

DEVELOPMENT OF ALTERNATIVE EDIBLE COATINGS FOR TURKISH DELIGHT
(LOKUM) AND DETERMINATION OF FILM PROPERTIES



by
Özlem Aslan

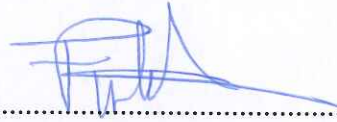
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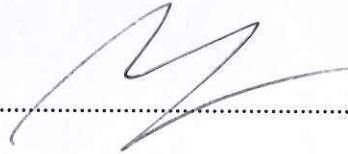
DEVELOPMENT OF ALTERNATIVE EDIBLE COATINGS FOR TURKISH DELIGHT
(LOKUM) AND DETERMINATION OF FILM PROPERTIES

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ABSTRACT

DEVELOPMENT OF ALTERNATIVE EDIBLE COATINGS FOR TURKISH DELIGHT (LOKUM) AND DETERMINATION OF FILM PROPERTIES

In the present study, polysaccharide based edible films were prepared, characterized and the optimal coating solution was applied to lokum samples. The films were targeted as packaging material for foods, which require controlled water vapor transport and good mechanical properties to extend the shelf life of products. Film formation procedures were deemed to be practical and economical at large scales. For this purpose carboxymethyl cellulose (CMC), starch and modified starch were chosen as film forming materials. Distilled water and glycerol were used as solvent and plasticizer, respectively. Calcium carbonate (CaCO_3) and polyethylene glycol (PEG) were used as stickiness reducing agents.

Film composition was optimized according to the film thickness and appearance (integrity, flexibility, homogeneity etc.) and the best formulation was fully tested for its physical (color, opacity, moisture content), barrier (water vapor permeability) and mechanical properties (tensile strength and elongation). These characteristics of the derived films were measured to assess their effectiveness as edible coatings for food.

Among the possible alternatives carboxymethyl cellulose, glycerol and polyethylene glycol suspensions were chosen to be the best components for the formation of homogeneous, thin and flexible films. The optimized concentrations were found as 0.5 % w/v, 0.1 % w/v and 0.5% w/v for CMC, PEG and Gly, respectively. The derived films were colorless, transparent and showed desired mechanical and physical properties.

It was also observed that CMC is a good matrix-forming material that allows the elaboration of edible films and glycerol is a plasticizer compatible with CMC, improving film flexibility, facilitating its handling and preventing pores and cracks.

ÖZET

TÜRK LOKUMU İÇİN ALTERNATİF YENİLEBİLİR FİLM ÜRETİMİ VE FİLM ÖZELLİKLERİNİN BELİRLENMESİ

Bu çalışmada, polisakkarit bazlı yenilebilir filmler hazırlanmış, karakterize edilmiş ve en uygun kaplama formülasyonu lokum örneklerine uygulanmıştır. Hazırlanan filmlerin, gıdaların raf ömrünü uzatabilmek için kontrollü su buharı geçirgenliğine sahip olan ve iyi mekanik özellikler gösteren paketleme materyalleri olması hedeflenmiştir. Film hazırlama prosedürlerinin geniş ölçekte pratik ve ekonomik olması dikkate alınmıştır. Bu amaçla, film ana materyali olarak karboksimetil selüloz (CMC), nişasta ve modifiye nişasta seçilmiştir. Çözücü olarak distile su, plastikleştirici olarak da gliserol kullanılmıştır. Kalsiyum karbonat (CaCO_3) ve polietilen glikol (PEG) yapışkanlık azaltıcı bileşen olarak kullanılmıştır.

Film kompozisyonu öncelikle film kalınlığına ve filmin görsel özelliklerine (bütünlük, esneklik, homojenite vb) göre optimize edilmiş, ardından en iyi formülasyon tüm fiziksel (renk, opaklık, nem içeriği), bariyer (su buharı geçirgenliği) ve mekanik özelliklerine göre (gerilme kuvveti ve uzama) test edilmiştir. Elde edilen filmlerin bu özellikleri, yenilebilir gıda kaplaması olarak etkinliklerini değerlendirmek amacıyla ölçülmüştür.

Olası alternatifler içinde karboksimetil selüloz, gliserol ve polietilen glikol ince, homojen ve esnek filmler oluşturmak için en iyi bileşenler olarak belirlenmiştir. Optimize edilmiş konsantrasyonlar % 0.5 CMC, % 0.1 PEG ve % 0.5 gliserol olarak bulunmuştur. Elde edilen filmler renksiz ve transparandır ve istenilen mekanik ve fiziksel özellikleri göstermiştir.

Ayrıca karboksimetil selülozun iyi matriks oluşturabilen bir materyal olduğu ve gliserolün film esnekliğini geliştiren, kullanımını kolaylaştıran, çatlak ve delikleri engelleyen ve karboksimetil selülozla uyumlu bir plastikleştirici olduğu gözlenmiştir.

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LIST OF SYMBOLS / ABBREVIATIONS

ΔE_{ab}	Total color difference
ASTM	American Society for Testing and Materials
Avg	Average
C	Chroma (yellowness index)
CaCl ₂	Calcium chloride
CaCO ₃	Calcium carbonate
CMC	Carboxymethyl cellulose
CO ₂	Carbon dioxide
E	Elongation at break
FDA	Food and Drug Administration
Gly	Glycerol
GRAS	Generally recognized as safe
HPC	Hydroxypropyl cellulose
HPMC	Hydroxypropylmethyl cellulose
MC	Methyl cellulose
min	Minutes
NaCMC	Sodium carboxymethyl cellulose
O ₂	Oxygen
PEB	Percentage elongation at break
PEG	Polyethylene glycol
RH	Relative humidity
Std	Standard deviation
TS	Tensile strength
UV/Vis	Ultraviolet /Visible
WVP	Water vapor permeability
WVTR	Water vapor transmission rate

1. INTRODUCTION

Nowadays market globalization and increasing amount of use of minimally processed foods causes an extension in the demand of longer product shelf life, additionally environmental concern encourages scientists to search for natural materials to be used in effective packaging systems. Using edible coatings based on naturally occurring polymers can be a solution for both of these issues. In order to obtain satisfactory results, the characteristics of basic materials in formulation of coating were needed to be modified. Moreover, as edible coatings are expected to act as a barrier for mass transfer of moisture, oxygen, carbon dioxide, aromas and lipids, the transport properties should be measured correctly for product development and properly for assessment of effectiveness [1].

Composition, structure and functional properties of biopolymer based films, as for synthetic polymers, determine their possible application areas. Mechanical and barrier properties of these materials can be tailored by controlling film formulation which improves finally efficiency of food packaging [2].

Turkish delight (lokum) is a sugar-based jelly-like confection made from starch and sugar. Its texture is soft and sticky and it is generally packaged and eaten as small cubes that are dusted with icing sugar to prevent sticking. Some recipes include small nut pieces, usually pistachio, hazelnut or walnuts. Raw materials or ingredients used in lokum production are sugar, water, corn starch, natural fruit flavors, cream of tartar and natural/artificial colors. The process of lokum production is given in Appendix A. Dusting lokum in icing sugar in the process postpones the desiccation of the surface of product, thus prevents the crust formation and deformation on the surface concurrently [3]. However, it complicates the consumption of lokum due to dust which may be smeared on hands or spilled around. Therefore, in the lokum production process, decreasing or abolishing of powder use is needed. In this sense, application of a thin edible coating to lokum may be an alternative method to decrease the stickiness and icing sugar use.

One of the most important criteria for choosing the right coating material is the compatibility of the coating material with the product surface. In this manner, coating

should provide integrity with the product itself [4]. In coating process it is expected that there should be a chemical interaction between film components and lokum constituents. In respect of polysaccharide based structure of lokum, the formulation of which consists of starch, sugar, citric acid and water, application of a coating with a similar structure to polysaccharide may meet the expectations.

The purpose of the present study was to investigate different polysaccharide raw materials and stickiness reducing agents in order to find the optimum conditions for film preparation, and apply the findings to lokum coatings. To do that, various polysaccharides (starch, modified starch and carboxymethyl cellulose) were tested to obtain most appropriate edible films. After optimizing composition, the best formulation was selected for the preparation of the films and lokum coating. Films obtained by casting were characterized for visual appearance, film thickness, barrier properties (water vapor permeability), mechanical properties (tensile strength and elongation at break), film color, opacity and film moisture content. Coated lokum samples were also evaluated for visual and textural (hardness) properties.

2. THEORY

2.1. FOOD PACKAGING

Organoleptic, nutritional, and hygienic characteristics of food products affect their quality but during storage and commercialization these properties are subject to change. Such changes are generally results of exchanges between the product and external environment. In order to prevent spoilage of foods and ensure food quality, several physical and chemical treatments such as sterilization, high pressure, radiations or actives agents were developed. But the ultimate stage of preservation needs to use a proper packaging which is considered superior for the durability of food quality [4].

Food packaging has always focused on the use of suitable packaging materials and methods in order to ensure the quality of products and to decrease the food loses. Besides this, consumer's preferences are oriented to better qualified, fresh-like, and safer food products recently. Therefore, several active packaging technologies have been developed for providing these demands and also to limit the damage of packaging which causes environmental pollution problems [5].

Synthetic polymeric films have been used widely in food industry due to their easy and cheap production from raw materials and additionally they are stable and flexible. But they are not biodegradable and that is a critical handicap for these films. The use of biodegradable alternatives from renewable sources instead of non-biodegradable plastics has taken attention due to the growth of environmental concerns [6]. Therefore, easily biodegradable agricultural biopolymers usage will solve both this problem and oversupply in farm production [7].

Food packaging focuses on the protection of food or food product from the environment and also providing organoleptically qualified and safer food products during the shelf life. Foods are dynamic systems with different packaging demands and limited shelf life therefore the packaging of foods is a complex issue. In order to select the proper biobased packaging material, it is very critical to know the properties and characteristics of food

product which are subject to packaging. Many biochemical and physical properties (moisture content, pH, matrix etc.) differ according to the food type to be packaged. Besides biodegradable packaging materials are expected to provide similar quality to that of conventional packaging materials which are used in food. These relate the properties such as barrier, optical, mechanical, microbiological, chemical and temperature resistance and the requirements such as migration and scalping. Also the biodegradable packaging material should ensure all mechanical and barrier properties during storage and handling of food. Moreover these properties depend on the type of material, its production and application processes [8].

2.2. EDIBLE FILMS AND COATINGS

Consumer preferences high quality and long shelf life products and regarding environmental concerns biodegradable packaging has gained interest recently [9]. The use of biodegradable films in agriculture is strongly suggested in order to reduce pollution resulted from plastic films. Therefore the studies have intensified on developing biodegradable and environmentally friendly films [10]. One of the alternatives is edible films.

Edible films and coatings differ from other biobased packaging by being edible besides being biobased and this places them in a unique category among packaging materials. Edible films and coatings are produced from polysaccharides, proteins, lipids, and derivatives which are biological materials. Obtained films and coatings protect food and enable better shelf life properties by acting as a barrier (of moisture, vapor, light and oil) for the product [8].

Many literature works have investigated physical and mechanical properties of edible films [7, 9, 11, 12, 13, 14, 15]. There are also several reviews on the formulation technology and application of edible films [4, 16, 17]. Edible films and coatings have been applied on fruits, vegetables, meat, poultry, candies, grains, or fresh, cured, frozen and processed foods [4].

Edible films are thin and continuous layers between foods or food components. They must fulfill two requirements to be called as edible films. Edible films are expected to be safe for consumer's health that is edible materials must be recognized as safe (GRAS) by Food and Drug Administration (FDA). Besides they must be composed of a film-forming material such as polymer. [8].

The aim of edible coating is to produce natural biopolymer-based coatings with desired properties which may be consumed with the food. The function of them is to provide a barrier in order to control mass transfer (water, gas and lipids) and/or to act as a carrier of food components such as ingredients and additives (pigments, flavors and so on). Edible films can also improve the appearance of food product. Besides edible coatings are expected to serve mechanical protection and protect all these properties during storage and handling [11, 18, 19].

The characteristics required for edible films and coatings are related to the needs of food product that may be coated. For example, oxidation-sensitive products like polyunsaturated fats require low oxygen permeability. Fruits and vegetables needs proper mass transfer selectivity that will allow respiration (O_2 , CO_2 , ethylene exchanges) while confining their dehydration during storage, or avoiding the solute penetration during the osmotic dehydration of fruits [4].

Besides the good barrier properties, edible films and coatings are expected to be organoleptically and functionally adaptable to foods. While edible packaging presents many possibilities to improve the food quality and shelf life, there are only a few industrial applications. In fact, the use and application of these packaging is not easy due to the complexity of formulation procedure. Therefore, more fundamental study is needed to understand the transfer processes in edible films and coatings such as agricultural polymeric polymers [4].

Under certain conditions of relative humidity (RH) and temperature, hydrophilic films and coatings (protein and polysaccharides based ones) are good oxygen and carbon dioxide barriers but a poor barrier to water vapor. In order to reduce water vapor transmission, lipid

and their derivatives may be added but the resulted films often possess poor mechanical and chemical stability and also bad organoleptic properties [20, 21].

Edible films are used for the protection of food products against loss of humidity and stickiness in different situations. Dry fruits like raisins, prunes and dates tend to absorb moisture and become sticky and often clump together if the ambient atmosphere humidity is high. On the other hand, these fruits lose their moisture and turn into a tough and even chewy product if they are stored in a dry atmosphere. Therefore, coating the individual pieces of dry fruit or other food products is desirable in order to protect food against these situations. Another example of stickiness is the case of hot candy which is a major problem during its manufacturing. Many types of coatings are used in order to retard the sticking of the hot candy to the metal surfaces with which it comes in contact. *Frey* [22] found that adding non-hygroscopic polyethylene glycols to the hot candy mass can reduce the stickiness dramatically. Polyethylene glycol in candy formulations acts as a preventative of stickiness rather than a cure and essentially, polyethylene glycol acts as an internal or built-in lubricant and reduces or in many cases eliminates the need for any external lubricants [23]. Besides, *Noborio* et al. [24] has used calcium carbonate (CaCO_3) as an anti-stick agent to keep the sticky surface of candy or chewing gum non-adhesive.

The main materials used in edible films are polysaccharides, proteins, lipids and their derivatives. Each film forming material produces different films with varying barrier and mechanical characteristics. Films can be formed by blending of film forming materials or adding some additives (plasticizers, emulsifiers etc.) according to the packaging necessities of food products [8].

In edible packaging, coatings are applied directly on the food product and the thin film is formed directly on the product. Dipping, spraying, brushing and foam applications are the methods of coatings. In the dipping method of coating, which was applied in this study, food is directly dipped into the coating suspension, then removed and left to be dried. On the other hand, films may be applied onto food product after formation. In that case, films are preformed structures, that is, firstly film is produced and later it is applied to foods. These biodegradable films are generally prepared by wet casting method, which is

performed by pouring of the aqueous solution on a suitable base material and later drying it in a suitable environment [16].

In any polymeric packaging film or coating, two types of forces are involved: one of them is between the film-forming polymer molecules for all polymeric films or coatings (cohesive force), and the other one is between the film and the substrate for coatings only (adhesive force). Film properties such as resistance, flexibility, permeability, etc. are affected by the degree of cohesion. Strong cohesion reduces flexibility, gas and solute barrier properties and increases film porosity. Cohesion depends on the structure and chemistry of biopolymer, the manufacture procedure and parameters (temperature, pressure, solvent type and dilution, application technique, solvent evaporation technique, etc.), the presence of plasticizers and cross linking additives and on the final thickness of the film [8].

Film cohesion intensifies by high chain order polymers. Besides when excessive solvent evaporation or cooling is applied generally due to the industrial reasons, non-cohesive films may sometimes be obtained due to premature immobilization of the polymer molecule [25].

2.2.1. Polysaccharide Based Edible Films

In both plants and animals, polysaccharides role in three important ways: They provide structural materials (cellulose, hemicelluloses, and pectic substances in plants; chitin and mucopolysaccharides in animals); they provide food reserves (starch, dextrans, and fructans in plants; glycogen in animals); and lastly they attract and retain water so that life's enzymic processes are not obstructed under dehydrating situations. Observing from nature, the food manufacturer sees opportunities to use polysaccharides as structural material and as hydrophilic agents, thus controlling the form, texture, and shelf life of processed foods [26].

Solution properties of various polysaccharides differ widely. In the case of high molecular weight ones, some disperse readily in water, some are quite insoluble and others disperse only as discrete, swollen particles or globules. A few results in nearly clear solutions with

low viscosity at moderate concentrations and others form turbid pastes that have pseudo-plastic rheology at low concentrations. Some of them form gels at low concentrations, some gel only at high concentrations; others do not gel at all. The gels of some polysaccharides are translucent whereas others are opaque; some are thermally reversible, whereas others are not. These differences and discrepancies are related to the monosaccharide composition of the polymer, to the pattern of the chemical linkages among the monosaccharide units, to hydrogen-bonding and ionic interactions within and among polymers, and gross conformations of the hydrated polymers in solution- subjects that need further investigation [26].

It is difficult to predict the behavior of hydrocolloids in foods. This can be attributed to the dynamic aspects of water-binding and intermolecular hydrogen-bonding forces in large molecules that contain multiple polar groups. The peripheral polar groups and central hydrophobic stems of polysaccharide molecules result in variable interactions with water and electrolytes that are still in investigation. Texture regulation of a processed food with polysaccharides is therefore problematical, because the initial state of hydration and interactions between molecules do not remain constant. Nevertheless, selection of certain polysaccharide types over others as food additives can provide better properties such as greater stability and convenient textures in many different food types [26].

Polysaccharide structure generally affects solution properties as follows:

- At the same concentration, linear polysaccharides form solutions with greater viscosities than branched polysaccharides of the same molecular weight.
- Linear polysaccharides can associate through intermolecular hydrogen bonding to form gels or, in more dilute solutions, precipitates. On the other hand, Branching, side chains (substitution on hydroxyl groups), or negative charges distributed along linear polysaccharide molecules hinder intermolecular associations.
- Viscosity is usually more affected from pH in solutions of polysaccharides containing carboxyl groups than in solutions of polysaccharides containing strongly acidic groups [26].

In industrial foods, polysaccharides (starch and others) are often used as a component. The films obtained from polysaccharides have good mechanical properties and form efficient

barriers against low polarity compounds [7]. In edible films and coatings, a variety of polysaccharides can be used. Polysaccharide and their derivatives such as starch, cellulose, their derivatives and gums have excellent film forming capacity. During short period storage, these coatings have been used to delay the moisture loss of some food products. However, polysaccharides, do not offer good barrier against humidity due to the hydrophilic structure. They retard the moisture by behaving as a sacrificial moisture barrier to the atmosphere which helps the food to maintain the moisture content. Besides the preventing moisture loss, some of the polysaccharide films are good barriers against oxygen which can help for preserving several food types. Polysaccharide based coatings may be produced from several sources, among them cellulose and starch are the most remarkable ones [27].

2.2.1.1. Cellulose and its derivative carboxymethyl cellulose (CMC)

- **Cellulose**

Cellulose is an almost linear polymer composed of anhydroglucose and is known as the most abundantly occurring natural polymer on earth. Structure of cellulose is shown in Figure 2.1. It is likely to form strongly hydrogen bonded crystalline micro fibrils and fibers due to its regular structure and array of hydroxyl groups and is most recognized in the form of paper or cardboard in the packaging issues. Although waxed or polyethylene coated paper is used in some areas of primary food packaging; the bulk of paper is used for secondary packaging [28].

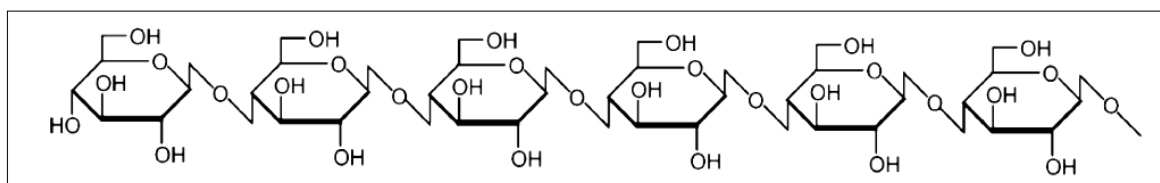


Figure 2.1. Structure of cellulose [16]

Cellulose is a cheap raw material, but difficult to use because of its hydrophilic nature, insolubility and crystalline structure. However it can be used after appropriate chemical

modifications to produce cellulose ether–ester films [12]. Nonionic methyl cellulose (MC), hydroxypropylmethyl cellulose (HPMC), hydroxypropyl cellulose (HPC) and ionic sodium carboxymethyl cellulose (NaCMC) are the cellulose ethers that have been used widely [8].

Cellulose derivative based edible films are transparent, flexible and very efficient barriers to oxygen and aroma compounds and have moderate strength, resistance to oil and fat migration [12, 19].

- **Carboxymethyl cellulose (CMC)**

Carboxymethyl cellulose (CMC) is the most important water-soluble derivative of cellulose having many applications in several industries such as food, cosmetics, pharmaceuticals, detergents, etc. It is produced by conversion of alkali cellulose swollen in aqueous NaOH and a surplus of an organic solvent with monochloroacetic acid or its sodium salt [29]. The production reactions are shown in Figure 2.2. NaCMC is a copolymer composed of two units: β -D-glucose and β -D-glucopyranose 2-O-(carboxymethyl)-monosodium salt, not randomly distributed along the macromolecule, which are linked via β -1,4-glycosidic bonds. The substitution of the hydroxyl groups by the carboxymethyl group is slightly most frequent at C-2 of the glucose [29]. The structure of CMC is shown in Figure 2.3.

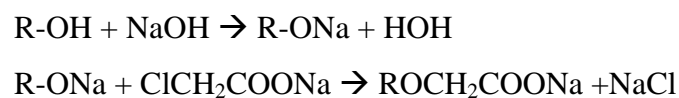


Figure 2.2. The production reactions of CMC [26]

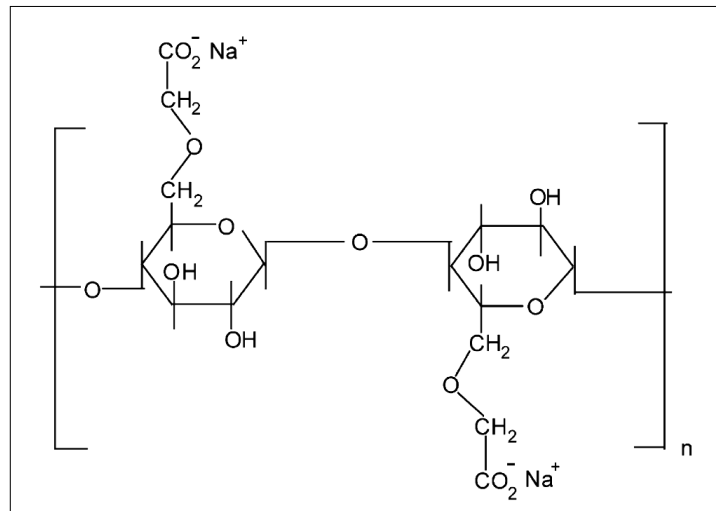


Figure 2.3. The structure of CMC [30]

CMC is colorless and odorless and can be categorized as a non-toxic water soluble polymer. The presence of metal salts slightly affects the viscosity of CMC solutions. Dispersions of CMC are stable between pH 2 and 10. CMC is insoluble in organic liquids and reacts with heavy metal salts to form transparent, relatively tough films which are insoluble in water and unaffected by organic materials [31].

CMC is an important polymer used in industry with many applications in flocculation, drag reduction, detergents, textiles, paper, foods, drugs, and oil well drilling operation. It has a number of sodium carboxymethyl groups (CH₂COONa) which induce water solubility. The various CMC properties depend on three factors: molecular weight of the polymer, average number of carboxyl content per anhydroglucose unit, and the distribution of carboxyl substituents along the polymer chains. Viscosity building and flocculation are the most important properties of CMC [30]. It has a role as a water binder, thickener, or as an emulsion stabilizer in food products, such as dietetic foods and ice cream. CMC is also used as a coating agent in the textile industry. Moreover it is added to the formulations of many pharmaceutical and cosmetics products as a suspending agent, tablet excipient, or as a viscosity-increasing agent [31]. Besides it is easily available and is also very cheap among all the polysaccharides [30].

CMC may affect the film properties of coatings. There are several studies which searched the effect of CMC on film characterization. In the study of *Gharbanzadeh* et al. [6], WVP of the biocomposite films (corn starch-CMC based films) diminished with the increase of

CMC content. Water resistance of CMC biopolymer is superior to that of starch one. This could be attributed to the more highly crystalline and more hydrophobic character of the cellulose fibers compared to starch polymer. The addition of CMC could bring in a tortuous path for water molecule to pass through. CMC at a low concentration probably disperses properly in the starch matrix, and inhibits the water vapor transmission. In the same study, the results showed that the CMC addition improves the water resistance of the starch matrix. The reason could be explained as follows: the starch is able to form hydrogen bonds with the hydroxyl and carboxyl groups of the CMC macromolecules and this strong structure could reduce the transmission of water molecules in the matrix. When CMC contents increased from 15% to 20%, the moisture absorption increased slightly from 20% to 21.33%. This result indicates that the combination of starch with cellulosic fiber improves water resistance to a certain degree since hydrophilicity of CMC is lower than that of starch.

Gharbanzadeh et al. [6] also found that the TS increased significantly from 6.57 to 16.11 MPa with the increase of the CMC concentration from 0% to 20%. This was explained by the interfacial interaction between the matrix and filler due to the chemical similarity (polysaccharide structure) of starch film and CMC.

Gharbanzadeh and *Almasi* [9] attributed the high TS and low strain to break value of the control sample (unplasticized) to hydrogen bonds between the CMC chains. These bonds promote high cohesiveness and low flexibility of the unplasticized films. An increase in strain to break value and decrease in TS with increasing glycerol concentration was observed in the study.

2.2.1.2. Starch

Starch is another widely abundant polysaccharide based raw material and is used to obtain biodegradable films since it has ability of forming a continuous matrix. It is generally produced from corn, potatoes, cereal grain and rice and is known as one of the most abundant renewable polymers in the nature. It is a mixture of amylose, and amylopectin. [6, 8, 32].

Amylose preponderance in amylo maize starch leads to stronger, more flexible films whereas branched structure of amylopectin generally results in films with poor mechanical properties (decreased tensile strength and elongation). Substitution of the hydroxyl groups in the molecule reduce the hydrogen bonding ability and thereby improve freeze thaw stability and solution clarity [16].

When the starch granules are heated in water, they start to swell, rupture and collapse while releasing amylose and amylopectin. Branched amylopectin structure in solution tends slightly to interact and, as a result, amylopectin gels and films are weak, cohesive and flexible, whereas linear chains of amylose in solution have high tendency interact by hydrogen bonds, and consequently, amylose gels and films are stiffer and stronger than amylopectin gels and films [33].

In packaging context, starch alone does not lead to films with proper mechanical properties (high percentage elongation, high tensile and flexural strength) unless it is not treated first by plasticization or mixing with other materials or genetic or chemical modification or combinations of the above situations [28]. Chemical modification such as cross-linking is a method that has been studied for years to diminish these problems and obtain low water sensitive and high strength materials [6].

Starch has been used in various methods for preparing compostable plastics and is economically competitive with petroleum but brittle nature of blends with high concentrations of starch is a challenge to the development of new starch materials. Brittleness of starch while providing full biodegradability in blends can be overcome by the addition of biodegradable plasticizers. Common plasticizers for hydrophilic polymers, such as starch, are glycerol and other low-molecular-weight-polyhydroxy-compounds, polyethers and urea. Plasticizers reduce the water activity thereby restricting the growth of microorganisms [28].

2.2.1.3. Plasticizers

Barrier and mechanical properties of biopolymer films are strongly dependent on the nature of the materials used in their formulation and final compositions [34]. The functional, organoleptic, nutritional and mechanical properties of an edible film can be improved by adding various additives such as plasticizers [32]. Plasticizer is also considered as a major component of edible films as well as film-forming polymer. In order to overcome film brittleness due to the high intermolecular forces, plasticizer addition is needed. Plasticizers improve film flexibility and extensibility by diminishing these forces and enabling mobility to the polymer chains. [7]. Plasticizers are also required to improve the mechanical properties in protein or polysaccharide-based edible films. However, plasticization may increase gas and vapor permeability due to the involvement of water and plasticizers [9].

Introducing plasticizers such as glycerol, sorbitol, ethylene glycol etc. in the film formulations has an advantage to provide flexibility, which improves handling [16]. There are several studies who studied the effects of plasticizers on film properties. According to *Parris et al.* [35] and *Alves et al.* [36], plasticizers in film formulations act as a component to reduce intermolecular hydrogen bonding between polymer molecules, thereby resulting spacing between macromolecules. This results in an increase in water vapor permeability because of the tendency of the network to adsorption and desorption of water molecules. Besides elongation of the films increases because of the spaces inside but the strength of the film decreases. *Alves et al.* [36] observed that when glycerol was introduced in the matrix, some structural modifications occurred in starch network resulting in less dense films and under stress, movements of polymer chains were facilitated, improving film flexibility.

Laohakunjit and Noomhorm [37] found that the appearance of all plasticized-rice starch films was clear and more uniform compared to control films (without plasticizer). Sorbitol- and glycerol-plasticized rice films were relatively smooth, whereas unplasticized rice films have a rough surface appearance. The number of insoluble particles and air bubbles were significantly decreased in the presence of plasticizers in film formulations. The plasticizer effectively reduced internal hydrogen bonding while increasing intermolecular spacing; as a result it decreased brittleness and increased permeability of the film materials. The

WVTR of plasticized rice starch films increased when glycerol and sorbitol contents increased. Glycerol-plasticized films showed significantly larger WVTRs in comparison to sorbitol-plasticized films. This result may be attributed to the larger polarity of sorbitol and its ability to retard the vapor evaporation rate more efficiently compared to glycerol-plasticized films. The large WVTR of glycerol-plasticized films can be attributed to the high tendency of glycerol to diffusion of water molecules. Glycerol is a relatively small hydrophilic structure and may be easily introduced between starch molecules to form hydrogen bonds with hydroxyl groups of amylose and amylopectin in starch. In the same study the TS of rice starch films significantly decreased with increasing plasticizer contents. Both plasticizers (glycerol and sorbitol) interfere with the hydrogen bonding of the polymer chains and this leads to a reduction in polymer interaction and cohesiveness which most likely has an effect on the crystallinity and other physical properties of the films including the flexibility of the film. Glycerol is the most popular plasticizer in edible films and has a superior effect. In all types of edible films, a small increase in the glycerol content leads to a large reduction in TS and significantly increased elongation. *Gibson and Ashby* [38] observed in their study on the mechanical properties of synthetic polymers that the tensile stress-strain curve was directly dependent on the structure properties of the polymer, and particularly to the glass transition. The increase in plasticizer content reduces the glass transition temperature of the polymer. Glycerol and sorbitol react with starch molecules thereby weakening the cohesive tension of the molecules in attached polymer chains and forming a more flexible structure. Glycerol and sorbitol are uniformly introduced within a network of hydrogen bonds between the starch molecules; therefore, the resulted film becomes more flexible, soft and transparent.

The relative per cent elongation increased significantly with increasing plasticizer concentration. Moreover, plasticized films showed a larger elongation in comparison to unplasticized ones. Sorbitol-plasticized starch films displayed a higher elongation ratio. The high percent elongation of sorbitol-plasticized films can be attributed to the relatively small, hydrophilic nature of sorbitol molecule with a large number of hydroxyl groups that establish hydrogen bonding. Generally, while the film structure softens, TS decreases and elongation increases. A higher elongation means that the film is more flexible under tension or mechanical stress. This indicates that the film might resist mechanical damage during machinery or rough handling in food processing [37].

In another study, when a plasticizer, as glycerol, was introduced into a starch matrix, direct interactions and the proximity between starch chains were reduced, which results in facilitating movements of starch chains under tensile forces, decreasing the glass transition temperature of these materials and improving their flexibility [33].

2.2.2. Water Vapor Permeability of Edible Films

Permeability can be described as the product of diffusivity and solubility only when Fick's and Henry laws are fully applied. Water vapor strongly interacts with polymer for most of the edible films which leads to diffusion [39].

The water vapor permeability of edible coating is a very important and widely studied property and receives much attention because of the role of water in deteriorative reactions. Water causes texture degradation, chemical and enzymatic changes while acting as a solvent or carrier. Also the water activity of foods is related with the shelf life of food product and therefore is considered as a significant parameter. Water activity should be low to decrease the deteriorative chemical and enzymatic reactions and to avoid the texture degradation in low-moisture foods. Water vapor permeability of the edible films depends on composition of film forming materials, ambient temperature, humidity and film thickness [8, 39]. As long as biodegradable or edible films function to impede moisture transmission between food and the surrounding media, water vapor permeability is expected to be as low as possible [14].

There are several methods to measure permeability. Weight gain or loss measurements are of importance to determine permeability. In many research, the method to measure the water vapor permeability is based on the standard method described in ASTM E96 (standard test method procedure for water vapor permeability) [40]. According to this method water vapor permeability of film sample is determined gravimetrically. In this procedure, the test film is sealed to a glass dish containing anhydrous calcium chloride or silica gel (Relative vapor pressure; RVP=0) and then the cell is placed in the desiccators or cabinets maintained at specific relative humidity and temperature. Glass dishes are continuously weighed and the water vapor transmission through the film and absorbed by the desiccant are determined by measuring the weight gain. Changes in weight of the cell

were plotted as a function of time [2, 8, 19, 27]. The slope of the plot between weight gain and time is used to calculate the water vapor transmission rate (WVTR) and water vapor permeability (WVP) [41]. WVTR ($\text{g s}^{-1} \text{m}^{-2}$) was calculated from the slope of the straight line divided by the test area.

The WVP (g mm/kPa s m^2) is calculated as;

$$\text{WVP} = \left[\frac{\text{WVTR}}{S (R_1 - R_2)} \right] d \quad (2.1)$$

where S = saturation vapor pressure (Pa) of water at test temperature, R_1 = RVP in the desiccator, R_2 = RVP in the permeation cell, and d = film thickness (mm). At least three replicates of each film should be tested for WVP and all films should be equilibrated with specific RH before permeability determination [14, 20, 27].

2.2.3. Mechanical Properties of Edible Films

Mechanical strength is an important property of edible film because it provides integrity of a film and enables resistance against minor defects such as a pin hole. In order to protect the food from environmental effects films must be durable to breakage and abrasion. Besides films are expected to adapt possible deformation without breaking which is provided by flexibility. Therefore a biodegradable or edible film is expected to resist the normal stress existed during its application, subsequent shipping and handling of the food to protect its integrity and barrier properties. The important parameters for the assessment of the formation, application and quality of films and coatings are tensile strength (TS) and percentage elongation at break (PEB). Tensile strength is defined as the maximum stress sustained by the film during a tensile test and expresses a measure of integrity and potential use of films for heavy duty. Moreover percentage elongation at break gives information about a film's ability to stretch and is expressed as the percentage of change of the original length of the specimen of a film between the grips while extending. High tensile strength is generally preferred, but deformation values must be adjusted according to the intended application of the films [8, 14].

Mechanical properties of cellulose based films depends on several parameters such as type of polymer and plasticizer, concentration of plasticizer, type of solvents, molecular weight of the film forming materials, film thickness and film formulation. The materials used in film formulation especially have significant effects on the mechanical strength of edible coatings. Besides all of these, film forming conditions such as the process, solvent, rate of drying and coating technique (dipping, spraying, spreading, etc.) generally influence mechanical properties of edible films and coatings [8].

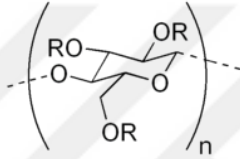
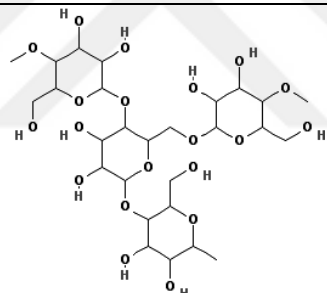
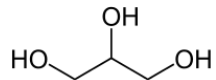
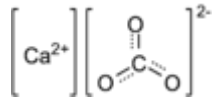
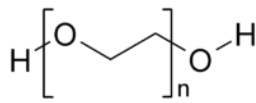


3. MATERIALS AND METHODS

3.1. CHEMICALS AND SAMPLES

The chemicals used in this study are shown in Table 3.1.

Table 3.1. Properties of chemicals used in film formulations

Chemical Name	Formula	Structure	Provider
Carboxymethyl cellulose	$C_8H_{16}O_8$	 $R = H \text{ or } CH_2CO_2H$	Shandong Yulong Cellulose Technology Co. Ltd. (Shandong, China)
Corn starch	$C_{27}H_{48}O_{20}$		Polen Un ve Gıda Katkı Maddeleri San. ve Tic. A.Ş. (İstanbul, Turkey).
Modified corn starch	-	different derivatives	Polen Un ve Gıda Katkı Maddeleri San. ve Tic. A.Ş. (İstanbul, Turkey).
Glycerol or 1,2,3-Propanetriol	$C_3H_8O_3$		Polen Un ve Gıda Katkı Maddeleri San. ve Tic. A.Ş. (İstanbul, Turkey).
Calcium carbonate	$CaCO_3$		Polen Un ve Gıda Katkı Maddeleri San. ve Tic. A.Ş. (İstanbul, Turkey).
Polyethylene glycol	HO-(CH_2CH_2O) $_n$ -H		Clariant International Ltd.

Lokum samples were purchased from a local market in İstanbul, Turkey.

3.2. METHODS

3.2.1. Visual Appearance

Visual appearance is an important parameter for choosing the ideal coating material. There are some properties that must be taken into account. The film samples should have integrity, smooth surface, flexibility and homogeneity. Films without pores and cracks are desirable. Besides, film samples should be easily removed from the plates and easily be handled in order to be used for further processes. Also, coatings should not affect the color of the sample. Therefore, the prepared film samples were evaluated visually according to the degree of providing these properties.

3.2.2. Film Thickness

As long as thin coating is aimed for food applications, film thickness is desired to be low. The film thickness was measured with a hand-held micrometer (Fowler Company, USA). Measurements were made at different points (at least five) on the films (at 25°C, RH= 50%). Average values were calculated.

3.2.3. Water Vapor Permeability (WVP)

WVP tests were carried out according to ASTM method E96/E96M-13 [40] with some modifications. Special cups, with an average diameter of 5.0 cm and a depth of 2.5 cm, were utilized to determine the WVP of films. Films were cut into discs with a diameter slightly larger than the diameter of the cup. After placing 3.00 g of anhydrous CaCl_2 (RH = 0%) in each cup, they were covered with film samples. Each cup was placed in a test chamber providing a RH of 60% at 25 °C. Air continuously circulated throughout the chamber with a velocity sufficient to maintain uniform conditions. Cups were weighed every one hour and water vapor transport was determined by the weight gain of the cup. Changes in the weight of the cup were recorded as a function of time. Slopes were calculated by linear regression (weight change vs. time). The water vapor transmission rate (WVTR) was defined as the slope (g/hour) divided by the transfer area (m^2). The WVP ($\text{g mm/m}^2 \text{ day kPa}$) was calculated as:

$$WVP = \frac{WVTR X}{P (R_1 - R_2)} \quad (3.1)$$

where P is the saturation vapor pressure of water (3.2 kPa) at the test temperature (25 °C), R_1 is the RH in the test chamber (0.60), R_2 is the RH in the cup (0) and X is the film thickness (mm). Under these conditions, the driving force [P ($R_1 - R_2$)] is 1920 Pa. All measurements were performed three times. Three samples were prepared from each individual film.

3.2.4. Mechanical Properties

The ultimate tensile strength (TS) and percentage elongation at break (PEB) of the films were determined at 23 ± 2 °C and RH= $50 \pm 10\%$ using a tensile tester (TAXT - Plus Texture Analyzer/Stable Micro Systems) according to the ASTM standard method D882-12 [42]. After conditioning in RH= 60% at 25 °C for 48 h, five film specimens, 15×2 cm strips, were cut from each of the film samples and were mounted between the grips of the machine. The initial grip separation and cross-head speed were set to 10.0 cm and 50.0 mm/min, respectively.

3.2.5. Film Color and Opacity

Color is an important parameter for food packaging in terms of general appearance and consumer acceptance [14]. Color values of the films were measured with a portable colorimeter (CR-300 Minolta Chroma Meter, Minolta Camera Co., Osaka, Japan). The results of the measurements performed on the color of the blend film were expressed in accordance with CIELAB system and the rectangular coordinates (L^* , a^* , and b^*) and the total color difference (ΔE^*) and chroma (yellowness values) were calculated. [$L^* = 0$ (black) to 100 (white); $a^* =$ green to red; and $b^* =$ blue to yellow]. Film specimens were placed on a white standard plate ($L = 97.07$, $a = 0.35$, and $b = 1.81$) and the L, a, and b color values were measured. All measurements were performed three times.

Total color difference (ΔE_{ab}) and chroma (C) were calculated using the following equations 3.2, 3.3, 3.4, 3.5 and 3.6:

$$\Delta L^* = L^*_{sample} - L^*_{standard}, \quad (3.2)$$

$$\Delta a^* = a^*_{sample} - a^*_{standard}, \quad (3.3)$$

$$\Delta b^* = b^*_{sample} - b^*_{standard}, \quad (3.4)$$

$$\Delta E^*_{ab} = \left[(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2 \right]^{0.5} \quad (3.5)$$

$$C = \left[(a^*)^2 + (b^*)^2 \right]^{0.5} \quad (3.6)$$

Film opacity was determined using a procedure described by Garcia et al [2]. A film sample was cut into a rectangle and placed on the internal side of a spectrophotometer cell. The absorbance spectrum (in the range of 400- 800 nm) was recorded for each sample by a Perkin Elmer Lambda 25 UV/Vis spectrophotometer. Film opacity was defined as the area under the recorded curve and determined by integration. The opacity was expressed as absorbance units x nanometers (Au x nm).

3.2.6. Moisture Content

Two grams from each of the sample films (conditioned at 25 ± 2 °C, RH= 50% for 48 h) were dried in an oven at 105 °C until constant weight was obtained. The water content can be calculated using equation 3.7:

$$\% \text{ water content} = \left(\frac{W_0 - W_f}{W_0} \right) 100 \quad (3.7)$$

where W_o is the sample weight before drying, W_f is its weight after drying. All measurements were performed three times.



4. EXPERIMENTAL STUDY

4.1. EXPERIMENTAL PROCEDURES

4.1.1. Choosing of Coating Material and Determination of the Formulation

One of the most important criteria for choosing the right coating material is the compatibility of the coating material with the product surface. In this manner, coating should provide integrity with the product itself [4]. Besides, the organoleptic properties of edible films and coatings should be as neutral as possible (colorless, odorless, tasteless, etc.) [43]. As a result, adaptability of the coating with the food is very important. In respect of polysaccharide based structure of lokum, the formulation of which consists of starch, sugar, citric acid and water, application of a coating with a similar structure to polysaccharide may meet the expectations [44].

The polysaccharide based coating formulation components which were planned to be used for film production are given in Table 4.1:

Table 4.1. Film formulation components

Polysaccharide	Plasticizer	Stickiness reducing agent
Carboxymethyl cellulose	Glycerol	CaCO ₃
Starch		Polyethylene glycol
Modified starch		

According to this table, film samples were prepared in different ratios and combinations which consist of polysaccharide, plasticizer and stickiness reducing agent. Film samples were firstly evaluated based on visual appearance and film thickness. After choosing the best formulation, physical and mechanical properties of film samples, which are water vapor permeability (WVP), tensile strength (TS), percentage elongation at break (PEB), film thickness, color, opacity and film moisture content, were investigated. Besides lokum appearance and texture were also evaluated after the application.

4.1.2. Film Preparation

Films were prepared as described by *Daniels* [23] with some modifications. Varying amounts of polysaccharide (CMC, starch or modified starch), plasticizer (glycerol) and stickiness reducing agent (PEG or CaCO_3) were dissolved in distilled water in different combinations at about 90 °C. The preparation procedure is described in Figure 4.1. After cooling and removing air bubbles, films were cast by pouring 20 g and 30 g of solutions onto Petri dishes resting on a leveled surface with 8.5 cm internal diameter and then dried for two days at 23 ± 2 °C. Three films were prepared for each formulation. Finally films were peeled off the Petri dishes for their evaluation. Totally four groups with different compositions (Group 1, Group 2, Group 3 and Group 4) of experimental formulation were planned. The abbreviations for the different film samples and their compositions are listed in Table 4.2, Table 4.3, Table 4.4 and Table 4.5. At least three films were prepared for each formulation, corresponding to three different replicates.

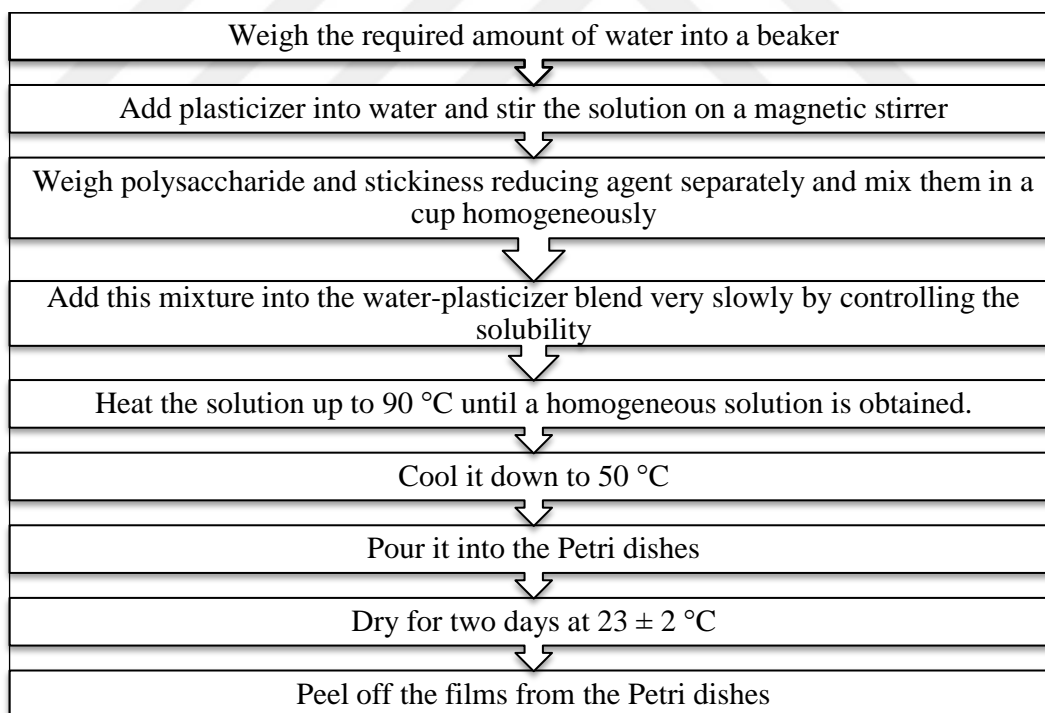


Figure 4.1. Film preparation procedure

- **Group 1**

In the beginning of the study, four formulations were determined to be prepared as shown in Table 4.2.

Table 4.2. Formulation of samples in Group 1

Sample No	Starch (%)	Gly (%)	CaCO ₃ (%)	Water (%)
1	3	1.5	0.1	95.4
	Modified Starch (%)	Gly (%)	CaCO ₃ (%)	
2	3	1	0.1	95.9
	CMC (%)	Gly (%)	CaCO ₃ (%)	
3	0.5	0.5	0.1	98.9
	CMC (%)	Gly (%)	PEG (%)	
4	0.5	0.5	0.5	98.5

- **Group 2**

To see the plasticizer effect, six film formulations were prepared as below in Table 4.3 which did not consist of Gly but consist of CMC and PEG.

Table 4.3. Formulation of samples in Group 2

Sample No	CMC (%)	PEG (%)	Water (%)
5	0.5	0.5	99.0
6	0.5	1	98.5
7	0.5	2	97.5
8	1	0.5	98.5
9	1.5	0.5	98.0
10	3	0.5	96.5

- **Group 3**

Five film solutions were prepared which consist of CMC as a main material and different concentrations of Gly and PEG.

Table 4.4. Formulation of samples in Group 3

Sample No	CMC (%)	Gly (%)	PEG (%)	Water (%)
11	0.5	0.1	0.5	98.9
12	0.5	0.2	0.5	98.8
13	0.5	0.5	0.5	98.5
14	0.5	0.5	1	98.0
15	0.5	0.5	2	97.0

- **Group 4**

3 and 4 were prepared again and besides new two formulations were decided to be prepared to be able to compare the samples with the same concentration of the stickiness reducing agent with each other. Totally four film trials were done. One surface of the lokum samples was coated with these film solutions.

Table 4.5. Formulation of samples in Group 4

Sample	CMC (%)	Gly (%)	CaCO ₃ (%)	Water (%)
3	0.5	0.5	0.1	98.9
	CMC (%)	Gly (%)	CaCO ₃ (%)	
16	0.5	0.5	0.5*	98.5
	CMC (%)	Gly (%)	PEG (%)	
4	0.5	0.5	0.5	98.5
	CMC (%)	Gly (%)	PEG (%)	
17	0.5	0.5	0.1	98.9

*this amount of CaCO₃ was hardly dissolved.

4.1.3. Application of the Coating Material onto Lokum Samples

Edible emulsified coatings were applied on lokum samples that were selected with a regular surface area to provide a uniform coating. For this application, film formulation was concentrated by evaporating 20% and 40% of its total weight. Some of the lokum samples were coated in one surface by applying one mL of polysaccharide based formulations; some of them were dipped once in the solution at room temperature for 15 minutes after removing the excess powder and dried for three days at 20 °C with forced ventilation incubator.

Lokum manufacturers have different ideas on the quality parameters of lokum such as color and texture of lokum. But they came in the agreement that appearance, structure and taste are the most important criteria for the quality of lokum. Most importantly, lokum should retain its shape and color, not have crack formation on the surface and have a transparent appearance. Softness and elasticity of lokum are the most important attributes for texture. But there is no certain measurement defined to assign the quality of texture by lokum manufacturers. The only expectation by the manufacturers is that lokum is neither too hard nor too soft [3]. In this study, lokum samples were subjected to texture analysis by texture analyzer and were also evaluated by their appearance.

5. RESULTS AND DISCUSSION

5.1. THICKNESS AND VISUAL APPEARANCE OF FILM SAMPLES

- **Group 1**

As explained in Section 3.2.2, thickness is an important parameter for food coating applications and it was measured by a hand-held micrometer (Fowler Company, USA). First of all, samples in different groups (ingredients of the samples in different groups were given in Tables 4.2-4.5.) were analyzed for their thickness and then preliminary visual appearance tests were done and the results were discussed.

Table 5.1. Film thickness results obtained from Group 1

Sample	Thickness (mm)
1 (30 g)	-*
1 (20 g)	0.102
2 (30 g)	-*
2 (20 g)	0.102
3 (30 g)	0.057
3 (20 g)	0.046
4 (30 g)	0.068
4 (20 g)	0.048

*: The sample became moldy during the drying process.

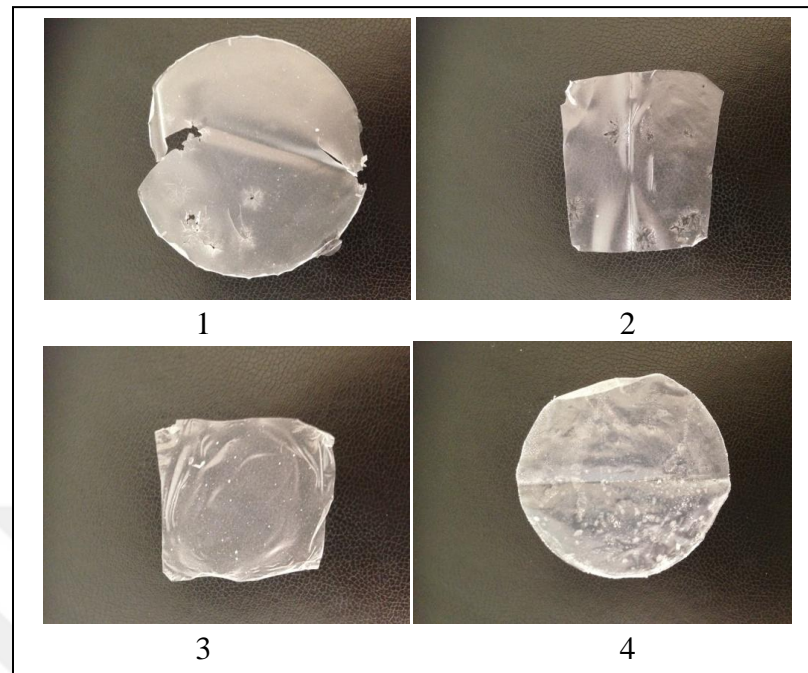


Figure 5.1. Visual Appearance of film samples (20 g) obtained from Group 1

Table 5.2. Results of preliminary visual appearance tests for Group 1

Sample	Integrity	Homogeneity	Flexibility	Smooth surface	Pores and cracks absence	Transparency	Easiness to handle	Easiness to peel off
1	-	+	+	+	--	++	-	-
2	+	++	+	+	--	++	-	-
3	+++	++	+++	++	+++	+++	++	+++
4	+++	-	+	+	+++	+	++	+

+++ excellent; ++ very good; + good; - poor; -- very poor.

According to film thickness values (Table 5.1), CMC based film samples (sample **3** and sample **4**) resulted in thinner films. This result can be attributed to the lower amount of ingredients (polysaccharide, plasticizer and stickiness reducing agent) used in the CMC based formulations (see Table 4.2 for formulations). Starch and modified starch based films (sample **1** and sample **2**) which were cast as 30 g became moldy due to the long

drying period (four days). As the water evaporation (drying) time increases due to the higher amount of water in starch based formulations, the film matrix may become more convenient for the growth of microorganisms. Besides the derived films showed poor visual properties (Figure 5.1, Table 5.2). Therefore it was decided not to use starch and modified starch in film formulations for further studies.

Film thickness and the visual appearance (integrity, homogeneity, flexibility, smooth surface, pores and cracks absence, transparency, easiness to handle and easiness to peel off from the plate) results were considered and sample **3** and sample **4** in Group 1 were determined as the best two formulations since they are thinner and have better visual appearance properties. In further studies, CMC was used as the main film forming material.

- **Group 2**

Table 5.3. Film thickness results obtained from Group 2

Sample	Thickness (mm)
5 (30 g)	0.047
5 (20 g)	0.049
6 (30 g)	-*
6 (20 g)	0.068
7 (30 g)	-*
7 (20 g)	0.109
8 (30 g)	0.101
8 (20 g)	0.076
9 (30 g)	0.103
9 (20 g)	0.079

*: the samples were broken into pieces during handling and therefore measurements couldn't be taken.

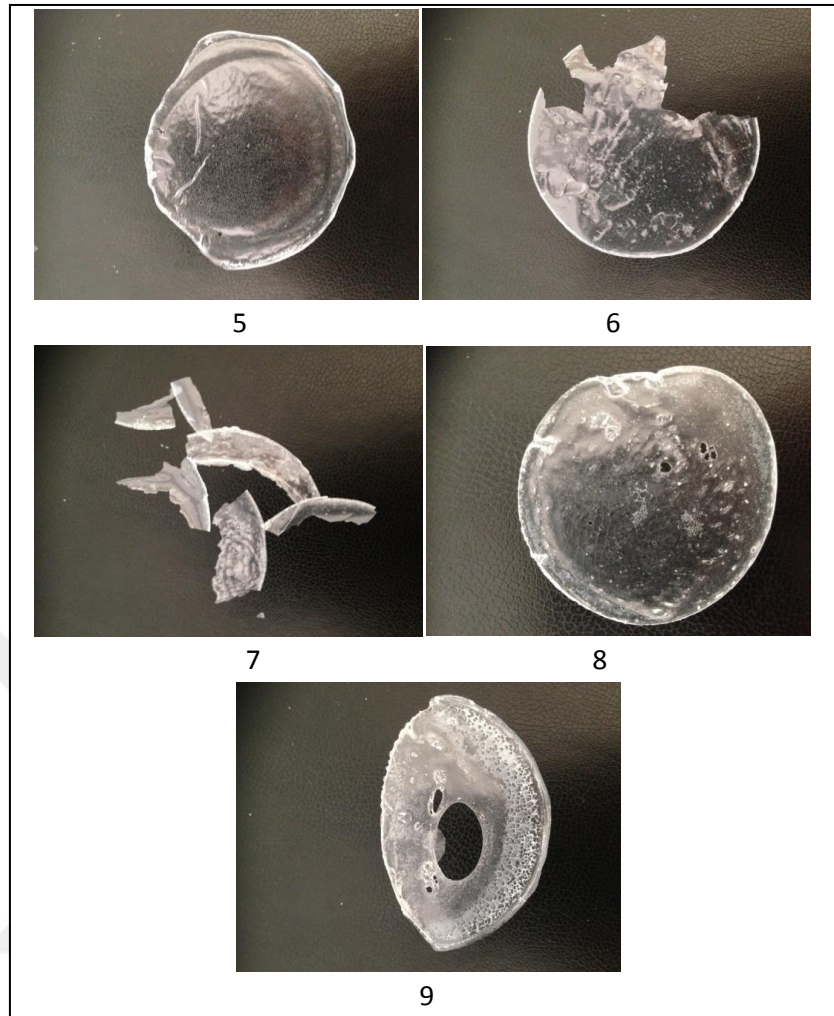


Figure 5.2. Visual Appearance of film samples (20 g) obtained from Group 2

Table 5.4. Results of preliminary visual appearance tests for Group 2

Sample	Integrity	Homogeneity	Flexibility	Smooth surface	Pores and cracks absence	Transparency	Easiness to handle	Easiness to peel off
5	++	++	--	+	--	++	--	--
6	--	+	--	-	--	++	--	--
7	--	++	--	-	--	+	--	--
8	-	--	--	--	--	-	--	--
9	--	--	--	--	--	--	--	--

+++ excellent; ++ very good; + good; - poor; -- very poor.

In group 2, CMC and PEG were used as film components. The thickness values were acceptable (Table 5.3), but they have poor visual properties (Figure 5.2 and Table 5.4.) The resulted film was too heterogeneous and spongy which ruined the film integrity when CMC quantity was more than 0.5% (1.0%, 1.5%) in the formulation. This result may be attributed to the strong cohesion forces between film forming polymer molecules (CMC) which increases as the polymer amount increases. Hence stronger cohesion reduces flexibility and increases porosity of the film. Therefore it was not possible to obtain intact films with more than 0.5% of CMC, without plasticizer. Besides in the formulation of **10**, it was very difficult to solve CMC (3.0%). This amount seemed higher than the maximum amount of CMC soluble in that amount of water (% 96.5). Hence the film solution could not be prepared and its result could not be discussed.

All film samples which did not include glycerol were too brittle and difficult to separate from the plate. The absence of glycerol decreased film flexibility, which makes the films difficult to handle. In order to overcome film brittleness due to the high intermolecular forces, plasticizer addition was needed. Plasticizers improve film flexibility and extensibility by diminishing these forces and enabling mobility to the polymer chains [7]. According to *Parris* et al. [35] and *Alves* et al. [36] plasticizers in film formulations act as a component to reduce intermolecular hydrogen bonding between polymer molecules, thereby resulting spacing between macromolecules which results in a decrease in brittleness.

The appearance of film samples in this group was in agreement with *Laohakunjit's* and *Noomhorm's* study. *Laohakunjit* and *Noomhorm* [37] found in their study that unplasticized rice-starch films displayed a rough surface appearance, whereas sorbitol- and glycerol-plasticized rice films were relatively smooth. The number of insoluble particles and air bubbles were significantly reduced in the plasticized films. The film surfaces in this study were also rough and not smooth in the absence of glycerol.

As a result the formulation of samples in group 2 was not adequate for film preparation.

- **Group 3**

Table 5.5. Film thickness results obtained from Group 3

Sample	Thickness (mm)
11 (30 g)	0.051
11 (20 g)	0.039
12 (30 g)	0.067
12 (20 g)	0.045
13 (30 g)	0.106
13 (20 g)	0.057
14 (30 g)	0.111
14 (20 g)	0.078
15 (30 g)	0.184
15 (20 g)	0.102

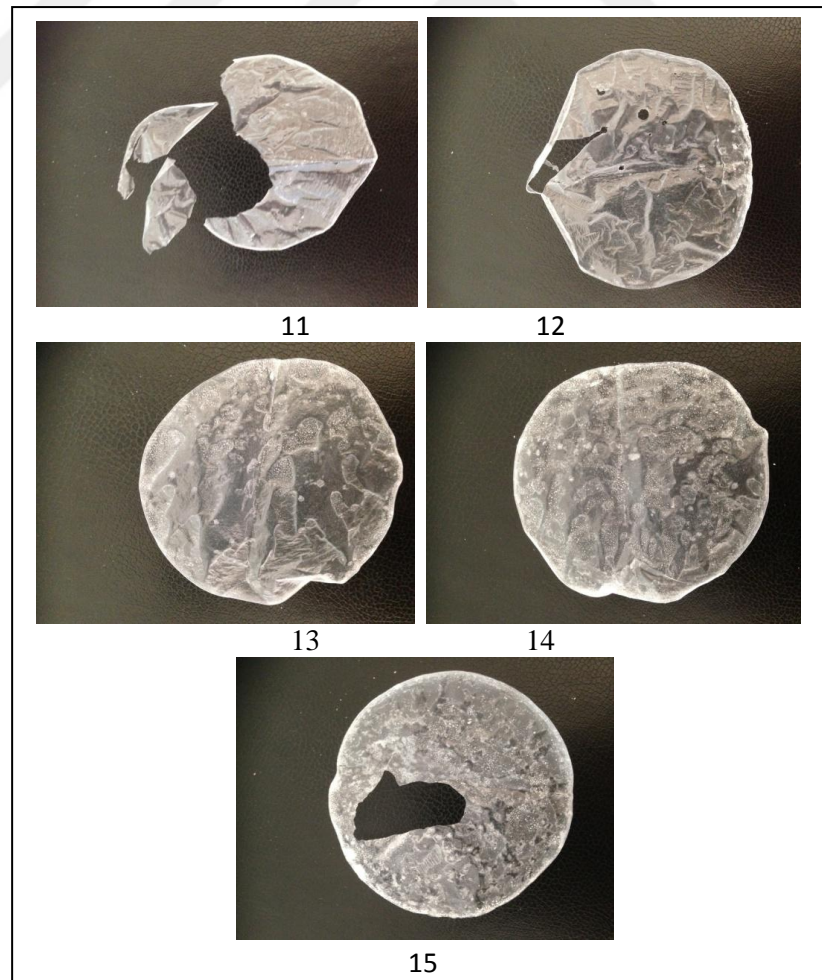


Figure 5.3. Visual Appearance of film samples (20 g) obtained from Group 3

Table 5.6. Results of preliminary visual appearance tests for Group 3

Sample	Integrity	Homogeneity	Flexibility	Smooth surface	Pores and cracks absence	Transparency	Easiness to handle	Easiness to peel off
11	--	-	+	+	--	-	--	--
12	-	+/-	+	+	-	-	-	-
13	+++	-	+	+	+++	--	++	+
14	+++	--	+	+	+++	--	+	+
15	--	--	+	+	--	--	-	--

+++ excellent; ++ very good; + good; - poor; -- very poor.

In Group 3, CMC, Gly and PEG were used as film components. Although the thickness values were seen to be appropriate (Table 5.5), the visual properties were seen not to be so well in most cases (Figure 5.3, Table 5.6). The brittleness of the films (sample **11** and sample **12**) which had less Gly than 0.5% (0.1% and 0.2%) was high and plus the film integrity of these samples was poor. This result may be related to the absence of efficient amount of Gly to overcome film brittleness due to the high intermolecular forces. Moreover solubility of film components in the formulation was not good enough, when PEG concentration was higher than 0.5 % (1% and 2%), and the derived films (sample **14** and sample **15**) were heterogeneous. These amounts seemed higher than the maximum amount of PEG soluble in that amount of water (98.0 % and 97.0% respectively). Therefore formulation of samples in group 3 was also not adequate for film preparation.

- **Group 4**

Lastly group 4 samples were evaluated.

Table 5.7. Film thickness results obtained from Group 4

Sample	Thickness (mm)
3 (20 g)	0.023
4 (20 g)	0.063
16 (20 g)	0.083
17 (20 g)	0.029

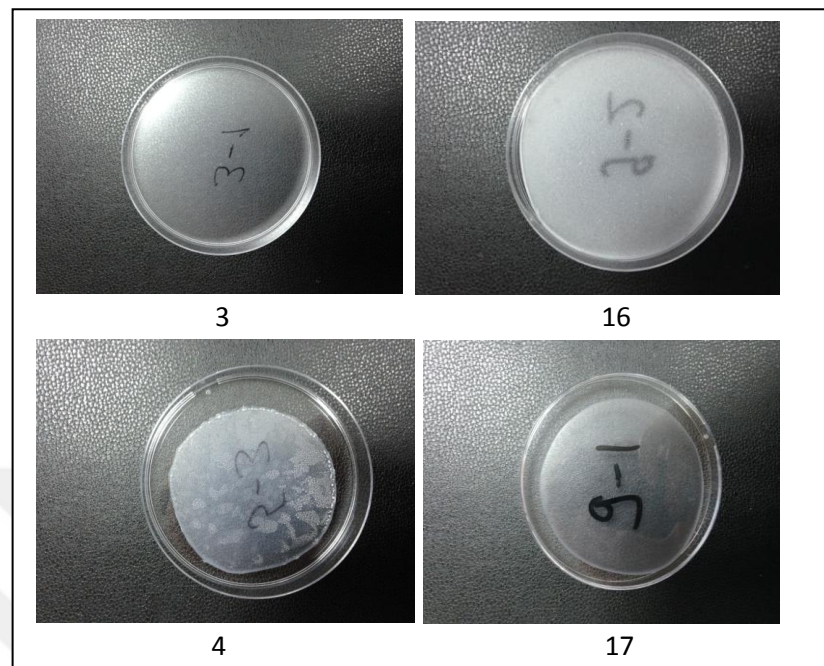


Figure 5.4. Visual Appearance of film samples (20 g) obtained from Group 4

Table 5.8. Visual Appearance of film samples obtained from Group 4

Sample	Integrity	Homogeneity	Flexibility	Smooth surface	Pores and cracks absence	Transparency	Easiness to handle	Easiness to peel off
3	+++	+++	+++	+++	+++	+++	++	+++
4	+++	-	+	+	+++	-	++	+
16	+++	+++	+++	++	+++	-	++	++
17	+++	+++	+++	+++	+++	+++	+++	+++

In Group 4, CMC, Gly, PEG and CaCO_3 were used as film components. As seen from Figure 5.4, Table 5.7 and Table 5.8, the films were thinner, smooth, homogeneous, elastic, translucent and easy to handle when the concentration of the stickiness reducing agents (CaCO_3 and PEG) was 0.1% (sample **3** and sample **17**). On the other hand, when they were applied onto lokum samples, the drying period was longer for the sample **3** compared to that of sample **17** (three days for sample **17**, five days for sample **3**). Therefore the best formulation for lokum coating was determined as that of sample **17**. Hence it was decided

to determine physical and mechanical properties of this film in order to evaluate its convenience for lokum coating.

5.2. PHYSICAL AND MECHANICAL PROPERTIES OF THE FILMS PREPARED ACCORDING TO THE FORMULATION 17

The results of thickness and visual properties tests ended up with choosing the formulation of sample **17** as the ideal formulation for film making. The film obtained from formulation **17** was analyzed in detail to define its properties clearly.

5.2.1. Film thickness values of sample 17

Seven samples were prepared with the formulation of **17** using the same amounts of ingredients. The thickness values were determined by micrometer five times independently that means measurements were taken at five different points on the films and the average value was found for each sample as seen from Table 5.9.

Table 5.9. Film thickness results obtained from formulation **17** (mm)

Measurement	1	2	3	4	5	Average
1	0.019	0.021	0.015	0.015	0.012	0.016
2	0.014	0.012	0.013	0.016	0.015	0.014
3	0.013	0.017	0.018	0.015	0.019	0.016
4	0.017	0.02	0.015	0.017	0.019	0.018
5	0.016	0.021	0.015	0.017	0.019	0.018
6	0.013	0.015	0.012	0.017	0.018	0.015
7	0.021	0.016	0.014	0.018	0.015	0.017
					Average	0.016

Finally the average thickness of the films from formulation **17** was found as 0.016 mm. This value is in agreement with the study of *Ayana and Turhan* [13] who found the thickness of MC based films between 0.016 mm – 0.019 mm and applied them onto kaşar cheese. Besides, the obtained film seems thinner than most of the edible films studied in the literature. *Ghanbarzadeh and Almasi* [9] found the thickness of CMC based films

between 0.075 mm – 0.092 mm. Su et al [45] found the thickness of CMC/soy protein based films between 0.094 mm – 0.109 mm. *Rodriguez et al* [32] measured the thickness of MC based films between 0.049 mm – 0.089 mm. Additionally thickness values of pectin films were found between 0.02 mm – 0.045 mm by *Mekkerdchoo et al* [46]. As a result the derived films from formulation **17** are promising for food applications based on thickness values.

5.2.2. Tensile strength, elongation values and water vapor permeability of the film sample 17

Mechanical properties of films have been characterized by the tensile strength (TS) and elongation (E %) values. For these properties, generally high values are required, which are the indicators of the high strength and high flexible films. For the tests four samples with the same concentration of formulation **17** were prepared and the results of the tensile tests have been shown in Table 5.10. The average result was found as 20.49 N/mm² and 48.54 % for tensile strength and elongation, respectively. Similar results have been previously reported for several films in the literature as shown in Table 5.11.

If the tensile test results of this study have been compared to those of the synthetic polymers, it can be concluded, that the studied films have comparable TS values to those of low and high density polyethylene, which have been reported between 10–20 MPa and 16–41 MPa, respectively, and also E% values of the studied samples (see Table 5.11) of which the average value was found as 48.54% were better generally than those of cellophane and cellulose acetate, which have been reported between 15–25% and 15–70%, respectively [15].

Gharbanzadeh and Almasi [9] attributed the high TS and low strain to break value of the control sample (unplasticized) to hydrogen bonds between the CMC chains. These bonds promote high cohesiveness and low flexibility of the unplasticized films. In the study an increase in strain to break value and a decrease in TS with increasing glycerol concentration were observed, which is consistent with the study of *Gharbanzadeh and Almasi* [9]. According to *Parris et al.* [35] and *Alves et al.* [36], plasticizers in film formulations act as a component to reduce intermolecular hydrogen bonding between

polymer molecules, thereby resulting spacing between macromolecules. This leads to an increase in the elongation of the films because of the spaces inside but the strength of the film decreases. As a result the increase in strain to break value and a decrease in TS with increasing glycerol concentration can be explained by the decrease of hydrogen bonding of CMC molecules.

This type of carboxymethyl cellulose film may be also suitable for other industrial applications where high tensile strength and high elongation values of films are required.

Table 5.10. Tensile strength and elongation values of film samples

Sample	Tensile Strength (N/mm ²)	Elongation (%)
1	22.87	48.10
2	19.43	52.06
3	17.72	44.21
4	21.94	49.80
Avg	20.49	48.54
std	2.35	3.31

One of the main purpose of food packaging is often to avoid or at least to decrease moisture transfer between the food and the surrounding media, or between two components of a heterogeneous food product, hence water vapor permeability should be as low as possible [33]. Water vapor permeability (WVP) of films was determined gravimetrically at 25 °C using a modified ASTM method E96/E96M-13 procedure. Measurements were performed for three samples with the same concentration three times. At Table 5.12 values of water vapor permeability results have been presented. The average value was found as 7.08 g mm/m² day kPa. These results are in good agreement with other previously reported studies for several films as summarized in Table 5.11. Although the samples have different thickness values, their physical properties are quite acceptable for film formation. Besides as seen from Table 5.12 the std value is quite low.

In the study of *Gharbanzadeh* et al. [6], WVP of the biocomposite films (corn starch-CMC based films) diminished with the increase of CMC content. Water resistance of CMC

biopolymer is superior to that of starch one. This could be attributed to the more highly crystalline and more hydrophobic character of the cellulose fibers compared to starch polymer. Therefore CMC is also a better choice considering its higher water resistance capacity compared to that of starch. The obtained result meets the expectations.

Table 5.11. Tensile strength (TS), elongation at break (E %) and water vapor permeability (WVP) of various films from the literature and this study

Film type	Test condition	Tensile strength (MPa)	Elongation at break (%)	Water vapor permeability (g mm/m ² day kPa)	Reference
Carboxymethyl cellulose	25 °C, 60% RH	20.49	48.54	7.08	Current study
Carboxymethyl cellulose	25 °C, 97% RH	8.7-20.7	6.6-28.8	1.2-15.5	[47]
Carboxymethyl cellulose	25 °C, 97% RH	2.2-17.8	1.4-89.9	5.9-22.9	[9]
Methylcellulose	25 °C, 53% RH	17.3-24.0	27.0-46.5	1.12-1.79	[13]
Carboxymethyl cellulose /soy protein	25 °C, 50% RH	42.0-59.2	1.3-159.0	-	[45]
Carboxymethyl cellulose /starch	25 °C, 52% RH	3.6-24.1	2.5-136.1	-	[15]
Methylcellulose/s starch	25 °C, 52% RH	2.5-28.4	8.8-109.7	-	[15]
Rice starch-chitosan	25 °C, 60% RH	27.5-38.1	8.1-13.0	4.11-7.08	[14]
Cassava starch	25 °C, 75% RH	4.0-26.0	6.0-46.0	-	[33]
Corn starch	25 °C, 75% RH	9.0-37.0	3.0-28.0	-	[33]
Chitosan	25 °C, 50% RH	39.1	10.8	13.22	[48]

Table 5.12. Water vapor permeability values of film samples

	Water Vapor Permeability (g mm / m ² day kPa)
1	6.97
2	7.32
3	6.95
Avg	7.08
std	0.21

5.2.3. Color and Opacity Values of Film Sample 17

Color of a film may influence the consumer's acceptability for a product. Color values of films may be determined by calculating ΔE . In this study, clear and transparent films were obtained from formulation **17**. Color values of the derived films are shown in Table 5.13. Experiments showed that ΔE value of the film was around 0.62. When compared ΔE values of this study with pectin film studied by *Mekkerdchoo* et al [46], ΔE values of the studied film was higher than *Mekkerdchoo*'s which were calculated as 0.017 - 0.045, but they were quite low compared to ΔE values in other studies. For example *Leceta* et al [49] found the ΔE values of Chitosan based films between 1.68 and 8.90, which are higher than those of films in this study. *Vercino and Garcia* [50] found the ΔE values of cassava starch based films between 2.63 and 11.41. It is generally known that ΔE values less than 3.0 cannot be detected by human eyes [46]. Even though, the intensity of the yellowness (chroma) was negligible compared to values reported for rice starch-chitosan based films which was calculated as 2.5-4.0 [14]. *Vercino and Garcia* [50] found the chroma value of cassava starch based films between 3.30 and 10.42. Therefore the resulted films were evaluated as suitable films for food coating according to their color values.

Table 5.13. Color values of film samples

Parameter	Standard	Sample+Standard	Sample
L	97.07	96.46	-0.61
a	0.35	0.40	0.06
b	1.81	1.94	0.13
ΔE			0.62
C			0.14

Film opacity is a critical property if the film is used as a surface food coating. Film opacity was found with the help of a UV/Vis spectrophotometer by using the procedure described by *Garcia et al* [2]. Transparent films are characterized by low values of the area below the absorption curve. Table 5.14 presents the opacity values of films obtained from formulation **17**. Similar results have been obtained from corn starch-chitosan films studied by *Garcia et al* [2]. *Slavutsky et al* [51] measured the opacity of starch based nanocomposite films higher than that of the studied film (93-249).

Table 5.14. Opacity values of film samples

Measurement	Au x nm
1	81.09
2	90.90
3	81.74
Avg	84.58
std	5.49

5.2.4. Moisture Content of Film Sample 17

The moisture content of films derived from formulation **17** was measured as 14.60 % by using gravimetric technique described in 3.2.6. This value is in agreement with other studies in the literature. *Garcia et al* [2] found the moisture content of corn starch and chitosan composite films between 9.1 and 25.2 % and *Garbanzadeh and Almasi* [9] measured the moisture of CMC based edible films between 15.32 and 26.18 %.

5.3. COATING OF LOKUM SAMPLES WITH FILM SOLUTION 17

5.3.1. Visual Appearance and Hardness Values of Lokum Samples after Coating

Some of the lokum samples were coated in one surface with film formulations which are described in Section 4.1.3 by applying one mL of solution onto the samples and some of them were dipped once in the solution at room temperature for 15 minutes after removing the excess powder. After coating process, all samples were dried for three days at 20 °C with forced ventilation incubator.

- **One surface coating**

The lokum samples were smooth, homogeneous, translucent and easy to handle after coating process. The film formed on lokum seemed to be adaptable to the surface. No pores or cracks were observed. The images of lokum samples after coating are shown at Figure 5.5. The results of visual appearance tests are shown in Table 5.15.



Figure 5.5. Lokum samples after coating one surface

Table 5.15. Visual appearance results of lokum samples coated in one surface

Integrity	Homogeneity	Absence of stickiness	Adsorption to lokum surface	Smooth surface	Pores and cracks absence	Transparency	Easiness to handle
+++	+++	++	+++	++	+++	++	++

+++ excellent; ++ very good; + good; - poor; -- very poor.

Texture measurement results of lokum samples after coating are shown at Table 5.16. The results indicate that coating with film solution decreased the hardness of samples resulting in softer Turkish delights when compared with uncoated lokum samples (control value). Besides, as evaporation percent increased, the hardness ascended also, but did not reach the value of uncoated lokum. This increase in hardness may be attributed to the increase in dry matter of solution while evaporating.

Table 5.16. Hardness values of lokum samples after coating in one surface

Evaporation percent (%)	Hardness (g)
0	559.8 ± 32.9
20	595.3 ± 37.8
40	647.9 ± 34.3
Control	1041.1 ± 22.8

- **Dipping**

The lokum samples after dipping were also smooth, homogeneous, translucent and easy to handle after coating. No pores or cracks were observed. The images of lokum samples after coating are shown at Figure 5.6. The results of visual appearance tests are shown in Table 5.17.



Figure 5.6. Lokum samples after coating by dipping

Table 5.17. Results of preliminary visual appearance tests for lokum samples coated by dipping

Integrity	Homogeneity	Absence of stickiness	Adsorption to lokum surface	Smooth surface	Pores and cracks absence	Transparency	Easiness to handle
+++	+++	++	++	++	+++	+++	++

+++ excellent; ++ very good; + good; - poor; -- very poor.

Results of texture measurements of lokum samples after coating process are given at Table 5.18. The results indicate that coating with film solution decreased the hardness of samples resulting in softer Turkish delights. On the other hand, as evaporation percent increased, the firmness has decreased opposite to the one surface coating results. This result may be associated with the long dipping period (15 min) which may allow more interaction between film components and lokum constituents. As a result this interaction may lead to an increase in softness.

Table 5.18. Hardness values of lokum samples after coating by dipping

Evaporation percent (%)	Hardness (g)
0	511.7 ± 29.7
20	446.1 ± 29.2
40	393.3 ± 26.7
Control	1041.1 ± 22.8

Results of lokum coating showed that CMC based structure of coating material used in this study is compatible with the product surface. This means there is a chemical interaction between film components and lokum ingredients especially between starch, water and CMC which are the main constituents.

Water molecules form hydrogen bonds with the hydroxyl groups of polysaccharides; also they do with hydroxyl groups of other molecules in the same way. Formation of this structure of associated water helps in dissolving or dispersing the large molecules. As the hydrated macromolecules rotate in solution, the water aggregates shift and can be rearranged or displaced. While folding or coiling, the polysaccharide molecule can associate with itself to form loops or helices, or possibly even double helices with other coiled macromolecules. By stretching out, it can align with sections of other molecules to form crystalloid regions which are called “micelles”. The micellar regions become hydrophobic as the bound water is replaced by the intermolecular hydrogen bonds of carbon-bound hydroxyl groups. If a sufficient number of polysaccharide molecules bind together, a three-dimensional network is formed which entraps considerable amounts of water (Figure 5.7) [26].

Considering the given information above the basic chemical reactions between the coating material and the lokum surface which provides integrity can be explained by the hydrogen bonds formed between hydroxyl groups of starch, CMC and water.

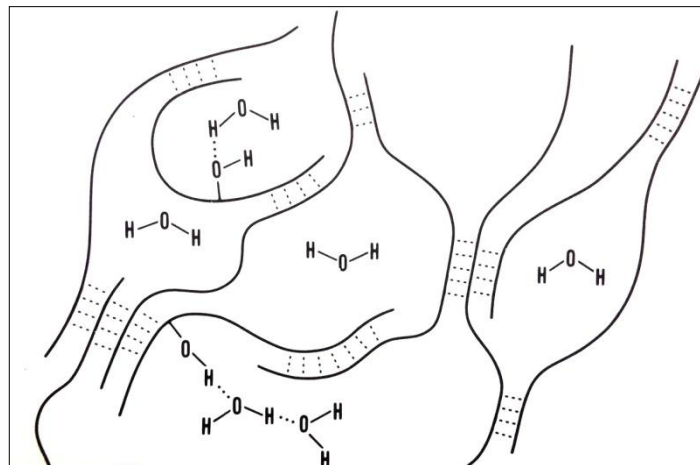


Figure 5.7. Scheme of intermolecular hydrogen bonding of polysaccharides.

6. CONCLUSION AND FUTURE WORK

Edible coatings are very promising systems for food storage in the future by providing good barrier and mechanical properties. They, alone or as carriers of useful additives, serve many benefits for food products.

Nowadays synthetic polymers are being replaced by renewable materials which are derived from natural sources. Using this kind of bio packaging will be beneficial and provide new economical potentials opportunities for farmers. Innovative techniques preserving food quality and safety as well as providing biodegradability must be adopted. Chemists, polymer technologists, microbiologists, chemical engineers, environmental scientists and bureaucrats should make an effort on researches for a successful implementation and commercialization of biopolymer-based ecofriendly packaging materials. It is a fact that biodegradation is an attractive route to environmental waste management [16].

As a result of this study, CMC based films can be described as biofilms with a homogeneous matrix, stable structure and interesting water barrier and mechanical properties to facilitate handling and transportation of food products and with the advantage of biodegradability. Furthermore this kind of films is promising and seems to have good potential in food applications improving sensorial properties such as color, shininess, transparency, roughness or sticking. The results of this experiment showed that using a coating based on carboxymethyl cellulose is a viable alternative for lokum coating. Among the possible alternatives carboxymethyl cellulose, glycerol and polyethylene glycol suspensions were found the best components for the formation of homogeneous, thin and flexible films with the optimized concentrations 0.5 % w/v, 0.1 % w/v and 0.5% w/v for CMC, PEG and Gly, respectively. The derived films were colorless, transparent and showed desired mechanical and physical properties. The average thickness value was found as 0.016 mm. The average results of tensile strength and elongation percent were found as 20.49 N/mm² and 48.54 %, respectively. Water vapor permeability was measured as 7.08 g mm/m² day kPa. Total color value and opacity value of resulted film were found as 0.62 and 84.58, respectively. And lastly the moisture content of film was measured as 14.60 %. The lokum samples after coating are also smooth, homogeneous, translucent and easy

to handle without pores and cracks on the surface. Besides the coating resulted in softer lokum samples which can be an advantage for lokum storage because of the tendency of lokum samples to get harder during storage due to the moisture loss. Lastly it can be concluded that dipping method of coating seems to be applicable in industrial processes and can be improved in the future applications by changing the duration time of the product in the solution or drying process.

As a future work, a shelf life study to determine the stability of this coating on lokum samples is planned to be performed with the necessary analyses. The coatings are expected to preserve their functions throughout the storage. If they do not preserve them, other ingredients such as methyl cellulose may be used as film components. Besides, this edible coating may be applied to other food products such as confectionaries, grains, dry fruits. Moreover, the formulation of coating may be enriched by adding some functional additives such as antioxidants, vitamins, sterols to improve the nutritional quality of the food.

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APPENDIX A: LOKUM PRODUCTION PROCESS