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Annals of Biological Research, 2013, 4 (2):253-256
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ISSN 0976-1233
CODEN (USA): ABRNBW

Properties of collagen based edible films in food packaging: A review

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ABSTRACT

Films are thin coatings of materials that protect the product against mechanical and corruption factors. The use of edible films and coatingsis developed these days because they can retain the quality, flavor and moisture content of the product and also are degradable and easy to use. Proteins are an apt choice for such film's base material as their suitable barrier property against oxygen, CO_2 and fat especially in low relative humidity. Collagen is a protein biopolymer used specially for meat products and has good mechanical properties although its permeability to O_2 increases with RH degrees. Higher water solubility and lower resistance of collagen to moisture has to be eliminated by increasing cross-link density with polysaccharide derivatives. Another way is blending of hydrophilic synthetic polymers with collagen that represents better mechanical properties. The best method for its extraction is acid hydrolysis which is a mediocre one.

Key words: Biopolymer, Edible films, Protein, Collagen.

INTRODUCTION

Films are thin layers of materials; they usually consist of polymers able to provide mechanical strength to the stand-alone thin structure. Edible films and coatings are produced from edible biopolymers and food-grade additives. Edible films and coatings enhance the quality of food products, protecting them from physical, chemical, and biological deterioration [1]. The application of edible films and coatings can protect food products from moisture migration, microbial growth on the surface, light-induced chemical changes, oxidation of nutrients etc [1]. Most commonly, edible films and coatings function as barriers against oils, gases or vapors, and as carriers of active substances, such as antioxidants, antimicrobials, colors, and flavors [1, 2, 3, 4, 5]. These protective functions are aimed to enhance the quality of food products, resulting in shelf-life extension and safety improvement [2].Film-forming biopolymers can be proteins, polysaccharides (carbohydrates and gums) or lipids [6].

Proteins are good film formers exhibiting excellent oxygen, carbon dioxide and lipid barrier properties, particularly at low relative humidity. Edible films based on proteins were found to possess satisfactory mechanical properties [1, 7, 8]. Protein film-forming materials are derived from many different animal and plant sources, such as animal tissues, milks, eggs, grains, and oilseeds [9]. Protein films are brittle and susceptible to cracking due to the strong cohesive energy density of the polymer [10]. The addition of compatible plasticizers improves the extensibility and viscoelasticity of the films [11]. Currently, edible films and coatings are used with several food products, mostly fruits, vegetables, candies, and some nuts [4, 12].

Collagen is the most commercially successful edible protein film. Film-forming collagen has been traditionally used in the meat industry, for the production of edible sausage casings. This protein has largely replaced natural gut casings for sausages.Collagen is a fibrous, structural protein in animal tissue, particularly skin, bones and tendons and represents about 30% of the total mass of the body [13].Collagen is readily available, non-toxic and provides an excellent basis for biomaterials. The main amino acids in collagen are: glycine, proline, hydroxyproline and alanine. The ordered triple helical structure of collagen is stabilized by both intra-chain hydrogen bonds and by structural water molecules Collagenfibrils are produced by self-assembly of collagen molecules in the extracellularmatrix, and provide tensile strength to animal tissues [14]. CollagenEdible films and coatings from animal origin proteins can be dissolved in dilute acid or alkali solutions, and in neutral solutions. Two majorcomponents are identified; α (MW 100 000 Da) and β(MW 200 000Da), and consistof two different types of covalent cross-linked chain pairs α_1-α_1 and α_2-α_2 [15, 16]. Hydrolysis of collagen results in gelatin. The molecular weight of gelatin covers a broad range, from 3000-200 000 Da, depending on the raw material employed duringgelatin production and handling conditions. Edible coatings made with gelatin reduce the migration of moisture, oxygen and oil.

Collagen films are not as strong and tough as cellophane, but have good mechanical properties [17]. Collagen films have an excellent oxygen barrier at 0% relative humidity, but the oxygen permeability increases rapidly with increasing relative humidity in a manner similar to cellophane [18]. Different cross-linking chemical agents have been used to improve the mechanical properties, to reduce the solubility, and to improve the thermal stability of these films. Carbodimide, microbial transglutarninase, and glutaraldehydeare usually used as cross-linkingagents [19, 20, 21].

Solubility of Collagen

Collagen is practically insoluble in water, but lowering the pH of solution can increase solubility.In the whole range of pH, solubility varied between 28.9% and 52.5% (Figure 1).Maximum solubility was observed at pH 2, whereas minimum solubility occurred from pH 6 to 11. The region of increasing solubility (pH 5 to 2) coincides with the range of increasing amount of proton combined with collagen fibers.High solubility observed at low pH´s because of conformation change induced by interactions between proteins and hydrogen ions in the acid medium, lead to higher hydration of collagen. Insoluble collagen is converted to soluble gelatin by acid or alkaline processing, but whereas products made from native collagen possess significant strength, this strength is lost when soluble collagen is used [22].

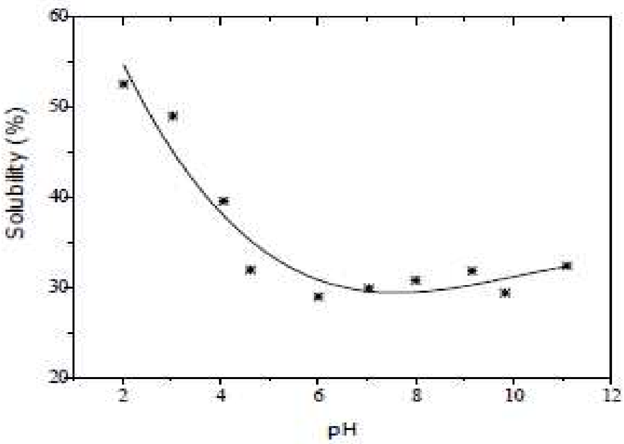

Fig1. Solubility of collagen

Hydrolyzate of Collagen

Collagen utilization in the way of a secondary industrial raw material is complicated by the quite high density of irreversible crosslinks introduced to stabilize collagen material against chemical and above all against microbial influences.

The first step in procedures proposed for processing such waste usually consists in partial hydrolysis which is realized as acid hydrolysis, alkaline, or as the comparatively least energy demanding, and thus economically most interesting, enzymatic hydrolysis. Processing collagen hydrolysates into edible packages has to take into account their lower molecular mass. That usually attains values around 15–30 kDa which, when compared with gelatin currently used for edible packages, is a level of 5–10 times lower. Higher water solubility and lower resistance of hydrolysate based packaging films and foils to moisture have to be eliminated by increasing cross-link density in hydrolysate [23].

Combination of Collagen with synthetic Polymer:

Blends of synthetic and natural polymers represent a new class of materials with better mechanical properties and biocompatibility than those of the single components.Collagen as a packaging material singly is not an ideal film, so it is better to combine it with other polymers likepolivinylalkohol(PVA), polivinylpyrrolidone(PVP), poliethyleneoxide(PEO) and poliethyleneglycol (PEG) that are water soluble.The miscibility and compatibility of two polymers depend on their ability to form specific interaction between them, which contributes to diminish or make negative the mixing enthalpy. Blends of collagen and synthetic polymer have been prepared mainly in the form of films using the solution casting method. [24]

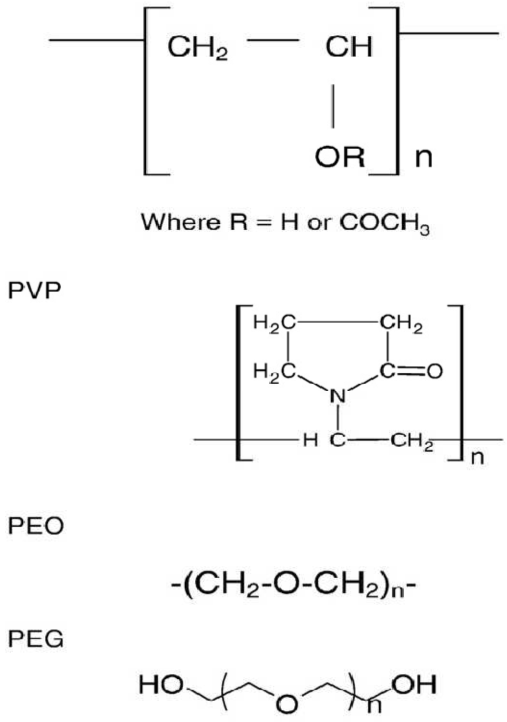

Fig2.Chemical formula of polivinylalkohol (PVA), polivinylpyrrolidone (PVP), poli ethylene oxide (PEO) and poliethyleneglycol (PEG)

Extraction of Collagen

Collagen is unique in its ability to form insoluble fibers that have high tensile strength (TS).
Traditional sources of collagen have mainly been sourced from pig skin and Cow hide but, fish offal such as bones, skin, scales and fins can serve as an alternative source of collagen.

Mammalian collagen differs from fish collagen in that fish collagens have lower gelling and melting temperatures but relatively higher viscosities than equivalent bovine forms

One possible commercial use for these fish-sourced collagens could be in applications where high viscosity solutions are required (films) [25].

a. ***Hydrogen Peroxide Extraction:***
In this way removed skins of fishes rinse with water and chill to 2˚C, then the skins mince and mix with distilled water & hydrogen peroxide (30% v/v). Following washing, the minced skins were dewatered using a screw press [25].
b. ***Enzymatic Extraction:***
In thismethodtwo types ofproteolytic enzymes (Protamex or Dizym) useto extract of collagen.One of the enzymes was added to cod skins (rinsed with water and minced) and a buffer solution with pH 7.5 and shaken for 2 hours. Skinswerethenseparatedandwashed with distilled water [25].
c. ***Acid Extraction:***
In this way thefishskin were ground in a grinder and extracted with 0.1 N sodium hydroxide to remove non-collagenous proteins,then washedwith distilled water andtheskinseparated bycentrifugation. The pelletwas removed and placed in butyl alcohol 10% for 1 hour to remove fat,thencentrifuged again. Theshellswerewashed with distilled waterandstoredincholoridric acid solution withpH 4.0 then freeze-dried [25].

Film Formation

For each film, 40 g of an aqueous solution of acid extracted fish collagen (1% w/w) was poured onto a level circular perspex plate and dried for 48 h to a constant weight. Films were peeled from the plates and stored. Glycerol was added as a plasticizer (0.08%, w/w) [25].

Plasticizers

In most cases, plasticizers are required for edible films and coatings, especially forPolysaccharidesand proteins. These film structures are often brittle and stiff due to extensive interactions between polymer molecules [9]. Plasticizers arelow molecular weight agents incorporated into the polymeric film-forming materials,which decrease the glass transition temperature of the polymers. They are able to positionthemselves between polymer molecules and to interfere with the polymer-polymerinteraction to increase flexibility and processability [3, 9]. Plasticizers increase the free volume of polymer structures or themolecular mobility of polymer molecules [26].

CONCLUSION

Increasing use of edible films with appropriate mechanical and barrier properties has occurred competitive field in food packaging. Edible film prevent moisture, oxygen, carbon dioxide, fatty and aromatic substances penetration, so they have major role in increasing shelf life of foods and maintaining their quality. Proteins are commonly used film-forming biopolymers and collagen is one of the most successful ediblefilmson commercial scale. Protein biopolymers are naturally sensitive and fragile, so plasticizers are used to increase flexibility of them but their use increases the permeability of the film. The type and amount of plasticizer used to achieve mechanical and barrier properties are important.

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