PAPER

THE PHYSICOCHEMICAL PROPERTIES OF EDIBLE PROTEIN FILMS

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ABSTRACT

In the present study, edible films from isolated or concentrated protein sources and from proteins of two different fish species were produced. The texture properties, light transmission (LT) and oxygen permeability (OP) of producing films were determined. The CL film settled in the second range according to both tension test parameters, thus outclassing the other tested films. The WG film possessed the lowest LT, so making it more effective in protecting of food products from light than the other tested films. The SPI film with the lowest OP value can be used for the purpose of protecting of food products from harmful effects of oxidation.

- Keywords: Coating, edible protein films, permeability, smoked fish, texture -

1. INTRODUCTION

Edible films and coatings are thin layers that can be eaten with food. They are derived from natural sources and are formed on the surface of a food for the purpose of protecting food and to prolong its shelf-life. For this agricultural function, protective coatings were improved as an alternative to commercial packaging materials such as glass, tin and polymer. Edible films and coatings do not carry carcinogen risk and do not cause a waste problem, which are important problems with plastic-based food packaging.

If edible films are prepared in appropriate conditions, they can perform all the functions of a useful package. Edible films are prepared utilizing hydrocolloids (protein and polysaccharide), lipids and composites (hydrocolloid+lipid). Edible protein films are separated, however, into two groups: plant origin proteins (corn zein, wheat gluten, soy protein, pea protein, sunflower protein, peanut protein and cotton protein, etc.) and animal origin proteins (keratin, collagen, gelatin, fish myofibrillar protein, egg white protein, casein and whey protein, etc.). Edible protein films can be manufactured from isolates or concentrated protein products that are purified from various protein sources, and by the evaluation of processing waste products (RHIM and NG, 2007).

The use of edible films for food is very old. So far, the most important application of edible films and coatings is an emulsion, made from oil and waxes (in 1930) that protect the important features of fruits such as brightness and color, prevents complications such as softness, initialing paleness and for improving fungicides, to better control the maturation and to delay water loss (DEBEAUFORT *et al.*, 1998; BALDWIN, 1999).

The advantages of natural biopolymer films can be summarized as follows: they are edible and biodegradable; to supplement the nutritional value of foods; enhance organoleptic characteristics of food, such as appearance, odor, and flavor; reduce packaging volume, weight and waste; incorporate antimicrobial agents and antioxidants; extended shelf-life and improved quality of usually non-packaged items; control over inter-component migration of moisture, gases, lipids, and solutes; individual packaging of small particulate foods, such as nuts and raisins; function as carriers for antimicrobial and antioxidant agents; for microencapsulation and controlled release of active ingredients; and have a possible use in multilayer food packaging materials together with non-edible film. They are low-cost and abundant; annually renewable resources (KROCHTA, 2002).

Despite the positive effects in the literature (GENNADIOS *et al.*, 1997), the industrial application of edible films is not very common yet. The theoretical, experimental studies related to different polymers will be used to compose edible films or coatings (using fresh, frozen, processed products and determining the permeability properties of films) are currently underway.

In the present study were used soy protein isolates (SPI), whey powder protein (WP), egg white powder protein (EWP), wheat gluten (WG), corn zein (Z), cattle gelatin (G) and collagen (CL), as well as rainbow trout protein (RTP) and Atlantic mackerel protein (MP) as the protein source. The texture properties, the light transmission and the oxygen permeability of edible films produced from these sources were established.

2. MATERIAL AND METHODS

2.1. Edible protein film manufacturing

The materials for the production of edible protein film were obtained from the Smart Chemicals Company (Izmir, Turkey). The edible protein films were manufactured as explained below, by pouring a determined amount film of solution into a Teflon pan (18 cm×18 cm), drying for a determined time and at a determined temperature.

2.1.1. Soy protein isolates (SPI) film

5 g SPI (produced in Germany and containing 90% protein), 100 mL distilled water and 2.5 mL glycerol (GLY) was stirred for 15-20 minutes at 55-60°C. This solution was then stirred for another 10-15 minutes at 75-80 °C and filtered through a cloth, after the solution's pH was adjusted to 10.5±0.1 with 2 M sodium hydroxide (NaOH) solution (DENAVI *et al.*, 2009). Prepared film solution (70 mL) was poured into a Teflon pan and dried for 24 hours at 35°C.

2.1.2. Whey protein (WP) film

5 g WP (produced by Lactoprot Company in Germany and containing 80% protein), 100 mL distilled water and 5 mL GLY was stirred for 15-20 minutes at 55-60°C. This solution then was stirred for another 15-20 minutes at 75-80 °C and filtered through a cloth, after the solution's pH was adjusted to 8.0±0.1 with 2 N NaOH (SARIKUS, 2006). The WP film solution (70 mL) was poured into a Teflon pan and dried for 48 hours at 35°C.

2.1.3. Egg white powder protein (EWP) film

9 g EWP (produced in Turkey and containing 80% protein), 100 mL distilled water, 4.5 mL GLY was stirred for 5 minutes at room temperature. Then the solution's pH was adjusted to 11.25±0.1 with 1 N NaOH. The solution was kept for 20 minutes in a water bath at 45 °C and filtered through a cloth (GENNADIOS *et al.*, 1997). The prepared film solution (70 mL) was poured into a Teflon pan and dried for 24 hours at 35°C.

2.1.4. Wheat protein (gluten-WG) film

7.5 g WG (produced in Belgium and containing 75-82% protein), 55 mL 95% ethyl alcohol, 45 mL distilled water and 3.75 mL GLY was stirred for 15 minutes at 55 °C. The solution's pH was adjusted to 4.0±0.1 with 50% acetic acid. The solution was filtered through a cloth, then stirred for another 15 minutes at 70 °C (TANADA-PALMU, 2000). All the prepared film solution was poured into a Teflon pan and dried for 48 hours at 45°C.

2.1.5. Corn protein (zein-Z) film

The film solution was prepared from zein protein (produced by Sigma Aldrich in USA and containing 90% protein), by modifiying the method developed by BAYSAL *et al.* (2009). 2.5 g Z, 60 mL 95% ethyl alcohol, 1 mL GLY was stirred for 30 minutes at 75-80 °C (BAYSAL *et al.*, 2009). The pH of the prepared Z film solution was measured as 5.8. The Z film solution (40 mL) was poured into a Teflon pan and dried for 24 hours at 45°C.

2.1.6. Gelatin (G) film

2 g G (produced by Rousselot Company in Argentina and containing 83% protein), 100 mL distilled water, 1.1 mL GLY was stirred for 30 minutes at 55-60 °C. The solution was then filtered through a cloth (THOMAZINE *et al.*, 2005). The pH of the prepared G film solution was determined as 5.1. The G film solution (130 mL) was poured into a Teflon pan and dried for 48 hours at 45°C.

2.1.7. Collagen (CL) film

3 g CL (produced in Turkey and containing 90% protein), 200 mL 3% acetic acid, 1.5 mL GLY was stirred for 30 minutes at 75-80 °C (HO *et al.*, 2001). When prepared according to this method, the pH of the CL film solution was 3.3. All the prepared film solution was cast into Teflon pan and dried for 24 hours at 45°C.

2.1.8. Rainbow trout protein (RTP) film

Rainbow trout (*Oncorhynchus mykiss*) were obtained from the Istanbul Fish market. The fish were transported in ice to the laboratory. The gutted and beheaded fish were minced, after skinning. The fish mince was washed 2-3 times to remove the water-soluble proteins, blood and dirty components, by keeping it for 5-10 minutes in cold water (water:fish ratio of 4:1, w/w). Following the washing process, fish mince was pressed through a cloth in order to remove water. Prepared in this way, washed fish mince constituted the raw material for the edible fish film. Previously produced edible film were tested for protein and moisture in this mince. The RTP ratio was found to be 18.48%, and the moisture ratio was found to be 73.35%. Because the protein ratio of the fish mince should be 2%, it was adjusted by adding the necessary amount of distilled water and then GLY at a ratio of 50% of the protein ratio was added. The mixture was blended and filtered. The solution's pH was adjusted to 3 with 50% acetic acid, after the solution was stirred for 10-15 minutes at 75-80 °C. The solution was stirred for another 10-15 minutes at 75-80 °C (CUQ *et al.*, 1997). The prepared film solution (100 mL) was poured into a Teflon pan and dried for 24 hours at 35°C.

2.1.9. Atlantic mackerel protein (MP) film

Used in manufacturing of edible film, Atlantic mackerel minces (*Scomber scombrus*) were prepared by cleaning and washing, as in the case of rainbow trout flesh. The MP ratio was found to be 23.38%, and the moisture ratio was found to be 72.62%. The MP film manufacturing method was similar to the RTP film manufacturing method. The only difference was that less distilled water was added, as when adjusting the protein ratio was to 2%, because of the MP ratio was higher. The film solution's pH was adjusted to 3 again (CUQ *et al.*, 1997). The MP film solution (100 mL) was poured into a Teflon pan and dried for 24 hours at 35°C.

2.2. The texture Profile of the films

Tension tests were made for the purpose of determining the resistance of the film against breakage and tensile forces. Test measurement values were as follows: target type: distance, test type: tension, target value: 40-90 mm, trigger load: 0.04 n, test speed: 0.5 mm/second, return speed: 4.5 mm/second, probe type: TA3/100, fixture: TA-DGA, load cell: 1500 g. The measured parameters were the tensile force (N) and the maximum elongation (mm). Three measurements were taken from three protein films belong to each group.

2.3. The Light Transmission (LT) of the films

The LT of edible protein films was measured according to the method in ASTM (2009) by using working visible position dual beam spectrophotometer at 560 nm, at 23±2 °C. This test method covers the measurement of the transparency of plastic sheeting in terms of regular transmittance (T_r). Although generally applicable to any translucent or transparent material, it is principally intended for use with nominally clear and colorless thin sheeting. Three measurements were taken from three protein films belong to each group. The LT of the films was calculated with the formula below accord-

Table 1 - The texture parameters, the light transmission and the oxygen permeability values of edible protein films.

Edible protein film	Tensile force (N)	Maximum elongation (mm)	Light transmission (%)	Oxygen permeability (mL/mm/day)
SPI	2.883±0.155AF	31.85±1.11AG	20.08±0.01A	17.10±0.01A
WP	0.668±0.001B	5.69±1.03B	23.35±0.01B	322.00±0.01B
EWP	1.972±0.117AC	82.00±2.94C	23.22±0.01C	45.40±0.01C
WG	1.275±0.147BC	57.40±2.07D	13.29±0.01D	218.00±0.01D
Z	0.948±0.427BC	0.50±0.02B	19.92±0.01E	181.37±0.01E
G	5.267±0.559D	35.12±1.88AF	63.30±0.01F	45.50±0.01F
CL	4.145±0.198DE	68.03±1.57E	18.70±0.01G	105.10±0.01G
RTP	3.559±0.720EF	39.94±0.03F	14.53±0.01H	97.10±0.01H
MP	1.273±0.082BC	28.95±0.96G	39.35±0.01I	281.00±0.01I

*Different letters (A, B, C) in the same column indicate the significant difference (P<0.05).

ing to light intensity value, measured by equipment (ASTM, 2009).

$$T_r = (I_r/I_0) \times 100$$

T_r: Light transmission, %
I_r: Light intensity value of spectrophotometer bath with sample
I_0: Light intensity value of spectrophotometer bath without sample

2.4. The Oxygen Permeability (OP) of the films

The OP of the films was measured during 4 hours at 23±2 °C by using Systech mark gas permeability test equipment, at 170 bar O_2 of pressure (ASTM, 2010). Three measurements were taken from three protein films belong to each group.

2.5. Statistical analysis

The resulting analysis data were evaluated by using an IBM SPSS Statistics 20® program. The results were given as an average ± standard deviation. The one-way analysis of variance (One-Way ANOVA) was applied. In the data parametric assumptions for multiple comparisons occurred. The Tukey test was used to locate the sources of the differences found within different groups in this test. P<0.05 variation was accepted as the significant discrepancy between the groups and the parameters.

3. RESULTS

The texture parameters, the light transmission and the oxygen permeability values of edible protein films are presented in Table 1. The lowest and the highest tensile force of edible protein films were 0.668±0.001 N (in the WP film), and 5.267±0.559 N (in the G film), respectively. The Z film had the lowest maximum elongation (0.50±0.02 mm), and the EWP film had the highest maximum elongation (82.00±2.94 mm) (Table 1).

It was reported by SABATO *et al.* (2007) that mechanical and barrier properties of protein-based films were generally better than polysaccharide (PLS)-based films. The properties of protein-based films were dependent on the various factors, such as the protein source, the pH of protein solution, the species and the amount of plasticizer, film thickness, the manufacturing conditions (temperature and relative humidity), and the structures, included film forming solution (enzymes, antimicrobials, etc.) (BENJAKUL *et al.*, 2008).

TEMIZ and YESILSU (2006) indicated that when made from WG strong films have mechanical properties like rubber. WG films, containing a low amount of GLY, had a higher tensile resistance (TR) and lower elongation at break (EAB) (TANADA-PALMU *et al.*, 2000). When the WG film was prepared from three different flours (commercial bread flour, hard red winter flour and soft white flour), it had a smooth tissue and film resistance, measured as TR, and the ratio increased by 50% by adding cysteine (cross-linking agent) (RAYAS *et al.*, 1997). When the mechanical and physical properties of the WG films, plasticized with GLY, were examined at different temperature (20°C, 50°C and 80°C) and the relative humidity (35% and 70%), the tensile strength (TS) increased too, by increasing the drying temperature at 35% relative humidity. TS decreased, when the temperature increased, however, at 70% relative humidity. The film thickness decreased with increasing temperature (KAYSER-ILIOGLU *et al.*, 2003). LIEBERMAN and GILBERT (1973) reported that the mechanical properties of edible films were considerably affected by the ratio of the plasticizer, used.

The composite films can be manufactured taking into account the different barriers and mechanical properties needed by different products and thus the effectiveness of the material was increased. The use of the plasticizers such as GLY, polyethylene glycol (PEG), sorbitol (SOR), etc. in the film formulations or the composites is advan-

tageous to impart pliability and flexibility, which improves handling. Utilization of the plasticizers reduces the brittleness of film by interfering with the hydrogen bonding between the lipid and hydrocolloid molecules (THARANATHAN, 2003).

In the study of MARINIELLO *et al.* (2003), whole soy flour and apple pectin were used as raw materials in order to obtain films, which due to their consistency could be perfectly handled. The films were also prepared in the presence of transglutaminase (T-Gase). The latter films showed a smoother surface and higher homogeneity, as demonstrated by microstructural analyses, whereas studies on the mechanical properties indicated that T-Gase increased their TS and reduced their flexibility. It was reasoned that by there was a possible use of the T-Gase polymerized pectin-soy protein films as edible food or drug coatings.

The proper pH value to prepare the SPI film with good mechanical and barrier properties was 10. Addition of PEG as a plasticizer at 60% of SPI weight gave better film properties comparing with other used plasticizers. Cross-linking of the SPI film by adding formaldehyde or glutaraldehyde at a different level into the film forming solution and the combination of SPI with the starch, also caused a noticeable improvement in the mechanical and barrier properties of the films (SOLIMAN *et al.*, 2007). According to DENAVI *et al.* (2009), the applied drying conditions when preparing the SPI film affected the mechanical properties, with the optimal drying conditions of 70 °C and 30% relative humidity and 60 °C and 60% relative humidity. Dried under these conditions, the SPI films presented a higher TS, lower EAB values. SHIH (1998) indicated that the TS and the EAB belonging to SPI was affected by pH. The mechanical properties of edible films improved with some of the applied methods. The mechanical properties of the CL film improved with glyceraldehyde and alcoholdiols; the TS of the CL film increased by exposing to UV beams; the TS of the Z film improved with aldehydes; the TS of the WG film developed with keratin; the TS of the WP film improved by heat treatment; the TS of the SPI film developed by heat treatment, UV and gamma radiation application, and by adding calcium chloride and calcium sulphate (MCHUGH and KROCHTA, 1994).

It was expressed by GENNADIOS *et al.* (1997) that the EWP films are highly hydrophilic; they could be used for water-soluble packets (pouches) for ingredients in the food, chemical, and pharmaceutical industries similar to cellulose ether-based water soluble packets in commercial use. The mechanical and barrier properties of such films can be modified by varying the types and amounts of added plasticizers.

When microbial T-Gase was employed as the catalyst for preparing the chitosan (CH)-ovalbumin films, the mechanical resistance of the CH-ovalbumin films increased from 24 MPa to 35 MPa. The improved mechanical and solubility properties of these new materials confirmed that this enzymatic approach could be a useful tool for preparing edible films for food coating and pharmaceutical applications (DI PIERRO *et al.*, 2007). In the study conducted by KOLODZIEJSKA and PIOTROWSKA (2007), the effect of GLY on the mechanical and water barrier properties, as well as on the water solubility, of fish gelatin-CH films (4:1, w/w) cross-linked with T-Gase or 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide (EDC) was determined. The TS of the films decreased after modification of the components with T-Gase or EDC, by about 25% and 40% respectively. The elongations of the enzymatically modified films containing 20% of GLY and of chemically modified films containing 15% of GLY were, respectively, about 8 and 13 times higher than those of unplasticized films. However, the TS of plasticized films were, respectively, 2.5 and 5 times lower. These properties widen the practical applications of modified films as packaging material. However, the cross-linking of components with commercial preparations of T-Gase, -different to modification with EDC- increased the fragility of films. Therefore, such films have should be plasticized.

The increase in the proportion of GLY caused a reduction of the puncture force, the TS, the modulus of elasticity, and an increase of the puncture deformation and the EAB of the G film (THOMAZINE *et al.*, 2005). When the G film and the Z film were prepared by incorporating nisin (NS) into the film-forming solutions, the Z film with the NS of 12.000 IU/mL had an increase of 11.6 MPa in the TS compared with the control, but the G film had a slight increase resulting from the increase of the NS concentration. These results suggested that the incorporation of NS into the Z film and the G film improved the physical properties of the films (KU and SONG, 2007).

In the study of CARVALHO *et al.*, (2008), the G films from the skins of Nile perch, a warm-water fish species, were reported to exhibit stress and EAB similar to that of bovine bone gelatin. The gelatin, extracted from halibut skins, showed a suitable filmogenic capacity, leading to transparent, weakly colored, water-soluble and highly extensible films. The intermediate evaporation step at 60 °C in the industrial procedure for drying the G film induced thermal protein degradation, caused the resulting films to be significantly less resistant and more extensible. It was seen that the G film with predominance of lower-molecular-weight fractions was apparently more plasticized by SOR molecules, favoring a higher extensibility and a lower resistance in the final film.

The edible films were successfully prepared from fish skin gelatin of brownstripe red snapper (*Lutjanus vitta*) and bigeye snapper (*Priacanthus macracanthus*). The films with the greater protein content had a higher thickness and me-

chanical properties (TS and EAB), but lower water vapor permeability than those with the lower protein content. The films without GLY were mostly brittle, and became more flexible in the presence of GLY. The TS generally decreased with increasing GLY concentration from 25% to 75% (JONGJAREONRAK *et al.*, 2006). IWATA *et al.* (2000) expressed that edible films prepared from water-soluble fish proteins, had better flexibility compared to most of the other protein films. The pH change, the various physical and chemical treatments and the properties of plasticizer affected the quality of fish protein film. Lower mechanical properties were found in the films prepared from the lower quality washed fish mince (BENJAKUL *et al.*, 2008). The TS of the films was higher, when prepared at acidic (pH 2, 3) and alkaline (pH 11, 12) conditions. The film with the lowest TS was made at pH 7. The mechanical resistance of the myofibrillar protein (MYFP) based films were substantially lower than the synthetic films -such as polypropylene (PP), polyethylene and polyvinyl dichloride- but was relatively close to low density polyethylene (LDPE) (SHIKU *et al.*, 2003).

GLY and PEG plasticizers gave flexible structure to the films prepared from water soluble fish protein. As the concentration of GLY increased, TS decreased with the concomitant increase of EAB. In contrast, PEG showed more marked influence on TS than on EAB. GLY:PEG ratio of 2:1 exhibited the maximum EAB value. It was confirmed that MYFP based films plasticized with the mixture of GLY-PEG showed lower TS (2.5-3.0 MPa) than with only GLY (5.0 MPa) or with only PEG plasticized films (7.0 MPa) (TANAKA *et al.*, 2001).

PARRIS and COFFIN (1997) observed that Z-based films plasticized with a mixture of GLY-polypropylene glycol (PPG) showed lower TS and lower elastic modulus than with only GLY plasticized films or PPG plasticized films. Moreover, the films plasticized with the mixture of GLY-PEG caused higher EAB (117.8%) than those with only GLY (2.6%) or PEG plasticized films (2.8%).

The functional properties of the fish protein films produced by the thermo-melting techniques were similar to known protein films and the TS of the films were similar to LDPE (CUQ *et al.*, 1998). The films obtained from Tilapia fish treated at 65°C/30 minutes were more resistant and more rigid than the films treated at 40°C/30 minutes (GARCIA and SOBRAL, 2005). When the protein concentration was treated at 90°C/30 minutes, the filmogenic solution was 2 g of sarcoplasmic protein (SRCP)-MYFP/100 g filmogenic solution, the prepared films were more resistant than the respective films (SOBRAL *et al.*, 2005). CUQ *et al.* (1995) expressed that MYFP films produced from sardine had the higher TR than that obtained from other protein films, such as Z, WG, SPI and WP.

The quality of Alaska pollack surimi (SRM) films was decreased in order to determine the influence of the SRM quality on the TS, and the EAB values. Thawed Alaska pollack SRM was incubated at 30°C for 20 minutes (slight protein denaturation) and at 30 °C for 5 hours (complete protein denaturation) in order to decrease the SRM quality. Slight protein denaturation caused a decrease in the EAB of the films and complete denaturation gave rise to a reduction of the TS, and the EAB values (SHIKU *et al.*, 2004). MYFP-based films were developed from a film-forming solution based on fish mince and the influence of plasticizers on the protein film quality was investigated. When no plasticizer was introduced in formulation the films were relatively brittle and needed to be handled very carefully, and GLY, SOR and sucrose were added in various concentrations. Plasticization of the MYFP-based films induced a large decrease in film strength and elasticity and an increase in deformation properties (CUQ *et al.*, 1997). SOR plasticized films were the most brittle, with the highest TS (3.14 MPa). In contrast, GLY and PEG plasticized films exhibited flexible structure, despite the low TS (2.13 MPa and 1.80 MPa, respectively). As plasticizer concentration increased, the TS decreased concomitant with an increase in EAB (BOURTOOM *et al.*, 2006).

Propylene glycol alginate (PGAL) was incorporated into Alaska pollack SRM film in order to improve their mechanical properties. The TS of the PGAL-SRM films prepared at pH 11 were twice as high compared to the SRM films prepared at pH 7. The EAB was not affected by the incorporation of PGAL. Results revealed that the formation of cross-linkages between epsilon-amino groups of lysine residues in SRM proteins and mannuronic acid esters of PGAL above pH 10 was responsible for the increased TS of the films (WENG *et al.*, 2006). The effect on the ratios of MYFP to SRCP from round scad (*Decapterus maruadsi*) muscle on the properties of the resulting films was investigated. The TS of the films decreased with an increased SRCP content. The films prepared from MYFP:SRCP ratio of 10:0 (w/w) exhibited the highest TS. The EAB of the films, prepared with SRCP content greater than 30%, had the decreased EAB (ARTHAN *et al.*, 2008).

A comparison could not be made, due to no mention in the literature to studies involving similar textural values of edible protein films obtained from the texture analyzer equipment used in our study. Moreover, when both tensile test parameters were evaluated, as seen clearly in Fig. 1 and Fig. 2, placing the CL film in the second range, this film group outclassed other film groups considerably. SARIKUS (2006) expressed that the CL film is used in sausage coating more than natural coatings. The most important advantages of these films are that they remain strong in producting process conditions, having a flexible structure with a high-tensility.

The G protein film obtained the highest LT value (63.30%±0.01); the WG protein film obtained, however, the lowest LT value (13.29%±0.01) (Table 1).

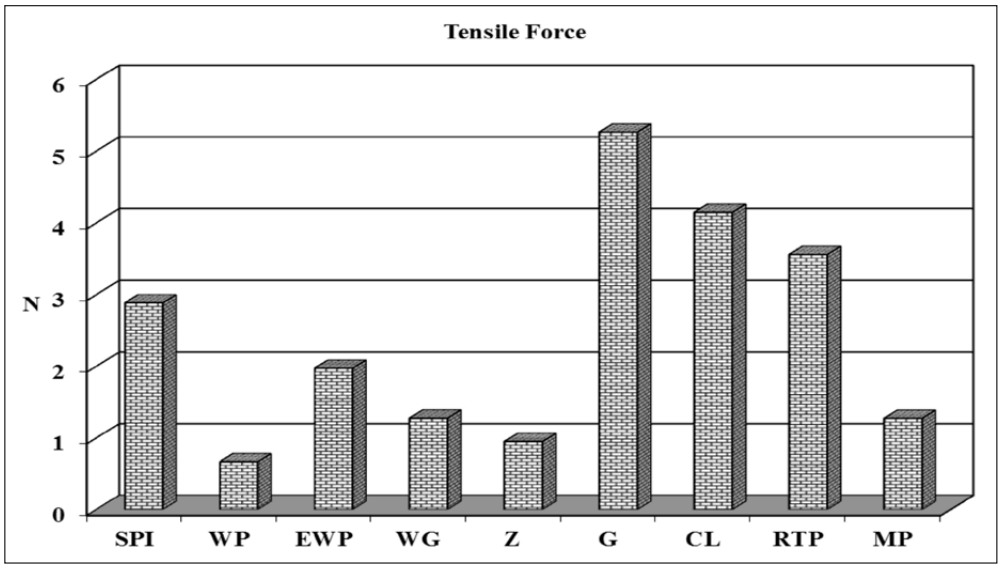

Fig. 1 -The changes of the tensile force values of edible protein films.

Because food products are exposed to light trigger oxidative reactions, the products were packed with non-light transmitting packaging material in order to protect them from the light. There are a limited number of studies mentioned in the literature about the LT value of edible films.

SHIKU *et al.* (2003) expressed that MYFP films, prepared from blue marlin flesh, have excellent barrier properties to UV light in the range of 200-280 nm regardless of pH. However, the UV barrier property of the films gradually became poor above the wavelength of 300 nm. In contrast, the MYFP film prepared at pH 7 blocked the most light in the UV-visible range from 350 to 800 nm because of its semi-transparency.

In our study, the LT of the WG film was measured as the lowest value (13.29%±0.01) at 560 nm/23±2 °C. The RTP film possessed the second lowest LT value after the WG film (Fig. 3). Comparisons could not be made, as there are no similar studies in the research literature of LT measurements conducted at the same wavelength as in our study. However, it is possible to say that the WG film can be more effective protecting products from light than other protein films.

The highest OP value was observed at 322.00±0.01 mL/mm/day in the WP film, and the lowest OP value was observed at 17.10±0.01 mL/mm/day in the SPI film (Fig. 4). The OP value of the EWP film and the OP value of the G film; the OP value of the CL film and the OP value of the RTP film was determined to be close to each other in.

The diffusion of gas and water vapor into film is called transition. These gases and the water vapor were absorbed by a surface of the polymer and oscillated by the other surface of the polymer during transition. The films have different barrier properties according to component properties and manufacturing techniques. The polar polymers, such as protein and carbonhydrates,

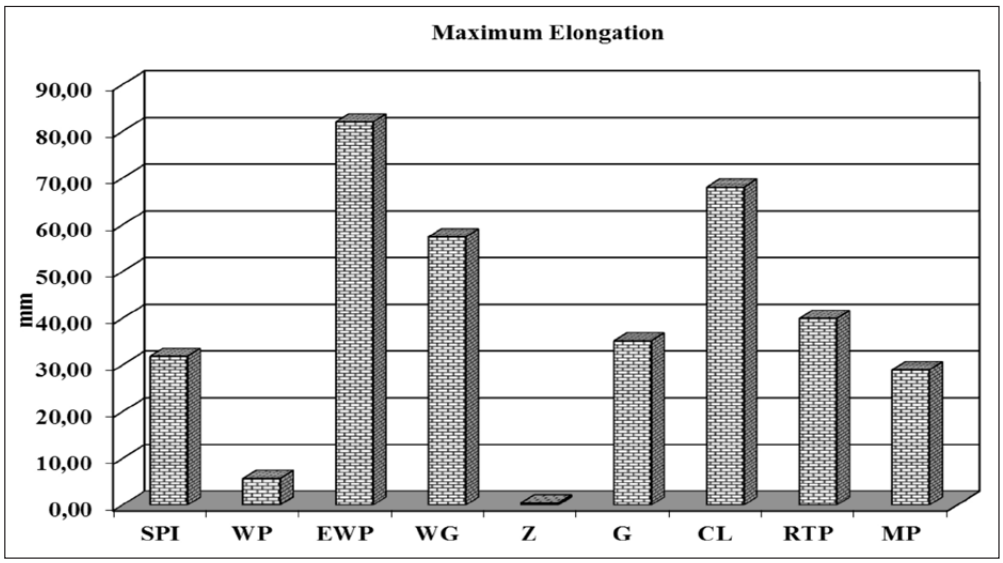

Fig. 2 -The changes of the maximum elongation values of edible protein films.

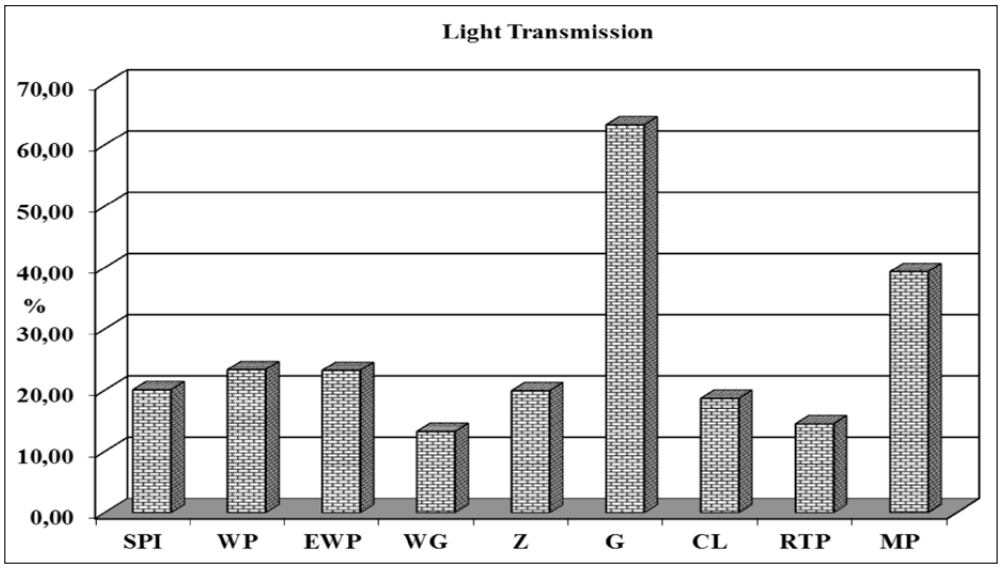

Fig. 3 -The changes of the light transmission values of edible protein films.

show low gas permeability and high water vapor permeability. In contrast, whilst materials (containing apolar hydrocarbon such as lipid) constitute an excellent barrier against the water vapor transition, they are not an effective barrier to gas transition. The chemical structure and the shape of the transition or absorbed film matrix substance is effective at the speed of diffusion and transfer. For example, the small molecules diffuse faster than the big molecules or the polar molecules diffuse faster than the apolar molecules in the polar films (CAGRI-MEHMETOGLU, 2010). The rate of rancidity, causing lipid oxidation and brown coloration, as well as causing myoglobin oxidation in meats, could be reduced by using edible coatings with the low OP (GENNADIOS *et al.*, 1997). It was implied by YILMAZ *et al.* (2007) that WP-based edible film and coating slowed gas (O_2, CO_2) transfer. The OP of the CL film was <0.04 $cm^3.\mu m/m^2.dk.Pa$; the OP of the Z film was 11.8 $cm^3.\mu m/m^2.dk.Pa$; the OP of the WG film was 3.9-6.1 $cm^3.\mu m/m^2.dk.Pa$; the OP of the SPI film was 1.6-4.5 $cm^3.\mu m/m^2.dk.Pa$; and the OP of the WP film was 18.5-76.1 $cm^3.\mu m/m^2.dk.Pa$ (LIEBERMAN and GILBERT, 1973). LIN and ZHAO (2007) expressed that the O_2 permeability ($7.84x10^{-19}$ $m^3.m/m^2.s.Pa$) of the Z-based coating was lower than the O_2 permeability of plastic films (such as LDPE, PP, polystyrene and polyvinylchloride) and of PLS, PLS/lipid composite coatings, but higher than the O_2 permeability ($2.89x10^{-17}$ $m^3.m/m^2.s.Pa$) of WG coatings. It was observed that the O_2 permeability of the WG coating was close to the O_2 permeability ($2.25x10^{-17}$ $m^3.m/m^2.s.Pa$) of LDPE. It was recognized in literature that the OP of edible films was affected considerably by factors such as the preparation conditions (temperature and relative

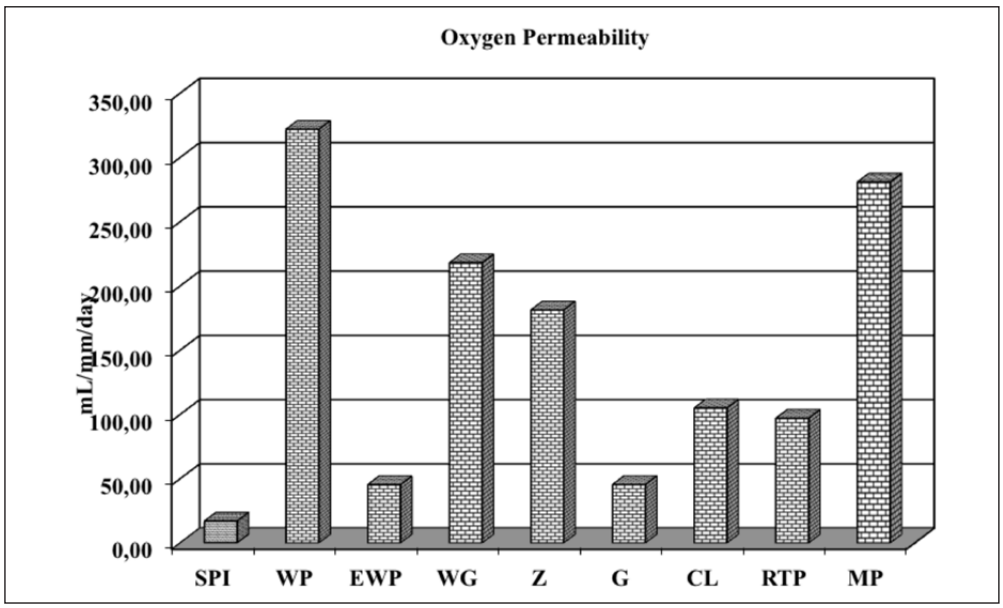

Fig. 4 -The changes of the oxygen permeability values of edible protein films.

humidity); the type and the amount of plasticizers, the incorporation of various chemicals; heat-treatments and pH levels. For example, MCHUGH and KROCHTA (1994) specified that the gas permeability of the CL film decreased with formaldehyde and chrome tannic acid, whilst the OP of the WP film and the SPI film improved with heat treatment. The OP (3.16 $cm^3.\mu m/m^2.dk.Pa$-at 23 °C and 50% relative humidity) of the WG film, made with 40% GLY, was found to be similar to the OP (3.82 $cm^3.\mu m/m^2.dk.Pa$-at 23 °C and %0 relative humidity) of the film obtained by GENNADIOS *et al.* (2006) (MUJICA-PAZ and GONTARD, 1997). Despite the fact that the OP of all WG films was low, the OP level could be raised by increasing the GLY concentration. It was seen that temperature has less effect on OP than the relative humidity. The low OP of the WG films may be due to their polar nature and linear structure, leading to the high cohesive-energy density and the low free volume (TANADA-PALMU *et al.*, 2000). SHIH (1998) expressed that the OP of the WG film decreased by adding of mineral oil and dipping in Ca^{+2}. It was specified that the SPI coatings were effective oxygen barriers (OP; $3.14x10^{-19}$ $m^3.m/m^2.s.Pa$) at low relative humidity conditions, especially as their high oxygen barrier properties made them suited to gave the facility their applications such as flavour and pharmaceutical microencapsulated agents or as coatings for fruit, vegetable and cheese. It was reported that the WP-based films also had excellent oxygen barrier properties (OP; $1.13x10^{-18}$ $m^3.m/m^2.s.Pa$) at low and medium relative humidity when they compared with synthetic polymers (LIEBERMAN and GILBERT, 1973). The proper pH value for the preparation of SPI film with good barrier properties was 10; the O_2 permeability of the SPI film was 1.06 $cm^3.\mu m/m^2.dk.Pa$ at this pH value. The addition of PEG as a plasticizer at 60% of SPI weight made the film properties better, compared with other plasticizers, and the O_2 permeability of the SPI film was 0.76 $cm^3.\mu m/m^2.dk.Pa$. The cross-linking of the SPI film by adding formaldehyde or glutaraldehyde at different levels into the film forming solution improved the barrier properties of the resulting films (SOLIMAN *et al.*, 2007). DENAVI *et al.* (2009) found that the applied drying conditions used in SPI film manufacturing affected the barrier properties of the film: the O_2 permeability of the film was 18.2 $cm^3.\mu m/m^2.dk.Pa$ dried at 70 °C and 30% relative humidity and the O_2 permeability of the film was 47.6 $cm^3.\mu m/m^2.dk.Pa$ dried at 60 °C and 60% relative humidity. In our study, the SPI film had the lowest O_2 permeability (17.10±0.01 ml/mm/day) (Table 1). The properties of SPI film can be improved with application of additional methods in light of the literature (LIEBERMAN and GILBERT, 1973; SOLIMAN *et al.*, 2007; DENAVI *et al.*, 2009) and it can be used for the purpose of protecting food products from the harmful effect of oxygen.

4. CONCLUSIONS

In our study of the mechanical properties of edible protein films, both tensile test parameters (tensile force and maximum elongation) were evaluated, placing of the CL film in the second range: this film group outclassed other film groups considerably. It was observed that the WG film possessed the lowest LT value. It is possible to say that the WG film is more effective in protecting products from light than other protein films. The lowest OP in our study belonged to the SPI film. The properties of the SPI film -which can be improved with additional methods in light of the literature- can be used for the purpose of protecting food products from the harmful effect of oxygen.

ABBREVIATIONS

CH:	Chitosan	PGAL:	Propylene glycol alginate
CL:	Collagen	PLS:	Polysaccharide
EAB:	Elongation at break	PP:	Polypropylene
EDK:	1-ethyl-3-(3-dimethylaminopropyl) carbodiimid	PPG:	Polypropylene glycol
EWP:	Egg white powder protein	RTP:	Rainbow trout protein
G:	Gelatin	SOR:	Sorbitol
GLY:	Glycerol	SPI:	Soy protein isolates
LDPE:	Low density polyethylene	SRCP:	Sarcoplasmic protein
LT:	Light transmission	SRM:	Surimi
MP:	Mackerel protein	T-Gase:	Transglutaminase
MYFP:	Myofibrillar protein	TR:	Tensile resistance
NaOH:	Sodium hydroxide	TS:	Tensile strength
NS:	Nisin	WG:	Wheat Gluten
OP:	Oxygen permeability	WP:	Whey protein
PEG:	Polyethylene glycol	Z:	Zein

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