WATER VAPOUR PERMEABLE EDIBLE MEMBRANES

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ABSTRACT

In this study, polysaccharide based edible films were prepared and characterized. Also water vapour sorption, diffusion and permeability characteristics of these films were studied. For these purposes cellulose ethers such as sodium salt of carboxymethyl cellulose (NaCMC) and hydroxypropylcellulose (HPC) were used as a film forming materials. Distilled water and glycerin were used as solvent and plasticizer respectively. To determine the effect of polymer concentration of the film forming solution on the film properties, NaCMC and HPC films were prepared from three different concentrations (3, 4, 5g polymer/100ml distilled water) of film forming solutions.

During the characterization studies of the films, to determine the elements and structural composition of the films, energy dispersive X-Ray and scanning electron microscopy analyze were applied to NaCMC and HPC based edible films. Also, X-Ray diffraction, Fourier transform infrared spectroscopy and differential scanning calorimetry analysis were applied to determine the form of elements, functional groups and glass transition temperature.

Water vapour sorption capacities of NaCMC and HPC based films were measured nearly 70%w and 25%w respectively. GAB and Halsey models were found to give the best fit for the water vapour sorption data of both NaCMC and HPC films.

Diffusion coefficient of water vapour in vacuum microbalance test was higher than that determined using the humidity chamber, this case could be result of the structural changes of films such as formation of porous structure in microbalance tests due to the fast drying of films by high vacuum. NaCMC based edible films showed higher diffusion coefficient values than HPC based films, due to the heterogeneous structure and bigger pore dimensions of the NaCMC films that was observed in the scanning electron micrographs.

Water vapour permeability (WVP) of both films increased with increasing thickness and increasing film forming solution concentration and WVP values of NaCMC based films were higher than the WVP values of HPC films.

In mechanical properties, while NaCMC films have brittle, stronger and stiffer structure, HPC films show elastic and ductile property.

ÖZET

Bu çalışmada poliskakkarit bazlı yenebilir filmlerin oluşturulması ve karakterizasyonu ile filmerin su buharı adsorpsiyon izotremleri, su buharı geçirgenlikleri ve mekaniksel özellikleri gibi bazı ambalaj özellikerinin incelenmesi amaçlanmıştır. Yenebilir filmlerin oluşturulmasında, karboksimetil selülozun sodyum tuzu (NaCMC) ve hidoksipropil selüloz (HPC) gibi selüloz eterleri film yapım malzemesi olarak, distile su ve gliserin sırasıyla çözücü ve plastikleştirici olarak kullanılmışlardır.

Film çözeltilerinin, akış davranışlarının film oluşturma özelliklerine etkisini ölçebilmek amacıyla, çözeltilerin viskoziteleri incelenmiştir. Yapılan viskozite ölçümleri sonucunda iki farklı polimer çözeltisinin tüm derişimlerinde aynı akış özelliğine rastlanmıştır. Film çözeltilerinin viskozitelerinde, kayma hızı arttıkça azalma gözlenmesi nedeniyle çözeltilerin Newtonion olmayan akış gösterdiği sonucuna varılmıştır. Elde edilen verilerin, Power Law viskozite modeline uygunluğu gözlenmiştir. Bu model polimer moleküllerinin akış yönünde yönlenmesi nedeniyle viskozite değerinin kayma hızı arttıkça azaldığını açıklamaktadır. Filmlerin karakterizasyonu için enerji dağılımı X ışınları (EDX), taramalı elektron mikroskopu (SEM), Fourier transform kızılötesi spektroskopisi (FTIR), X ışınları kırınımı (X-ray) ve taramalı diferansiyel kalorimetri (DSC) gibi analizler yapılmıştır. EDX ölçümleri sonucunda NaCMC filmerinin %8, %39 ve % 53 oranlarında sodyum, oksijen ve karbon, HPC filmlerinin ise %70 aranında karbon ve %30 oranında oksijen içerdiği gözlenmiştir. Taramalı elektron mikroskopu ile yapılan incelemelerde, NaCMC bazlı filmlerin yaklaşık 3 mikrometre çapında gözenekler içerdiği, HPC filmlerinin ise daha küçük boyutlarda, yaklaşık 0.5-1 mikrometre çapında, homojen olarak dağılmış gözenekler içerdiği görülmüştür. X ışını kırınımı ile toz haldeki ve film haldeki polimerlerin kristal yapıları incelenmiş ve HPC polimerinin amorf yapısında herhangi bir farklılık gözlenmezken, NaCMC polimeri toz halde amorf yapıda olmasına rağmen film halde kristal yapıda olduğu gözlenmiştir. Taramalı diferansiyel kalorimetri ölçümleri sonucunda filmlerin camsı geçiş sıcaklıklarının oda sıcaklığının altında olduğu saptanmıştır. Filmler bu nedenle oda sıcaklığında visko-elastik özellik göştermişlerdir. Filmlerin su buharı soğurma özellikleri nem kabini cihazı ile incelenmiş ve sonuçların geçerliliğini kanıtlamak amacıyla mikrobalans cihazından da

yararlanılmıştır. Ölçümler sonucunda, nem kabini ile bulunan su buharı soğurma izotermlerinin, mikrobalans ile tespit edilen izotermlere göre daha yüksek çıktığı gözlenmiştir. Bu farklılığın filmlerin kurutulması sırasında farklı kurutma sıcaklıklarının uygulanmasından kaynaklandığı düşünülmektedir. Genel olarak soğurma izotermlerine bakıldığında, NaCMC filmlerinin % 70 oranında, HPC filmlerinin ise % 25 oranında su sorpsiyon kapasitesine sahip olduğu ve filmlerin su buharı sorpsiyon kapasitelerinin, film çözeltilerinin polimer derişimlerine çok bağlı olmadığı gözlenmiştir. İki farklı polimer yapısındaki yenebilir filmlerin sorpsiyon kapasitesi, ortamın bağıl nemi arttıkça artmıştır. Bu artış 0.7 su aktivitesine kadar lineer daha sonra hızlı bir yükeliş göstermiştir. Bu çeşit bir adsorpsiyon izotermi Tip II izotermini tanımlamakta ve hidrofilik polimerin tipik su buharı adsorpsiyon davranışını sergilemektedir. Kütle artış hızı grafiklerinde, film örneklerinin, Fickian tipi difuzyon davranışı gösterdiği gözlenmiştir. NaCMC filmerinin adsorpsiyon ve desorpsiyon izotermlerinin üst üste çakışması da difuzyonun Fickian tipi olduğunu kanıtlamakta ve bu tip bir sorpsiyon izotermi su buhari difuzyon hızının, polimer zincirinin gevşeme hızından daha yavaş olmasına bağlı olarak oluşmaktadır. Bu durumun su buharı sorpsiyon analizlerinin, camsı geçiş sıcaklığının üzerinde yapılması nedeniyle filmlerin kauçuk yapı kazanmalarından oluşabileceği düşünülmektedir. HPC filmleri Fickian tipi difuzyon davranışı göstermesine rağmen adsorpsiyon ve desorpsiyon izotermleri üst üste çakışmadığı ve filmler tarafından içe çekilen suyun, filmin dışarıya bıraktığı sudan az olduğu gözlenmiştir. Bu durumun nedeni, ölçümler sırasında nem ile şişen filmden, şişmeyen filme göre su buharının daha hızlı taşınması ile açıklanabilir. Su buharı soğurma verilerine çeşitli model denklemleri uygulanmış ve NaCMC için GAB, HPC filmleri içinde Halsey modellerinin en uygun modeller olduğu gözlenmiştir.

Su buharının film içinde difuzyon katsayısı hesaplanmış ve NaCMC filmlerinde, HPC filmlerine göre su buharı difuzyon katsayısının daha yüksek olduğu gözlenmiştir.

Yapılan su buharı geçirgenlik ölçümlerinde NaCMC filmlerinin su buharını HPC filmlere göre daha fazla geçirdiği ve geçirgenlik miktarının her iki film örneği için film kalınlığına ve film çözeltisinin derişimine bağlı olarak arttığı gözlenmiştir.

Filmlerin mekanik dayanıklılığını ve esnekliğini ölçmek amacıyla çekme testleri yapılmış ve NaCMC bazlı filmlerin daha kuvvetli, sert, kırılgan bir yapıya, HPC filmlerinin ise güçsüz ama esnek bir yapıya sahip olduğu gözlenmiştir.

Yapılan çalışmalar ve analizler sonucunda NaCMC bazlı filmlerin yüksek su buharı geçirgenliği ve soğurma özelliklerine sahip olmasının yanı sıra esnek olmayan ama güçlü bir yapıya sahip olduğu, HPC filmlerinin ise su buharını geçirme ve soğurma özelliklerinin NaCMC filmlerine göre daha düşük olduğu, ve daha esnek ancak plastik deformasyona uğrayabilen bir yapıda olduğu bulunmuştur.

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CHAPTER 1

INTRODUCTION

The increased consumer demand for high quality, long shelf-life ready to eat foods has initiated the development of mildly preserved products that keep their natural and fresh appearance as long as possible. For this purpose; over the past 30 years, considerable research effort has been devoted to the uses of edible films and coatings. An edible coating or film has been defined as a thin, continuous layer of edible materials, which may be eaten together with the food, formed or placed, on or between foods or food components. Their function is to provide a barrier to mass transfer (water, gas and lipids), to serve as a carrier of food ingredients and additives (pigments, flavours and so on), or to provide mechanical and microbial protection

The structural and barrier properties of edible films are affected by some parameters such as viscosity of film forming solution, film formation procedure, film thickness, water vapour sorption characteristics, etc. Viscosity of the film forming materials plays the main role in controlling the film properties. Peressini et al. (2003), demonstrated the importance of flow behaviour of MC-starch based film forming dispersions which strongly affect the smoothness of the surface and affect the coating appearance. Coating quality in the solid state is affected by the flow properties of a liquid film. The water vapor permeability (WVP) is the most extensively studied property of edible films (McHugh et al. 1993, Park et al. 1993, Aydınlı and Tutaş 2000, Anker et al. 2001) mainly because of the importance of the role of water in deteriorative reactions. Factors affecting WVP of edible films are composition of film, temperature and relative humidity. The work of Kamper and Fennema (1984) is one of the few that regarded the temperature effect on WVP of edible films. They also studied the relative humidity effect on WVP of an edible film. Park et al. (1993) reported the effect of molecular weight of methylcellulose (MC) and hydroxypropyl cellulose (HPC) on oxygen permeability and WVP as well as tensile strength and elongation of edible films. Water vapor adsorption data give the hydration properties of polymer. Mechanical, water vapor, gas or solute barrier properties of many edible films could be strongly affected by environmental conditions such as relative humidity and temperature. Because of this case, sorption isotherms (adsorption and desorption) of these films have been extensively studied. (Turhan and Sahbaz, 2003, Park et al. 1993, Buonocore et al. 2003, Coupland et al. 2000) Ayrancı (1996) investigated the moisture sorption behaviour of MC films in order to evaluate some functional properties of films such as barrier property and stability of the films

The objective of this work is to produce and make the characterization of cellulose-based edible films that are water vapor permeable. For this purpose sodium carboxymethylcellulose (NaCMC) and hydroxypropylcellulose (HPC) were used as the cellulose-based film forming materials. To study some characteristics of NaCMC and HPC based edible films, film forming solutions were prepared in different concentrations (3, 4, 5g polymer in 100ml water). These different concentration values were used as comparison factor during the studies. The applied characterization studies include; Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), energy dispersive X-ray (EDX), differential scanning calorimetry (DSC) and X-ray diffraction (XRD) analysis. After characterization studies, film samples were examined for the water vapour sorption and permeability characteristics and also for mechanical properties. These properties affect the protection ability of the films on to the any food or food products.

CHAPTER 2

BIODEGRADABLE PACKAGING AND EDIBLE FILMS

2.1. Biodegradable Packaging

Biodegradable packaging means the packaging materials are made of biodegradable polymers based on renewable (natural) sources. These polymers are called as biobased polymers or biopolymers (See Figure2.1.).

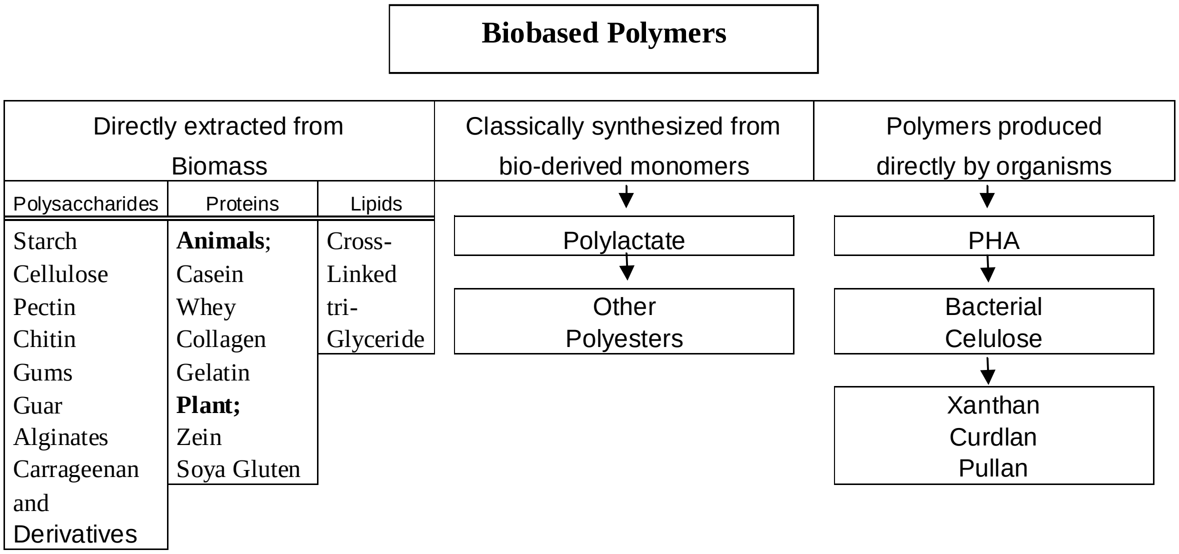


Figure 2.1. Schematic presentation of biobased polymers based on their origin and method production (Source: Weber 2000).

Biobased polymers allow full recycling and completely biodegradable with a considerably short period of time. They can be used to make biodegradable packaging materials to replace short-shelf life plastics. Biobased polymers can also be used for food packaging applications called as food biopackaging (Arvanitoyannis and Biliaderis 1999, Guilbert et al. 1996).

2.1.1. Food Biopackaging

A biodegradable packaging material is suitable for the packaging of biologically active foods; degradation of the packaging material does not occur, within the shelf life of the food.

The main purposes of food packaging are to protect the food or food product from the surroundings and to maintain the sensory quality and safety of the food throughout the products shelf life. The packaging requirements of foods are complex because foods are often dynamic systems with limited shelf-life and very specific packaging needs. When selecting biobased packaging materials, it is very important to know the characteristics of the applicable food product. Deteriorative reactions in foods include enzymatic, chemical, physical, and microbial changes. The foods to be coated or packaged differ in many biochemical and physical aspects (moisture content, pH, matrix polarity, etc). Biodegradable packaging materials must meet all the criterias that apply to conventional packaging materials associated with foods. These relate to barrier properties (water, gases, light, aroma), optical properties, mechanical and microbial protection properties, strength, welding and moulding properties, migration and scalping requirements, chemical and temperature resistance properties, and so on. Also interactions between the food and biopackaging material must not compromise food quality or safety. (Narayan 2003, Weber 2000). The biodegradable packaging material must remain stable for maintaining mechanical and / or barrier properties and should function efficiently during storage and handling of the food. These packaging properties depend on the type of used packaging materials, its formation and its application procedures (Guilbert et al. 1996).

There are a variety of foods or food products that have different needs and properties. But many of the conventional packaging materials can not provide optimal conditions for product storage. To design of packagings for specific food products a number of approaches have been used. Such product specific packagings are edible films and coatings, active packagings, modified atmosphere packaging and combination of packaging materials. In this study coatings and films are subjected in the field of biobased packagings.

2.1.2. Edible Film and Coating Manufacture

Edible films and coatings have a unique category of packaging materials differing from biobased packagings and conventional packagings by being edible. Edible films and coatings are produced from biological materials such as polysaccarides, proteins, lipids, and derivatives. Films and coatings act as barrier (to the moisture, vapour, light, oil), protect the food and improve the shelf-life of the food. Films and coatings differ in their mode of formation and application to foods.

Coatings are applied and formed directly on the food products, the thin film is formed directly on the product. Coatings may be applied by dipping, spraying, foam application and brushing. In dip method coating, food is directly dipped into the composite coating formulations (in aqueous medium), then removed and allowed to air dry. Continuous dipping builds up decay organisms, soil and trash in the dipping solution, which needs to be removed for better performance characteristics. Another coating method is foam application method that is used for coating emulsions. 'Coating by spraying' is the conventional method generally used in most of the cases. (Tharanathan 2003, Weber 2000)

Whereas, films are freestanding (preformed) structures, first film structure is formed and later applied to foods. Biodegradable packaging films are generally prepared by wet casting of the aqueous solution on a suitable base material and later drying on a drum drier or using traditional plastic processing techniques, such as extrusion. Optimum moisture content (~5-8 %) is desirable in the dried film for its peel off from one edge of the base material (Tharanathan 2003, Weber 2000).

In any polymeric packaging film or coating, two sets of forces are involved: between the film-forming polymer molecules for all polymeric films or coatings (cohesion), and between the film and the substrate for coatings only (adhesion). The degree of cohesion affects film properties such as resistance, flexibility, permeability, etc. Strong cohesion reduces flexibility, gas and solute barrier properties and increases porosity. Cohesion depends on the biopolymer structure and chemistry, the fabrication 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 (Guilbert et al. 1996).

2.2. Edible Films

Edible polymer film is a thin, continuous layer of edible material formed on or between foods or food components. Edible films are defined by two principles. First, edible implies that it must be safe to eat or that it is generally recognized as safe (GRAS) by the Food and Drug Administration (FDA). Second, it must be composed of a film-forming material, typically a polymer. You can dip, and you can coat, but the term edible film refers to a continuous barrier that is formed as the film adheres to the surface of the foodstuff.

Edible films can be used to reduce the mass transfer (water, gas or lipids) between component of multicomponent food products by acting as a barrier, to serve as a carrier of food additives and ingredients or to provide mechanical and microbial protection. Edible films can also be used to protect the properties of foods during their storage and handling, to improve the appearance of food or to increase the shelf life of the foods. Films can help to maintain desirable food quality characteristics such as colour, flavour, spiciness, acidity, sweetness and saltiness (Aydınlı and Tutaş 2000, Peressini et al. 2003, Turhan and Şahbaz 2003).

Polysaccharides, proteins, lipids and their derivatives are the main constituents of the edible films. The composition of edible films is chosen as a function of the desired properties of the films (Debeaufort et al. 2000). Each film forming material produced a film with different barrier and mechanical properties. According to the packaging needs of the food or food products, films can be produced by combination of film forming materials or adding some additives such as plasticizers and emulsifiers.

2.2.1. Types of Edible Films

2.2.1.1 Polysaccharide Based Edible Films

Edible coatings and films can be made from a variety of polysaccharides. Polysaccharide and their derivatives (cellulose and derivatives, starch and derivatives, gums etc) have excellent film forming ability. Such coatings have been used to retard moisture loss of some foods during short term storage. However, polysaccharides, being hydrophilic in nature, do not function well as physical moisture barriers. The method which they retard moisture loss is by acting as a sacrificial moisture barrier to the atmosphere, so that the moisture content of the coated food can be maintained (Cheng et al. 2002). In addition to preventing moisture loss, some types of polysaccharide films are less permeable to oxygen. Decreased oxygen permeability can help preserve certain foods. Polysaccharide coatings can be made from a variety of sources Cellulose and starch receive the most attention (Cheng et al. 2002).

Cellulose is the structural component of the plant and the most abundant source of complex carbohydrate. Cellulose is a linear polymer of anhydroglucose (See figure 2.2.).

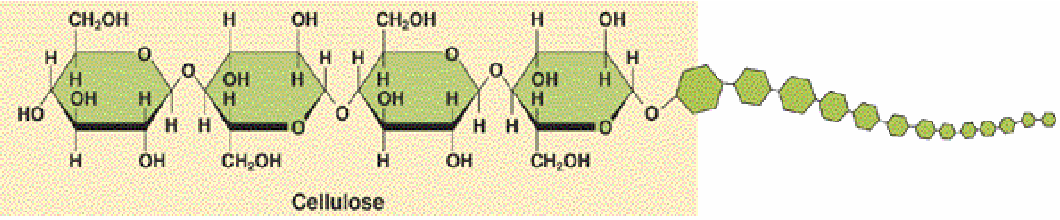


Figure 2.2. Structural formula of cellulose (Source: WEB_6 (2004)).

Although is a cheap raw material, because of the insoluble, crystalline and hydrophilic nature of cellulose it is difficult to use. This problem can be solved by derivatization of cellulose with etherification and esterification reactions. The water insoluble cellulose is brought into aqueous solution to produce edible films with appropriate chemical modification (such as etherification reaction) (Arvanitoyannis and Biliaderis 1999). The most widely used cellulose ethers are non ionic methyl cellulose (MC), hydroxypropylmethyl cellulose (HPMC), hydroxypropyl cellulose (HPC) and ionic sodium carboxymethyl cellulose (NaCMC). Carboxymethyl cellulose is used for the production of edible films and coatings. 'TAL-Prolong' and 'Semperfresh' are two commercially available composite coating formulations based on CMC. They contain sucrose fatty acid esters, sodium salt of CMC and emulsifier WEB_1 (2004). They are used for the shelf-life extension of a variety of fresh fruits and vegetables. 'Nature-Seal' is another cellulose based coating formulation used for delayed ripening of some vegetables and fruits (for example; tomatoe, mangoe, apple, potatoe, pear, avocado, carrot, onion, etc.). It is edible and it protects color, flavor, texture and firmness of foods. (Tharanathan 2003, WEB_4 (2004)). Cellulose derivative based edible films are transparent and flexible and have poor water vapor but relatively good oxygen, aroma and carbondioxide barrier properties (Turhan and Şahbaz 2003, Cheng et al. 2002).

Starch is another raw material widely abundant polysaccharide, especially obtained in granular form from potatoes, cereal grain, rice and corn and is one of the most abundant renewable polymers found in nature. Starch is a mixture of amylose, and amylopectin (Peressini et al., 1999). (See Figure 2.3.)

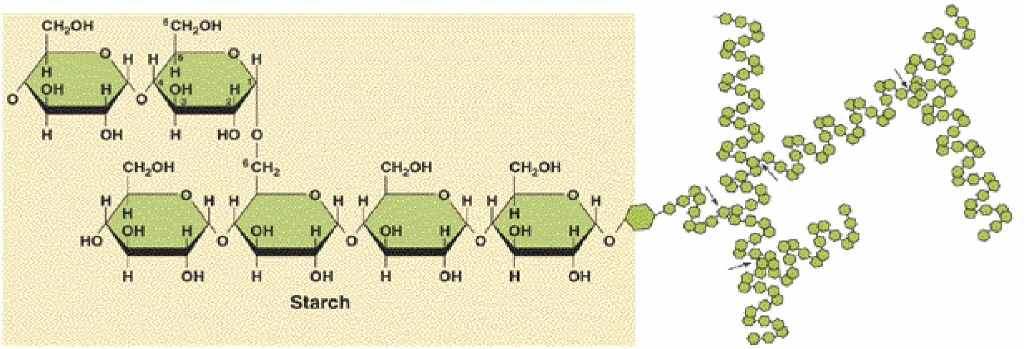


Figure 2.3. The structural formula of starch (Source: WEB_6 (2004))

The linear starch polymer amylose produces films that have low oxygen permeability, flexible and hydrophilic character. Branched structure of amylopectin produces a film with poor mechanical property (Tharanathan 2003, Miller and Krochta 1997). As general films based on starch have suitable mechanical property, moderate gas barrier and poor moisture barrier properties. By applying plasticization, chemical crosslinking and esterification reactions to the starch, the final structure and properties of the starch based film is all affected to varying degrees. For example; starch hydrolysates that have good aroma barrier properties used dried apricots and coating apple slices to protect their flavour (Miller and Krochta 1997). Hydroxypropyl starch composites are used for candies, raisins, nuts and dates to protect these foods from oxidative rancidity. Starch is more applicable polysaccharides for food packaging, because of it is low cost and easier to process than cellulose (Petersen et al. 1999).

2.2.1.2. Protein Based Edible Films

Proteins are essentially polymers of amino acids. The amino acid has the basic structure:

$$H_2N\text{-}CHR\text{-}COOH$$

The H_2N- part of the molecule is, of course, the amino group. The -COOH part of the molecule is the carboxylic acid group. The center carbon has a hydrogen substituent, and also a R group. By the formation of peptide bond between amino and carboxylic acid group of amino acid, polypeptide is obtained (See Figure 2.4.). Polypeptide or longer chains of amino acids is called protein.

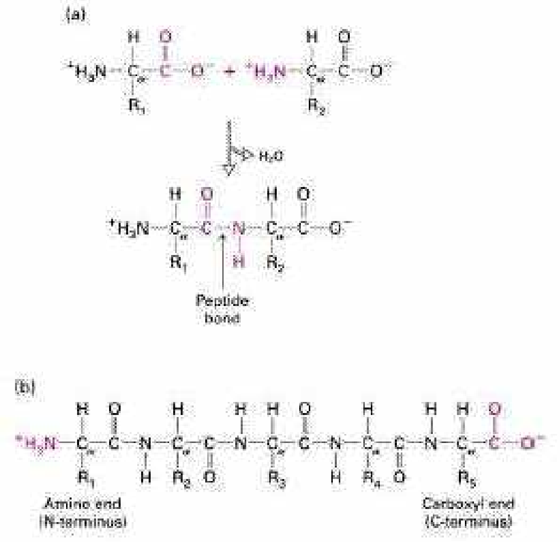


Figure 2.4. The main structural formula of protein (Source: WEB_6 (2004))

Proteins from plants (soy, zein, corn protein) and animal (whey, collagen, gelatin protein) origins are used in some edible film formulations. Generally, protein based edible films are good barriers to oxygen, carbon dioxide and aroma compounds but not to water (Tharanathan 2003, Jangchud and Chinnan 1999). They are highly affected from humidity and temperature (Koyuncu and Savran 2002). The increased molecular interaction that depends on the sequence of hydrophobic and hydrophilic amino acid residues and the protein structure cause the formation of strong but less flexible and less permeable films. The influence of moisture on the mass transport properties of protein films is controlled by the degree of hydrophilicity of the amino acid residues in protein (Miller and Krochta 1997). Protein based films can not be applied to fruits and vegetables because of their poor moisture barrier property. Zein–based films produce glossy and grease resistant films that have great potential focused in edible films and coatings. Zein proteins have also been used effectively as coatings for confectionery products (Park et al. 1993). Appropriately processed whey proteins produce flexible but brittle films (Kaya S. and Kaya A. 2000). Casein proteins, derived from milk, have been used in emulsion based coatings to reduce water loss in zucchini (Avena-Bustillos et al. 1994).

2.2.1.3. Lipid Based Edible Films

Lipid based edible films and coatings can be made from a wide array of lipid substances including acetylated monoglycerides, oils, natural waxes, fatty acids and surfactants (Weber 2000).

Waxes are naturally found on fruits and vegetables as a coating to prevent moisture loss especially in the dry humid season. Wax coatings (bees wax, paraffin wax, candellia wax) have been applied since time immemorial for preservation of fresh and dry fruits and nuts (Tharanathan 2003). Lipid based edible films are used especially for their hydrophobic characters that provide good water vapour barrier property. Waxes are the most effective ones but show poor sensory characteristics. Lipid based edible films are widely applied to fresh fruits and vegetables to provide glossy surface and to increase the shelf life of the product by decreasing the respiration rate and water vapour transfer (Koyuncu and Savran 2002). Mineral oil is commonly used for coating fruits and vegetables, and as a food release agent.

2.2.2. Application of Edible Films on Foods

Many foods we consume every day take advantage of edible coatings. It remains, however for food scientists to apply edible films and coatings in order to settings to fully utilize some of the properties of these "unique packaging materials". Edible films and coatings play an important role in the quality, safety, transportation, storage and display of a wide range of fresh and processed food. They can coat food surfaces, separate different components, or act as casing, pouches or wraps.

Moisture loss due to transpiration during storage is inevitable, edible films and coatings can provide extending post-harvest life of fruits and vegetables. They can retard ripening and water loss and reduce decay but may also alter flavour (McGuire and Hallman 1995, Baldwin et al.1995). Some examples for this case are;

Edible wheat gluten coatings can applied to strawberries in order to reduce weight and firmness losses during storage WEB_1 (2004). A cellulosic film-former, such as carboxymethyl cellulose or hydroxypropyl methylcellulose can be used as a moisture barrier for cut vegetables that tend to turn white as they dry out WEB_3 (2004). Water dispersible forms of corn protein (zein) can be applied as a film or coating to provide a moisture or gas barrier for nut meats or fruits. In nut meats, zein coating act as oxygen barriers and increase shelf life 50% by preventing rancidity according to Paul Freeman of Freeman Industries, Tuckahoe, NY, which markets corn zein formulations (Kruchta and Johnston 1997). Methyl cellulose, hydroxypropyl cellulose, gellan gum and calcium reactive pectin all have been used as film coatings in fried foods to maintain moisture and limit fat uptake in food to produce lower fat finished product and reduce moisture migration into the oil and conceivably extend the frying oil's shelf life WEB_5 (2004). Methyl cellulose and hydroxypropyl cellulose manufactured by the Dow Chemical Co., Midland MI, have been used to decrease oil absorption during frying of French fries and onion rings. Hydroxypropyl cellulose films are marketed by Watson Foods, West Haven, CT. are used to form pouches that allow processors to add premeasured amount of additives such as colorants and vitamin premixes directly without further handling (Kruchta and Johnston 1997).

Combining the advantages of polysaccharides, proteins and/or lipids offer multicomponent edible films and coatings that have good mass transfer barrier properties. The barrier properties of these systems strongly depend upon their structure and chemistry, the interaction between different film components as well as surrounding environment conditions. Multicomponent edible films and coatings could be beneficial to the food industry by leading to innovative applications. (Weller et al. 2002). In the study of Xu et al. (2001) the edible film composed of soybean protein isolate, stearic acid and pullulan had been applied to preserve the kiwifruit, so the shelf life of kiwifruit coated with edible film being extended to about 3 times. Laminate of chitosan (14.5% by weight), cellulose (48.3%) and polycaprolactone (glycerol (36.2%) and protein (1.0%)) have been used as a moisture, oxygen and carbondioxide barrier and for mechanical protection of fresh products (shredded lettuce and cabbage, head lettuce, cut broccoli, whole broccoli, tomatoes, sweet corn and blueberries) (Mokino and Hirata 1997). The some other examples have been shown in the following table (Table 2.1.)

Table 2.1. Food application of an edible films and coatings.

Product example	**Critical functions of packaging**	**Examples of materials**	**References**
Fish	Oxygen and moisture barrier	Whey protein and acetylated Monoglycerides	Stuchtell and Khrochta (1995)
Pizza base/sauce	Moisture barrier	Alginate, whey protein	Kemper and Fennema (1985)
Mushrooms	Oxygen and moisture barrier	Alginate	Nussinovitch andKampf (1993)
Avocados	Oxygen and carbondioxide barrier	Nature SealTM (polysaccharide based film)	Bender et al. (1993)
Carrots	Moisture and gas barriers	Nature SealTM 1000 (cellulose based)	Howard and Dewi (1995)
Pears	Moisture, oxygen and carbondioxide barriers	Corn zein Semperfresh^{TM}	Park and Jo (1996)

CHAPTER 3

CELLULOSE BASED EDIBLE FILMS

3.1. Cellulose Derivatives

Cellulose is fibrous, crystalline and insoluble natural polymer (see Figure 3.1.). Cellulose derivatives have excellent film making properties (Park et al. 1993). Derivatization of cellulose from the solvated state can be made by esterification or etherification of individual hydroxyl group on the polysaccharide backbone (Petersen et al. 1999).

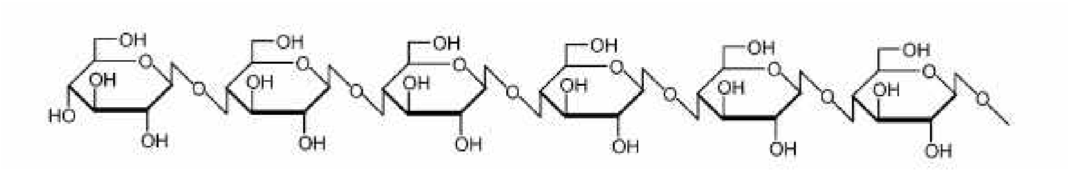


Figure 3.1. Chemical structure of cellulose (Source: Tharanathan, 2003).

The etherification of water insoluble cellulose by using propylene oxide, sodium monochloroacetate or methyl chloride cause the formation of aqueous solution that used to produce a nonionic methylcellulose (MC), hydroxypropyl cellulose (HPC), hydroxypropyl methylcellulose (HPMC) and ionic sodium carboxymethylcellulose (NaCMC) based edible films. Cellulose ether films are flexible, transparent, resistant to oils and fats, have good aroma and barrier properties and moderate strength, and also all are edible (Weber 2000). Although long recognized to possess good film forming characteristics, CMC and HPC have not received as much attention as other cellulose derivatives such as MC and HPMC (Cheng et al. 2002).

3.1.1. Hydroxypropyl Cellulose (HPC)

Hydroxypropyl cellulose is nonionic water soluble cellulose ether. HPC is the only edible and biodegradable cellulose derived polymer that has thermoplastic and extrusion property. The structural formula of HPC is shown in Figure 3.2.

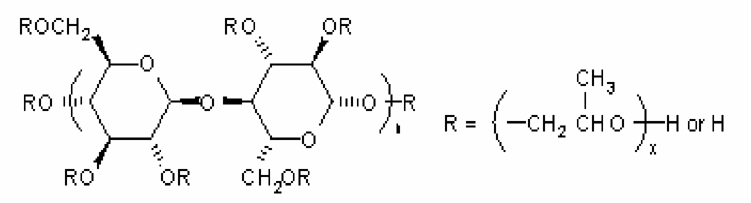


Figure 3.2. Chemical structure of HPC (Source: WEB_7 (2004))

HPC can be used as an emulsifier, thickener, stabilizer, binder, suspension agent and for edible coating formation WEB_7 (2004). HPC based edible films have good oxygen barrier properties, so these films can be used for prevention of lipid oxidation for snacks and roasted peanuts (Weber 2000). HPC has been used as film coatings in fried foods to maintain moisture and limit fat uptake.

3.1.2. Ionic Sodium Carboxymethylcellulose (NaCMC)

Sodium carboxymethyl cellulose (NaCMC), the most important cellulose ether is formed by the reaction of cellulose with sodium hydroxide and chloroacetic acid (Kötz et al 2001). Sodium salt of carboxymethylcellulose has a number of sodium carboxymethyl groups (CH_2COONa) that introduced into the cellulose molecule (See Figure 3.3.). NaCMC is an ionic water soluble white powder.

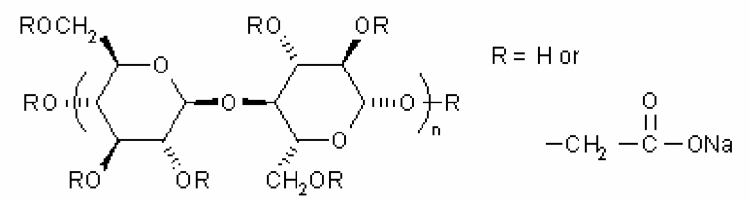


Figure 3.3. Chemical structure of NaCMC (Source: WEB_7 (2004))

NaCMC is easily available and very cheap material. It has high shear stability and has a property of viscosity building and flocculation. NaCMC can be used with a wide range of application primarily in foods, drugs and cosmetics as a viscosifier, emulsion stabilizer, thickener and to improve the texture and for all well drilling operation. As an edible film and coating NaCMC can be used as moisture barrier for carrots to provide retention of flavour, oxygen and carbondioxide barrier, for avocados to delay and onset ripening with the name of NatureSeal^{TM} (Bender et al. 1993). By combining with the sucrose ester of fatty acid or mono and diglycerides that called Tal Pro-long^{TM} and Semperfresh^{TM} can be used as moisture and oxygen barrier for some fresh fruits and vegetables (Weber 2000).

3.1.3. Methylcellulose (MC)

Methylcellulose is cellulose ether that has excellent film forming properties. Methylcellulose is formed by the alkali treatment of cellulose, followed by the reaction with methyl chloride (Peressini et al. 2003). The resulting product is white, odorless, water soluble and tasteless powder. The structure of MC is shown in Figure 3.4.

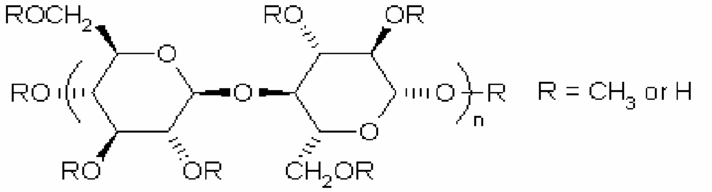


Figure 3.4. Chemical structure of MC (Source: WEB_7 (2004))

Methylcellulose exhibits thermal gelation and forms excellent films that can be used in pharmaceautical and food industries. It is used as thickener for aqueous and non-aqueous systems, binders and lubricants, and to make clear films with grease resistance or edible film and coating for food products. As an edible film MC can be used as fat and moisture barrier for breading and deep fat frying starch products (Mallikarjunan et al. 1997). Park et al. reported that MC based films that laminated with corn zein and stearic acid can be used as a barrier to oxygen, light and moisture for potatoe chips. Methylcellulose has also been used to coat fruit and prevent moisture loss.

3.1.4. Hydroxypropyl Methylcellulose (HPMC)

Hydroxypropyl methylcellulose is cellulose ether, derived from alkali treated cellulose that is reacted with metyl chloride and propylene oxide. Figure 3.5. shows the structure of HPMC. It has white to off white colour, fibrous powder and granule structure, can swell in water to produce a viscous colloidal solution, and it is non ionic, dissolves slowly in cold water, insoluble in hot water and soluble in most polar solvents, insoluble in anhydrous alcohol, ether, and chloroform WEB_7 (2004).

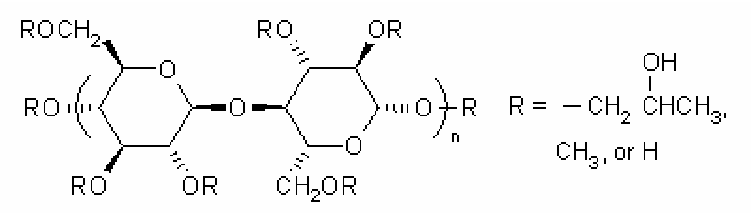


Figure 3.5. Chemical structure of HPMC (Source: WEB_7 (2004))

HPMC can be used in foods as an emulsifier, thickening agent, stabilizer, gellant, film former, protective colloid, fat barrier and suspending agent in food products like ice cream, breading, bakery goods, etc. MC and HPMC have properties known as reversible thermal gelation that is the basis for many applications; they form gels when heated but return to solubility when cooled. By acting as a fat barrier, MC and HPMC based edible films are used to reduce absorption of fat in products being fried WEB_7 (2004).

3.2. Properties of Cellulose Based Edible Films

3.2.1. Viscosity

Rheology is the science of flow and deformation of materials WEB_2 (2004). Design of film processing operations requires accurate data on the rheological properties of film forming solutions or dispersions (Peressini et al. 2003). Viscosity plays the main role in controlling the film quality and properties. The rheological properties of a material are determined with the parameters temperature, pressure, strain or shear rate by using the fundamental rheological instruments such as rheometers. Measurement data can be fitted to different flow models such as Power Law, Bingham, Herschel Bulkley and Casson to simplify the presentation of rheological measurement data over a wide shear rate. The measurement results can be used to evaluate the characterization of material (like film forming solution) because the flow behaviour allows to study the different material properties such as storage stability, consistency, melting temperature, hardening temperature, shear stability, molecular weight, quality during production and chemical, mechanical and thermal treatments. They are also a way to predict and control a host of product properties, end use performance and material behaviour. Viscosity measurements are made in conjunction with product quality and efficiency. Similarly, the rheological properties of polymeric film forming solutions directly affect the final product edible films and coatings. The presence or absence of defects influence the appearance and decrease the protective properties of the coatings. These defects depend partly on the rheological properties of film forming solutions. The rheology of the film forming solution, the methods and mechanics of application and the changes in properties associated with the transition from the liquid to the solid state, influence the coating surface. The pseudoplastic, viscoelastic and thixotropic properties of film forming solution are important factors during the film formation (Peressini et al. 2003).

Viscosity of polymer solution properties depend on the both nature of the materials mixed and the amount present in the mixture. A particularly important example is the viscosity of a solution of a polymeric material in a small-molecule solvent. The viscosity of a dilute solution of spherical particles is shown in Equation 3.1 which is an important equation for the polymer viscosity.

$$\frac{\eta}{\eta_0} = 1 + 2.5\phi \qquad (3.1)$$

η is the viscosity of a solution of volume fraction, Ø, of the spheres, η_0 is the viscosity of the pure small- molecule solvent. For particles of other shapes, a similar relationship occurs, but the numerical coefficient of the volume fraction is different.

To evaluate the viscometric property of cellulose based edible films some studies related to the viscosity of aqueous polymer solutions were given below.

In the study of Peressini et al. (2003), flow behaviour of MC-starch based film forming dispersions had been studied to obtain information relevant to the food coating. The steady-state flow curves of the film forming dispersions had showed shear thinning behaviour under steady state shear flow (See Figure 3.6.).

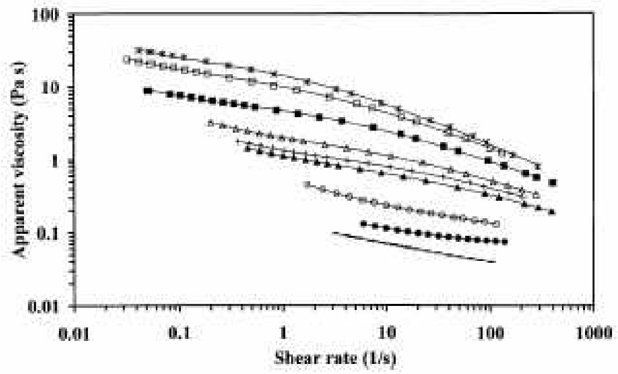


Figure 3.6. Apparent viscosity as a function of shear rate for film-forming dispersions examined. Lines: calculated curves. Symbols: experimental data (1(); 2( ); 3( ); 4( ); 5(); 6(*); 7( ); 8( ); 9(+)) (Source: Peressini et al. 2003).

On the viscosity-shear rate plot, three different profiles can be seen at low, intermediate and high MC contents (numbers from 1 to 9 represent the different MC/glycerol values (g/100g) from 31.09% to 62.18%). The flow property models can be used to identify the appropriate coating system design and to optimize operating conditions. In this study, Herschel-Bulkley model (Eq. 3.2) had been applied when MC content was lower than 31%;

$$\tau = \tau_0 + K\gamma^n \qquad (3.2)$$

Where τ (Pa) is the shear stress, $\dot{\gamma}$ (s^{-1}) is the shear rate, τ_0 is the apparent yield stress, K (Pas^{-n}) and n (dimensionless) are the consistency and flow indexes, respectively.

MC content at 31%, 53% and 62%, modified version of Cross model (Eq. 3.3) had been applied to fit the data.

$$\tau = \tau_0 + \eta \ \gamma + [\eta_0\gamma / (1+ (\lambda\gamma)^{1-n})] \qquad (3.3)$$

where η_0 and η (Pas) are the zero-shear viscosity (when $\tau_0 = 0$) and the infinite-shear viscosity, respectively, λ (s) is a characteristic time and n (dimensionless) is the flow index.

Viscosity (η_0) had increased in line with MC content and had been strongly influenced by glycerol (samples 3 and 4). MC had been the prime factor affecting the apparent viscosity. The effect of glycerol on viscosity had been observed in association with MC. According to the experimental conditions, very viscous dispersions can be obtained with high MC and low glycerol content. The smoothness of the surface, which is primarily governed by low shear viscosity strongly affect the coating appearance. Coating quality in the solid state is affected by the flow properties of a liquid film.

In the study of Wanchoo and Sharma (2003), dilute solution viscosity behaviour of CMC and MC had been studied at 20^0C by determining with their intrinsic viscosity. Both the polymer-polymer interactions and polymer-solvent interactions can be determined with dilute solution viscometry method.

The classic Huggins equation when adapted to polymer-solvent system has the following form (Wanchoo and Sharma 2003).

$$\frac{\eta_{sp}}{C_i} = [\eta]_i + b_{ii} C_{ii} \tag{3.4}$$

where the interaction parameter, b_{ii} is related to the Huggins coefficient K_i by $b_{ii} = K_i[\eta]_i^2$, and $[\eta]_i$ is the intrinsic viscosity that are defined in Equation 3.5. Intrinsic viscosity gives an information about the concentration dependence of specific viscosity.

$$[\eta_i] = \lim\left(\frac{(\eta_{sp})_i}{C_i}\right) \tag{3.5}$$

$[\eta_{sp}]_i$, C_i represent the specific viscosity and the polymer concentration respectively. Equation 3.6 shows the specific viscosity,(η_{sp}), specific viscosity is the fractional increase in the viscosity over that of the pure solvent caused by the addition of the polymer.

$$\eta_{sp} = \frac{\eta - \eta_0}{\eta_0} \tag{3.6}$$

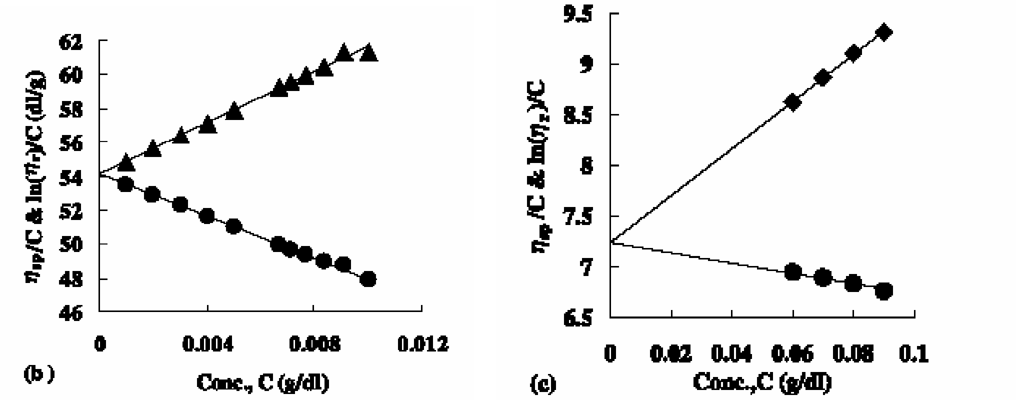


Figure 3.7. Huggins Plot (n_{sp}/C and lnη_r/C vs C) for the (a) CMC/distilled water, (b) MC/distilled water at 20^0C. (Source: Wanchoo and Sharma 2003).

By using the experimental data obtained from Figure 3.7. with Huggins equation, the intrinsic viscosity of CMC and MC had been calculated (See table 3.1.). As seen in table 3.1. the intrinsic viscosity (n) of CMC is greater than the intrinsic viscosity of MC. Intrinsic viscosity describes the interaction of a single average polymer molecule with a sea of solvent.

Table 3.1. Intrinsic viscosity data of polymers (Source: Wanchoo and Sharma 2003).

Polymer	Solvent	Temperature (^{0}C)	[n] (dl/g)
CMC	Distilled water	20	54.1
MC	Distilled water	20	7.25

In the study of Biswal and Singh (2004), the rheological properties of the aqueous CMC solution had been evaluated. The viscosity versus shear rate graph had showed that the aqueous solution of CMC behaved as non-Newtonian fluid (see Figure 3.8.). The intrinsic viscosity of CMC had been found to be 6.7 dl/g.

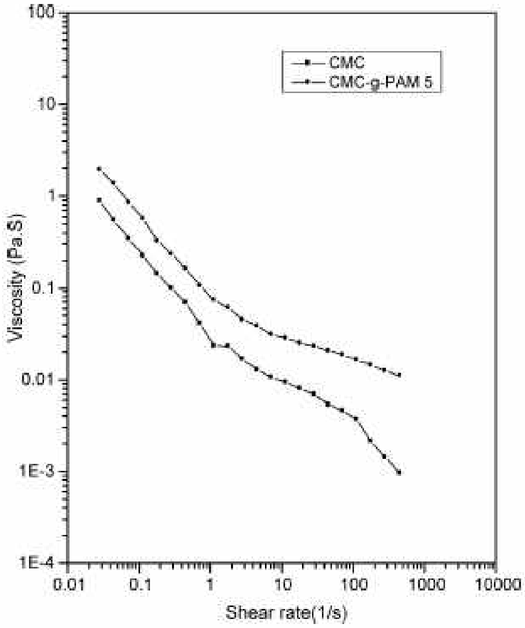


Figure 3.8. Viscosity versus shear rate curves of CMC and CMC-g-PAM 5. (Source: Biswal and Singh 2004)

Ghannam and Esmail (1997) reported the rheological properties of carboxymethyl cellulose (CMC) solutions. They showed that 1- 5% CMC aqueous solution with degree of substitution 0.7, obey power law, k values increased from 0.05 Pas to 28.0 Pas and n values decreased from 0.95 to 0.53 as the % of CMC increased from 1 to 5 %.

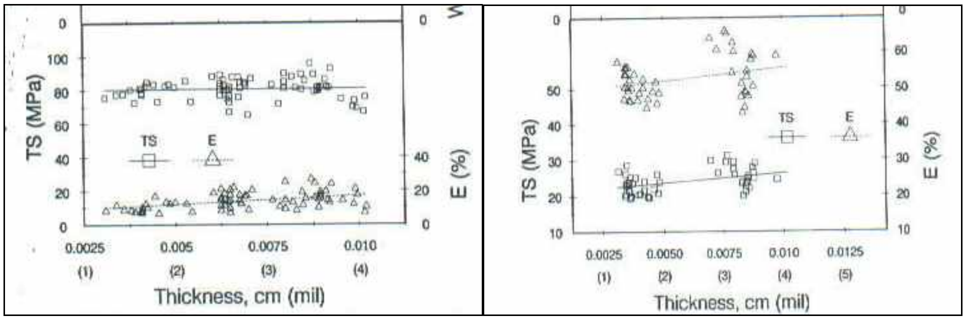
3.2.2. Mechanical Properties of Cellulose Based Edible Films

Adequate mechanical strength provides the integrity of a film and its freedom from minor defects, such as pin hole that ruin the barrier property (Chen 1995). To strengthen the structure of a food filling and to protect the food from environmental effects films must be generally resistant to breakage and abrasion, and films must be flexible in order to adapt to possible deformation of the filling without breaking (Guilbert et al. 1996). The mechanical properties (tensile strength (TS) and elongation (E)) of the films and coatings are important parameters for the formation, application and quality of the films and coatings. Tensile strength expresses the maximum stress developed in a film during a tensile test and offers a measure of integrity and heavy duty use potential for films and percentage elongation at break is a quantitative representation of a film's ability to stretch (Gennadios et al. 1993).

Mechanical properties of cellulose based films can be affected by several factors, such as polymer structure, plasticizer selection and plasticizer concentration, molecular weight of the film forming materials, type of solvents, film thickness and film formulation (Park et al. 1993). The film forming materials and especially their structural cohesion have important effects on the mechanical properties of edible films and coatings. Cohesion is the result of a polymer's ability to form strong and/or numerous molecular bonds between polymeric chains, thus hindering separation (Guilbert et al. 1996). The geometry, molecular weight distribution, molecular strength and the type of position of polymer's lateral groups are important factors for the structure of polymer. All have an important effect on the cohesion ability of the polymer. The film forming conditions e.g. types of process and solvent, rate of cooling and evaporation, coating technique (spraying, spreading, etc.) generally affect the mechanical properties of edible films and coatings.

Some studies were given below to evaluate the mechanical property of cellulose based edible films;

In the study of Park et al. (1993), the effect of film thickness and type of plasticizer on the mechanical properties (tensile strength and elongation) of MC and HPC based edible films had been studied. Figure 3.9. (a) and (b) shows the thickness effect on the mechanical properties of MC and HPC based edible films respectively.



(a) (b)

Figure 3.9. Thickness effect on barrier and mechanical properties of (a) methyl cellulose films (molecular weight = 20.000) and (b) hydroxypropyl cellulose films (molecular weight = 1.000.000). (TS = tensile strength; E = elongation) (Source: Park et al. 1993)

According to Figure 3.9. (a) it can be seen that although TS of MC films is constant with thickness, E of MC films seems to increase slightly as thickness increase. In Figure 3.9. (b) TS of HPC films seem to increase as thickness increase, E of HPC films shows a trend similar to MC films and increase slightly as thickness increase.

Plasticizers make films more flexible due to their ability to reduce hydrogen bonding between polymer chains and plasticizer molecules while decreases the attractive forces between polymer chains and increases the free volume, molecular spacing and segmental motions (Cho and Rhee 2002, Turhan and Sahbaz 2001). Plasticizers can also be used to change the barrier and physical properties of films. The most effective plasticizers are resembled most closely in structure of the polymers they plasticize. For cellulose based films polyethylene glycol (PEG) has been commonly used as plasticizer. In the study of Park et al. (1993), the effect of different type of plasticizer on the mechanical properties (TS and E) of MC and HPC films had been evaluated. Figure 3.10. shows the plasticizer effects on tensile strength (TS) and elongation (E) of MC and HPC films. As shown from Figure 3.10. TS of both (a) MC and (b) HPC films decrease but E of both films increases as concentration of plasticizers increase. TS of MC films were usually greater than those of HPC films.

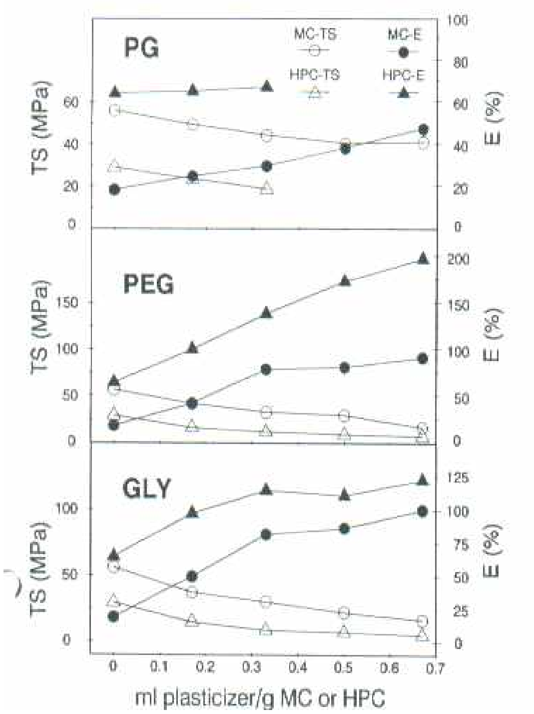


Figure 3.10. Plasticizer effects on tensile strength (TS) and elongation (E) of (a) MC and (b) HPC films. (PG = propylene glycol; PEG = polyethylene glycol; GLY = glycerin) (Source: Park et al. 1993).

Plasticizer properties e.g shape, number of carbons in molecules and number of hydroxyl groups can affect the mechanical properties of cellulose based films (Park et al. 1993). As a plasticizer PEG has a longer carbon chain (number of carbons in chain ~ 16) against to glycerin and propylene glycol (PG) (number of carbons in chain = 3). The formation of hydrogen bonding between polymer and PEG occurred, reducing intermolecular attraction; thereby improve flexibility and extensibility (Turhan and Sahbaz, 2001). As a result of this case, increased PEG concentration cause the extend of increase in flexibility that is greater than for other two plasticizers. PG has less functional group (two hydroxyl group) compared with glycerin, and its molecule is smaller than those of the other two plasticizers. So the extent of reduction of TS and increase of E by PG addition is less than for other two.

The effect of MC concentration on the mechanical properties of films had been evaluated by Turhan and Şahbaz (2003). Table 3.2. shows the effect of MC concentration on the mechanical properties of films. As shown from the Table 3.2., when the MC concentration increase, TS and E properties of film decrease. This case can be explained by the partial insolubility of MC at high concentrations.

Table 3.2. Effect of MC concentration on the mechanical properties of films (Source: Turhan and Şahbaz 2003).

MC (g/100ml solvent)	TS (MPa)	E(%)
1.5	16 ±1	10 ±0.4
3	33 ±3	14 ±1
4	23 ±3	11 ±1
5	11 ±1	8 ±1
6	8 ±1	6 ±2

Prodduturi et al. (2004) reported the mechanical properties of 10% clotrimazole added melt extruded HPC film mechanical properties depend on humidity of environment. At 0% RH films had TS above 63 MPa and E below 11%. As RH increases the brittle behaviour of the film was changed to ductile mode. TS was lowered and E was increased.

3.2.3. Water Vapour Sorption Isotherms of Edible Films

Water activity is defined as the ratio of the partial pressure of water in equilibrium with the food to the partial pressure of pure water at the same temperature

(Coupland et al. 2000). Water activity (a_w) is important to determine the stability criteria for foodstuffs and it is function of the equilibrium moisture content and the temperature. Water activity of the product effects the microbial growth, browning, lipid oxidation, etc., and other physical properties (such as color, texture, etc.) of the food (Pinedo et al. 2004). Because of these effects water activity is important factor in the preservation of moisture sensitive material for food applications against microbial, chemical and physical deterioration.

An important role of edible films is to reduce the exchange of water between the food and the environment, in particular to reduce drying of moist foods. The moisture barrier property of a film depends on the solubility of water in the film matrix. The moisture sorption isotherm (adsorption and desorption), is a way to characterize the solubility of water in the film matrix, so it is especially important for edible films (Coupland et al. 2000). A water sorption isotherm gives an information about the relationship between the water content (w) and water activity (a_w) of a material or the relative humidity (RH) of air measured at a constant temperature in thermodynamic equilibrium (Tsiapouris and Linke 2000). Sorption isotherms are also important to improve the conditions of several processes as dehydration, packing or storing. The sorption isotherms obtained from experimental data result in an estimation of equilibrium moisture content that is necessary to predict the hygroscopic properties of the film (Baldev Raj et al. 2001).

Sorption isotherms describe equilibrium sorption of porous materials in the non-saturated region as a function of the penetrant activity, including adsorption (i.e.formation of multilayers) and capillary condensation. In the saturated region, equilibrium sorption is described by the so called capillary pressure curve. Five types of sorption isotherms according to the BET-classification are shown in Figure 3.11. Type I is the well-known Langmuir isotherm, which is applicable to microporous solids. Type II and Type III isotherms describe adsorption of gases on macroporous or non-porous solids, and Type IV and Type V isotherms are applicable to both mesoporous or microporous solids. The presence of hysteresis loops is characteristic for Type IV and Type V, but may also appear in the other isotherms.

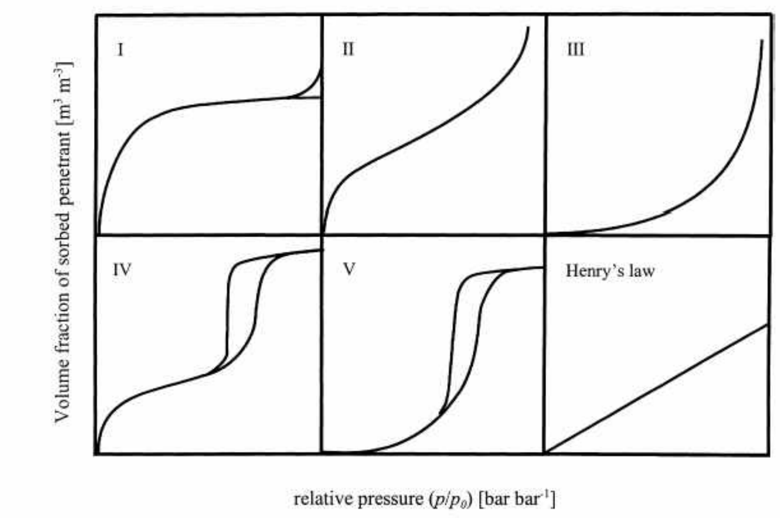


Figure 3.11. Five types of the sorption isotherm according to the BET-classification (Source: van der Wel and Adan 1999)

A variety of equations can be used to model the general sorption function M = f (a_w) (Coupland et al. 2000). To be successful, any modeling equation should fit as good as possible to experimental data, over a range of water activity (a_w) by using a minimum number of adjustable parameters. These parameters can be related with some physical meanings such as monolayer value, the amount of water required to coat all the primary binding sites (Coupland et al. 2000). Generally, the Bruanuer-Emmet-Teller (BET), Guggenheim-Anderson-de Boer (GAB) and Halsey and Smith equations applied to describe the isothermal water vapour adsorption data. BET and GAB models do not include the temperature dependence relationship directly, but this relationship is reflected in the model's coefficients, which are temperature dependent (Lin et al. 2005). The water vapour sorption isotherm models have special interest in many aspects of food preservation by dehydration (Baldev et al. 2002).

Bruanuer-Emmet-Teller (BET) Isotherm Model

$$1/[(1-a_w)\times M] = 1/M_m + [1/(C\times M_m)]\times[(1-a_w)/a_w] \qquad (3.7)$$

where M_m is the monolayer moisture content, and C is the constant related to the net heat of sorption. M is the equilibrium moisture content on a dry basis and a_w is the water activity. BET monolayer equation is an effective method for estimating the amount of water bound to specific polar sites in dehydrated systems used for food applications (Baldev et al. 2002). The BET model is considered to give good agreement with experimental values for water activities between 0 and 0.5 in hydrophilic glassy polymers (van der Wel and Adan 1999).

Guggenheim-Anderson-de Boer (GAB) Isotherm Model

$$M = \frac{m_0 C k a_w}{(1 - k a_w)(1 - k a_w + C k a_w)} \qquad (3.8)$$

Where M is the equilibrium moisture content (g/g polymer), at a water activity a_w, m_o is the monolayer value, and C and k are the constants. k is assumed to be less than 1 (Cho and Rhee, 2002). According to the van der Wel and Adan (1999), GAB equation is effective for fitting data of non-ideal water sorption in polymers (Type II or III) over activity ranging from 0 to 0.95, which is not the case for the classic BET model.

Halsey Isotherm Model

$$\ln(M) = a + b \text{ X } \{\ln[-\ln(a_w)]\} \qquad (3.9)$$

where a and b are Halsey constants, which can be estimated from a linear plot of $\ln(M)$ versus $\ln[-\ln(a_w)]$. Halsey model is another sorption isotherm model that expresses condensation of a multilayer at a relatively large distance from the surface.

Smith Isotherm Model

$$M = M_b - M_a \text{ X } [\ln(1-a_w)] \qquad (3.10)$$

where M_b and M_a are constants. From a linear regression of M versus $\ln(1-a_w)$, the Smith constants can be computed.

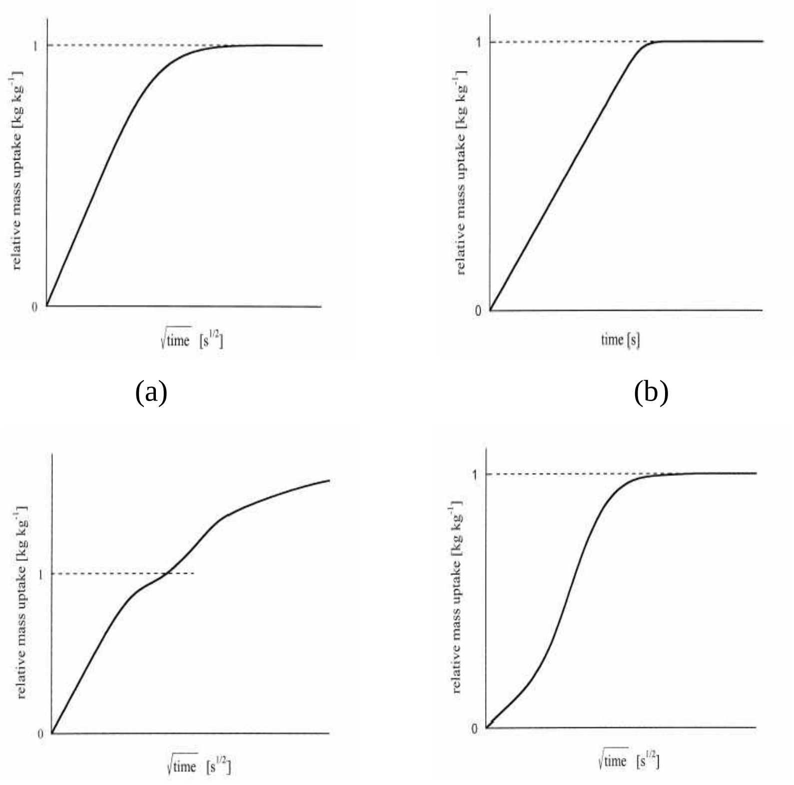
The water adsorption capacity of edible films depend greatly on the distribution of polar groups, accessibility of these groups to water, degree of crystallinite of the matrix, relative strength of water-water and water-macromolecule interactions and relative humidity conditions (Roman-Gutierrez et al. 2002). Polysaccharides are generally hydrophilic and interact strongly with water and water vapours through hydrogen bonds. Absorption of water into the structure of polysaccharides may change the physical and chemical properties of polysaccharides.

Amorphous saccharides usually absorb water into their bulk structure, which may cause crystallization or in the case of large polysaccharides the cleavage of polymer-polymer bonds , the formation of water-polymer bonds, separation of polymer chains, swelling and finally the dispersion of polymer chains in the medium. Sorbed water can accelerate the hydrolytic degradation, isomerisation and / or crystallization processes, that all are usually undesirable for food processing. When water penetrates solid polymer, it inserts itself into the hydrogen-bonded links between adjacent polymer chains and make them more and more independent of each other because more and more water comes between polymer-polymer chains. As the individual chains gain rotational freedom, they occupy more space, which results in the swelling of the polymer mass. By forcing additional chain apart, the penetrating water fills the voids between the polymer chains and diffuses into denser regions of the polymer (Alvarez-Lorenzo et al. 2000). According to the Wan et al. (1991), model of water uptake kinetics, (Eq. 3.11) there are two water uptake mechanisms; capillary-driven uptake through interparticle porous (k_1) and diffusive uptake through the swollen polymer (k_2).

$$U = k_1 t^{0.1} + k_2 t^{0.5} \tag{3.11}$$

Where U is the water uptake achieved by time t, expressed as a percentage of the total mass of the polymer and water system, and k_1 and k_2. are kinetic constants related to the mechanisms of water uptake (capillary-driven and diffusive, respectively).

Polymers can show different responses to the diffusion of penetrants in to the polymeric systems. The typical sorption kinetics for polymers are shown in Figure 3.12. If the polymer relaxation is much faster than the penetrant diffusion, diffusion is followed by instantaneous response to the system, resulting in Fickian behaviour. Instantaneous response of the system requires large flexibility of the polymer chains in the system. This is generally accepted to be the case for the polymers above their glass transition temperature (Tg), which are rubbery polymers (polymers below Tg are glossy). This type of sorption kinetics is called as Fickian diffusion or Case I diffusion. As seen in Figure 3.12. (a), absorption curve smoothly levels off to a saturation level M . Desorption and absorption curves should be overlapped in the Fickian diffusion. If the rate of penetrant diffusion is greater than the rate of polymer relaxation then Case II diffusion occurs. Other type is the Case III sorption that also known as anomalous diffusion. Types of anomalous diffusion are Two-stage sorption and Sigmoidal sorption are shown in (c) and (d) in Figure 3.12. In two-stage sorption there are two parts, first part indicates fast Fickian absorption, and second part indicates slow non-Fickian absorption (van der Wel and Adan 1999).



(a) (b)

(c) (d)

Figure 3.12. Typical sorption curves (a) Fickian absorption curve, (b) Case II absorption curve, (c) Two-stage absorpiton curve, (d) Sigmoidal absorption curve (Source: van der Wel and Adan 1999)

Strong interactions occur between the sorbed water and the polymer, because water molecules close to the polymer more slowly than the water molecules in contact with other water molecules, which indicate that they are located in a highly restrictive environment. Interactions of water vapour with cellulose ethers affect the flow and compaction properties and physical and chemical stability of the polymer (Alvarez-Lorenzo et al. 2000). The chemical structure and physical properties of the solid material and the ambient relative humidity that determines the equilibrium moisture content of given solid greatly affect the uptake of water vapour by a solid material (Alvarez-Lorenzo et al. 2000). The water adsorption / desorption capacities of edible films can be characterized by the kinetics of water gain / loss during equilibration at different levels of RH (between 0% and 95%) at 30^0C.

The changes in sample mass as a function of time are generally associated with the diffusion phenomena and can be modeled using the Fick's laws of Fickian type diffusion (Roman-Gutierrez et al. 2002). The Fick's first and second laws, are shown in Equations 3.12 and 3.13 respectively,

$$Ji = -Di \frac{dCi}{dx} \tag{3.12}$$

$$\frac{dc}{dt} = d(Ddc/dx)/dx \tag{3.13}$$

J is the amount of permeant passing through the unit area of the film in unit time, D is the diffusion coefficient, C is the concentration of penetrant molecules, x is the coordinate in the direction of flux, and t is the time. If during the measurement of sorption isotherm the changes in the thickness of the sample can be ignored and diffusion coefficient is independent from the concentration, Equations (3.14) and Equation (3.15) can be used to measure the diffusion coefficient of thin membranes.

$$M_t / M \; = (16D/h^2\pi)^{1/2}. \, t^{1/2} \qquad \text{when } Mt/M \; < 0.5 \tag{3.14}$$

$$\ln(M \; - Mt) = \ln(8\, M \; / \pi^2) - \pi^2 Dt/h^2 \qquad \text{when } Mt/M \; > 0.5 \tag{3.15}$$

where Mt is the mass of vapour absorbed by a membrane, M is the mass sorbed by the membrane at equilibrium, h is thickness. Equation 3.14 enables the diffusion coefficient to be obtained from plots of Mt/M against $t^{1/2}$ for the initial period of water sorption, whereas at the end of the sorption process, logarithmic plots of M - Mt against time also yield the diffusion coefficient.

The diffusion of low molecular weight compounds in polymers is generally governed by two simultaneously occurring phenomena: (1) a substantionally stochastic phenomenon, where the penetrant flows exclusively driven by a concentration gradient; (2) a relaxation phenomenon driven by the distance of the local system from the equilibrium (Buonocore et al. 2003).

There are a number of extensive studies focused on sorption properties of edible films. Chinnan and Park (1995) studied the sorption isotherms of methyl cellulose and hydroxypropyl cellulose films. Another study about sorption isotherm of HPC was made by Alvarez-Lorenzo et al. (2000). In this study Young-Nelson and GAB equations had been used to fit the experimental moisture sorption data of different type of hydroxypropyl cellulose that are L-HPCs (Low-DS hydroxypropylcelluloses) and HPCs (Medium/high-DS hydroxypropylcelluloses) (DS is the degree of substitution). For Young-Nelson analysis Alvarez-Lorenzo et al. (2000) had used, non-linear and stepwise multiple regression analyses (Statgraphics® v. 7.0) as proposed by Nokhodchi et al. (1997) to fit the sorption and desorption data with Equations 3.16 through 3.20.

$$M_s = A(\theta + \beta) + B\theta H \tag{3.16}$$

$$M_d = A(\theta + \beta) + B\theta H\mathrm{max} \tag{3.17}$$

respectively, where *M* is moisture content, the subscripts ‘s’ and ‘d’ indicate sorption and desorption respectively, *H* is relative humidity

$$\theta = H/[H+E(1-H)] \text{ and} \tag{3.18}$$

$$\beta = -\frac{EH}{E-(E-1)H} + \frac{E2}{E-1}\ln\left(\frac{E-(E-1)H}{E}\right) - (E+1)\ln(1-H) \tag{3.19}$$

A, B and E being fitting constants that are characteristics of each material. θ is interpreted as the fraction of the polymer surface covered by at least one layer of water molecules; $A\theta$ as the mass of water in a complete monolayer, expressed (like all masses in the model) as a fraction of the dry mass of the polymer; $A(\theta + \beta)$ as the externally adsorbed moisture (so that $A\beta$ is the mass of water which is adsorbed beyond the mass of the monolayer); B as the mass of water adsorbed internally at 1.0 relative humidity; $B\theta H$ as the mass of internally absorbed water when the monolayer coverage is θ and the relative humidity H; and E as a kind of equilibrium constant (though without regard to entropy effects) between monolayer water and the 'normally condensed' water adsorbed externally to the monolayer

$$E = \exp\left[-(q_l - q_L)/(k_B T)\right] \tag{3.20}$$

q_L (Jmol^{-1}) is the heat of condensation of water, q_l (Jmol^{-1}) is the heat of adsorption of water on the polymer, T(K) is the temperature and k_B is the Boltzman constant (1.38x10^{-23} J K^{-1}). The fraction moisture present in different zones of the hydroxypropylcellulose particles were estimated by fitting Young-Nelson [3.20] and GAB [3.8] equations to the experimental moisture sorption-desorption data. Figure 3.10. shows the sorption-desorption isotherms of a typical L-HPCs(LH-11) and typical HPC (Klucel®MF).

Table 3.3. Optimized values of the parameters of Young and Nelson's model of uptake of water vapour (Source: Alvarez-Lorenzo et al. 2000)

Polymer	E	A	B	r^2	*F* value
LH-11	0.82	0.033	0.126	0.9930	987.2
Klucel®MF	1.2	0.045	0.047	0.9975	2753.1

Table 3.4. Optimized values of the parameters of GAB model of uptake of water vapour (Source: Alvarez-Lorenzo et al. 2000)

Polymer	W(%)	Cg	K	r^2	*F* value
LH-11	3.96	44.65	0.918	0.9082	70.2
Klucel®MF	2.64	60.89	0.962	0.9490	131.3

To judge by the r^2 columns of Tables 3.3 and 3.4. the Young-Nelson model (Table 3.3.) fits the data well than the GAB model (Table 3.4.), possibly because the sharp rise in water uptake at relative humidities greater than about 0.70 (see Figure 3.13.) may be incompatible with the GAB assumption that adsorption is restricted to the particle surface. This implies that the water vapour is not adsorbed onto the particle surface, but is also adsorbed into the interior of the polymer particle.

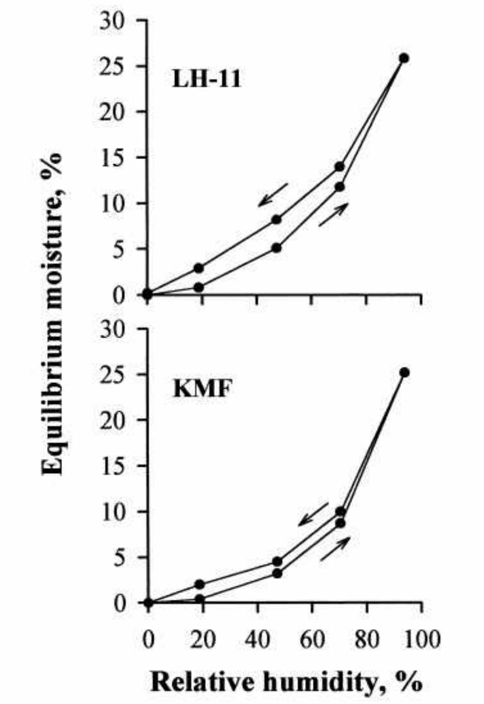


Figure 3.13. Sorption-desorption isotherms of the L-HPC (LH-11) and the HPC (Klucel®MF) (Source: Alvarez-Lorenzo et al. 2000)

Alvarez-Lorenzo et al. have also studied the water uptake kinetics of L-HPC compacts and HPC compacts. (See Figure 3.11.). According to the Figure 3.14. it can be seen that; L-HPC compacts had took the water just 5 min. but HPC compacts had took over 1 h. The researchers suggest that; this difference may depend to the rapidly swelling and disintegrating ability of L-HPCs that have less complex structure than HPCs.

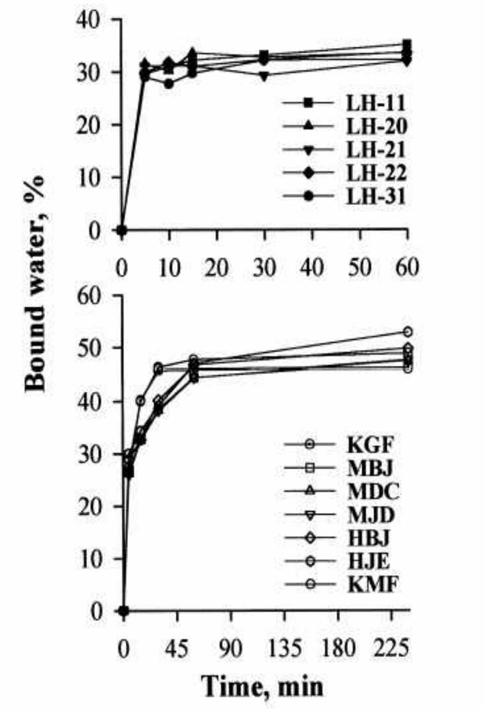


Figure 3.14. Kinetics of uptake of non-freezing water hydroxypropylcellulose compacts (Source: Alvarez-Lorenzo et al. 2000)

In the study of Cheng et al. (2002), water vapour adsorption capacity of edible films that were made from konjac glucomannan (KGM) solutions, with or without added alkali (KOH) and/or sodium carboxymethylcellulose (NaCMC) had been evaluated. Figure 3.15. shows moisture sorption isotherms of the films studied. The relationship between moisture content and water activity has sigmoid-shaped and characteristically similar to those of most biopolymeric materials. According to the Figure 3.15. they had concluded that, KOH and NaCMC, and their interaction, have significant effects on the sorption isotherms of the films studied. KGM-KOH films exhibited a substantially lower water-binding capacity than the control KGM films in the absence of NaCMC over the whole range of RVP tested. The researchers suggested that alkaline deacetylation of the KGM polymer reduced steric hindrance and the polymer chains become freer to associate. In the absence or presence of KOH, the addition of NaCMC, have the effect of enhancing the hydration capacity of KGM-based films (Cheng et al. 2002).

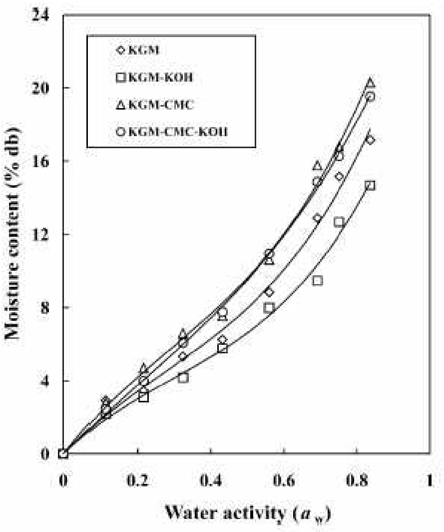
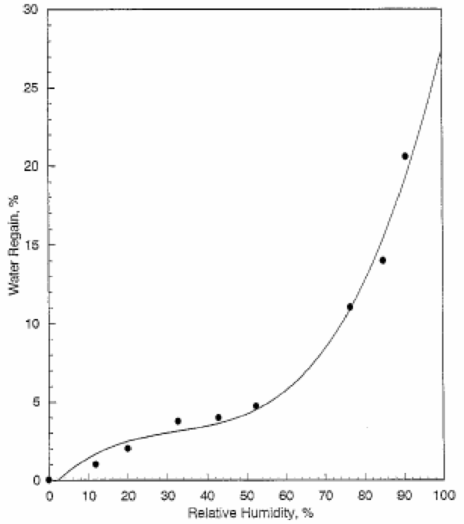


Figure 3.15. Moisture sorption isotherms of konjac glucomannan-based edible films at 30^0C (Source: Cheng et al. 2002).

In an another study the sorption isotherm of HPC based films had been evaluated by Yano et al. (1998). In this study film form of HPC had been obtained by using ethyl alcohol and water a solvent and then drying of this mixture on petri dish for one week. The sorption isotherm of HPC films were shown in Figure 3.16. HPC is hydrophilic polymer and adsorbs water, so the sorption isotherm of HPC film had showed typical isotherm for hydrophilic polymers (Type II).



igure 3.16. The sorption isotherm of HPC at 30^0C (Source: Yano et al. 1998).

Prodduturi et al. (2004) studied the moisture-sorption characteristics of HPC films. They showed that the water vapour adsorption of the 10% clotrimazole added HPC was independent from molecular weight of HPC.

3.2.4. Water Vapor Permeability of Edible Films

The water vapour permeability is the most extensively studied property of edible films mainly because of the importance of the role of water in deteriorative reactions. Water acts as a solvent or carrier and cause texture degradation, chemical and enzymatic reactions. Also the water activity of foods is an important parameter in relation with the shelf-life of the food. In low-moisture foods, low levels of water activity must be maintained to minimize the deteriorative chemical and enzymatic reactions and to prevent the texture degradation. The composition of film forming materials (hydrophilic and hydrophobic character), temperature and relative humidity of the environment affect the water vapour permeability of the edible films. (Ayrancı and Tunc 2003, Anker et al. 2002).

When considering a suitable barrier in foods and food packaging the barrier properties of biopolymeric films are important parameters (Anker et al. 2002). Edible polysaccharide films and coatings are generally good barriers against oxygen and carbondioxide and have good mechanical properties but their barrier property against water vapour is poor because of the their hydrophilic character (Aydinli and Tutas 2000).

To add an extra hydrophobic component e.g. a lipid (waxes, fatty acids) in an edible film and produce a composite film is one way to achieve a better water vapour barrier. Here the lipid component serves as the barrier against water vapour (Anker et al. 2002). By adding lipid, the hydrophobicity of the film is increased and as a result of this case water vapour barrier property of the film increases (Gallo et al. 2000).

Moisture transport mechanism through a composite depends upon the material and environmental conditions. Permeability has two different features in case of composites. First; permeation can occur by solution and diffusion in non-porous membranes; and the other; simultaneous permeation through open pores is possible in porous membrane.

There are various methods of measuring permeability. Weight loss measurements are of importance to determine permeability characteristics (Ulutan and Balköse 1996). Water vapour permeability is usually determined by direct weighing because, despite its inherent problems, mainly related to water properties such as high solubility and cluster formation within the polymer and tendency to plasticize the polymer matrix, it is simple and relatively reliable method. The major disadvantage of this method resides in its weakness to provide information for a kinetic profile, when such a response is required (Arvanitoyannis and Biliaderis 1999).

In many research, measurements are mostly based on the standard method described in ASTM E96–80 (standard test method procedure for water vapour permeability) (Turhan and Sahbaz, 2003, Cheng et al, 2002, Anker et al. 2002, Xu et al. 2001, Gallo et al. 2000). According to this method water vapour permeability is determined gravimetrically and generally, the applied procedures are nearly the same in many research papers that are related with this purpose. In this procedure; firstly, the test film is sealed to a glass permeation cell which contain anhydrous calcium chloride ($CaCl_2$), or silica gel (Relative vapor pressure; RVP=0) and then the cell is placed in the desiccators maintained at specific relative humidity and temperature (generally 30^0C, 22% RH) with magnesium nitrate or potassium acetate (Turhan & Sahbaz 2003; Cheng et al. 2002; Gallo et al. 2000). Permeation cells are continuously weighed and recorded, and the water vapour that transferred 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 (Turhan and Sahbaz 2003, Cheng et al. 2002). When the relationship between weight gain (Δw) and time (Δt) is linear, the slope of the plot is used to calculate the water vapour transmission rate (WVTR) and water vapour permeability (WVP) (Gallo et al., 2000). Slope is calculated by linear regression and correlation coefficient (r^2>> 0,99) (Arvanitoyannis and Biliaderis, 1999).

The WVTR is calculated from the slope ($\Delta w/\Delta t$) of the straight line divided by the test area (A), (g s^{-1} m^{-2});

$$\text{WVTR} = \Delta w / (\Delta t \cdot A) \qquad (g.m^{-2}.s^{-1}) \qquad (3.21)$$

where $\Delta w / \Delta t$ = transfer rate, amount of moisture loss per unit of time ($g.s^{-1}$); A= area exposed to moisture transfer (m^2) (Cheng et al. 2002).

The WVP (kg Pa^{-1} s^{-1} m^{-1}) is calculated as;

$$\mathrm{WVP}=[\mathrm{WVTR} / S\,(R_1-R_2)]\times d \quad (3.22)$$

where S = saturation vapour pressure (Pa) of water at test temperature, R_1 = RVP in the desiccator, R_2 = RVP in the permeation cell, and d = film thickness (m). At least three replicates of each film should be tested for WVP and all films should be equilibrated with specific RH before permeability determination (Turhan and Sahbaz, 2003; Cheng et al, 2002; Gallo et al., 2000).

The water vapour permeability can also be calculated from the WVTR as follows;

$$P = \mathrm{WVTR} \times l / \Delta p \qquad (\mathrm{g.m^{-2}.s^{-1}Pa^{-1}}) \quad (3.23)$$

l = film thickness (m); Δp = water vapour pressure gradient between the two sides of the film (Pa); P = film permeability ($\mathrm{g.m^{-2}.s^{-1}Pa^{-1}}$) (Debeaufort et al. 1993).

These equations were derived from Fick's and Henry's laws for vapour and gas diffusion through the film.

When the vapour transport from the film have one dimensional, permeation model can be represent by the first law of the Fickian diffusion with an effective diffusivity, D_{eff} ,

$$J = D_{eff}\,(\frac{dc}{dx}) \quad (3.24)$$

D_{eff} is the effective diffusivity. If it is considered that diffusion coefficient is independent of concentration, and it is assumed that film with a thickness of L is thin, so steady-state condition is achieved in the film even though the concentrations of the lower and upper sides of the film may change with time. Then Equation 3.25 can be used to measure the effective permeability;

$$\ln\frac{P_{IL}-P_{Iui}}{P_{IL}-P_{Iu(t)}} = \frac{P_{eff}\,ART}{VL}\,t \quad (3.25)$$

Where P_{IL} and P_{Iu} are the vapour pressure at the lower and upper part of the permeation cell respectively. Therefore the rate of permeation is generally expressed by the permeability (P) rather than by a diffusion coefficient derived from Equation 3.25 and the solubility (s) of the penetrant in the film. When there is no interaction between the water vapour and film, these laws can apply for homogeneous materials. Then, permeability follows a solution - diffusion model as;

$$P = DxS \tag{3.26}$$

where D is the diffusion coefficient and the S is the slope of the sorption isotherm and is constant for the linear sorption isotherm (McHugh et al., 1993; Debeaufort et al., 1993, van der Wel and Adan 1999). The diffusion coefficient describes the movement of permeant molecule through a polymer, and thus represents a kinetic property of the polymer-permeant system.

As a result of the hydrophilic characteristics of polysaccharide based edible films, the water vapour permeability of films are related to their thickness. The permeability values increase with the increasing thickness of the films (McHugh et al. 1993).

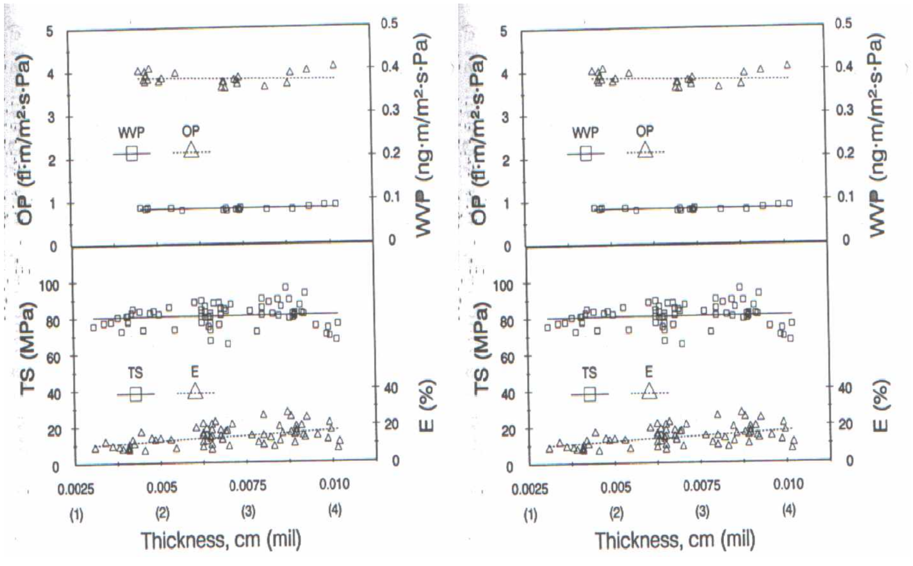
To evaluate the water vapour permeability property of cellulose based edible films some studies that are related with this subject were given in the following part;

In the study of Park et al. (1993), the effect of thickness of films and the molecular weight (MW) of the film forming materials on water vapour permeability (WVP) and oxygen permeability (OP) of MC and HPC films had been compared. The effect of MW was shown in Table 3.3. The comparison of means and standard deviations of OP and WVP for MC and HPC films had been compared. They conclude that OP of MC films generally increased as the MW of MC increased and OP of HPC films increased as MW of the polymer increased. WVP of MC and HPC films also increased as the MW increased. WVP of MC based edible films were generally higher than HPC based films (Table 3.5.).

Table 3.5. Changes in oxygen and water vapour permeability of MC and HPC films with molecular weight (Source: Park et al. 1993).

Films (MW)	Oxygen Permeability (fl.m/m^2.s.Pa)	Water Vapour Permeability (ng.m/ m^2.s.Pa)
MC		
13.000	3.1 ±0.30	0.084 ±0.0047
20.000	3.6 ±0.56	0.094 ±0.0056
41.000	4.6 ±0.31	0.103 ±0.0099
63.000	5.3 ±0.72	0.110 ±0.0065
86.000	5.1 ±0.59	0.121 ±0.0152
HPC		
100.000	3.0 ±0.23	0.052 ±0.0035
370.000	3.2 ±0.14	0.059 ±0.0037
1.000.000	3.7 ±0.10	0.066 ±0.0040

Thickness effect to water vapour permeability and oxygen permeability properties of MC and HPC based films were shown in Figure 3.17. (a) and (b) respectively. According to Figure 3.17. OP and WVP of MC films were relatively constant over a thickness range from 1.8mil to 4.2mil. The OP and WVP of HPC films were constant over a thickness range from 0.9mil to 5.5mil (Park et al. 1993).



(a) (b)

Figure 3.17. Thickness effect on WVP and OP of (a) MC films (molecular weight = 20.000) and (b) HPC films (molecular weight = 1.000.000) (Source: Park et al. 1993)

In the study of Ayrancı et al. (1997), the effect of molecular weights of cellulose based edible films on their water vapour permeability properties had been studied. Table 3.6. shows the WVTR, permeance and permeability values of MC and HPMC based edible films with varying molecular weights of the polymers.

Table 3.6. Average thickness, water vapour permeability (WVTR), permeance and permeability values of films with HPMC and MC of varying molecular weights (Source: Ayrancı et al. 1997)

MW	Av. Film Thickness (µm)	WVTR (g.h^{-1}.m^{-2})	Permeance (g.h^{-1}.m^{-2}Pa^{-1})	Permeability (g.h^{-1}.m^{-2}Pa^{-1})
HPMC				
22000	1.4±0.1	6.79±0.06	4.05x10^{-3}	5.7x10^{-8}
26000	1.3±0.2	6.85±0.05	4.08x10^{-3}	5.3x10^{-8}
86000	1.0±0.2	6.79±0.05	4.05x10^{-3}	4.1x10^{-8}
MC				
13000	1.3±0.1	3.16±0.01	1.88x10^{-3}	2.5x10^{-8}
20000	1.0±0.2	3.17±0.05	1.89x10^{-3}	1.9x10^{-8}
41000	1.5±0.1	3.35±0.01	1.99x10^{-3}	3.0x10^{-8}
63000	1.2±0.2	3.31±0.05	1.97x10^{-3}	2.4x10^{-8}
86000	1.0±0.2	3.42±0.05	2.04x10^{-3}	2.0x10^{-8}

As seen from the table 3.6. there in no clear trend in variation of WVTR and permeance values with molecular weights of HPMC and MC. Permeability values of HPMC films decrease with increasing molecular weight of HPMC. In the study of Park et al. 1993, permeability values of HPC based films increase with increased molecular weight of HPC. They explain this disagreement with the present of the extra methyl group of HPMC that makes this polymer more hydrophobic. Concerning permeability values of MC, above a molecular weight of 41.000, there is a regular decrease with increasing molecular weight. The researchers had explained this result the by possibility of decreased mobility of the molecule with increasing molecular weight and this case cause contribution to water vapour transfer becomes less. On the other hand, Park et al. 1993, found that WVP values of MC based edible films increase with increasing molecular weight of MC.

CHAPTER 4

EXPERIMENTAL

4.1. Materials

The film forming materials Hydroxypropyl cellulose (HPC) (Mw = 370.000) and Carboxymethylcellulose sodium salt (NaCMC) (Mw = 250.000 - D.S = 1,2) used in this study were supplied from Sigma- Aldrich. Glycerol used as plasticizer was purchased from Merck . Deionized water was used as a solvent throughout the experiment.

4.2. Methods

4.2.1. Film Preparation Method

Three, four and five grams of HPC or NaCMC were dissolved in a 100ml deionised water at room temperature by mixing with magnetic stirrer for 4 hours. After complete dissolution of film forming materials, glycerol was added as a plasticizer at 10% dry weight. The concentration of glycerol was determined by preparing each cellulose-based film with different glycerol content (1%, 5%, 10% and 15%). Then it was concluded that 10% glycerol based on dry weight shows the best result according to the flexibility and appearance of films. The solutions with glycerol were homogenized with a magnetic stirrer at room temperature for 1 hour. Then film forming solutions were kept in a vacuum oven for about 48 hours to remove air bubbles or dissolved air.

Finally, solutions were spread by using Sheen Automatic Film Applicator 1133N on glass plates. Solution films with 6cm x 20cm x 0.12cm dimensions were obtained. The spread films were dried at room temperature for 48 hours, than at 60^0C in an oven for 25 minutes. The films were detached from the glass plates and used for testing. The prepared film samples were covered with paper and stored at room temperature The thickness of films were measured with digital micrometer to the nearest 0.001mm at ten locations. Films were prepared with a thickness of nearly 10, 20 and 30 micrometer for HPC and NaCMC films obtained by 3, 4 and 5 percent concentration film solutions. The film forming process is shown in Figure 4.1.

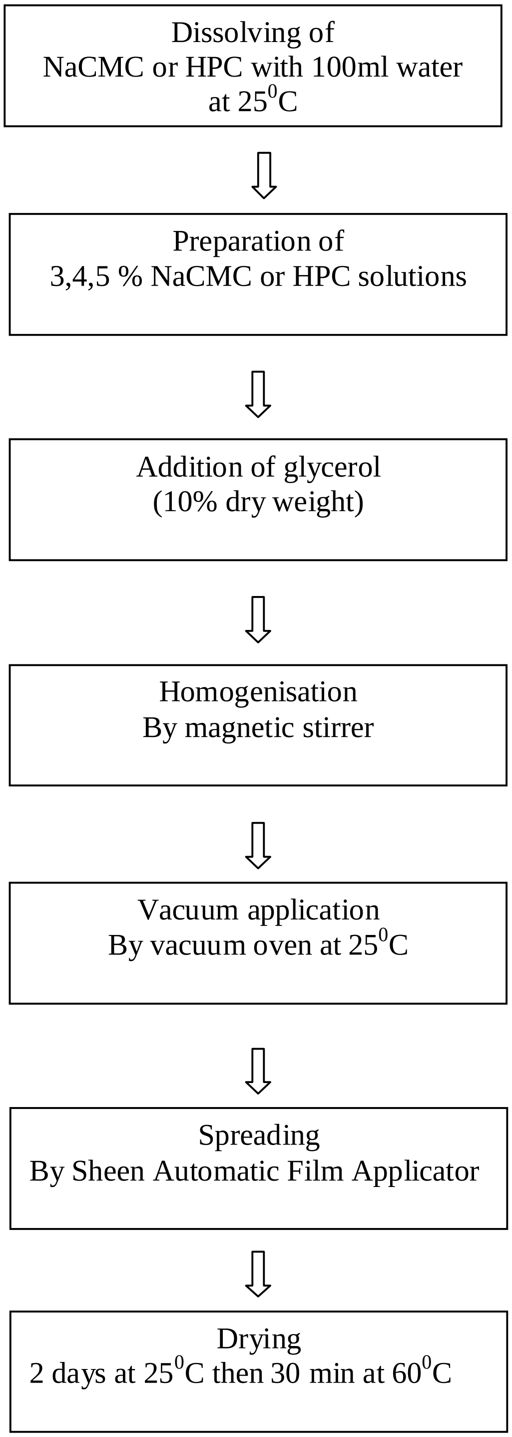


Figure 4.1. Film formation process

4.2.2. Viscosity Measurement of Film Forming Solutions

Viscosity of film forming solutions were measured by Brookfield viscometer (Model No: DVIII Programmable Rheometer) by using the thermocell SC4-27 unit at a 23-25^{0}C temperature interval. As a measurement condition, speed increment = 1.00; speed ramp interval = 0.005; set speed = 5.00; wait for speed = 50.0 were chosen. Two measurements were done for each film forming solutions.

4.2.3. Characterization of Films by FTIR, SEM, XRD, EDX, DSC and TGA Analyses

Fourier Transform Infrared Spectroscopy (FTIR);

To determine functional groups in the NaCMC and HPC based edible films FTIR spectrometer (Digilab FTS300MX) was used with a resolution of 4 cm^{-1}, in the range of wave number between 750 and 4000cm^{-1}. DTGS element was used as a detector. All analysis were carried out at room temperature.

Scanning Electron Microscopy (SEM);

Each film was mounted on aluminum stubs using aluminum sticky tape and coated with gold palladium film in a VG Microtech SC 7610 Sputter coater. Then specimen was examined using a Philips XL 30S FEG electron microscope.

X-Ray Diffraction Analysis (XRD);

NaCMC and HPC based films and powder form of these cellulose ethers were analyzed by using a Philips X' pert Pro. Diffractometer with $CuK_{\acute{\alpha}}$ radiation. The scattering angle (2θ) was varied from 5 to 70^{0}.

Energy Dispersive X-Ray (EDX);

EDX analysis was carried out to determine the elements in the HPC and NaCMC based edible films. In this analysis, data were collected from 6 randomly chosen points and by taking arithmetic mean of these values, average weight percent of the elements found in the film was calculated.

Differential Scanning Calorimetry (DSC);

DSC analysis was used to determine the glass transition temperature values of the HPC and NaCMC based edible films. Film samples (3.4-5.2mg) were stored in ambient condition and examined in aluminum crucible under nitrogen purge (flow rate = 40ml/min) by differential scanning calorimetry (Shimadzu DSC-50) using a temperature rate of 10^0C/min over 600^0C for CMC and 200^0C for HPC based film samples.

Thermal Gravimetric Analysis (TGA);

Thermal properties of the NaCMC and HPC films were stored in ambient condition and analyzed by the thermobalance (Shimadzu TGA-51). ~10mg and 11mg NaCMC and HPC film samples were scanned up to 200^0C at a heating rate of 10^0C/min. Nitrogen atmosphere (40ml/min) was used for all analyses.

4.2.4. Measurements of Sorption Isotherms of Films

The water sorption isotherms of the cellulose - based films were measured by using the Environmental Chamber. This procedure is based on the determination of the moisture content of samples being at equilibrium in a closed chamber whose temperature (accuracy $\pm 0.5^0$C) and relative humidity (accuracy ±1%) are controlled with the vaporization of water at a given temperature.

Before measuring each sorption isotherm, films were dried at 80^0C through the 0% moisture in an oven (Nüve FN 500 / TS 6073 model) and then weighed using an analytical balance (Sartorius BP 2215) with a precision of 0.1mg in order to determine the mass of dried films. After each equilibrium condition the mass of the films at a specific RH was measured again with an analytical balance which was placed in the chamber. Film samples were reached to equilibrium condition in nearly 15 - 20 minutes. The RH values between 20% and 90% at 25^0C were increased at 10% steps after each equilibrium condition. During changing of RH values, all film samples were covered with an aluminum-foil to protect the films from air ventilation in the chamber. The adsorption capacities of films were determined by the kinetics of water gain during equilibration at different level of RH between 20% to 90% at 25^0C as a function of time. The desorption capacities of films were determined by the kinetics of water loss at RH from 90% to 20% at 25^0C as a function of time.

To control the accuracy of the sorption isotherms, Magnetic Suspension Balance was also used. In this system, film samples were placed into the measuring cell with multi-tray sample holder. Then the column enclosing the sample was heated to up to 60^0C by using a water bath and vacuum was applied to the column by rotary vane pump up to 0.0001 mbar to remove the water that desorbed from the samples during the heating process. The column was kept at 30^0C after drying process. After starting the software program, the system was allowed to reach equilibrium in 24 hours. Water was heated in a flask by using constant temperature bath and water vapour was sent to the column until equilibrium is reached. When equilibrium was obtained, valves of the column were closed. The vapor pressure of the water was controlled by changing temperature of water in the flask. Then again by opening the valves of the column water vapour was sent to the column until new equilibrium is reached. This procedure was applied until the temperature difference between the water vapor and column reached to 5^0C

4.2.5. Water Vapour Permeability Measurements of Edible Films

The water vapour permeability of edible films were determined by Permeability Measurement System (Figure 4.2.). This system consists of an air pump, flowmeter, zeolite filled column, hygrometer, permeation cell, valves of the permeation cell, and the computer. The permeation cell contains lower and upper parts. Water is present in an open container in the lower part and upper part contains hygrometer. The film was placed between two parts of the permeation cell. Open surface of film was 16.6cm^2, the upper part of the permeation cell (Volume = 56.53 cm^3) was dried as much as possible by means of sweeping with dry air obtained by passing ambient air through a zeolite filled column. The valves of the permeation cell were closed after drying. The relative humidity values in the upper cell were measured by a hygrometer, (Datalogger SK - L200TH) and were recorded by a computer with respect to time. Three replicates of each film type were tested for water vapour permeability measurements.

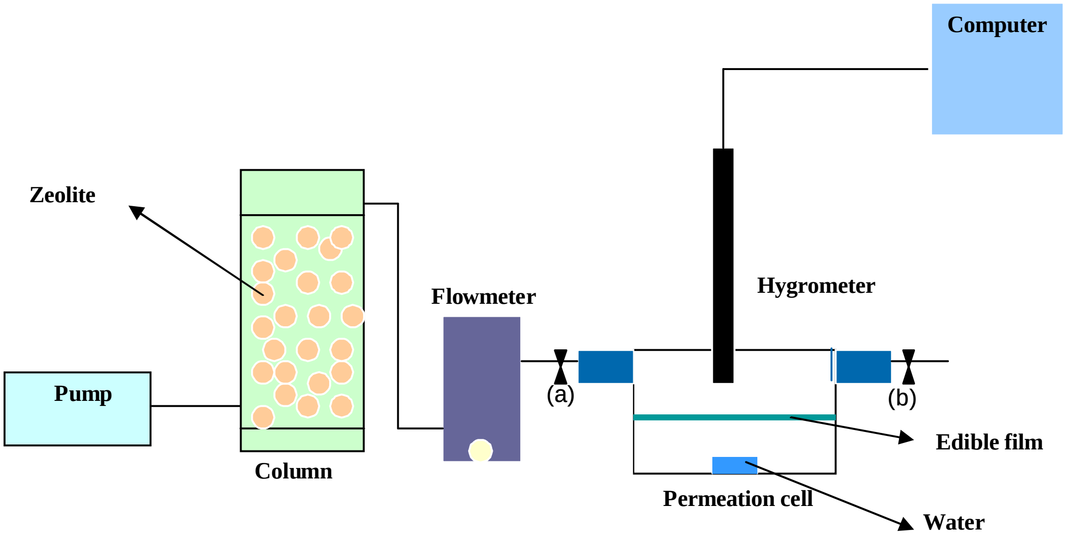


Figure 4.2. Permeability measurement system

4.2.6. Determination of Mechanical Properties of Films

An Instron Universal Testing Instrument (Model 4210) was used to determine mechanical properties (TS and %E) of films in accordance with ASTM D882-83 (1984). The Enviromental Chamber was used to condition each film specimens at 20^0C and 50% RH for 48 hours. Testing film strips were 100mm long and 10mm wide. The initial grip separation was set at 100mm and crosshead speed at 5mm/min. Young's modulus (MPa) (E), stress at break (N/mm^2) and strain at break (%), stress at yield (N/mm^2) and strain at yield (%) parameters were collected and obtained directly from the computer. At least five replicates of each NaCMC and HPC films were tested

CHAPTER 5

RESULTS AND DISCUSSIONS

5.1. Viscosity Analysis of Edible Film Forming Solutions

Viscosity plays the main role in controlling the film quality and properties. Viscosity analyses of the film forming solutions were made to measure the flow properties of the solutions. The rheological properties of the solutions directly affect the structural, mechanical and barrier properties of the films. The steady-state flow curves of the film-forming solutions were shown in Figure 5.1. and Figure 5.2. for NaCMC and HPC polymers, respectively. At shear rates higher than 30 s^{-1}, viscosity of 5% concentrated film forming solutions could not be measured due to flow instability

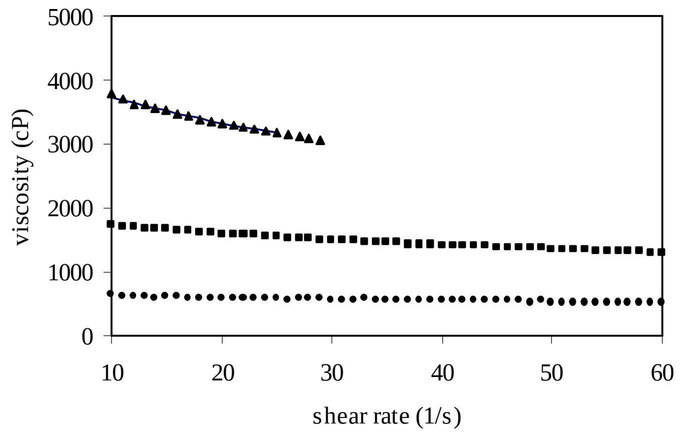


Figure 5.1. Apparent viscosity as a function of shear rate for NaCMC film forming solutions with different concentrations ( ) % 3; ( ) %4; ( ) %5 (3, 4, 5g NaCMC / 100ml water)

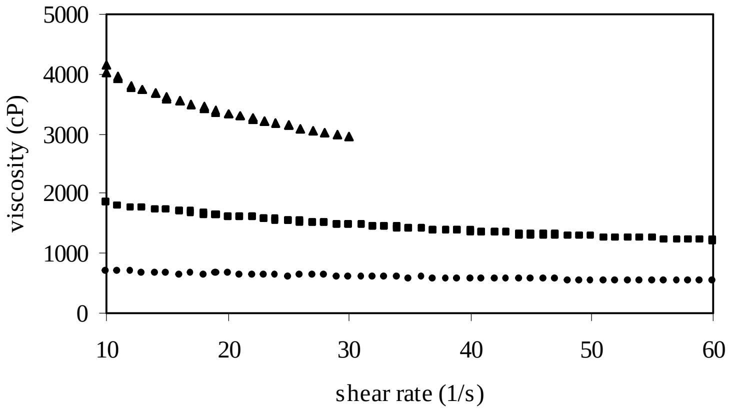


Figure 5.2. Apparent viscosity as a function of shear rate for HPC film forming solutions with different concentrations ( ) % 3; ( ) %4; ( ) %5 (3, 4, 5g HPC / 100ml water)

As shown from Figure 5.1. and Figure 5.2. dilute NaCMC and HPC based film forming solutions (3g polymer/100g water) acted as a Newtonian fluid because viscosity remained constant as the shear rate varied. In comparison to dilute solutions, all other solutions showed non-Newtonian behaviour such as pseudoplastic due to a decrease on viscosity with increasing shear rate. Biswal and Singh (2004) also reported about non-Newtonian behaviour of CMC solution. The viscosity of 0.5 wt% CMC solution decreased from 0.010 to 0.007 (PaS) when shear rate was increased from 10 to 30 (1/s).

To evaluate the relationship between η_{sp}/C_i and concentration (C) of these solutions Equation 3.5 were used to calculate η_{sp}/C_i values that were reported in Table 5.1. and the Figure 5.3. Since the solution showed shear thinning, viscosity at shear rate $10s^{-1}$ was taken for η_{sp}/C_i calculations.

Table 5.1. η_{sp}/C_i values of polymers

Solution Concentration (%)	NaCMC	HPC
3	248	223
4	431	460
5	772	793

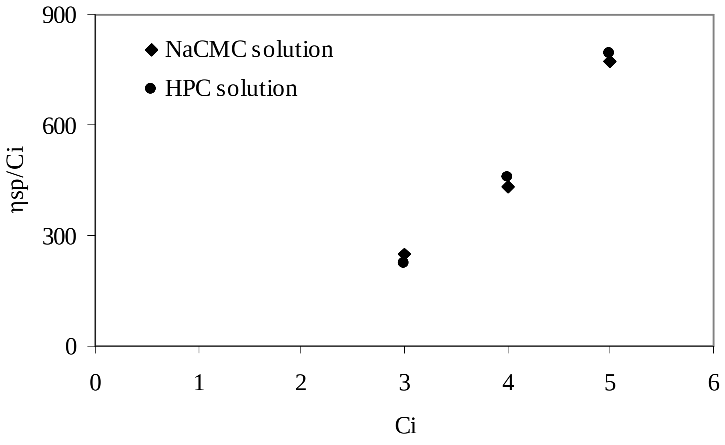


Figure 5.3. The intrinsic viscosity graphs of NaCMC and HPC film forming solutions.

As shown from Table 5.1. the η_{sp}/C_i values of these solutions increased with increasing solution concentration. Also the η_{sp}/C_i values of the same concentration film-forming solutions were similar with each other. So it can be concluded that the effect of solution concentrations on the specific viscosity values were nearly same for HPC and NaCMC film forming solutions. In Figure 5.3. there was a linear relation between η_{sp}/C_i versus C_i but the η_{sp}/C_i intercept at zero C_i value was negative. This may be caused by the hydro gel formation at this high concentration range (3, 4, 5g polymer/100ml water) that were the optimum concentration interval to make films. For molecular weight determinations Wanchoo and Sharma (2003) studied up to 0.012 g/dl concentration CMC solution, on the other hand in the present study film forming solutions having 3 to 5 g/dl concentration viscous behaviour was studied.

Flow property modeling of film-forming dispersions is useful technologically to identify the most appropriate coating system design and optimize operating conditions. For this purpose to measure the flow characteristics of these solutions, some models were applied to fit the data. In this study Power Law model was found to be the best fit model for all film-forming solutions. The power law equation can be seen in Equation 5.1 and the calculated parameters were given in the Table 5.2.

$$\tau = k.\gamma^n \tag{5.1}$$

where τ is shear stress, γ is shear rate, k is consistency index and n is the flow index.

Table 5.2. Viscosity model for NaCMC and HPC film-forming solutions

MODELS	Solution Concentration (g NaCMC/ 100g water)			Solution Concentration (g HPC/100g water)		
POWER LAW	3	4	5	3	4	5
CONSISTENCY INDEX, k (mPas)	851.6	2700	5966	1143	3446	7609
FLOW INDEX, n	0.88	0.82	0.8	0.81	0.75	0.72
CONFIDENCE OF FIT (%)	**99.7**	**98.9**	**99.6**	**98.7**	**98.8**	**99.7**

Power law model is typical for polymers. This model indicates that, the polymer molecules were oriented in flow direction, so it can be explained that why viscosity decreased with increasing shear rates. In the present study degree of substitution of NaCMC was 1.2, while in the study of Ghannam and Esmail (1997) degree of substitution was 0.7 for CMC and the k values were 2.30, 8.30, 28.8 and n values were 0.73, 0.61 and 0.53 for 3, 4 and 5 % NaCMC solutions respectively. Different k and n values were found in the present study for NaCMC with degree of substitution 1.2 and presence of 10% glycerin.

5.2. Characterization of the Edible Films

5.2.1. Fourier Transform Infrared Spectroscopy (FTIR) Analysis

The graft copolymer structure of HPC and NaCMC was confirmed by IR spectroscopy. The IR spectrum of NaCMC based film is shown in Figure 5.4. As seen from the IR spectrum of NaCMC based film there is a broad band of 3300 cm^{-1} which belongs to vibration of hydrogen bonded -OH group and there is band at 2914cm^{-1} that is due to C-H stretching vibration. The presence of a strong absorption band at 1583.8 cm^{-1} confirms the presence of COO^- group. The bands around 1414 and 1323cm^{-1} are assigned to $-CH_2$ scissoring and –OH vibration, respectively. The band at 1020 cm^{-1} is due to $>CH-O-CH_2$ stretching. The spectrum in Figure 5.4. was identical with the study of CMC that was reported by Biswal and Singh (2004).

The IR spectrum of HPC based film is shown in Figure 5.5. There is a broad band at 3450 cm^{-1} and 1630 cm^{-1} due to vibration of hydrogen bonded -OH group. The bands around 2968, 2909 and 2872.6 cm^{-1} are assigned to C-H stretching vibrations. The presence of a strong absorption band at 1410 cm^{-1} confirms the presence of $-CH_2$ scissoring. The bands at 1325cm^{-1} is assigned to –OH vibration. The band at 1040 cm^{-1} is due to $CH-O-CH_2$ stretching (Biswal and Singh 2004).

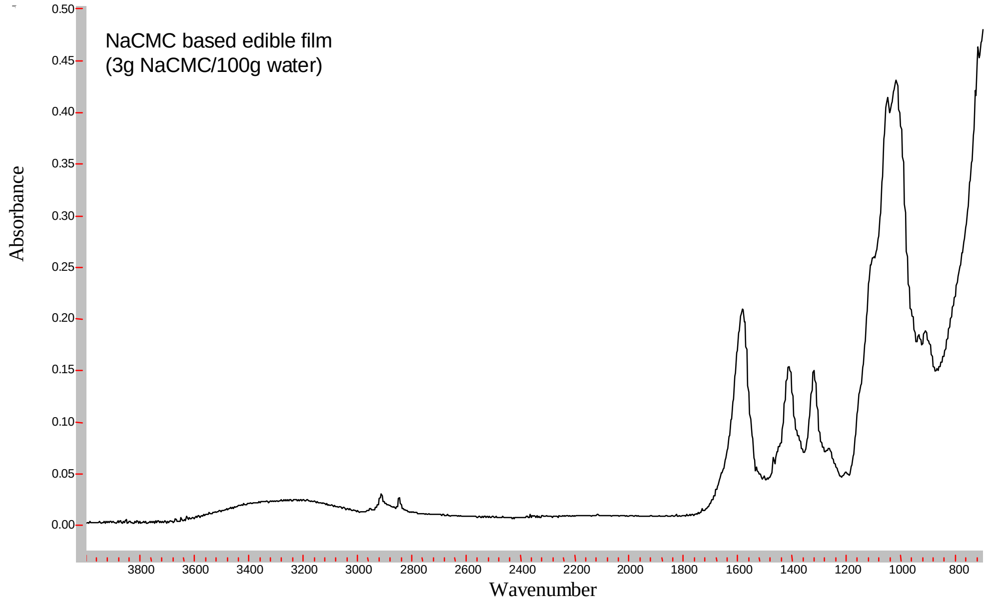


Figure 5.4. IR spectrum of NaCMC based film.

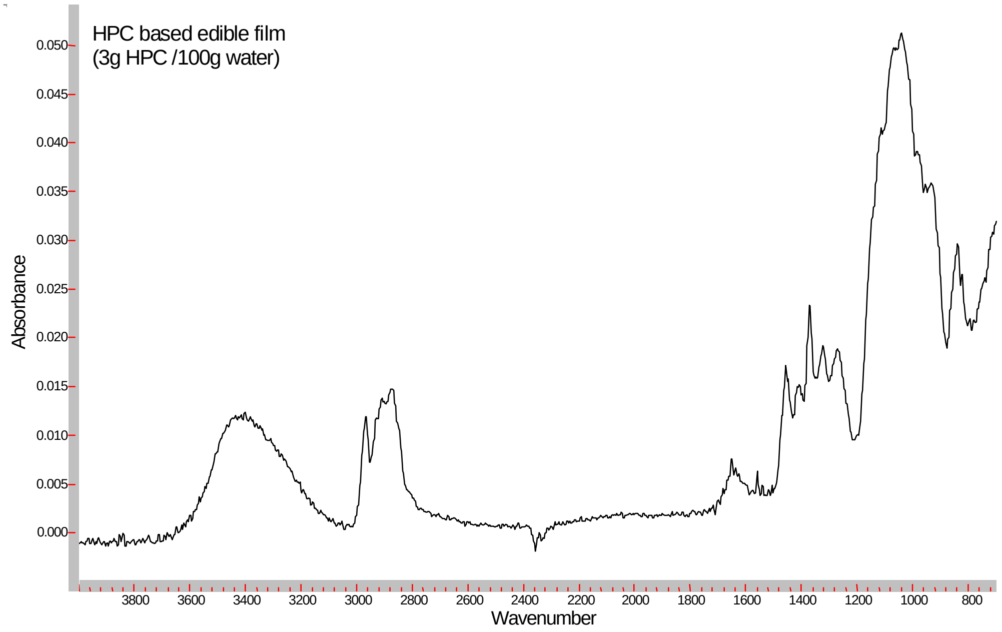


Figure 5.5. IR spectrum of HPC based film.

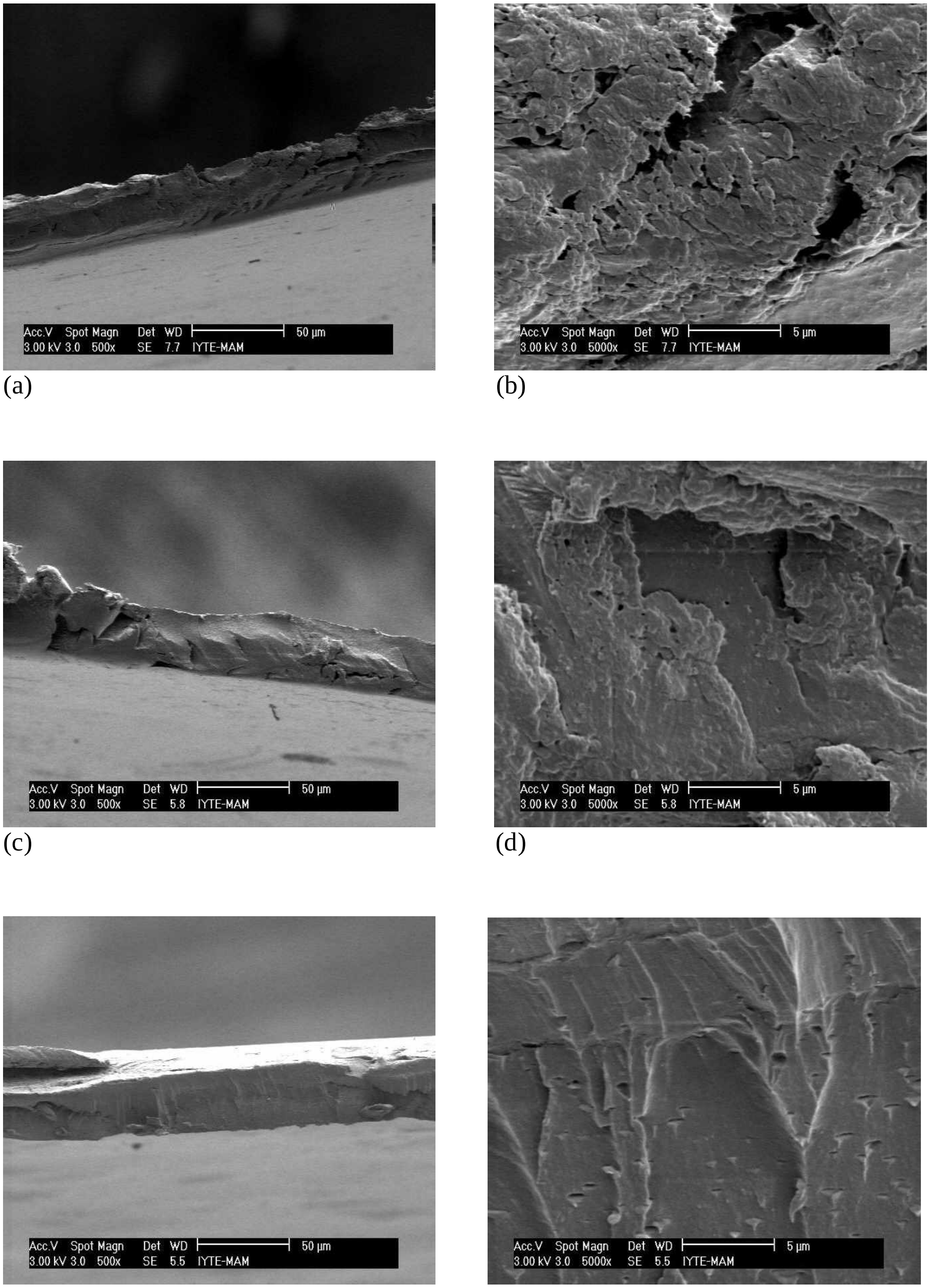
5.2.3. Scanning Electron Microscopy (SEM) and Energy Dispersive X- Ray (EDX) Analysis

Energy Dispersive X-Ray analyses were applied to get information about the main elements of the two different cellulose ether based edible films. HPC and NaCMC based film samples obtained from 3% film forming solutions were analyzed and the results were obtained by taking the average of the values that were randomly selected from 6 different points of film samples. The elemental analysis of the NaCMC and HPC based edible films were shown in Table 5.3. As shown in Table 5.3, NaCMC based edible films contain 8 % Na, with different from HPC based films. From the degree of substitution of NaCMC, theoretical composition was calculated. Experimental carbon (C) content was higher, oxygen (O) and sodium (Na) content was lower than their theoretical values.

Table 5.3. Chemical composition of NaCMC and HPC based edible films in mass %

Elements	NaCMC	Theoretical	HPC
C	53.2 ± 2.1	44	70.1 ± 1.9
O	38.8 ± 2.7	43	29.9 ± 1.9
Na	8 ± 1	12	-

Scanning electron microscopy was used to determine the structure of the NaCMC and HPC based edible films. It can be seen from the Figures 5.6. and 5.7. both NaCMC and HPC based edible films have a porous structure and HPC based edible films have relatively more homogenous porous structure in comparison to NaCMC based edible films. As seen in the cross sectional micrographs of film samples with magnification at 5000; the pore dimensions of NaCMC based films (~3µm) produced from %3 film forming solution were larger than other two NaCMC based films. HPC films contain so many little pores with dimensions of ~0.5-1µm in their homogenous structure. In the study of Biswal and Singh (2004), scanning electron micrographs of powdered CMC, had showed a granular structure.

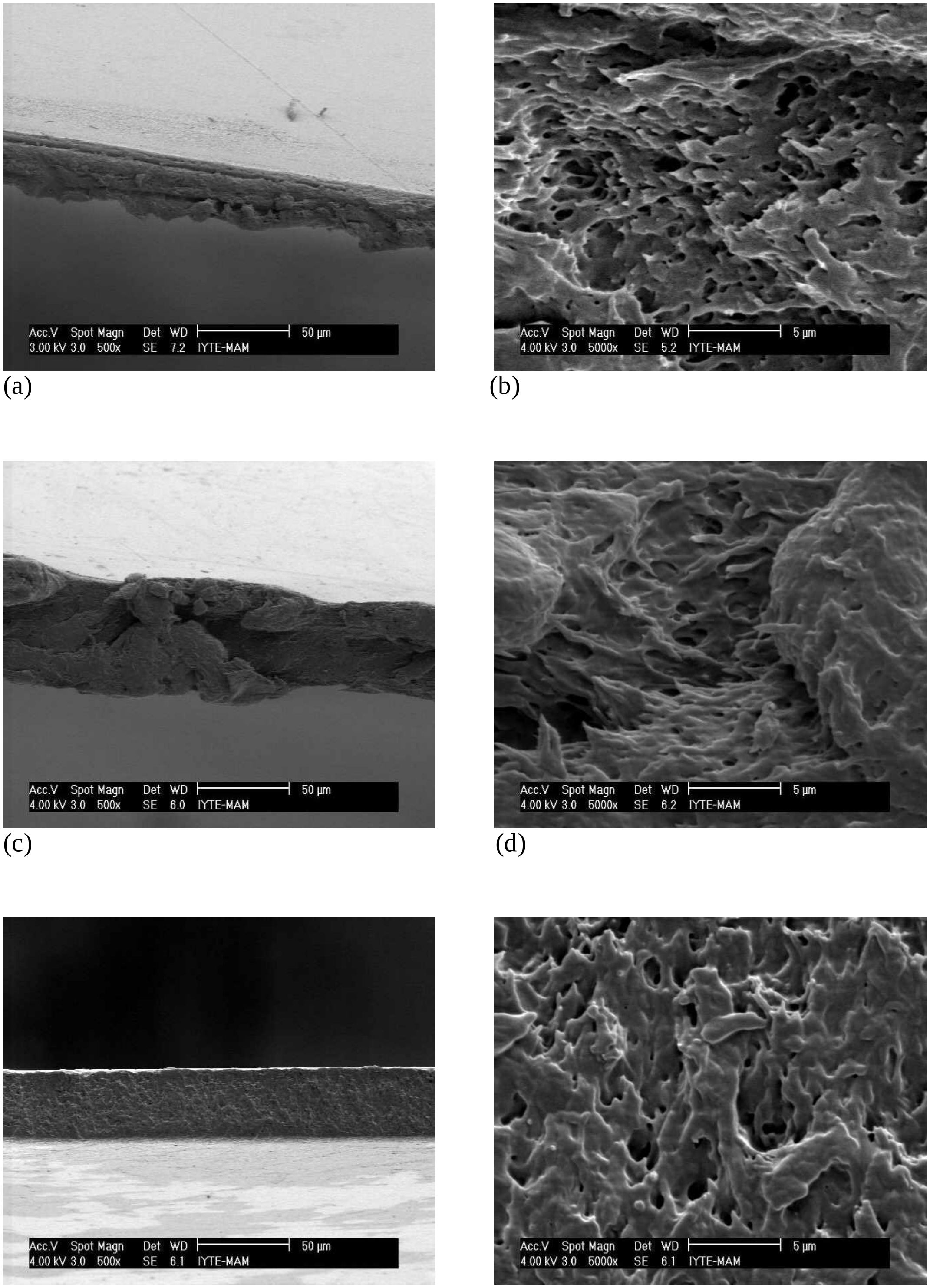


(a) (b)

(c) (d)

(e) (f)

Figure 5.6. Scanning electron micrographs of the NaCMC films obtained from 3% (a) and (b), 4% (c) and (d), 5% (e) and (f) NaCMC solutions (Magnification at 500 and 5000 respectively).



(a) (b)

(c) (d)

(e) (f)

Figure 5.7. Scanning electron micrographs of the HPC films obtained from 3% (a) and (b), 4% (c) and (d), 5% (e) and (f) HPC solutions (Magnification at 500 and 5000 respectively).

5.2.3. X-Ray Diffraction Analysis (XRD)

X-Ray Diffraction (XRD) analyses were applied to confirm the crystallinity of the NaCMC and HPC based edible films. The film forming cellulose ethers NaCMC and HPC in powder form were also analyzed to observe the differences in crystallinity between powder and film forms of these cellulose ethers. Figures 5.8 through 5.11. show the X-ray diffraction diagrams of the HPC and NaCMC in powdered and film forms, respectively. According to the Figure 5.8 and 5.9. it can be seen that HPC show an amorphous structure, there are no changes in the amorphous structure of the HPC between the powder and film form.

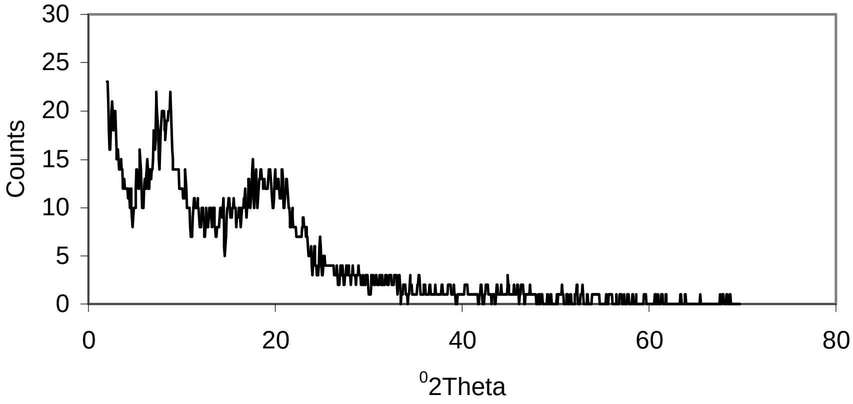


Figure 5.8. X-ray diffraction diagram of the powdered form of the HPC

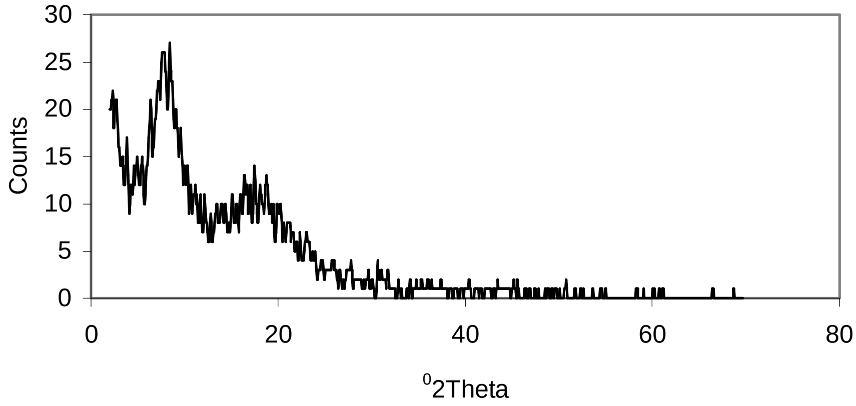


Figure 5.9. X-ray diffraction diagram of the HPC based films

As shown in Figure 5.10. and 5.11. crystallinity of the edible NaCMC based film is different from the powder form of NaCMC. The X-ray analysis of the powdered form of NaCMC polymer shows an amorphous structure. Films form of NaCMC showed crystalline peaks at 2θ = 25.2^0, 16.9^0, 14^0. In the study of Biswal and Singh (2004) powdered form of CMC had showed very small crystallinity against to the results of present study.

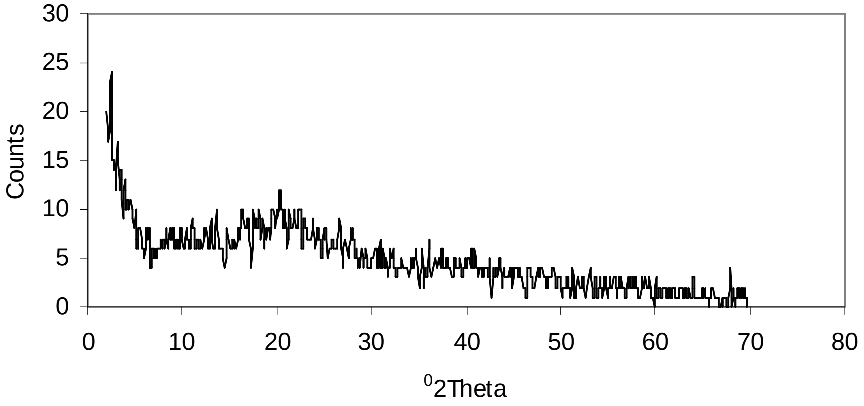


Figure 5.10. X-ray diffraction diagram of the powdered form of NaCMC

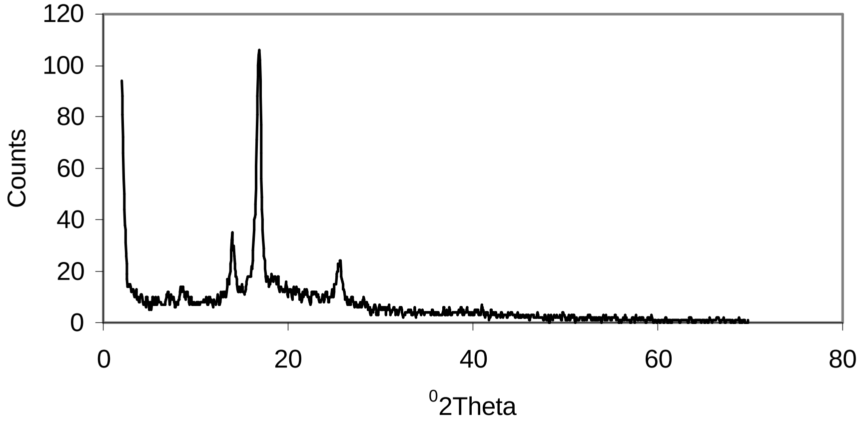


Figure 5.11. X-ray diffraction diagram of the NaCMC based films

5.2.4. Differential Scanning Calorimetric (DSC) Analysis of the Edible Films

Figures 5.12 and 5.13 show the DSC curves of the edible films. The DSC curves of NaCMC based edible films were obtained from 3%, 4%, and 5% polymer solutions were shown in Figure 5.12. As shown in figure DSC curves for all NaCMC based edible films show similar behaviour with each other. An endotherm being maximum between 83-98 ^{0}C were observed due to dehydration and evaporation of water from the films that already above their glass transition temperature. Indeed all films had 10% glycerin to lower their Tg value below room temperature. The DSC analysis results of all NaCMC edible films show similar result with the DSC curve of the CMC which had been studied by the Biswal and Singh, (2000). In this study, CMC had showed a distinct feature in the DSC curve having one endotherm at 76 ^{0}C.

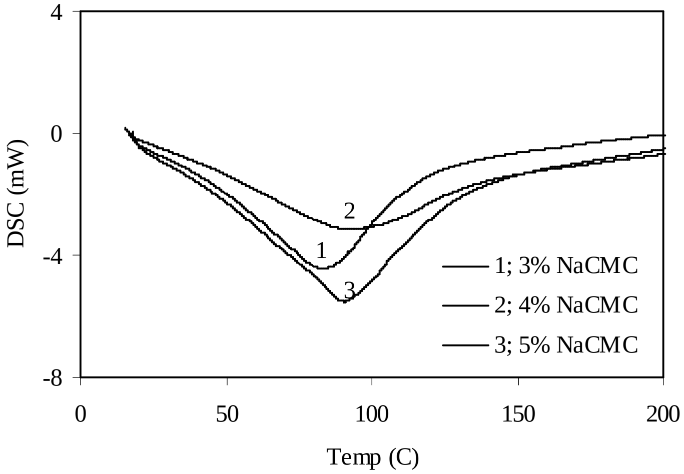


Figure 5.12. DSC curves of NaCMC based edible films from 3%, 4%, 5% solution

The DSC curves of HPC based edible films obtained from 3%, 4%, and 5% polymer solutions are shown in Figure 5.13. All the thermograms show a broad endotherm in the range of 70-85 ^{0}C, corresponding to the loss of residual water.

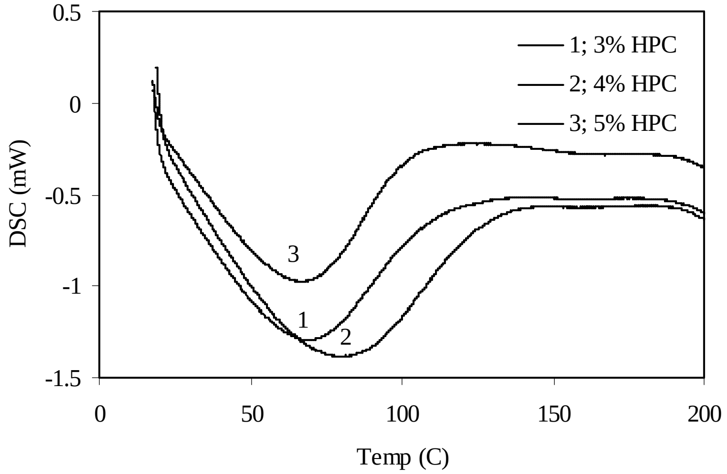


Figure 5.13. DSC curve of HPC based edible films from 3%, 4%, 5% solution

The glass transition phenomena separates materials into two domains according to clear structural and property differences, thus dictating their potential applications. Below glass transition temperature (T_g) the material is rigid, and above it becomes visco-elastic or even liquid (Guilbert et al. 1996). In this study, DSC curves indicated that NaCMC and HPC based films had Tg values that were lower than room temperature. So these samples showed a visco-elastic behaviour in the sorption and desorption experiments.

5.2.5. Thermal Gravimetric Analysis (TGA)

Figure 5.14 shows the TGA curves of the NaCMC and HPC films. The TGA curves of films were obtained from 3% polymer solutions. As shown from Figure 5.14. the analyses starting temperature was nearly 30 ^{0}C for HPC films and 20 ^{0}C for NaCMC films. The weight loss of the HPC film was 3% and the weight loss of the NaCMC film was 15% when the temperature was 200 ^{0}C. Drying of HPC film was completed up to 100 ^{0}C, but NaCMC film continued to dry at 200 ^{0}C.

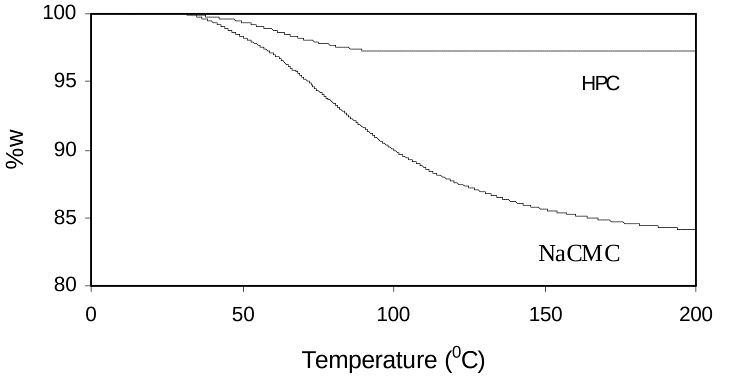


Figure 5.14. TGA curves of NACMC and HPC films from 3% solution

5.3. Sorption Isotherms of Edible Films

The amount of water adsorbed by the edible films greatly influences different properties of these materials, such as their mechanical strength, their mass and their storage stability against microorganisms.

The relationship between water activity (a_w) and the moisture content of films (at constant temperature) was described by moisture sorption isotherms. The equilibrium water content was calculated from an increase in mass of the dried sample after equilibration at a given RH compared to dry sample mass. Figure 5.15. shows the equilibrium water content of the NaCMC and HPC based edible films as a function of water activity at 25^0C and also shows the effect of polymer concentration on the moisture-sorption isotherms of films.

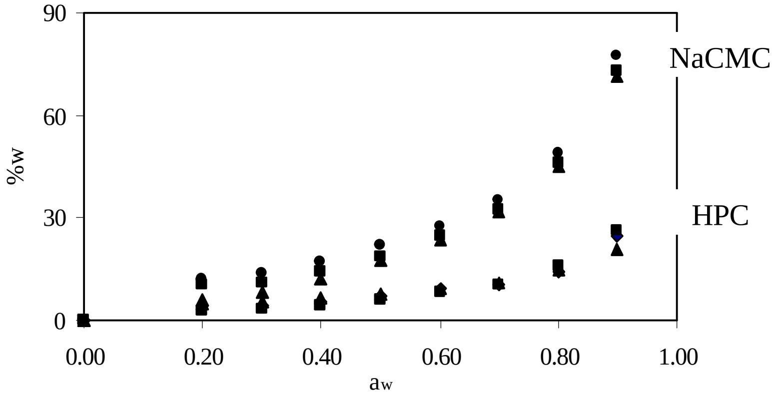


Figure 5.15. Moisture sorption isotherm of NaCMC and HPC based edible films from solution concentrations (   ) % 3; ( ) %4; ( ) %5.

For NaCMC based edible films (Figure 5.15.) it can be seen that their sorption capacity is higher than HPC based edible films. As seen from Figure 5.15. at 90 %RH water vapour sorption capacity of the NaCMC based films was 70 %w, and for HPC films water vapour sorption capacity was 25 %w. For all different HPC solution concentrations, films had same capacity through the 0.7 water activity, above this water activity value sorption capacity of high concentrated films decreased in comparison to low concentrated films and this case is also valid for NaCMC films. The obtained sorption isotherms for HPC based edible films are similar with the sorption isotherm of HPC film at 30^0C in the study of Yano et al. (1998). In their study the sorption isotherm of HPC film (that produced with ethyl alcohol and water solvents) gave typical isotherm for hydrophilic polymers. From 0% RH to about 70% RH, the water regain of HPC films had increased gradually until 70% RH at which point increases sharply, reaching about 28% water gain at 100% RH (see Figure 3.16.).

As evident in Figure 5.15. the sorption curves of HPC and NaCMC based edible films were typical of cellulose films were reported by Gontard et al. (1993). The curves showed a relatively slight slope at a low water activity, with an exponential increase at high water activity (above 0.7) solely due to the higher sorption of water molecules by NaCMC and HPC.

To control the accuracy of the sorption isotherms, Magnetic Suspension Balance was also used to determine the sorption characteristics of the NaCMC and HPC based films. The water activity was calculated with the ratio of column pressure to saturation vapour pressure of water at column temperature. The microbalance tests were applied only films that formed with 3% concentration polymer solution up to 0.8 water activity. The obtained results were shown in Figure 5.16 and Figure 5.17 for NaCMC and HPC films respectively. From these two figures it can be seen that microbalance analysis showed lower sorption values than humidity chamber results above 0.4 water activity. This could be the result of using lower drying temperature (60^0C) in microbalance than that (80^0C) in humidity chamber experiments. As seen in DSC curves (Figure 5.12 and 5.13) of two polymeric films, moisture desorption from the films were not completed at 60^0C. The difference in moisture content of film dried at 60 ^{0}C and 80 ^{0}C were 1% and 3.5 % for HPC and NaCMC films. Thus initial states of the films were different as well as sorption medium in microbalance and humidity chamber. Films in microbalance contained higher amount of moisture initially and sorption and diffusion of water molecules are involved. In humidity chamber sorption of moisture from air occurred.

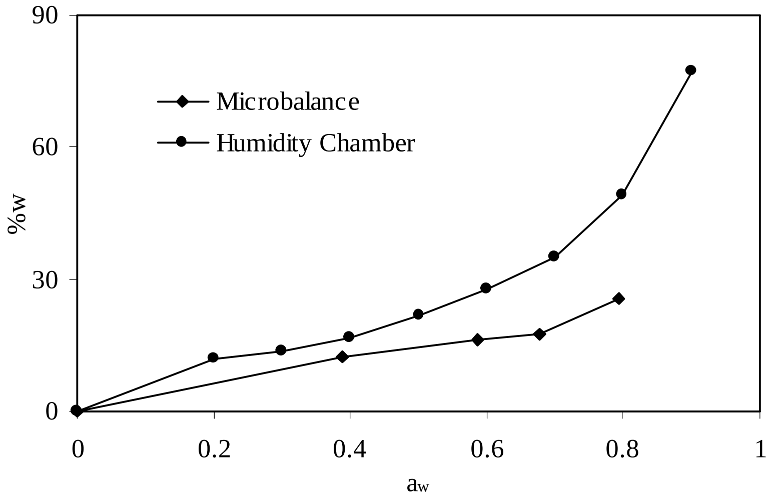


Figure 5.16. Comparison of sorption isotherms of NaCMC films from microbalance and humidity chamber experiments

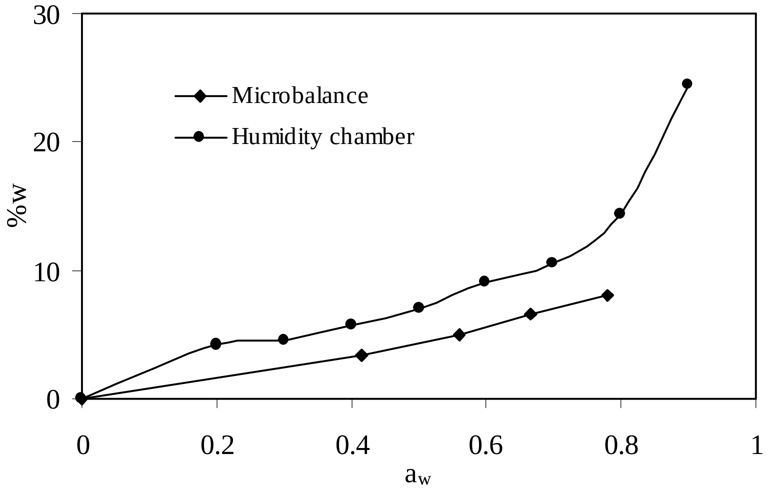


Figure 5.17. Comparison of sorption isotherms of HPC films from microbalance and humidity chamber experiments

Figure 5.18. shows the desorption isotherms of NaCMC and HPC based edible films. From this figure it can be seen that the moisture desorption behaviours of these films show similarities with the moisture sorption isotherms of films.

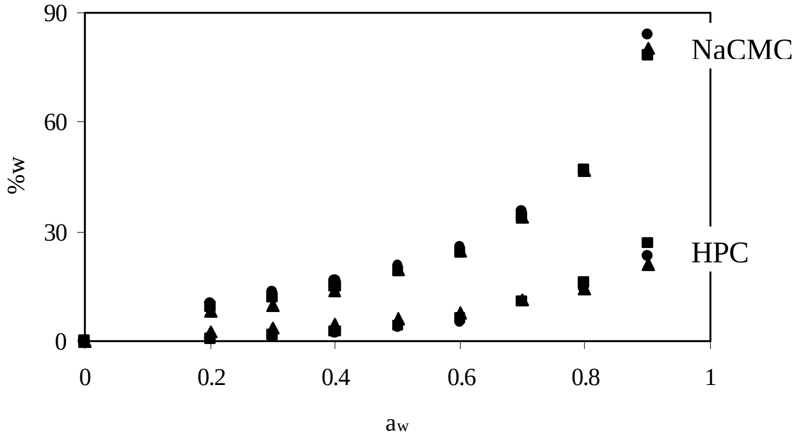


Figure 5.18. Moisture desorption isotherms of NaCMC and HPC based edible films for all solution concentrations (   ) % 3; ( ) %4; ( ) %5.

The comparison of desorption and sorption isotherms of different NaCMC based films which were prepared with 3, 4, 5 percent concentrated solutions are shown in Figures 5.19. - 5.21. respectively. According to the following three figures, it can be seen that desorption isotherms of NaCMC based films were same with the sorption isotherms of 3, 4 and 5% solution concentrated films and there is no hysteresis between desorption and sorption isotherms. It can be seen that, all sorption isotherms of NaCMC films showed Type II isotherm that describes the sorption of water on macroporous solids. The macroporous structures of NaCMC films were also determined in the scanning electron micrographs. The mass uptake (Mt/M) versus $t^{1/2}$ graphs of NaCMC based films (see Figure 5.22.) showed a Fickian sorption behaviour after linear part all sorption curves smoothly reached to a saturation level like in Figure (3.12.). Also overlapping of the sorption and desorption curves indicated the presence of Fickian sorption. This case indicates that the rate of diffusion is significantly slower than the rate of relaxation of the polymer chains. This could be due to the rubbery structure of NaCMC based films that might be observed with sorption above glass transition temperature.

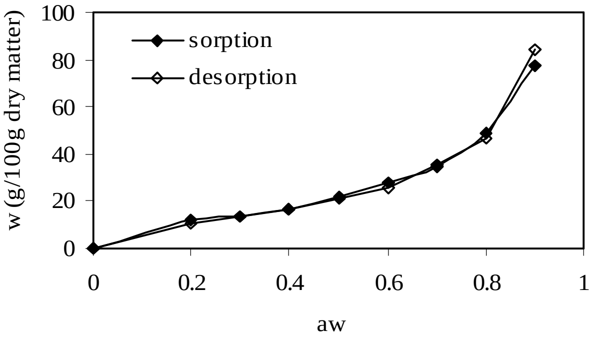


Figure 5.19. Desorption and sorption isotherms of NaCMC based edible film prepared with (3g NaCMC / 100ml water) solution.

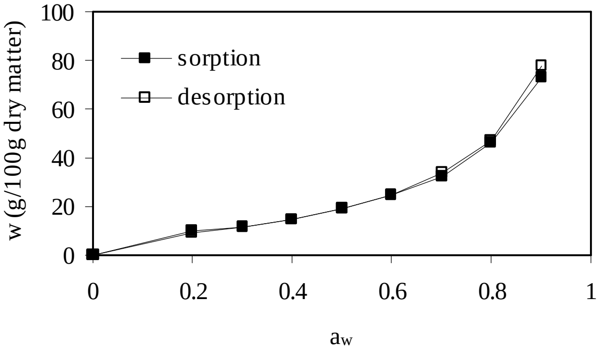


Figure 5.20. Desorption and sorption isotherms of NaCMC based edible film prepared with (4g NaCMC / 100ml water) solution.

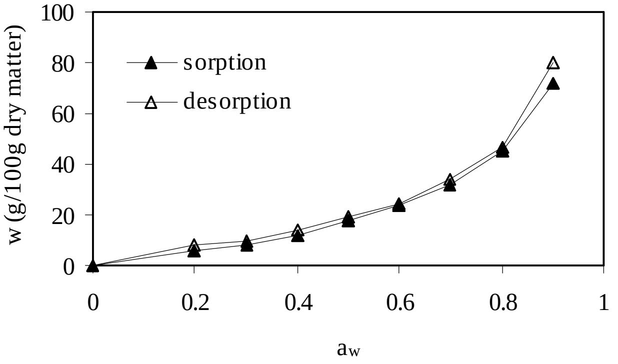


Figure 5.21. Desorption and sorption isotherms of NaCMC based edible film prepared with (5g NaCMC / 100ml water) solution.

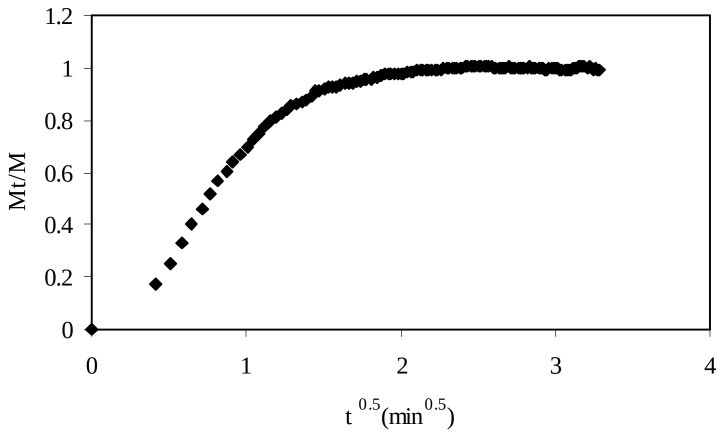


Figure 5.22. Mass uptake curve for NaCMC based film (Microbalance analysis) at 0.4 a_w

The comparison of desorption and sorption isotherms of HPC based films that were prepared from 3, 4, 5 percent concentrated solutions were shown in Figure 5.23., 5.24. and 5.25. respectively. In general, sorption isotherms of HPC films showed Type II sorption isotherm that indicates the macroporous structure of HPC films. Figure 5.26. shows mass uptake curves of the HPC films obtained from microbalance experiment, from this figure it can be seen that HPC based films showed Fickian sorption similar with NaCMC films. When the process is a Fickian, the sorption and desorption isotherms should be overlapped. But in the present study as seen from Figure 5.23. through 5.25. sorption and desorption isotherms did not agree with each other at water activities between 0.2-0.7. At this water activity interval, amount of moisture desorbed from films, were higher than the sorbed moisture amount. This disagreement with the Fickian sorption might be the result of insufficient drying of HPC films before sorption experiment or moisture sorption during transfer of the film from drying oven to humidity chamber.

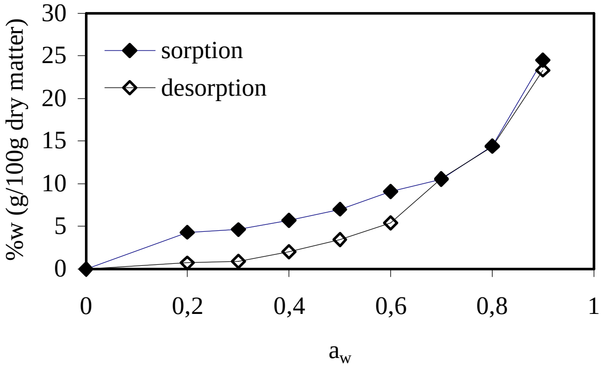


Figure 5.23. Desorption and sorption isotherms of HPC based edible film prepared with (3g HPC / 100ml water) solution.

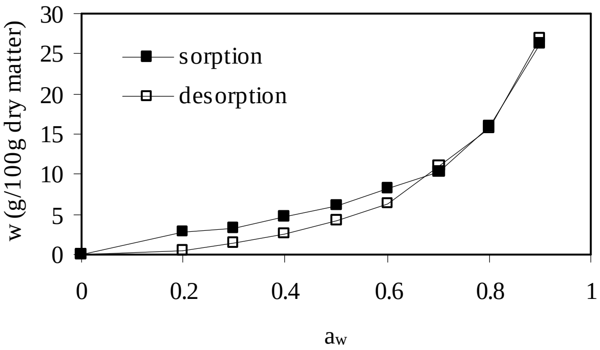


Figure 5.24. Desorption and sorption isotherms of HPC based edible film prepared with (4g HPC / 100ml water) solution.

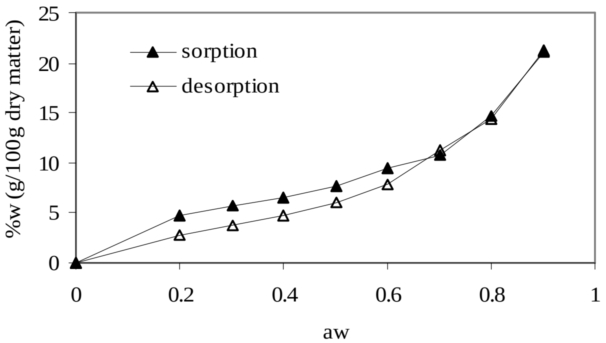


Figure 5.25. Desorption and sorption isotherms of HPC based edible film prepared with (5g HPC / 100ml water) solution.

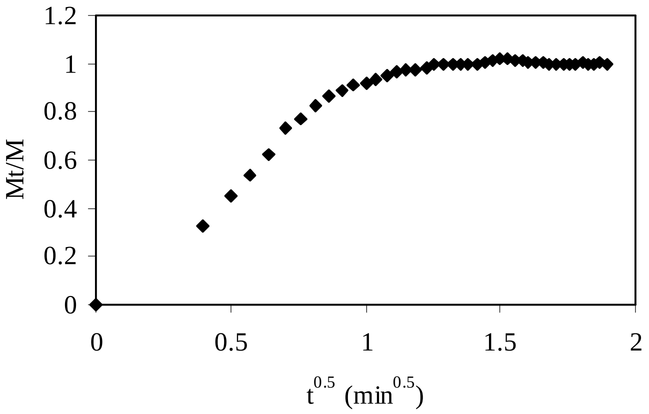


Figure 5.26. Mass uptake curve for HPC based film (Microbalance analysis) at 0.4 a_w

HPC and NaCMC based film samples exposed to various relative humidities showed no DSC melting transitions. All the water sorbed under these conditions is therefore bound to the hydrophilic groups of polymers. However, since DSC provided no information on the topological distribution of the water in these samples, the fraction of moisture present in different zones of the films were estimated by fitting some sorption models. For this purpose BET, GAB, Smith and Halsey models (see Eq. 3.7, 3.8, 3.9, 3.10 respectively) were applied to the sorption isotherms of NaCMC and HPC based edible films. The calculated parameters of the models were used to evaluate the fit of each equation to experimental data (see Table 5.4.). BET and GAB models were applied to data up to 0.6 and 0.9 a_w respectively. Smith and Halsey models were also applied up to 0.9 a_w.

Table 5.4. Optimized values of the parameters of the GAB model of uptake of water vapour

MODEL	Solution concentration	Constants			R^2	SE	MRD
GAB		m_0	C	k			
	%3NaCMC	**12.96**	**10.03**	**0.93**	**0.98**	**0.61**	**-0.0006**
	%4NaCMC	**12.22**	**6.06**	**0.93**	**0.99**	**0.83**	**0.0015**
	%5NaCMC	**17.83**	**1.36**	**0.88**	**1.00**	**1.02**	**-0.0197**
	%3HPC	3.64	77.85	0.95	0.95	0.38	0.0000
	%4HPC	416	4.11	0.94	0.99	0.30	0.0031
	%5HPC	4.33	60.36	0.88	0.97	0.21	0.0004
BET		m_o	C				
	%3NaCMC	11.43	15.65		0.98	0.42	-0.0010
	%4NaCMC	10.19	11.15		0.99	0.57	-0.0016
	%5NaCMC	14.68	1.28		1.00	0.78	-0.0021
	%3HPC	11.43	15.65		0.99	10.85	-1.2340
	%4HPC	10.19	11.15		1.00	9.49	-1.3800
	%5HPC	14.68	1.28		1.00	6.78	-0.4630
Smith		Ma	Mb				
	%3NaCMC	31.28	1.08		0.93	2.96	0.0230
	%4NaCMC	30.35	-0.84		0.98	2.93	0.0290
	%5NaCMC	32.03	-4.81		0.99	1.88	0.0430
Halsey		A	B				
	%3HPC	**1.71**	**-0.65**		**0.99**	**0.04**	**-0.0002**
	%4HPC	**1.46**	**-0.84**		**0.99**	**0.07**	**-0.0040**
	%5HPC	**1.84**	**-0.55**		**1.00**	**0.02**	**-0.0002**

In the study of Alvarez-Lorenzo et al. (2000) Young Nelson and GAB models had been applied to fit the sorption isotherm data of powdered HPC samples. And according to the r^2 values of the models they concluded that Young-Nelson model was the most suitable. The calculated GAB parameters for HPC films (m_0, C, k) were not same with the parameters that found in the study of Alvarez-Lorenzo et al. (2000) that were shown in Table 3.4. In the present study, as seen from the Table 5.4. together with r^2 values, standard error (SE) and mean relative deviation (MRD) values were also calculated to measure the accuracy of the r^2 values. High r^2 value gives information about the suitability of the model, but besides high r^2 values, low SE and MRD (<0.5) values should be obtained to determine best fit model. As a result of the calculations (see Table 5.4.) Halsey model were chosen as the most suitable model for sorption isotherms of HPC films. For NaCMC films GAB model were determined as the best fit model. Experimental data and sorption isotherms predicted for the HPC and NaCMC based films are shown in Figure 5.27. and Figure 5.28. respectively.

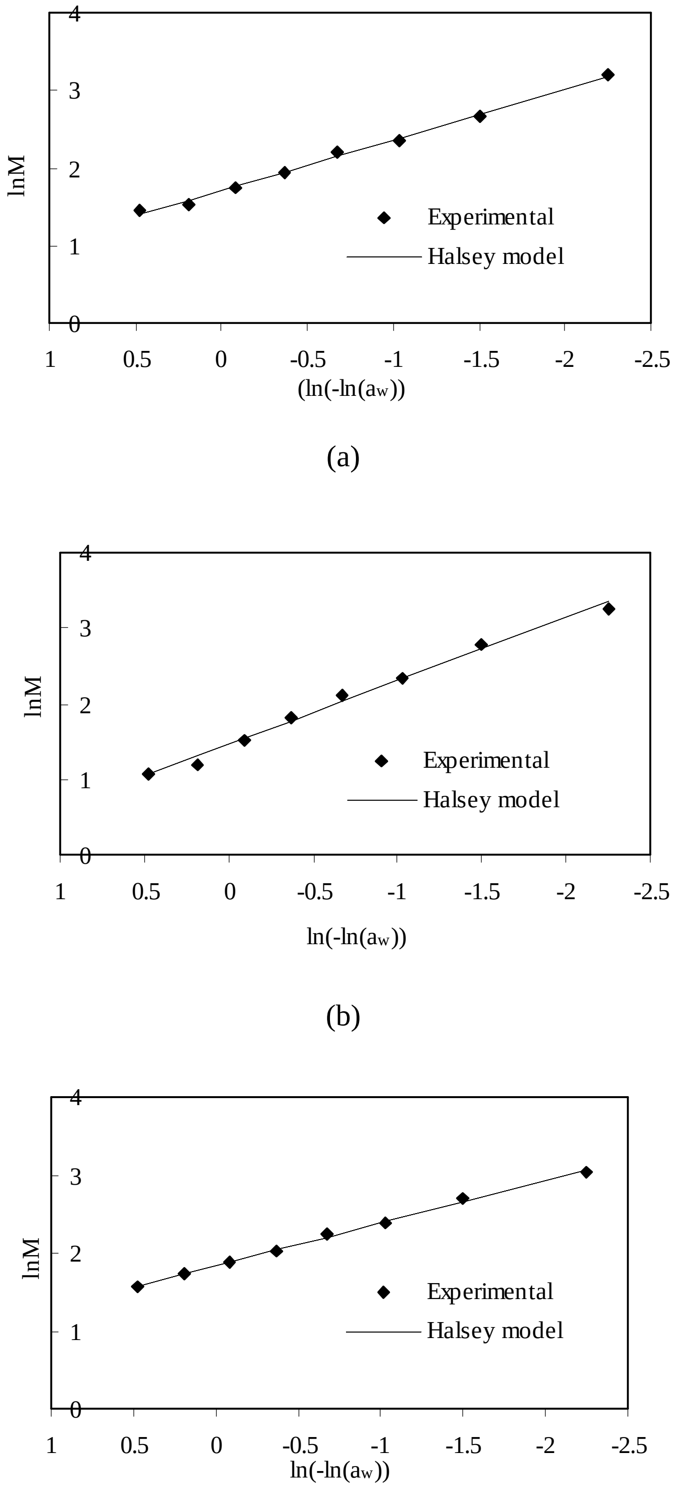
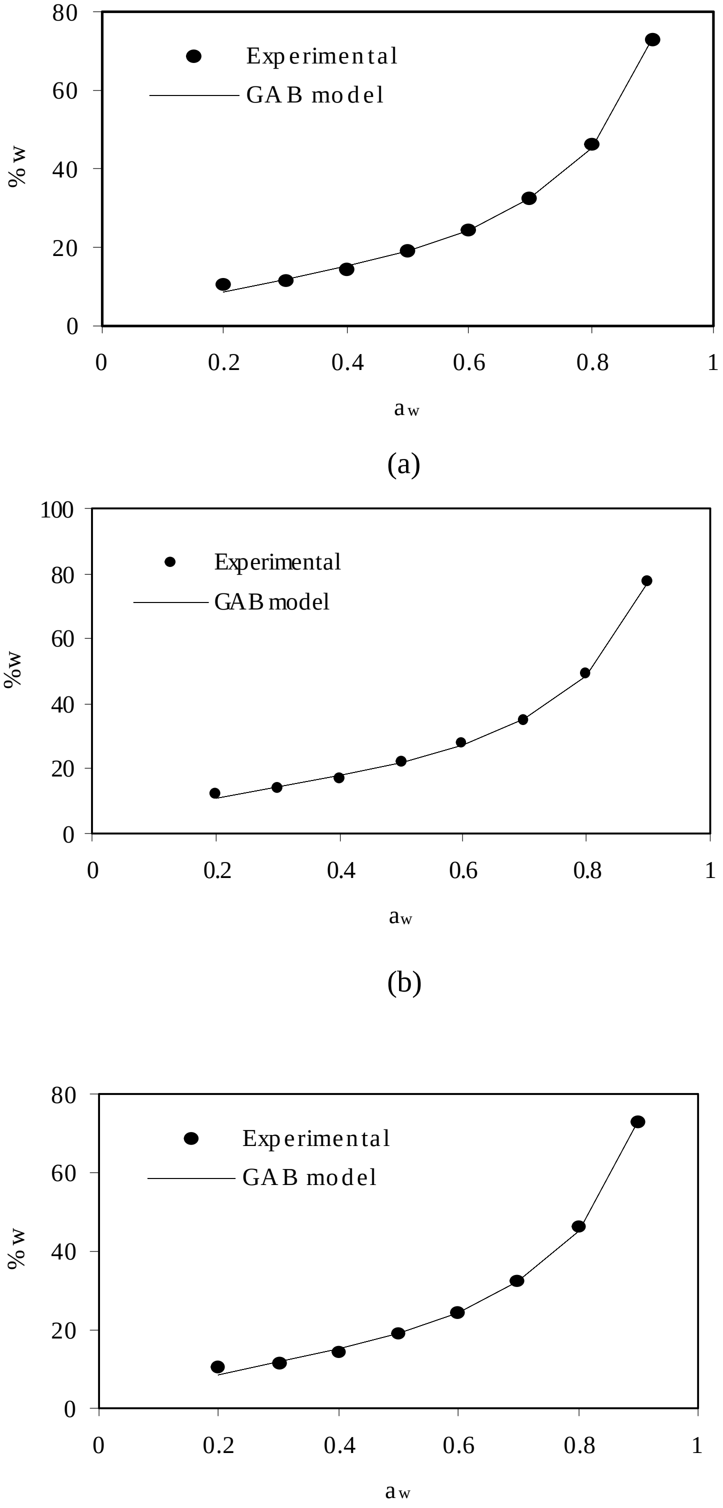


Figure 5.27. Experimental and predicted sorption values of HPC films with Halsey model. (a), (b), (c) indicates films with 3, 4, 5% solution concentrations respectively.



(a)

(b)

(c)

Figure 5.28. Experimental and predicted sorption values of NaCMC films with GAB model. (a), (b), (c) indicates films with 3, 4, 5% solution concentrations respectively.

5.4. Water Vapour Diffusion in Films

The effective diffusivities of water vapour through the both NaCMC and HPC based edible films have been determined from the humidity chamber and microbalance sorption data by using Equation 3.14. This model relies on the diffusion through a slab for a short time, i.e. Mt/M < 0.5 experiments.

The diffusion coefficients were obtained from plots of Mt/M against $t^{1/2}$ for the initial period of water sorption for NaCMC and HPC based films which solution concentration of 3% polymer.

Table 5.5. and 5.6. show the diffusion coefficients of water vapour in films during sorption and desorption measurements in humidity chamber.

Table 5.5. Diffusion coefficients of water vapour in NaCMC and HPC films for sorption, reported as $\ln(Dx10^{14}m^2s^{-1})$.

Relative Humidity	%3 NaCMC	%4 NaCMC	%5 NaCMC	%3 HPC	%4 HPC	%5 HPC
20	1.07	5.62	3.78	5.62	3.78	2.14
30	2.02	2.41	2.97	2.41	2.97	1.93
40	0.81	2.15	2.77	2.15	2.77	2.01
50	1.47	2.39	3.29	2.39	3.29	2.01
60	2.25	3.31	4.11	3.31	4.11	2.36
70	2.09	3.50	4.31	3.50	4.31	2.08
80	1.52	2.87	3.85	2.87	3.85	2.59
90	1.74	3.27	4.09	3.27	4.09	3.47

Table 5.6. Diffusion coefficients of water vapour in NaCMC and HPC films for desorption , reported as $\ln(Dx10^{14}m^2s^{-1})$.

Relative Humidity	%3 NaCMC	%4 NaCMC	%5 NaCMC	%3 HPC	%4 HPC	%5 HPC
90	0.94	2.42	2.06	2.42	2.06	1.77
80	0.79	2.28	2.00	2.28	2.00	1.28
70	1.84	2.98	2.59	2.98	2.59	0.96
60	0.77	2.26	1.90	2.26	1.90	1.10
50	1.90	3.67	2.65	3.67	2.65	2.40
40	1.21	3.20	2.89	3.20	2.89	1.07
30	1.23	2.97	2.35	2.97	2.35	0.70
20	1.38	2.87	2.31	2.87	2.31	2.30

Figure 5.29 and 5.30 show the relationship between diffusion coefficient results of HPC and NaCMC films in sorption measurements. Both films show similar results for different solution concentrations. Figure 5.31 and 5.32 show diffusion coefficients in NaCMC and HPC film samples in desorption experiments. These two graphs indicate that both films have similar diffusion coefficient values.

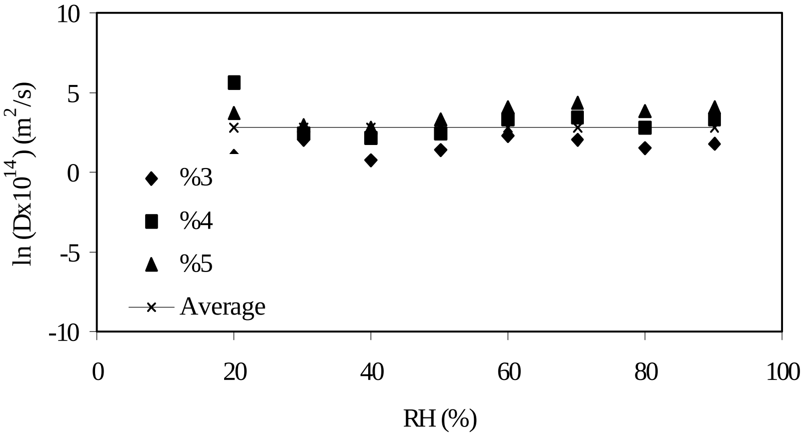


Figure 5.29. Diffusion coefficient results of NaCMC films in sorption measurements.

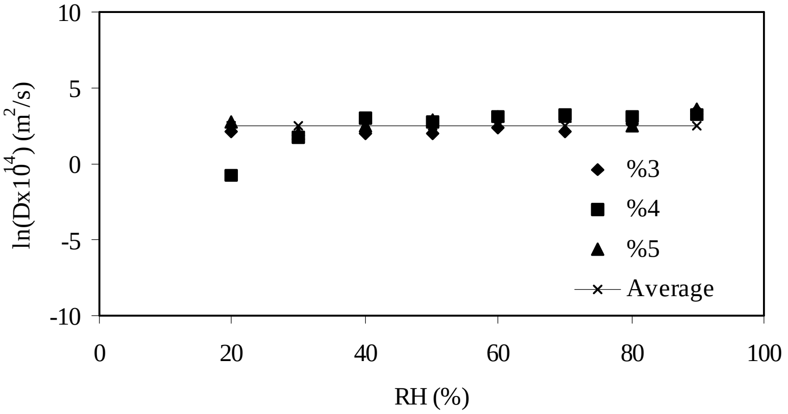


Figure 5.30. Diffusion coefficient results of HPC films in sorption measurements.

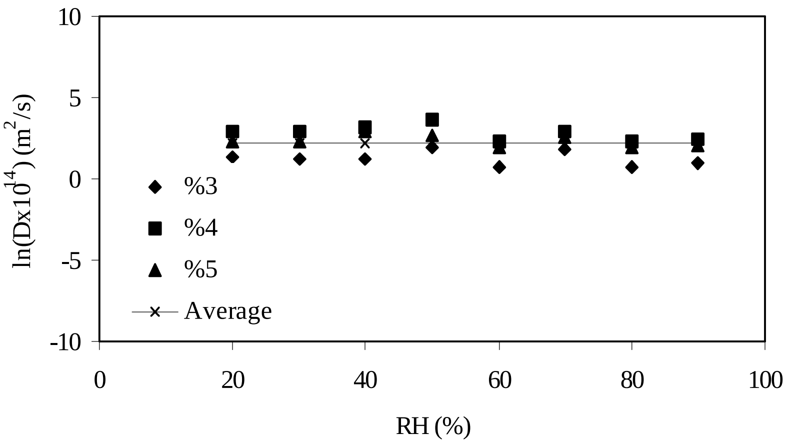


Figure 5.31. Diffusion coefficient results of NaCMC films in desorption measurements

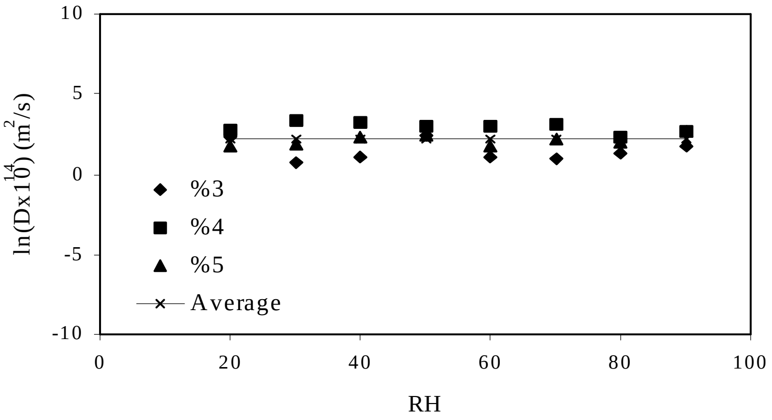


Figure 5.32. Diffusion coefficient results of HPC films in desorption measurements

Diffusion coefficients of water vapour in NaCMC and HPC films varied with relative humidity around an average value. The average values of diffusion coefficients from sorption data were greater than desorption data while the diffusion coefficient for NaCMC and HPC films were 1.66x10^{-13} m^{2}s^{-1} and 1.25x10^{-13} m^{2}s^{-1} from sorption data and were 0.85x10^{-13} m^{2}s^{-1} and 0.87x10^{-13} m^{2}s^{-1} from desorption data. If no structural changes occurred during sorption and Fickian diffusion occurred same diffusion coefficients would not be obtained from sorption and desorption data

Figure 5.33. and Figure 5.34. show Mt/M versus $t^{1/2}/l$ graph of microbalance and humidity chamber results for NaCMC and HPC films at 40 % relative humidity. While the relative humidity changed from 0 to 40 % in microbalance, it changed from 30 to 40 in humidity chamber. Faster diffusion occurred in microbalance.

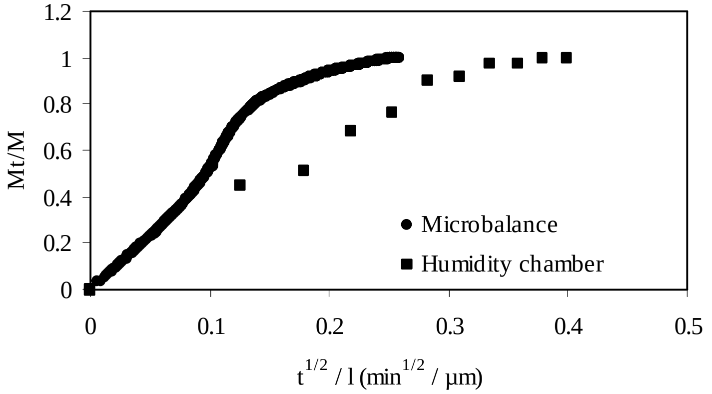


Figure 5.33. The mass uptake (Mt/M) versus $t^{1/2}$ / l graph for NaCMC based films (with 3% solution concentration)

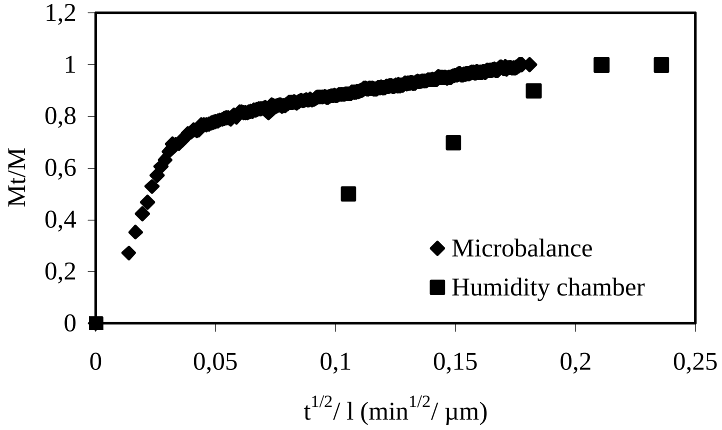


Figure 5.34. The mass uptake (Mt/M) vs $t^{1/2}$ / l graph for HPC based films (with 3% solution concentration

In figure 5.35. and 5.36, mass uptake versus square root of time for microbalance tests are seen. From the initial slopes, D values were found.

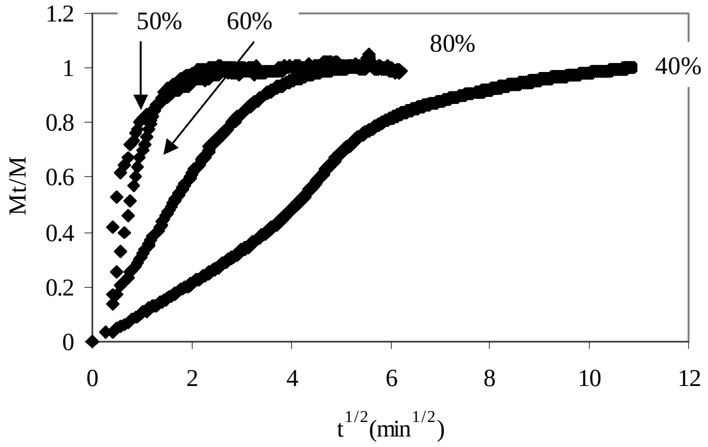


Figure 5.35. Mass uptake curves of NaCMC film that obtained from 3 % solution concentration in microbalance at different relative humidity values.

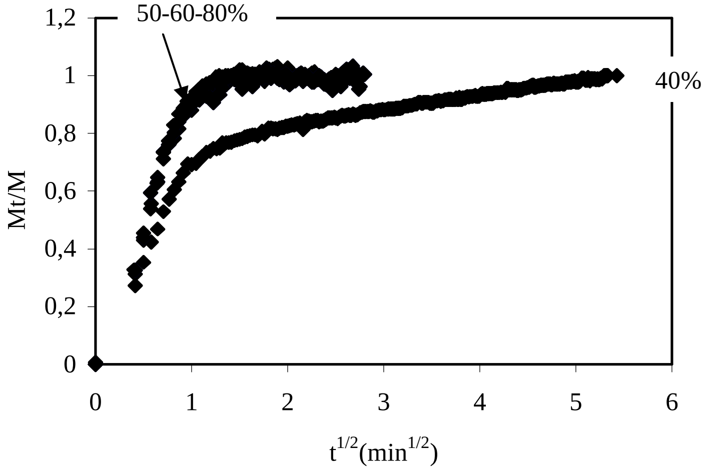


Figure 5.36. Mass uptake curves of HPC film that obtained from 3 % solution concentration in microbalance at different relative humidity values.

Table 5.7 shows the diffusion coefficients of water vapour in NaCMC and HPC films in microbalance and humidity chamber.

Table 5.7. Diffusion Coefficients for NaCMC and HPC based edible films prepared from 3 % solution concentration.

Film type	RH (%)	Humidity Chamber $D \times 10^{14}$ (m^2/s)	Microbalance $D \times 10^{14}$ (m^2/s)
NaCMC	20	2.9	-
	30	7.5	-
	40	2.2	7.4
	50	4.4	-
	60	9.5	275
	70	8	818
	80	4.6	87.6
	90	5.7	-
HPC	20	8.5	-
	30	6.9	-
	40	7.4	165
	50	7.5	-
	60	11	283
	70	4	241
	80	13	235
	90	32	-

The calculated results show that (Table 5.7.) humidity chamber and microbalance results are not same with each other. These differences may be result of the differences in the measurement conditions. During humidity chamber analysis, film samples reach to equilibrium moisture content for 10-15 minutes. But in microbalance measurements equilibrium moisture value of films were obtained in very short times e.g. between 0.5-1 minutes. Fast drying in high vacuum causes the drying of the swollen films without finding time to shrink. Thus more porous structure could be obtained in microbalance experiments thus diffusion coefficients were found higher than humidity chamber. HPC based edible films showed higher diffusion coefficient values than NaCMC based films. This can be result of the presence of high number of pores in the structure of HPC films that was showed in the scanning electron micrographs. Or plasticization tends to facilitate diffusion, since rubbery polymers entail higher diffusion coefficients than glassy polymers. This result may be due to the highly presence non-freezing water that a water is strongly bound to the polar groups in the polymer. This strongly bound water is an important plasticizer in highly hydrophilic polymers and causes a transition from glass to rubber to occur upon water absorption and rubbery polymers entail higher diffusion coefficients than glassy polymers. In NaCMC film diffusion coefficient value at 70 %RH was 818 m^2s^{-1} but at 80 %RH was 87.6 m^2s^{-1} for microbalance experiment. The decrease of diffusion coefficient may be due to the clustering of water in film structure at high relative humidity.

5.5. Water Vapour Permeability Analysis of Edible Films

Water vapour permeability studies were carried out to measure the water vapour barrier efficiencies of the films. Water has a deteriorative effect on foods, so water vapour barrier property of edible films is an important factor in the packaging area.

Permeability values of water vapour were calculated from the slope of linear portion of ln $[(P_{lL} - P_{lui})/(P_{lL} - P_{lu(t)})]$ vs time (Eq. 3.25) graph (see Figure 5.37.) and from the sorption-diffusion mechanism P=D.S (Eq. 3.26), the results were compared in Table 5.8. Solubility (S) values of the film were found by approximately and calculated from Equation 5.1. Using experimental adsorption isotherms diffusion (D) values were found from the lag time values of permeation tests and by calculated by using Equation 5.2. Lag time is defined as the time to start of increase of relative humidity.

$$S = c/p \qquad (\text{gmol/cm}^3\text{kPa}) \qquad (5.1)$$

where c is the concentration of permeant, p is the vapour pressure of the permeant. When the relationship between c and p becomes linear, S is referred to as Henry's law solubility coefficient than sorption isotherms (Miller and Krochta 1997).

$$D = h^2/6t \qquad (\text{m}^2/\text{s}) \qquad (5.2)$$

where h is the thickness of the film and t is the lag time (Park 1986). It was assumed that the upper part of the permeation cell was completely dry, so it contained very low amount of moisture.

Actually, the sorption isotherm were not linear they fitted to GAB model for NaCMC and HPC films. Thus an approximation to linear isotherm data up to 0.7 water activity was made for application of solution and diffusion model.

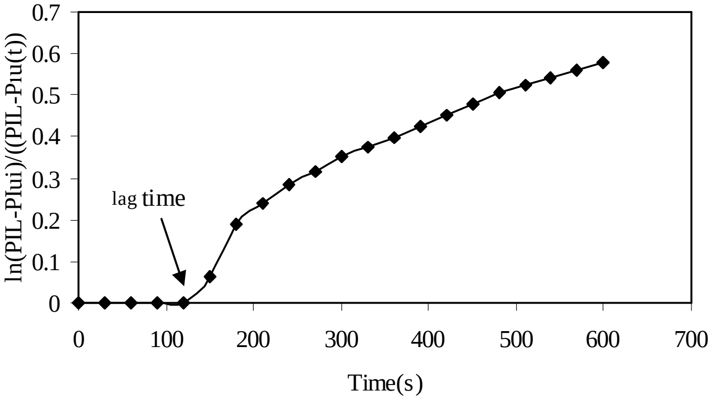


Figure 5.37. Linear portion of permeability graph of HPC film with a solution 3% concentration as a function of time. (See Appendix A.1. for other WVP graphs)

Table 5.8. Comparison of water vapour permeability values of NaCMC and HPC based edible films

Concentration of polymer solution (%)	Solubility (S)	Diffusion coeff. (D)	P = D x S	P = LxVxs / RxAxT
NaCMC	(gmolH_2O/cm^3.kPa) x10^3	(m^2/s) x10^{12}	(g.molH_2O/s.cm.kPa) x10^{10}	(g.molH_2O/s.cm.kPa) x10^{10}
3	14 ± 2	0.89 ± 0.4	1.32 ± 0.53	0.058 ± 0.02
4	13 ± 0.7	2.57 ± 0.9	3.44 ± 1.35	0.098 ± 0.012
5	13 ± 0.6	3.27 ± 0.6	4.12 ± 0.65	0.12 ± 0.0003
HPC				
3	4 ± 0.4	0.2 ± 0.02	0.14 ± 0.035	0.033 ± 0.0011
4	4.8 ± 0.4	0.93 ± 0.4	0.44 ± 0.17	0.049 ± 0.0056
5	5.5 ± 0.3	1.57 ± 0.8	0.83 ± 0.39	0.056 ± 0.0087

The differences between water vapour permeability values of NaCMC and HPC films may be the result of the porous structure of films. The transfer of water may occur by diffusion and solution mechanism and on the same time by the migration from the holes in films. Water has high solubility and cluster formation property within the polymer and tendency to plasticize the polymer matrix. Natural polymers are characterized by extensive water clustering and plasticization of their matrix, properties regarded as important shortcomings in packaging applications (Arvanitoyannis and Biliaderis 1999).

Permeability values from Equation 3.25 were much lower than the predicted by solution diffusion model (Eq. 3.26.) indicating non-linear permeation behaviour. While Equation 3.26 could be applied to initial period of permeation, Equation 3.25 covers a longer period. The differences between pressures of two sides of the film decreases with time thus permeation rates decreases. The scanning electron micrographs of the films in Figure 5.6. and Figure 5.7. indicated the presence of pores of ~3μm and ~0.5-1μm size for NaCMC and HPC films respectively. The experimental permeability values of HPC film prepared from ethyl alcohol and water reported by Park et al. (1993) was 0.059 ± 0.0037 ng.m/m^2.s.Pa or $3.3x10^{-11}$ g.molH_2O/s.cm.kPa was nearly 5 fold higher than that of the prepared film in the present study. This difference could be attributed the different morphologies of film prepared from alcohol-water solution. The WVP values of both NaCMC and HPC films were 10^5 times lower than the MC based edible films that were reported by Turhan and Şahbaz (2003).

Figure 5.38. shows the experimental water vapour permeability values of films as a function of thickness. From this figure it can be seen that WVP values of NaCMC and HPC based films increased with increasing thickness. Same WVP behaviour had been observed for polysaccharide based edible films in the study of Aydınlı and Tutaş, (2000). This case can be result of the increasing hydrophilicity of the films with increasing thickness due to non-linear nature of sorption isotherms. Permeation of water vapour is a dynamic process. Water vapour spends longer time in thick films causing closer approach to equilibrium moisture level. Thus thick films have higher moisture content and have higher solubility value. According to the Miller and Krochta (1993), increasing of water vapour permeability with increasing thickness can depend on the ionic structure of polymers. Since NaCMC is an ionic polymer, water vapour permeability values of these films are high. But in the study of Park et al. (1993), no thickness dependence was observed for HPC films.

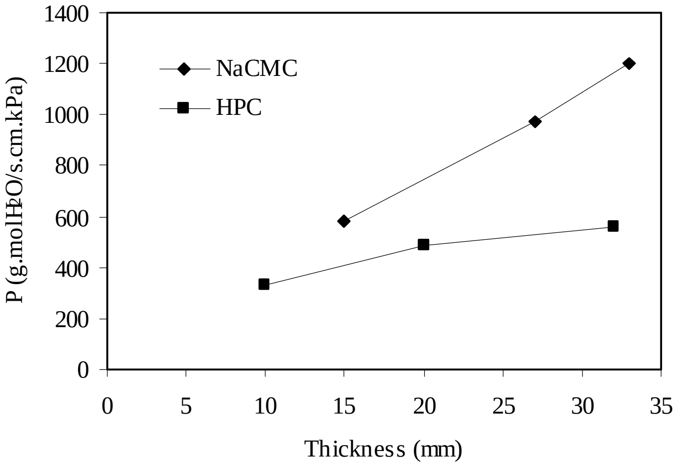


Figure 5.38. Water vapour permeability values of films as a function of thickness.

Figures 5.39. shows the WVP at 30^{0}C for HPC and NaCMC based edible films as a function of film forming solution concentration. It displays a different behaviour between two polymers, the WVP through NaCMC based films are 5-10 times higher than through HPC based edible films (1.32x10^{-14} and 0.14x10^{-14} g.molH$_2$O/s.cm.kPa respectively). (See Table 5.8.). Therefore HPC based films were better moisture barriers than NaCMC based films. This can be due to the hydrophilicity, (high level of hydrophilicity increases the WVP) and probably to the different crystalline structure of the two polymers. The mass transfer of water vapour in a semi-crystalline polymer is primarily a function of the amorphous phase, because the crystalline phase is usually assumed to be impermeable (Miller and Krochta, 1997). High crystalline structure may provide more dense and compact structure which contains less free volume for water molecule migrations, so WVP decrease. This case is not valid for HPC, because it has low crystalline structure and the experimental results showed that their WVP property is low, compared to NaCMC based films. A straightforward relationship between polar groups and solubility is not feasible because of the complexity of interactions and inherent difficulties in assessing factors such as accessibility of polar groups, the relative strength of water-water versus the water-polymer bonds and crystallite size, shape and degree of crystallinity of the polymer matrix affect the water vapour permeability property of the polymers. The lower solubility and lower diffusion coefficients of water vapour in HPC films than NaCMC resulted lower WVP values in HPC films. The crystalline fraction of NaCMC was not expected to be effected by water vapour.

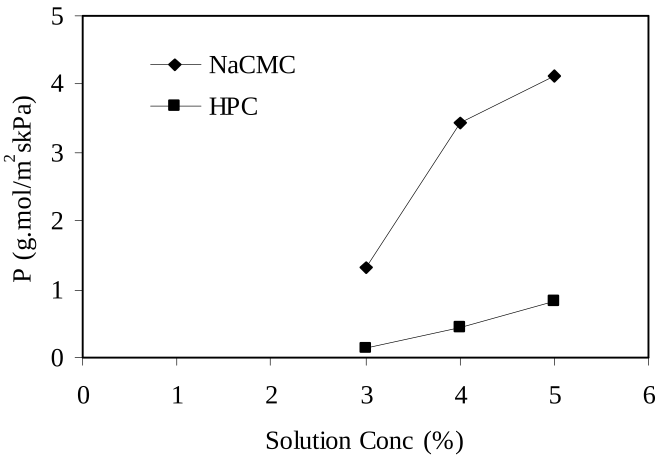


Figure 5.39. Water vapour permeability values of films as a function of solution concentrations

5.6. Mechanical Properties of Edible Films

Mechanical properties of films were evaluated to determine the physical resistance and flexibility of the films. The mechanical properties of films can give information about the function, stability or shelf life of the films as packaging material. Table 5.9. and Figure 5.40. give a general information about mechanical properties of prepared edible films by showing some mechanical properties,

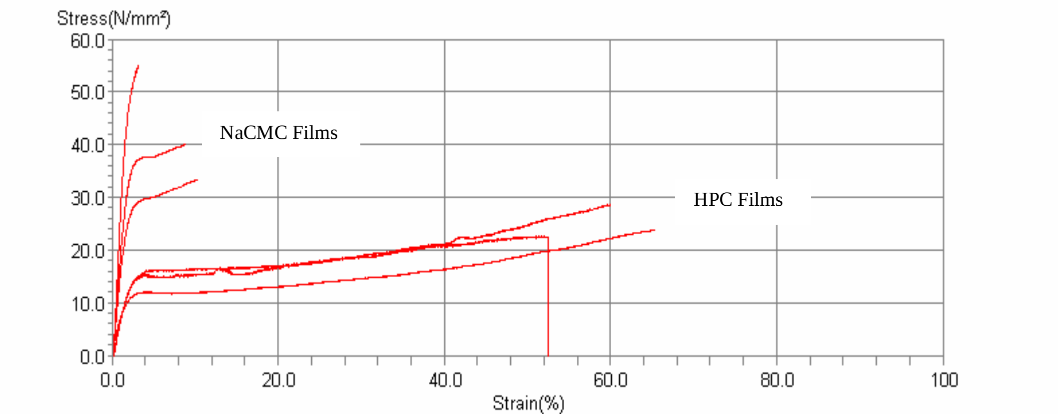


Figure 5.40. Stress-strain curves of HPC and NaCMC based edible films

Table 5.9. Mechanical properties of NaCMC and HPC films

Solution Conc. (%)	Yield Stress (MPa)	Yield Strain (%)	Young Modulus (MPa)	Stress at Break (MPa)	Strain at Break (%)
NaCMC					
3	68 ±12	4.4 ±1.8	3329 ±334	68 ±12	4.4 ±1.8
4	38.9 ±4.5	5.5 ±1.7	2282 ±228	39 ±4	7 ±1.6
5	33 ±4.4	7.8 ±2.6	1827 ±260	35 ±3.6	10 ±2.5
HPC					
3	15.5 ±1.8	3.8 ±0.9	729 ±88	15.5 ±0.7	58 ±21
4	10.4 ±4.6	3.5 ±1.8	487 ±213	13 ±15.45	82 ±20
5	8.7 ±2.8	4.5 ±0.5	399 ±117	8.5 ±13	91 ±20

As a sum of the all graphs; Figure 5.40. shows clearly the mechanical property differences of NaCMC and HPC based edible films. According to this figure it can be easily seen that, NaCMC based films had higher yield stress value, so they were more stronger films than HPC based films. On the other hand, yield strain values of HPC based edible films were higher than NaCMC films, so these films were more elastic, than NaCMC based films. In the study of Yano et al. (1998), the stress versus strain curve of the HPC based film had been evaluated. In their study, the stress at yield value had nearly 6 MPa, and strain at yield value had found approximately 5%. These results shows similarities with the results of HPC based films in the present study. In the study of Tharanathan (2003) tensile strength and elongation of HPC films (Mw = 370.000) were reported as 15.32 MPa and 204 % respectively. On the other hand in the present study similar stress at break (tensile stress) values around 8.5 – 15.5 MPa but lower strain at break (elongation) 58-91% were obtained for HPC films with same molecular weight in the present study.

The tensile strength values of both polymeric film samples were very low as a packaging material. So strength of these films was too low compared to other packaging materials. However these cellulosic films can be used to protect the food from the environment by covering the food or to increase the shelf life of the food by decreasing the respiration rate or can be used to prevent the water or molecule migration from the food, etc. So the lower tensile strength values should not be negative parameter for these films to be used as a packaging material. Figures 5.41. through 5.44. show the mechanical behavior of the films as a function of film forming solution concentrations. As seen from Figure 5.41. as the concentration of film forming solutions increased, tensile strength of the NaCMC based films decreased and elongation of these films increased due to an increase in overall porosity of the films. NaCMC films that were prepared from low concentrated solution had high tensile strength, high young modulus (see Figure 5.45.) and low elongation values, so these low concentrated films had strong and stiff structure but showed less elasticity (brittle structure). Increase of elongation values with the increasing solution concentration made films ductile at high concentration values.

The mechanical properties of HPC based edible films showed similar behaviours with NaCMC based edible films with respect to the solution concentration (see Figure 5.42.).

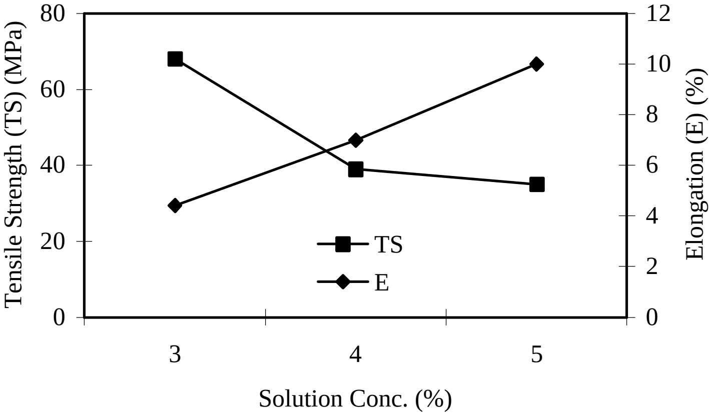


Figure 5.41. Effect of solution concentration on mechanical properties (TS and E) of NaCMC based edible films

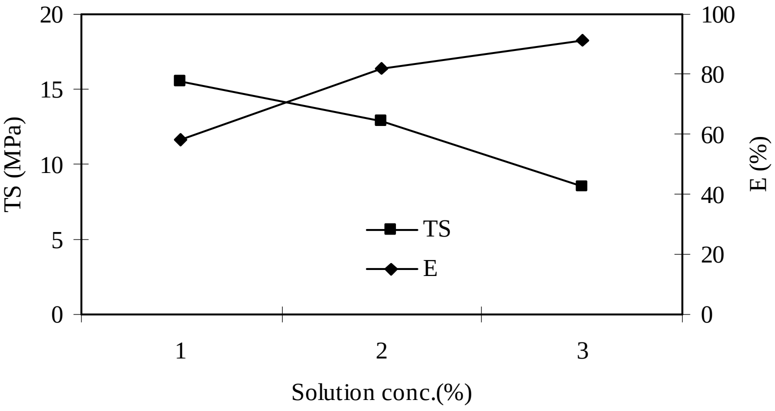


Figure 5.42. Effect of solution concentration on mechanical properties (TS and E) of HPC based edible films

Tensile strength of NaCMC and HPC based edible films are shown in Figure 5.43. From this figure it can be seen that TS of NaCMC based edible films were higher than HPC based films, so NaCMC based edible films were stronger than HPC films. The low tensile strength property of HPC based edible films could be result of the homogenous and more porous structure of the films.

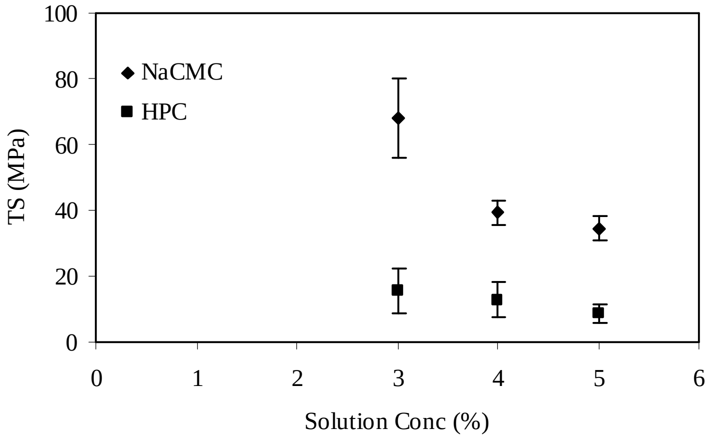


Figure 5.43. Effect of solution concentration on tensile strength (TS) of the edible films

Elongation of NaCMC and HPC based edible films were shown in Figure 5.44. Elongation of the HPC based films were higher than the NaCMC based films, so it can be concluded that HPC polymers produce more elastic films. High elongation of the HPC based films could be result of the thermoplastic and porous structure of the HPC films. Increases in %E mainly occur when films become rubbery, i.e., when structure changes from ductile to elastic (Turhan and Şahbaz, 2003). On the other hand the high elongation at break of the HPC film in the present study was due to plastic deformation after yield.

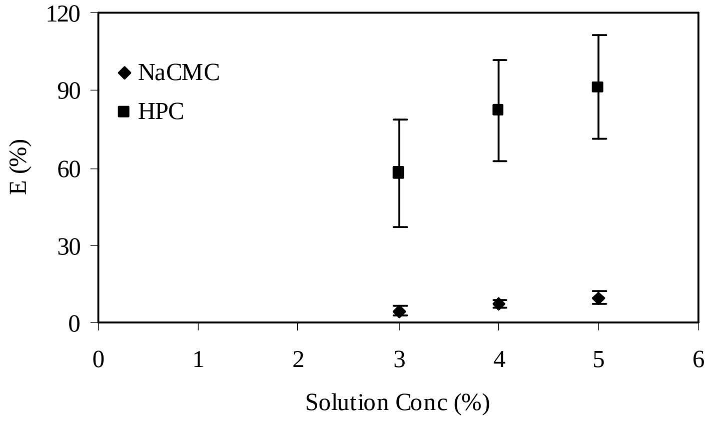


Figure 5.44. Effect of solution concentration on elongation (E) of the edible films

High viscosity of high concentration films causes difficulties in removing entrapped air bubbles by vacuum application. Thus film with higher porosity formed with increasing solution concentration. Higher porosity decreases tensile strength and increases elongation of the films

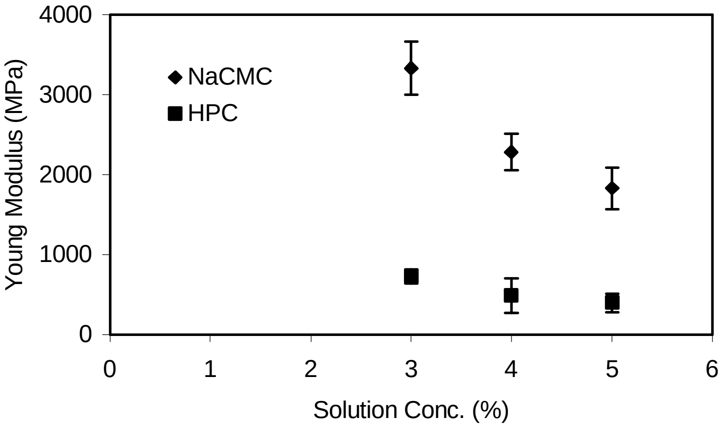


Figure 5.45. Effect of solution concentration on Young Modulus of films

Young modulus values gives information about the stiffness of the films. Figure 5.45. shows the young modulus values of NaCMC and HPC films as a function of solution concentration. According to Figure 5.45. NaCMC based edible films showed more stiffness than HPC films. Lower young modulus of HPC film indicated their more elastic behaviour.

CHAPTER 6

CONCLUSIONS

In this study, polysaccharide based edible films were obtained and characterized using some characterization analysis to obtain information about the packaging properties of these films. Water vapour sorption, diffusion and permeability characteristics of these films were also studied. Cellulose ethers; Sodium carboxymethylcellulose (NaCMC) and Hydroxypropyl cellulose (HPC) were used as edible film forming materials, distilled water and glycerin were used as solvent and plasticizer, respectively.

Viscosities of film forming solutions were determined for the effects flow behaviour on the film formation properties. As a result of the viscosity measurements, both NaCMC and HPC based film forming solutions with a concentration of 4% and 5% showed non-Newtonian flow behaviour such as pseudo plastic due to the decreasing of viscosity with increasing shear rate. On the other hand, the dilute solutions (3%) of HPC and NaCMC showed a Newtonian fluid behaviour because viscosity remained constant as the shear rate varied.

According to the EDX analysis, NaCMC based edible films contained 8 % Na, different from HPC based films. Scanning electron microscopy was used to determine the structure of the NaCMC and HPC based edible films. HPC based edible films had high porosity with homogenous dispersion but NaCMC based edible films showed lower porosity. The amount and volume of pores can affect the mechanical and permeability properties of the films. Actually during the mechanical property measurements of films HPC based edible films showed high elongation and low tensile strength that could be due to the its high porosity. Based on X-Ray diffraction, it was observed that the powder and film form of HPC have an amorphous structure. While powder form of NaCMC showed and amorphous structure, film form of NaCMC had low crystallinity. Differential scanning calorimetry indicated that, there was an endotherm being maximum between 83-98 ^{0}C for NaCMC films and 70-85 ^{0}C for HPC films due to dehydration and evaporation of water from the films that are above their glass transition temperature (Tg). Indeed all films had 10% glycerin as plasticizer to lower their Tg value below room temperature.

Water vapour sorption characteristics of NaCMC and HPC films were determined with sorption and desorption analysis in microbalance and humidity chamber at 25 ^{0}C. Microbalance was used to control the accuracy of the sorption isotherm analysis. Microbalance analysis showed lower sorption values than humidity chamber results above 0.4 water activity. These differences might be the result of the different drying temperature that used 60^{0}C in microbalance and 80^{0}C in humidity chamber experiments. According to the both sorption experiments water vapour sorption capacity of the NaCMC based films (70%w) was higher than HPC based films (25%w).

GAB, BET, Halsey and Smith models were applied to fit the water vapour sorption data. GAB and Halsey models were found to give the best fit with NaCMC and HPC films

The diffusion coefficients of water in film were obtained from plots of Mt/M against $t^{1/2}$ for the initial period of water sorption for NaCMC and HPC based films which solution concentration was 3% polymer. Diffusivities of water vapour through the films were studied by comparing the diffusion coefficients found by the humidity chamber and microbalance tests. Diffusion coefficient of the films determined in microbalance test were higher than that of the ones determined in humidity chamber. This case could be result of the structural changes of films like formation of porous structure in microbalance due to the fast drying of films by high vacuum and slow relaxation of the polymer. NaCMC based edible films showed higher diffusion coefficient values than HPC based films, due to the heterogeneous structure and bigger pore dimensions of the NaCMC films with a solution concentration of 3% polymer.

Water vapour permeability properties of films were evaluated as a function of solution concentration, film thickness and type of polymer of the films. Water vapour permeability data showed that WVP of both films increased with increasing thickness and increasing film forming solution concentration. WVP values of NaCMC based films were measured to be higher than the WVP values of HPC films.

Mechanical property experiments indicated that, NaCMC films have stronger and stiff structure in comparison to HPC films due to the high tensile strength and young modulus values. However HPC films showed more elastic structure compared to

NaCMC films was brittle with low elongation at break values.

As a conclusion of all studies, NaCMC and HPC are good polymers to produce films and each of them can produce films with different properties. Edible sodium carboxymethylcellulose polymer can produce films with high water vapour sorption capacities, and low water vapour barrier properties, also these films have good mechanical properties such as high strength and stiff structure. On the other hand edible hydroxypropylcellulose polymer can produce films that have lower water vapour sorption capacity, with a high water vapour barrier ability and high elasticity. For both types of films; different film forming solution concentrations caused the formation of films with similar properties with each other.

Future work about these two edible films should be related with the gas permeability measurement of films or application of these films to the food, food products and pharmaceutical products to evaluate the effects of these films on some quality characteristics of foods such as texture, microbial activation, freshness, shelf life and controlled release of drugs.

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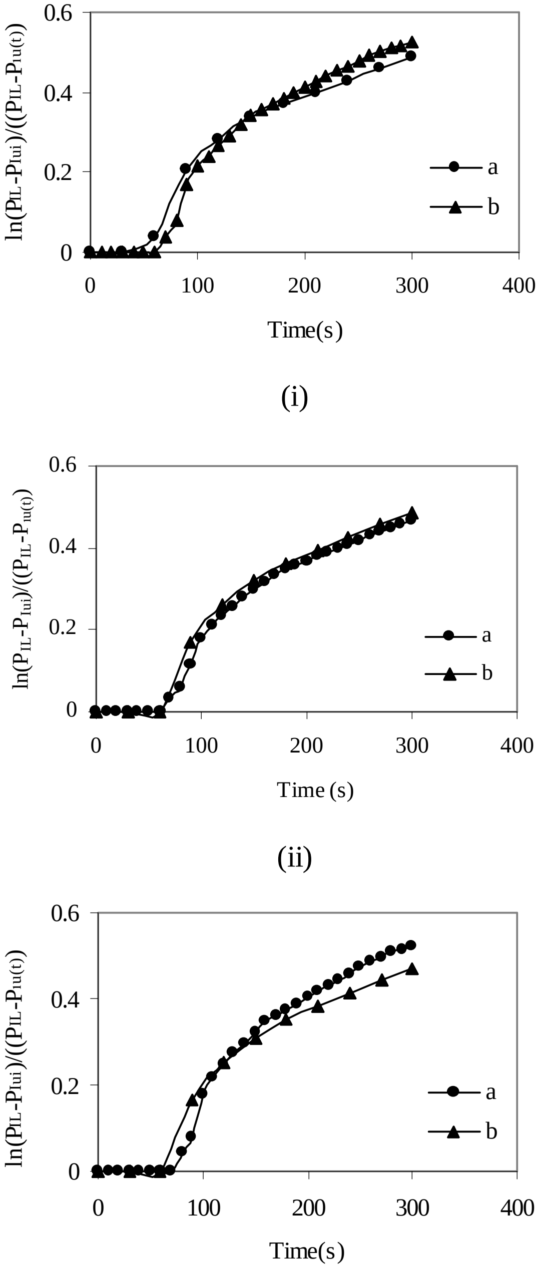
APPENDIX

A.1. Linear portion of permeability graphs

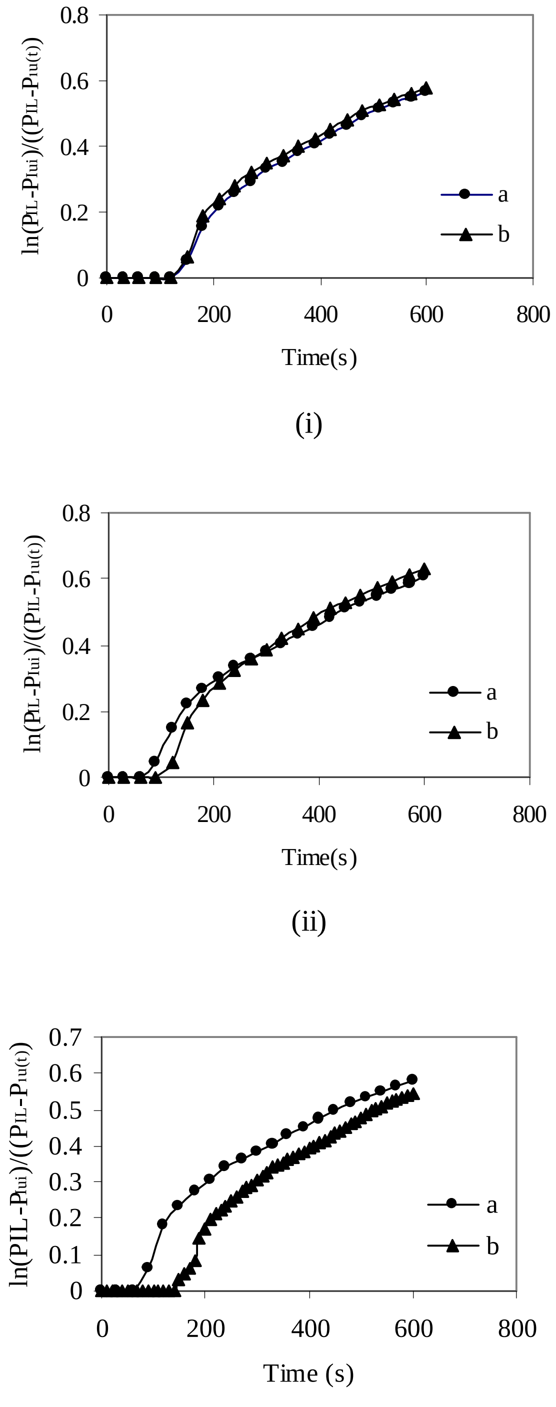


(i)

(ii)

(iii)

Figure A.1. Linear portion of permeability graph of NaCMC based edible films with solution concentration (i) 3%, (ii) 4%, (iii) 5%. (a and b represent the parallel studies)



(i)

(ii)

(iii)

Figure A.2. Linear portion of permeability graph of HPC based edible films with solution concentration (i) 3%, (ii) 4%, (iii) 5%. (a and b represent the parallel studies)