been used for wrapping food products for more than 80 years. Saran consists of polymerized vinylidene chloride with monomers; unsaturated carboxyl groups and acrylic esters, forming long chains polymers of vinylidene chloride. It results in a film by copolymerization of molecules bound tightly together so that very little gas or H_2O can penetrate. Thus, it's a barrier against oxygen, moisture, H_2O, chemicals, and high temperatures used to protect food for the consumer, as well as industrial products. PVDC films are found to be resistant to oxygen, H_2O, acids, bases, and solvents. The first cling film designed for household was in 1953 and commercial use in 1949, Saran films now are marketed as Saran Wrap® films commercially by S. C. Johnson. After World War II, it was prior sanctioned in 1956 by Society of the Plastics Industry and then was approved for food packaging [2]. PVDC can now be used as a base polymer, in food packaging gaskets, also with direct contact with dry foods, with fatty and aqueous foods for paperboard coating. To improve the barrier performance of PVDC about 85 % is used as a thin layer between paper, plastic, and cellophane.

The relationship between the food and contact with the packaging material contributes to the changes that can occur over time in food products. High levels of chemicals can leach into food from the cardboard used in cereal and pizza boxes and can contaminate food as recently found out by a government report [3]. Cling film now is found to be safer than before because phthalates (toxic oestrogen-mimicking chemicals) are no longer used in its manufacture. Cling films provide a means to preserve, protect, merchandise, market and distribute foods. It plays a significant role in how the food products reach the consumers in a safe form without compromising the quality. For choosing the right packaging material for a particular food product, several factors have to be considered [4]. Research is going on to develop a class of food wrapping cling films which will revolutionize food packaging, preserve the quality of food by preventing it from external contamination. Commonly used synthetic plastic films include those made from polyvinylidene chloride, polyethylene, polyvinyl chloride, polystyrene, polypropylene etc. Table 1 represents the various synthetic cling films with their specific properties that are used worldwide for various packaging applications. Nowadays cutting edge work is going on to develop cling wraps which can be used with microwaves easily and which can bear enormous amount of heat without getting leached to the food particles. fig. 2 shows food packaging films available in the market.

Natural polymer based cling films

Since synthetic polymers for food packaging are resistant to all forms of degradation, are non-biodegradable, and are costly in terms of materials for production of large quantities of petrochemicals, research is going on for more than a decade, to develop natural polymer based cling films for food packaging which unlike other petrochemical-based polymers that take centuries to degrade after disposal are completely converted to CO_2, H_2O and biomass by the action of microorganisms without any negative environmental impact. Ongoing research has shown that it is possible to establish natural polymer based cling films which can be tailor made to prevent food from microbial spoilage thereby increasing its shelf life, with enhanced tensile strength and poor oxygen barriers with low water vapour permeability. Examples of natural polymers include proteins, polysaccharides, and nucleic acids. Protein-based edible films have received considerable attention in recent years because of various advantages they offer, including their use of edible packaging materials, as compared to the synthetic films.

Table 1: It shows various synthetic cling films used worldwide for food packaging (Source: Food Packaging-Roles, Materials, and Environmental Issues) [5]

Type of cling films: Synthetic polymer based cling films		
Synthetic polymer	**Properties**	**Packaging applications**
Low Density Polyethylene (LDPE)	Processing ease, strength and flexibility, toughness, easily sealable, moisture barrier.	Frozen plastic bags, squeezing bottles, (honey, and mustard) cling films for vegetables, lids of containers.
Polyethylene Terephthalate (PE)	Toughness and strength, effective gas and moisture barrier.	Dressing salads & fruits, peanut and butter packaging jam bottles.
High Density Polyethylene (HDPE)	Stiffness and toughness, moisture & gas permeability resistance.	Yogurt, jellies, margarine, milk and juice bottles.
Polyvinylidinechloride (PVDC)	Provides excellent oxygen gas & moisture blocking properties that are minimally affected by humidity (applicable in a variety of environments).	Layer in medical packaging, packaging of meat & sausages.

Fig. 2: It shows commercially available PVC based food packaging film

Edible protein films

For the individual packaging of small portions of food protein-based edible films can be used, particularly for products like beans and cashew nuts. They can also be applied inside heterogeneous foods at the interfaces between different layers of components. Protein films can prevent the deterioration of inter-component moisture and solute migration in foods such as pizzas, pies, and candies. They can function as carriers for antimicrobial and antioxidant agents and can be used on the surface of food to control the diffusion rate of preservative substances from the surface to the interior of the food. Multilayer food packaging materials can be made from proteins together with edible non edible films. Mechanical and barrier properties of protein based edible films can substitute synthetic polymer films. The formulation of protein edible films with low water vapor permeability is by the addition of hydrophobic components analogous to the situation with synthetic polymers. Polymers which have higher hydrophobic contents are found to be poor oxygen barriers but excellent moisture barriers. Proteins contain hydrophilic amino acid residues and the fact that they are not totally hydrophobic limits their moisture-barrier properties. To limit the ability of water and to reduce barrier properties, moisture-sensitive O_2 barrier polymers must be either copolymerized with a hydrophobic polymer or sandwiched between hydrophobic polymer layers. Protein based edible films are now being investigated because of their poor water vapor resistance and their lower mechanical strength in comparison to synthetic polymers.

Edible films and coatings are made from edible biopolymers and food-grade additives. These films consist of thin layers of polymers able to provide mechanical strength to the stand-alone thin structure. Edible films protect food from physical, chemical, biological deterioration, migration of moisture, microbial growth on the surface, oxidation of nutrients, and enhance the quality of food products [6]. Edible films offer the barrier to oils, gasses, vapors and can be used as carriers of active substances like antioxidants, colors, antimicrobials, and flavors [6, 7, 8, 9, 10]. It results in shelf-life extension and safety improvement [7]. Film forming biopolymers include proteins, polysaccharides (carbohydrates and gums), or lipids [11]. At low relative humidity proteins are good film formers exhibit excellent O_2, CO_2, and lipid barrier properties [6, 12, 13]. Certain animal and plant sources, such as animal tissues, milk, grains, eggs, and oilseeds are protein film formers [14]. These films are found to be brittle and susceptible to cracking due to the strong cohesive energy density of the polymer. Compatible plasticizers addition to these films improves the extensibility and viscoelasticity [15, 16]. Proteins generally exist as either fibrous proteins in their native form, which are water insoluble and serve as the main structural materials of animal tissues, or globular proteins, which are soluble in water or aqueous solutions of acids, bases or salts and function in the living systems [17]. Wheat gluten, corn zein, soy protein, and whey protein, are all globular proteins and have been investigated for their film properties. Solutions or dispersions of the protein as the solvent evaporates can form protein films. Water, ethanol or ethanol-water mixtures can be used as solvents for such films [6]. Proteins have to be denatured by heat, acid, base, and/or solvent in for film formation. Once extended, protein chains can associate themselves through hydrogen, hydrophobic, ionic, and covalent bonding. Protein films are expected to be good oxygen barriers at low relative humidities [18]. His researchers explained that polymers containing groups that can associate via hydrogen bonds or ionic bonds and result in films that are excellent oxygen barriers, but are susceptible to moisture. Protein which has been used as edible films include gelatin, casein, whey protein, corn zein, wheat gluten, corn zein, mung bean protein, and soy protein [19, 20].

Collagen films

Collagens constitute about one-third of the total body protein in mammals and are structural proteins of connective tissue of bone, hide, tendons cartilage, and ligaments. Collagen is used as sponges, films, and membranes. Commercially successful edible protein films can be made from collagen as it possesses characteristics as a biomaterial. These films have the following advantages: it has well-documented structural, chemical, physical, and immunological properties; it is biocompatible and non-toxic to most tissues; and it is readily isolated and purified in large quantities [21]. The production of collagen films from animal hides using a dry or wet process with some similarities [22].

Collagen fibrils provide tensile strength to animal tissues which were produced by self-assembly of collagen molecules in the extracellular matrix [23]. Two major components identified from collagen edible films and coatings from animal origin proteins; α (MW 100 000 Da) and β(MW 200 000Da), and consist of two different types of covalent cross-linked chain pairs α1-α1 and α2-α2 by dissolving them in dilute acid or alkali solutions, and in neutral solutions [24, 25]. Collagen hydrolysis results in gelatin. Gelatin edible films reduce the migration of moisture, oxygen, and oil. Their research has led to the conclusion that, collagen films are not as strong and tough as cellophane, but have good mechanical properties. Collagen films have found to have excellent oxygen barrier at zero percent relative humidity, but increased oxygen permeability increases with increasing relative humidity in a way similar to that of cellophane. Carboxamide, microbial transglutaminase, and glutaraldehyde are different cross-linking chemical agents which were used to improve the mechanical properties, to improve the thermal stability of these films, and to improve reduce their solubility.

By lowering the pH of the solution, can increase solubility collagen is practically insoluble in water. Solubility varied between 28.9% and 52.5% range of pH. At pH, 2 maximum solubility was observed whereas minimum solubility occurred from pH 6 to 11. Higher hydration of collagen results in high solubility observed at low pH´s because of conformation change induced by interactions between proteins and hydrogen ions in the acid medium [26], worked on hydrolysates of collagen by partial hydrolysis (acid hydrolysis, alkaline) comparatively least energy demanding, and thus economically feasible, enzymatic hydrolysis. Lower molecular mass of collagen hydrosylates around 15–30 kDa which, when compared with gelatin is currently used for edible packages, is a level of 5–10 times lower. By increasing cross-link density in hydrolysate higher water solubility and lower resistance of hydrolysate based films and foils to moisture can be eliminated [27]. Work on the combination of collagen with synthetic polymer, blends of synthetic and natural polymers is going on. Collagen as a packaging material alone is not an ideal film; therefore it is essential to combine it with other polymers like PVA, PVP, PEO and PEG that are water soluble. Collagen and synthetic polymer blends have been prepared as films using the solution casting method having high tensile strength [28].

Fish offal such as bones, skin, scales and fins can serve as an alternative source of collagen as compared to the traditional sources of collagen from pig skin and cowhide. Fish collagens have lower gelling and melting temperatures but relatively higher viscosities than equivalent bovine forms than mammalian collagen. Fish-sourced collagens could be in applied where high viscosity film solutions are required [29].

Gelatin films

Gelatin is a hydrocolloid that can form a thermo-reversible substance with a melting point close to body temperature; therefore it is particularly significant in edible film formation and pharmaceutical applications. Gelatin contains a high content of glycine, proline, and hydroxyproline. Gelatin films contain a mixture of single and double unfolded chains having hydrophilic character. Gelatin aqueous solutions at 40^{o}C, are in the sol state and they form physical, thermo-reversible gel on cooling. The chains undergo a conformational disorder–order transition and tend to recover the collagen triple-helix structure during gelation [30]. Gelatin films can be used as coatings on meats to reduce oxygen, moisture and transport of oil. Gelatin is also able to form clear and strong films and can be used for microencapsulation as well as capsule coatings in food and pharmaceutical manufacturing [31]. Gelatin films were formed with 20-30% gelatin, 10-30% plasticizer (using glycerin or sorbitol) and 40-70% water followed by drying the gelatin gel. However, gelatin films do not possess ideal water vapor barrier, as compared to protein films, which limits its application as edible films [32].

Nano TiO_2 was reinforced into gelatin films by the following method: Dispersion of TiO_2-N was formed in water at different concentrations- 1%, 2%, 3%, and 5%; w/w of total solid, stirring was done for 1 hour, and then sonicated in an ultrasonic bath (Marconi model, Unique USC 45kHz, Piracicaba, Brazil) for about 30 minutes to ensure complete homogenization. Aqueous gelatin dispersion at 8% (w/w) was made from the same. Mixture of sorbitol and glycerol in the ratio 3:1 at 40% (w/w) of total solid was added as a plasticizer by Abdorreza and his colleagues in 2011 [33]. Nanocomposites of gelatin were heated at about 60 °C to prevent protein denaturation and then held for 1 h. A 16×16 cm^2 film was formed from 45 g of the dispersion by casting them on plates fitted with rims around the edge. Films were dried at 25°C and 50% RH in a humidity chamber. Control films without nanoparticles were similarly prepared. Dried films were peeled carefully and stored at 25 °C.

- **Water vapor permeability**

Water vapor permeability (WVP) tests of the films were carried out by following the modified method of ASTM standard E96-05 [34]. Water containing test cups (1.5 cm below the film) were taken and a plot of weight gained versus time was used to determine the WVTR. The slope of the linear portion represented the steady state amount of water vapor transmission through the film per unit time (g/h). The slopes had regression coefficients of 0.99 or more. The WVP of film was calculated.

- **Oxygen permeability (OP)**

Oxygen permeability measurements were performed using the ASTM standard method D3985-05 on films (with Mocon Oxtran 2/21 (Minneapolis, USA) equipped with a patented colorimetric sensor (Coulox®) and WinPermTM permeability software). Films were mounted in diffusion cells by placing them on an aluminum foil mask with an open area of 5 cm^2 and tests were carried out at 25ºC temperature, using 21% oxygen as test gas. The permeability coefficients (in cc-μm/m^2day atm) were calculated on the basis of oxygen transmission rate at steady state taking into account the thickness of films.

- **Antimicrobial activity**

Using the agar diffusion method antimicrobial activity tests on the films were carried in 2007 [35]. Inhibition zone against E. coli and S.

Aureus on solid media were used to determine antimicrobial effects of the films.

Corn zein films

Most important protein in corn is zein. In 2002, it was found that zein being a prolamin protein dissolves in 70–80% ethanol. Due to the high content of non-polar amino acids zein is relatively hydrophobic and thermoplastic. Films made from an alcohol soluble protein zein show relatively high barrier properties compared to other proteins [36]. Zein films were formed through the development of hydrogen, hydrophobic and the presence of limited disulfide bonds between zein chains [32]. There is a development of hydrophobic and hydrogen bonds between zein chains in the film matrix. The addition of plasticizer for increasing the flexibility of the films makes them non-brittle [31]. Zein films offer good water vapor barrier properties as compared to other edible films. Zein films showed the ability to reduce moisture, loss of firmness, and delay colour change in fresh fruits by the reduction of O_2 and CO_2 transmission. Zein shows high water vapor permeability compared with typical synthetic polymers apart from the fact that it is not water soluble at a neutral pH. Addition of fatty acids or by using a cross-linking reagent water vapour barrier properties of the films can be improved [32].

Wheat gluten films

Wheat gluten is a water insoluble globular protein of wheat flour. Gluten being cohesive and elastic gives integrity to wheat dough and facilitates film formation. It comprises of gliadins and glutenins. Glutenins form stronger films and posses better barrier properties than films from gliadins or whole gluten. Gliadin films show good optical properties but are not water resistant. Gliadin is soluble in 70% ethanol, but glutenin is not [7]. Wheat gluten is insoluble in natural water but dissolves in aqueous solutions of low or high pH at low ionic strength [37]. The films from wheat gluten can be biodegraded completely after 36 days in aerobic fermentation and within 50 days in farmland soil without releasing toxic products [38].

Wheat gluten films can be formed by drying aqueous ethanol solutions; results in cleavage of native disulfide bonds during the heating of film-forming solutions. The formation of new disulfide bonds in wheat gluten during film drying is believed to be important along with hydrogen and hydrophobic bonds. Glycerin in gluten films as a plasticizer is necessary to improve the flexibility of wheat gluten films [7]. Addition of a large amount of plasticizer may reduce the elasticity, strength and water vapor barrier properties of the films. Greater the purity of wheat gluten stronger and clearer is the gluten films. Gluten films are supposed to be effective oxygen barriers, but poor water vapor barriers due to the hydrophilic nature of the protein and to the substantial amount of hydrophilic plasticizer added to impart adequate film flexibility.

Mung bean protein films

Mung beans seeds contain 25-30% of proteins. Proteins of mung bean have a molecular weight of 24 and 55 kDa. It is rich in essential amino acids such as lysine, leucine, phenylalanine, and isoleucine also in acidic amino acids such as glutamic acid and aspartic acid. Sulfur containing amino acid, cysteine and methionine were also detected in mung bean protein (2.75 and 3.62%) [39]. Mung bean protein films were prepared and found that the mechanical properties-tensile strength and elongation at break of mung bean protein films were superior and water vapor barrier properties were excellent [20]. However, the films exhibited lower mechanical and water vapor barrier properties compared with some synthetic polymers like HDPE, PVC, CA, and PE. Mung bean protein films show resistance to water vapor permeability due to the inherent hydrophilicity of proteins. A hydrophilic plasticizer, which favored adsorption of water molecules was added.

Applications of protein based edible films

Protein edible films offer an alternative source of packaging with sustained environmental costs. These films can be used for versatile food products and can reduce the loss of moisture, can restrict the absorption of oxygen, can lessen migration of lipids [6]. Oxygen permeability of soy protein-based film was 540, 670, 500 and 260 times lower than that of LDPE, PE, MC, starch and pectin when they are not moist [13]. Protein-based edible films if used alone can contaminate food but can be used to wrap foods inside a secondary synthetic package during food distribution and storage. His researchers found that these wraps are biodegradable and can also be eaten, and do not cause any harm to the environment. The wraps can cover leftovers in the refrigerator at home, peeled fruit mixtures or as a sandwich bag for lunch [40]. An excellent review of protein based edible films is presented. Gennadios and his researchers reviewed the applications of various protein-based edible films; corn zein on nut and fruit products, casein emulsion film [31].

To maintain the quality of frozen king salmon work on whey protein isolate and acetylated monoglyceride were done and the result was a delay in the lipid oxidation onset and a reduction in moisture loss rate [41]. To maintain the quality of cooked turkey work on corn zein with an antioxidant and emulsifier was done. The result was that as compared with the PVDC films corn zein with an antioxidant and emulsifier reduced hexanol after 3 days [42]. Sodium caseinate films for wrapping bread were made in 2005 [43]. The unwrapped bread samples had a higher value in the compression tests as compared to the bread samples wrapped with single or double layered sodium caseinate films. As the polyvinyl chloride films, these films prevented the hardening of bread after 3 hours of storage but were not that effective after 6 hours of storage.

Cellulose & derivatives films

Cellulose is the linear polymer of anhydroglucose and one of the most abundantly occurring natural polymers on earth. Cellulose is one of the complex carbohydrates consisting of 3000 or more repeating glucose units. Fig.3 shows the structure of cellulose. It is the basic structural component of plant cell walls non-digestible by man. Cellulose is crystalline, and infusible because of its regular structure and array of hydroxyl groups, as well as it tends to form hydrogen-bonded crystalline microfibrils and fibres and is used in the form of paper or cardboard in the packaging context. Work on cellulose derivatives in 1993 was done and was found out that cellulose is swollen and dissolved using a solvent to films, coatings, or filaments. The swollen cellulose structure can be chemically modified to improve its properties [44].

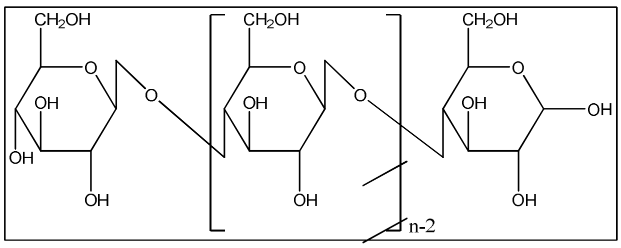

Fig. 3: It shows structure of cellulose (Source: Edible films and coatings: characteristics and properties) [45]

Cellulose derivatives can be formed by partially or totally reacting the three hydroxyl groups present on the anhydroglucose unit with various reagents. Table 2 represents the commonly synthesized derivatives of cellulose. Derived celluloses are more resistant to microbial attacks as well as enzymatic cleavages than native cellulose forms. A variety of films can be formed from these derivatives, their applications range from food packaging films to water-soluble edible films [46]. Soroka in 2009 established the functions of food packaging material. He enlisted that packaging should provide mechanical protection and structural support for food products. It should also prevent penetration of liquids, gases (O_2 and CO_2), light, microbes, and grease in or out of the package [47].

Table 2: It shows derivatives of cellulose used for food packaging applications (Source: Cellulose Derivative Films-A Review) [48]

Cellulose ethers	Cellulose esters
Methylcellulose	Cellulose acetate
Hydroxypropyl methylcellulose	Cellulose acetate butyrate
Ethylcellulose	Cellulose triacetate
Hydroxyethyl methylcellulose	
Carboxymethylcellulose	
Hydroxyethylcellulose	

Cellulose derivatives are a class of natural polymers that are most relevant for packages that come into direct contact with foods. Research on the properties of different cellulose derivatives used for film formation is going on to develop blends and layers of cellulose derivatives with other biopolymers or synthetic polymers to enhance the mechanical, barrier properties, and shelf life of food packaged. Another research topic is the expansion of cellulose acetate (CA), methylcellulose (MC), and carboxymethylcellulose (CMC) as cellulose derivatives which are being extensively used for film formation. The potential of cellulose derivatives for food packaging is evaluated against properties of petro-plastics in food packaging, HDPE and LDPE and the typical oxygen barrier properties of PET. They serve as a reference for comparing the properties of cellulose-based packaging and edible films, even if LDPE and PET are not specifically used as edible films.

Cellulose acetate films

Derived cellulose acetate (CA) is a general term for a variety of acetate esters of cellulose [46]. Cellulose acetate along with cellulose diacetate and cellulose triacetate is used in food packaging as a rigid wrapping film widely. Membranes are also formed by these cellulose derivatives [49]. Esterification of 92% of the hydroxyl groups of the cellulose molecule in cellulose triacetate was done [50]. Fig.4 represents the structure of cellulose acetate. The tensile strength of commercial cellulose acetate is 41 MPa-87 MPa (at 23 °C, ISO 527-2), and the elastic modulus is found to be 1.9 GPa-3.8 GPa (at 23 °C, ISO 527-2). The WVP is 1.1·10-12 to 1.7·10-12 g·m/m²·s Pa (The iDES Inc. 2012) of vinyl-coated, CA films used for packaging. Casting of CA dense membranes give an OP of 3.7·10-12 cm³·m/m²·s Pa (at 20 °C, 0% RH) [51]. CA films by the addition of naturally occurring antioxidants L-lysozyme and L-tyrosine can be rendered [52].

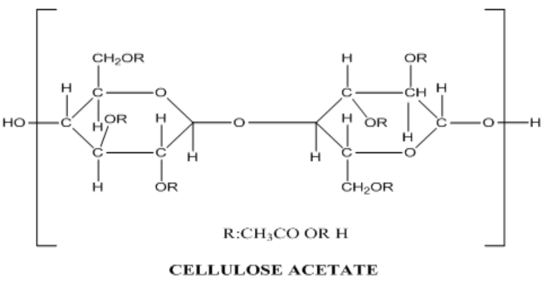

Fig. 4: It shows structure of cellulose acetate (Source: Edible films and coatings: characteristics and properties) [45]

Immobilization of fungal derived naringinase on CA films was done. These films reduced the bitterness components of citrus juices [53]. Antimicrobial CA films were made by adding the potassium salt of sorbic acid (potassium sorbate) [54], lysozyme [55], and sodium proprionate [56]. Antimicrobial films affect the growth of pathogens in food by slowly releasing the active agent from the film and dissolving onto the surface of the food through direct contact. This extends the shelf life of the food product. The porosity of the film and the release rate of the active agent are critically important.

CA films by the dry phase inversion technique were prepared [54]. Different porosities containing films were made by changing the initial casting composition, drying temperature, and wet casting thickness. Crystallization of the antimicrobial agent (potassium sorbate) is affected due to a degree of porosity during drying. Dense films showed a low degree of crystallization. The release rate of the antimicrobial agent was controlled by the dissolution of the emerged crystals. Entrapping behavior of the active agents into pores of the film was carried out in 2010 [52]. The release direction can be controlled by asymmetric films, where one side is denser than the other. By changing the chemical linking of the active agent into the matrix, the release kinetics of the active agent can be manipulated. Compostable packaging by recovered keratin from wool waste and forming a keratin-filled translucent CA composite film was created [57]. Work on cellulose diacetate (CDA) mixed with potato or corn starch was carried out in 2000. Triacetylglycerol was added as a plasticizer and was hot-molded into films [58].

Methylcellulose films

Methylcellulose (MC) is formed when one or several of the hydroxyl groups (-OH) in an anhydroglucose unit are replaced by a methoxide group (-OCH_3). Fig.5 represents structure of methyl cellulose. If the other two hydroxyl groups in the sugar unit can be replaced by; ethyl (-OC_2H_5) or a hydroxypropyl (-$OCH_2CH(OH)CH_3$) group, the corresponding compound is called methylethylcellulose (MEC) or hydroxypropyl methylcellulose (HPMC).

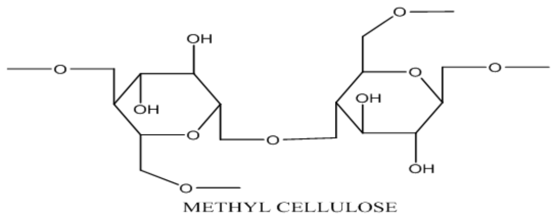

Fig. 5: It shows structure of methylcellulose (Source: Edible films and coatings: characteristics and properties) [45]

The degree of substitution of MC is within the range 1.4 to 2.0 is soluble in cold water [44]. In 2011, it was reported that it forms continuous, flexible, transparent, tasteless non-toxic films that have good oxygen barrier properties but poor water vapor properties [59]. In the starch whey protein MC films were found that the oxygen barrier properties of these films could be predicted by the relative amounts of the components and their OTR. MC has relatively high tensile strength and elastic modulus due to which it showed reinforcing effect [60]. MC is a film-forming substance which shows enhanced mechanical properties in blends containing proteins, lipids etc [61]. MC content in the blends increases the mechanical properties also increase but at the same time the resistance to water vapor penetration decreases [62].

As the amount of glycerol is increased it gradually reduces the tensile strength, increases the elongation at break, and reduces the oxygen barrier [60]. The addition of lipids as a moisture barrier in these films usually leads to a decrease in mechanical properties [63]. The addition of gelatin to polysaccharide based films was carried out and it was concluded that gelatin improves the moisture barrier only at a certain pH and reduced the mechanical properties in all cases [64]. MC films which were filled with microcrystalline cellulose at a loading level of 0.25% and found that it improved the puncture strength by 117% and simultaneously decreased the water vapor permeability by 26% [65].

Carboxymethylcellulose films

Carboxymethylcellulose (CMC) is a cellulose derivative in which some of the hydroxyl groups of the glucpyranose units in cellulose are replaced by carboxymethyl groups. CMC is formed by an alkali catalyzed reaction with chloracetic acid ($ClCH_2CO_2H$) and is represented in Fig.6. CMC has a film forming capability as it readily absorbs moisture, dissolves easily in cold water, and shows thermal gelatinization. CMC is used as edible films for food packaging. Recently in 2012 work on agricultural waste materials as well as alternative cellulose sources for preparation of CMC was carried out and found that durian rind and the invasive, weed-like tree Mimosa pigra are among one of the important sources [66]. In 2011, CMC films by suspension casting method were prepared. CMC is first dispersed in the water then mechanically stirred, and fillers and other additives are added. Then the films are cast onto a suitable flat surface such as a Petri dish [67]. Incorporation of hydrophobic lipids into hydrophilic CMC blends by emulsification was carried out in 2008 [68].

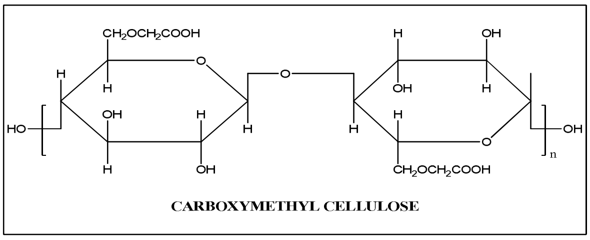

Fig. 6: It shows structure of carboxymethyl cellulose (Source: Edible films and coatings: characteristics and properties) [45]

CMC blends have been made with chitosan, gelatin, starch, Glucomannan, sodium caseinate, PVA, polyvinyl amine, sunflower oil and oleic acid. Sometimes the interaction between CMC and the copolymers is identified and the cross-linking of dialdehyde-CMC (DCMC) in gelatin-based films was established [69, 70] andonCMC in starch films [71]. Cross-linking in these films enhances the mechanical and barrier properties of the composites against water vapor. CMC was studied as a hydrogel polymer. Roy and his researchers found that dry hydrogels are considered biodegradable alternatives to petroplastic food packaging materials [72]. Blends prepared with synthetic polyvinyl pyrrolidone and CMC have a tensile strength of 1.42 GPa. In a compost bed biodegradation experiment, the films maintained their elastic properties for two weeks. The films were found to be hygroscopic and absorbed moisture released by packed foods (fruits and vegetables). The concentration of alkali during the fictionalization of cellulose had a direct effect on the tensile properties of CMC films. The higher is the concentration of carboxymethyl groups in the cellulose molecule, the stronger the CMC film is due to strong intermolecular forces. In addition to using fillers in CMC blends (clay, microcrystalline cellulose, and chitosan) an improvement in the mechanical properties is usually observed. The tensile strength and the E-modulus are increased, and the strain at break of the films is reduced. Fillers like glycerol in CMC based films can be seen increases the ductility of the film significantly but also decreases the tensile strength and the modulus of elasticity [66, 67].

- **Water vapor barrier properties**

CMC may reduce the WVP of the composite, depending on the polymer materials like starch [73]. CMC films are found to be permeable to water vapor, and several approaches like an addition of lipids have been tested to reduce their permeability. On increasing the mass fraction of lipids will reduce the WVP of CMC films and also decreases the mechanical properties of the films. The degree of substitution (DS) of CMC directly affects the hydrophilicity of the film, which in turn is directly proportional to the WVP of the CMC films [66]. During the preparation of CMC at a certain alkaline concentration, the DS reaches its maximum, which coincides with the maximum permeability to water vapor.

- **Oxygen barrier properties**

Noncellulosic hydrolysate containing oligo polysaccharides and lignin prepared from the nonpurified wastewater of a wood pulping process. When these are mixed with CMC it forms homogeneous films with very low oxygen permeability of 9.3·10-15 cm^3·m/m^2. s·Pa (at 23 °C, 760 mmHg) for a CMC/hydrolysate-(mixing ratio 1:1). A good oxygen barrier film material has an OP smaller than 1.2·10-13 cm^3·m/m^2·s·Pa. [74].

Chitosan MC Films

Chitosan (CH) is derived from crustacean chitin, and finds its use as a food packaging material. The second most abundant polysaccharide chitosan is a non-toxic, biocompatible, biodegradable derivative of chitin. Fig.7 shows the structure of chitosan. Its antimicrobial activity against a large spectrum of bacteria and low toxicity toward mammalians was found out recently [75, 76]. One of the drawback to utilizing chitosan is its cost. Binary blends of chitosan with MC were made [59, 77-85]. Also, ternary blends with MC and PVA to create edible films were formed [82]. Chitosan due to its rigid character has been shown to increase the elastic modulus and tensile strength of the MC films in binary blends [78, 81]. The addition of CH increases the solubility of the films in water by and decrease the WVP of the composites [59].

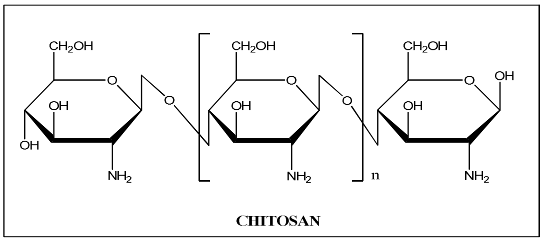

Fig. 7: It shows structure of chitosan (Source: Edible films and coatings: characteristics and properties) [45]

Chitosan containing methylcellulose can act as a matrix in a composite. Silica nano-particles have been used as filler in these [59]. Work on antimicrobial Chitosan containing MC solutions and it was found that it inhibited the growth of Listeria monocytogenes, a virulent food-borne bacterium causing listeriosis [77]. Vanillin was used as an antimicrobial agent in CH-MC based blends [82]. Antimicrobial MC films containing no CH have been prepared with olive leaf extract [87]. The films contained glycerol and 0.5-3.0 w/v% of olive leaf extract (OLE-containing physiologically active polyphenols). The OLE increased the tensile strength, but reduced the elongation at break as well as reduced the water vapor permeation and inhibited the growth of Staphylococcus aureus in cheese. Cinnamaldehyde (obtained from cinnamon bark), eugenol (extracted from essential oils such as clove oil), and carvacol have also been used as antimicrobial agents in the MC matrix [88]. Table 3 enlists preservation requirements of common food categories.

Future prospects

Intervention of nanotechnology in food packaging:

In 2007 it was found that nano composites are now known to exhibit increased barrier properties, increased mechanical strength, and improved heat resistance and stability as compared to the native polymers [90]. The importance of nanotechnology to food sector arose from 2002 from 150 million US dollars and has risen to 860 million US dollars in 2004 [91]. Nanotechnology is used nowadays to encourage active packaging which involves incorporation of antimicrobial activity to food packaging materials which can control the microbial surface contamination of food. Both migrating and non-migrating antimicrobial materials were investigated. Contact between the food product and packaging material is found to be an essential factor and therefore potential food applications include vacuum or skin-packaged products like fish & poultry etc. Graphene nanosheets that are used as fillers (nanoclays, kaolinite, carbon nanotubes) had potential that can improve the ability of plastic packaging against migration of gases, flavour compounds, and as well as boosting the shelf life [92]. There are also possibilities to combine antimicrobial compounds with different types of carriers used for food packaging like plastic and rubber articles, food-packaging materials, and paper-based materials. Antibodies can also be coupled to fluorescent nanoparticles to detect various toxic chemicals or food borne pathogens over food. Still the complete life cycle of polymer nanotechnology for the packaging material is being explored [93].

Table 3: It shows requirements of packaging and preservation of common food categories (Source: Development of Packaging for Food Products-AARON L. BRODY) [89]

Food item	Type of packaging film	Properties
Non-vegetarian		
Ground Meat	Plasticized polyvinyl chloride (PVC) film.	Being a poor gas barrier, these films permit access air and hence the oxymyoglobin red color is for the short duration of retail distribution.
Case-Ready Meat	Polyester/Polyolefin film.	Gas / moisture barrier whose internal atmospheres are carbon dioxide to retard the growth of aerobic spoilage microorganisms.
Case-Ready Meat	Polyester/Polyolefin film.	Gas / moisture barrier whose internal atmospheres are carbon dioxide to retard the growth of aerobic spoilage microorganisms.
Processed Meat	Polyvinylidene chloride (PVDC) film.	Oxygen barrier.
Poultry	Polyvinyl chloride(PVC)/ Polyethylene film	Moisture and microbial barrier.
Fish	Polyethylene film.	Moisture resistant, protect the structural case against internal moisture.
Dairy products		
Milk	Polyethylene coated paperboard or bottles.	Retards the loss of moisture and resist fat intrusion and avoidance of contamination.
Cheese	Polyester/Polyvinylidene chloride	Gas barrier packaging under elevated carbon dioxide which is used to retain the internal environmental condition.
Fruits and vegetables		
Apples, pears, strawberries, lettuce, tomatoes, etc.	Monolayer Polyethylene film	Retards moisture loss to extend the refrigerated shelf life and provide controlled atmosphere preservation.
Dry foods		
Beverage mixes, soup mixes, blends of dry sugars, dehydrated meat	Polyolefin film	Total barrier to water vapor and oxygen after removal of air.

CONCLUSION

The novel synergistic combination of biopolymers, with their modified derivatives and additives, is at par with commercially available and widely used synthetic polymer based packaging films available in the market. Also, economically the wholesale rate of starch, guar (biopolymers used in the preparation of these cling films) are cheap enough when compared to petroleum-based synthetic raw materials. So therefore, these films can produce sound effect both economically as well as environmentally. Some films can be synthesized with antimicrobial activities using antimicrobial agents as fillers which not only extends the shelf life of food products, but also keeps food items safe from microbes. The qualities of these films have been standardized using ASTM standards for Packaging of Food Products and good results have been obtained on the laboratory scale. Therefore it is concluded that, future belongs to Biodegradable Green Plastics Packaging Materials and the study carried out reveals that these packaging films can be prepared and validated on an industrial scale and can be used after further standardized for commercial application. These natural polymer based cling films for food packaging will become relevant and will revolutionize the packaging industries in a span of time.

CONFLICT OF INTERESTS

Declared None

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