MANUFACTURING A NEW PROTECTIVE POLYETHYLENE BASED FILM CONTAINING ZEOLITES FOR PACKAGING OF FOOD

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This is to certify that we have read this thesis and that in our opinion it is fully adequate, in scope and quality, as a thesis for the degree of Doctor of Philosophy.

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ABSTRACT

MANUFACTURING A NEW PROTECTIVE POLYETHYLENE BASED FILM

CONTAINING ZEOLITES FOR PACKAGING OF FOODS

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The main objective of the study was to manufacture a zeolite containing new polymer based packaging film and test it for the permeabilities of oxygen, carbondioxide and water vapor.

For the manufacture of a polyethylene film containing zeolite particles six different manufacturing methods; hot pressing, adding zeolite to molten polyethylene and dissolved polyethylene solution, coating polyethylene beads with zeolite in a druggie pan, extrusion of polyethylene bead with zeolite and hot pressing of the extruded mix film were tried. For each method three different particle sizes of zeolite 53, 106 and 212μ, prepared by grinding the one received from Bigadiç mine of Etibank, were used. Of the films obtained by the six manufacturing methods used, the film produced by the last one being successful, was subjected to permeability tests for the selected gases.

As the first set of measurements the permeabilities for water vapor were determined. For water vapor transmission rates, a direct relationship between temperature and the rates were observed with increased temperature for all films. In addition, the the permeabilities of the produced films were between the permeability of polyethylene and permeability of FH film.

As the second set of measurements the permeabilities for oxygen and carbondioxide were determined. The ratio of the carbondioxide to oxygen permeabilities for these films increased with increasing zeolite particle size.

Key words : Packaging film, Polyethylene, Zeolite, Gas Permeability

ÖZ

GIDALARIN PAKETLENMESİ İÇİN ZEOLİT İÇEREN POLİETİLEN ESASLI BİR PAKETLEME MALZEMESİNİN ÜRETİLMESİ

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Bu çalışmanın ana amacı polimer esaslı bir paketleme malzemesi üretmek ve üretilen malzemeyi oksijen, karbondioksit ve su buharı geçirgenliği yönünden denemektir.

Zeolit parçacıkları içeren, kabul edilebilir bir filim üretilmesi için altı farklı üretim yöntemi denenmiştir. Bu yöntemler sıcak baskı, zeolitin eritilmiş polietilene katılması, zeolitin çözünmüş polietilen çözeltisine katılması, polietilen boncukların draje makinesinde zeolitle kaplanması, zeolit kaplı polietilen boncukların sıcak çektirilmesi ve bu bileşik filmin tekrar sıcak basılmasıdır. Bu yöntemler denenirken Etibank Bigadiç İşletmelerinden sağlanan madenden hazırlanmış 53, 106 ve 212μ büyüklüğünde elenmiş olan zeolit örnekleri kullanılmıştır. Denenen altı yöntem içinde zeolit kaplı polietilen boncukların sıcak çektirilmesi ve bileşik filmin sıcak basılması yöntemi en başarılı olmuş ve seçilen gazlara karşı geçirgenliği ölçülmüştür.

Ölçümlerin ilk bölümünde su buharına karşı geçirgenlikler ölçülmüştür. Su buharı geçiş hızı denemelerinde tüm filimler için geçiş hızı ve sıcaklık arasında doğrusal ilişki bulunmuştur. Ayrıca, üretilen filimlerin geçitgenlikleri polietilen filim ve FH filim geçirgenlik değerleri arasında olmuştur.

Ölçümlerin ikinci bölümünde oksijen ve karbondioksit gazlarına karşı geçirgenlik değeri hesaplanmıştır. Karbondioksit geçirgenliğinin oksijen geçirgenliğine oranının zeolitin parçacık büyüklüğü ile arttığı gözlenmiştir.

Anahtar kelimeler : Paketleme malzemesi, Polietilen, Zeolit, Gaz Geçirgenliği

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TABLE OF CONTENTS

CHAPTER

LIST OF TABLES

TABLES

LIST OF FIGURES

FIGURE

CHAPTER I

INTRODUCTION AND SPECIFIC OBJECTIVES

I. 1. INTRODUCTION

Fresh fruits and vegetables harvested seasonally in high amounts from different areas are mostly stored in suitable environments until marketed and consumed. During storage and transportation, the conditions for well maintanance should be practised since fresh fruit and vegetables are living systems and very sensitive to detoriative effects.

Among the chemical, biological and physical methods of preservation, physical methods are the most convenient due to causing least change in the properties of the produce.This complies with the recent studies in food science which aimed to minimize the processing so that the food resembles its natural features to the maximum extent. In this aspect, for food processing modified atmosphere (MA) and controlled atmosphere (CA) storage and packaging are especially important for fresh produce.

Packaging a food product is an operation aimed to prevent most of the possible kinds of degradation that render it unsuitable for consumption or of a lower sensorial value. Stability of a packaged foodstuff greatly depends on the characteristics of the packaging material and proper conditions of harvesting, storage and distribution (Mathlouthli and Leiris,1990).

It has been estimated that about one-third to a half of the fresh produce grown around the world is spoiled before it is consumed. This can be prevented by extending shelf life of fresh produce by packaging. As a feature of proper packaging in a sealed package a fresh product creates a modified atmosphere by respiratory gas exchange and gas permeation through the packaging material. In addition to providing and maintanining MA, packaging leads to ease of handling, improved sanitation by reducing contamination, protection from physical and chemical influences, exclusion of light, maintanence of high relative humidity, reduction of water loss, facilitation of brand identification and provision of a barrier to the spread of decay from one unit to another.

For this purpose, for a packaging material primarily permeability of the film to oxygen, carbondioxide and ethylene gases, commodity diffusion resistance and their effects on quality parameters must be established together with the effect of temperature on these (Kader, et.al., 1989). This will enable selection of a suitable packaging material among possible alternatives.

Polyethylene is the mostly used polymer film for packaging with the advantages as being inert, permeable to gases and impermeable to water vapor. A commercial product FH film^{TM} (Evert - Fresh Co.Inc., Japan) was reported to be extremely suitable for extending the shelf life of the produce containing minerals which are natural zeolites embedded into polyethylene. Although zeolites have unlimited uses in planting, animal feeding, waste treatment and solar heat collectors, in Turkey they are unfortunately being wasted in unrelated areas, e.g., as filling material in cement. With regard to these and above facts considering the large amount of zeolite deposits in Turkey, in this study it is aimed to produce a packaging material using polyethylene and zeolites.

I.2. SPECIFIC OBJECTIVES

The objective of this study was to devise an acceptable manufacturing process to use zeolites in the production of a new polyethylene based packaging material and test it for the permeabilities of oxygen, carbondioxide and water vapor.

For the production of a suitable packaging film, zeolite particles were introduced into the various forms of polyethylene as film, melt, solution or bead by possible manufacturing techniques. In this respect, in the first phase of the work, size and amount of zeolites that can be used per polymer mass and film thicknesses were studied. Then, for the relevant zeolite sizes and zeolite/polyethylene ratios determined, various manufacturing techniques were applied. Finally for the films produced by the most satisfactory manufacturing technique carbondioxide, oxygen and water vapor permeabilities were tested and compared with those of the conventional materials.

Thus, principally it is aimed to find a suitable manufacturing process in which commercial polyethylene and zeolites of our country can be combined in the production of a functional packaging film.

CHAPTER II

THEORY

II. 1. PACKAGING

II. 1.1. Need for Packaging

Most food is consumed far removed in time and space from the point of its production and hence proper packaging is a necessary aid for the storage and distribution of the food. There are a number of important functions of packaging materials. They serve as a material handling tool and a processing aid as well as a convenience item for the consumer and marketing . Further, when properly used they are cost saving devices (Fennema, 1975).

A food product is packaged for prevention of possible kinds of degradation that may render it unsuitable for consumption or impart a lower sensorial value (Mathlouthi and Leiris, 1990). In this aspect, it is important that the food should be fresh, intact and suitable for being packaged. That is, a package can function to preserve an existing quality at the state of wrapping.

In the economical aspect of packaging, instead of a maximum protection against all sources of degradations it is proposed that the packaging material should only posses a protection efficiency in relation with the choosen shelf life.

II. 1.2. Packaging Materials

There are various types of packaging materials according to the need as; metals, metal foils, paper, plastic films, wood, edible films and some combinations of them. In choosing a packaging material to protect a food product during the storage, primarly the physical and chemical properties of the packaged food is considered (Mathlouthi and Leiris, 1990).

Plastic films have become the mostly used material for packaging during the last century due to their advantages and the resulting wide application areas. These are various polymeric materials with densities in the range 900 to 1400 kg/m^3 for most of them. The ability of a plastic to provide lightweight packages, which is an important consumer convenience and a way for processors to reduce shipping costs, is one of the largest driving force behind the well acceptance of plastics in the market for food containers that were once the exclusive province of metal and glass.

The neccessity that nearly all packages must be closed in some way, to protect its contents from enviromental factors renders plastics an advantage as vast majority of such materials can be closed by heat sealing. Polymer coatings and adhesives are universally used to perform this function. No other packaging material can match the ability of plastics to create strong, hermetic sealed at low temperatures (35-125^{0}C). Many plastic film substrates can be heat sealed to themselves without an additional adhesive coating. This greatly increases the productivity of the machines since mechanisms for applying adhesives can be eliminated.

All common plastics can readily converted into thin, strong and clear films. This means that for thousands of flexible packaging applications metal and glass can not be used and only paper, glassine and cellophane can compete. In addition, plastics are unsurpassed in the ease with which special shapes can be readily created particularly important for rigid containers.

Unmodified plastic films and sheets range in appearance from crystal clear to hazy. Pigments or soluble dyes can be added to produce total opacity in virtually any color or to produce transparent colored films and sheets. For example, if the food being packaged is sensitive to light catalyzed oxidation, as many foods are, pigmentation or metallization can be used to screen out light. No other packaging material offers the package designer such a wide range of choices.

Tear and puncture resistance gives plastics a major edge over paper, cellophane and aliminum foil in flexible packages.

Many food products are sensitive to attack by water vapor and oxygen. Glass, metal and pinhole-free aluminum foil are totally impermeable to these two gases which damage so many food products. Plastics rank well below these materials but they are far more impermeable than uncoated paper. Even simple uncoated, homo-polymer plastics such as polyethylene and polypropylene exhibit sufficient moisture barrier for many applications. Although all-plastic packages will never have the infinite oxygen barrier provided by metal and glass, they are now close to providing enough oxygen barrier in order to compete for all food packaging applications.

The finite permeability of plastics to gases becomes a positive attribute in the design of packages for products such as fresh produce which continue to respire after being harvested.

II. 1.3. Production of Packaging Films

In the industry, several methods have been used for the manufacture of polymer films. Most thin sheets and films are made by calendering or extrusion.

In extrusion, the compounded material in the feed hopper is heated and forced into the die area by a screw conveyor. By the combination of the choker bar and die opening, the thickness of the sheet is controlled. After extrusion the sheet passes through oil or water cooled, chromium-plated rolls before being cut to size (Begeman 1963).

In calendering, the material composed of resin, plasticizer, filler and color pigments is first compounded and heated before being fed into the calender. The thickness of the sheet produced depends upon the clearance between the rollers in the squeezing process and the speed of the finishing rollers which strech the plastic. Before the film is wound it passes through water cooled rolls.

In manufacturing laminated products, the resin material is dissolved by a solvent to convert it into a liquid. Rolls of paper or fabric are then passed through a bath for impregnation. This is a continuous operation and as the sheet leaves the resin bath, it goes through a drier which evaporates the solvent, leaving a fairly stiff sheet impregnated with the plastic material.

II. 1.4. Active Packaging Technologies

Active packaging is the term used when the packaging performs some role other than providing an inert barrier to external conditions (Rooney, 1995). Active packaging has developed as a series of responses to unrelated problems in maintanence of the quality and safety of foods. Accordingly, a range of types of active packaging has been developed.

In one sense active packaging is considered as a means of maintaining the optimum conditions to which a food was exposed at the immediately preceeding step in its handling or processing. Passive packaging has been used in an effort to minimize the deletorious effects of a limited number of external variables such as oxygen, water, light, dust microorganisms, rodents and to some extend heat. Hence, active packaging has the potential to continue some aspects of the processing operation or to maintain chosen variables at particular levels.

II. 1.4.1. Modified Atmosphere Packaging

Modified atmosphere packaging is the alteration of the gaseous environment produced as a result of respiration or by the addition or removal of gases from small sized food packages to manipulate the levels of O_2, CO_2, N_2 and C_2H_4 in order to extend storage life of the fresh produce.

Fresh produce continue to actively metabolize during postharvest phases. After a short period of adjustment, steady-state conditions will be established inside an intact polymeric film package once the appropriate relationship among produce and package variables is achieved. Oxygen inside the package is consumed by the produce as it respires and an approximately equal amount of CO_2 is produced. The reduction in O_2 concentration and increase in CO_2 concentration create a gradient causing O_2 to enter and CO_2 to exit the package. Initially, however, the gradient is small and the flux across the package is not sufficient to replace the O_2 that was consumed or to drive out all of the CO_2 that was generated. Thus, inside the package, O_2 content decreases and CO_2 content increases. As this modified atmosphere is created inside the package, respiration rates start to fall in response to that new atmosphere concentrations. Thus, eventually new equilibrium concentrations of the gases surrounding the fruit are established. At this state, O_2 consumption equals O_2 diffusion into the package and CO_2 production equals CO_2 diffusion out of the package (Kader, et.all.,1989). By this way a beneficial modified atmosphere can be passively created within a package.

In order to avoid uncontrolled levels of O_2, CO_2 and C_2H_4 that can be deteriorative, active modification can be applied in a number of ways. It can be done by creating slight vacuum and then replacing the package atmosphere with the desired gas mixture. This mixture can be further adjusted through the use of absorbers or adsorbers in the package to scavenge these gases.

Selection of a film that will result in a favorable modified atmosphere should be based on the expected respiration rate of the commodity at the transit and storage temperature to be used and the known optimum O_2 and CO_2 concentrations for the commodity.

II.1.4.2. Control of Oxygen Amount in a Package

Lowering the O_2 level around fresh fruits and vegetables reduces their respiration rate in proportion with the O_2 concentration. Removal of oxygen also protects the loss of any vitamins that are oxidation sensitive. The most appropriate method of removal of oxygen from a food package depends on the nature of the food, its processing history and the packaging machinary and the way its distributed.

One major way to directly control oxygen levels in a package is the use of an oxygen scavenger system. The simplest scavenger is reduced iron and iron containing sachet that is directly put into the package. If the oxidation rate of the food and the film oxygen permeability are known, the amount of iron required for the desired shelf life can be calculated. Other chemical scavenger systems include reactive dyes, ascorbic acid and oxidizing enzymes namely glucose oxidase and alcohol oxidase. The problem is the diffusion of the reaction products from the enzymes, since if too slow, the enzyme activity will decrease. Other approaches are incorporating an organic chelator that binds oxygen into the packaging material and incorporating free radical scavengers that react with oxygen (Labuza, 1990)

Sachets merely inserted into the food package constitute most of the present systems in commerce. Alternatively, the scavenger can be hot-melt bonded to the inner wall of the package or sachets are inserted in the form of cards, sheets or layers coated onto the inner wall of the package (Rooney, 1995).

II. 1.4.3. Control of Cabondioxide Amount in a Package

A carbondioxide generating or scavenging system is incorporated into the film or added as a sachet. Since, high CO_2 levels are desirable for some foods and plastic films are generally 3-5 times more permeable to CO_2 than O_2 a generator will be needed for some applications. On the other hand, high CO_2

levels cause fruits to enter anaerobic glycolysis which is undesirable. One commercial application is a mixed iron powder- CaOH sachet in which both O_2 and CO_2 are scavenged (Labuza, 1990).

II. 1.4.4. Control of Ethylene Amount in a Package

Ethylene has diverse and profound effects on the physiology of plants, but has been recognised as a problem in postharvest handling of horticultural products. This must be removed from the headspace otherwise the product quickly matures and shortens shelf life (Labuza, 1990).

Most commonly used ethylene removal agents are potassium permanganate ($KMnO_4$) based scavengers. Typically, such products contain 4-6 % $KMnO_4$ on an inert substrate such as perlite, alumina, silica gel, vermiculate, activated carbon or celite. These products are available in sachets for packages and on blankets that can be placed in produce-holding rooms. Potassium permanganate is not contacted with food because of its toxicity.

Various metal catalysts on activated carbon will effectively remove ethylene from air passing over the bed of carbon. Activated charcoal impregnated with palladium catalyst and bromine-type inorganic chemicals are some examples.

In the past several years a number of packaging products have appeared based on the putative ability of certain finely dispersed minerals to adsorb ethylene. Typically, these minerals are local kinds of clay that are embedded in polyethylene bags which are then used to package fresh produce.

A product called Ever-Fresh bags is marketted by the Evert-Fresh Corporation in the U.S.A. The bags are, presumably, polyethylene with Japanese Oya stone dispersed within the film matrix. Oya stone has putative ethylene adsorbing capacity.

There are many other similar bags being sold throughout the world offering improved postharvest life of fresh commodities due to the adsorbtion of ethylene by the minerals dispersed within the film. The evidence offered in support of this claim is generally based on the shelf life experiments comparing common polyethylene bags with mineralized bags. Such evidence generally shows an extension of shelf life and/or reduction of headspace ethylene but yet are unconvincing. Although the finely divided minerals may adsorb ethylene, they will also open pores within the plastic bag and alter the gas-exchange properties of the bag. Because ethylene will diffuse much more rapidly through open pore spaces within the plastic than through the plastic itself, one would expect ethylene to diffuse out of these bags faster than through pure polyethylene bags. However, by the same phenomena exchange of CO_2 and O_2 with the ambient shall be taking place more readily than is the case for a normal polyethylene bag. These effects can improve shelf life and reduce headspace ethylene concentrations independent of any ethylene adsorption. In fact almost any powdered mineral can confer such effects without relying on expensive Oya stone or other speciality minerals (Zagory, 1995).

Although the minerals in question may have ethylene adsorbtion capacity, the data supporting the commercial products incorporating these minerals fail to demonstrate such capacity. Even if they do have ethylene-adsorbing capacity, it is possible that they will lack significant capacity while embedded in plastic films. The ethylene would have to diffuse through the plastic matrix before contact with the dispersed mineral, thus greatly slowing any process of adsorption. Once the ethylene has diffused half-way through the plastic film, venting to the out side may be nearly as fast and effective as adsorption on embedded minerals.

II. 1.4.5. Control of Moisture in a Package

The respiratory metabolism of fresh produce produces water and in turn tends to increase the humidity of the container unless removed by suitable means. As most films that are available for use in modified atmosphere packaging typically have low permeability to water vapor, the humidity formed within the packages can cause condensation and favor the development of molds and bacteria (Kader, et.all., 1989).

For reducing the in-pack relative humidity one or more humectants are placed between two layers of a plastic film which is highly permeable to water vapor. An example is described as placing propylene glycol and a carbohydrate both of which are humectants (Rooney, 1995)

One approach is using microporous sachets of inorganic salts for transport of chilled sensitive fruits and vegetables. When chilled, these foods may suffer chill injury loosing their quality attributes especially with regard to color and flavor. If stored at room temperature this loss is prevented to a degree but the moisture accumulation leads to rot. Some of the chemical compounds used for this purpose are $CaSiO_4$, KCl, xylitol, NaCl and sorbitol.

II. 1.4.6. Polyethylene Film as the Most Common Packaging Material

Polyethylene is a thermoplastic hydrocarbon polymer composed of unit mers of ethylene. It is one of the most important packaging material among the polymer films.

Polyethylene may be produced either by high pressure or low pressure processes. Low density polyethylene (LDPE) is the product of the high pressure process and contains short and long side branches. These branches prevent packing into a crystal lattice in their immediate vicinity and thus lower the degree of crystallinity. Therefore, its permeability is respectively high. High density polyethylene (HDPE) has the least branching and as a result has the greater thermal stability and the lower permeability.

LDPE is the most widely used polyethylene since it is flexible both at room and lower temperatures, considerably waterproof, capable of being heat sealed, can be produced in a variety of colors and the most inert and stable of all polymers.

II. 1.4.7. FH Film as an Example of Active Packaging Material

It has been known that respiring produce will generate its own modified atmosphere, but doing so it may reach a stage of ripeness which is not desired.

Choices have been made between packaging films in an effort to achieve a modified atmosphere which can supress respiration and lenghten shelf life. Since there was difficulty in achieving satisfactory performance with many produce-film combinations, highly permeable porous patches were introduced. This enabled packers to use film of any suitable material provided that there is adequate exchange of oxygen and carbondioxide. These films have been made porous by inclusion of porous powders such as zeolites or volcanic rocks, or by inclusion of crushed rocks (Rooney, 1995).

Some films containing inorganic powders are claimed to offer multiple benefits for packaging of horticultural produce. In this respect it is reported by the manufacturers that Ever-Fresh (FH) film containing Oya stone dispersed on the film surface adsorbs ethylene, preserves freshness and controls levels of water vapor, oxygen and carbondioxide in the pack by means of the minute pores. The bags are re-usable if rinsed and turned inside out to dry.

Ever-Fresh bags sold as FH film are reported to be impregnated with processed Oya stone which has its origins in a cave in Japan. The cave has been used for three centruies to store fresh produce. The success of this cave as an ideal storage space can be attributed to constant levels of high humidity, static temperature, darkness and most importantly, the ability to adsorb the gases discharged by the stored produce. The study of the caves gave scientists the key to developing the Ever-Fresh film that absorbes ethylene, maintains humidity, permeable to other gases and when refrigerated maintains temperature control. All of these are major factors in successful long-term storage of produce (Sacharow, 1995).

II. 2. GENERAL FEATURES OF FRESH PRODUCE

The most important characteristic of harvested intact plant tissues is the persistence of aerobic respiration throughout the storage life of the product. Aerobic respiration involves metabolism of carbohydrates and organic acids in the presence of atmospheric oxygen, with the ultimate production of carbonioxide, water, heat and small amounts of organic volatiles and other substances.

For maintaining high quality and extending postharvest life of the fresh produce the primary factors as; harvesting at optimum maturity, minimizing the mechanical injuries, using proper sanitation procedures and providing optimum temperature and relative humidity during all marketing steps should be done.

Modification of oxygen, carbondioxide and ethylene concentrations in the atmosphere surrounding the fresh produce are the secondary factors which are referred to as either controlled atmosphere (CA) or modified atmosphere (MA). The beneficial effects of controlled atmosphere or modified atmosphere have been assumed to be the reduced oxygen and/or elevated carbondioxide causing a reduction in respiration rate. Lowering oxygen level and elevating carbondioxide level around fresh fruits and vegetables reduces their respiration rate in proportion to the gas composition which must carefully determined since a minimum of 1-3 %O_2 and a maximum of 20 % CO_2 may lead to a shift from aerobic to anaerobic respiration.

However, posharvest deterioration of fresh produce can be caused by many factors in addition to high respiration rates. Ethylene biosynthesis and action is one of the reasons for this. Ethylene being a gaseous plant growth hormone leads to maturation and subsequent senescence. For most produce there exist a close relationship between respiration and ethylene production and respiration rates could be measured by the produced ethylene amount. As the produce matures they produce more ethylene and if ethylene accumulates this accelerates the senescence of the produce.

Reduced oxygen levels (below 8 %) decrease ethylene production by fresh produce unless anaerobiosis starts and reduce their sensitivity to ethylene since O_2 is required for ethylene production and action.

Effect of CO_2 on ethylene production rates differs depending on the commodity and the CO_2 concentration. Increase in ethylene production occurs only when the CO_2 concentration is high enough to cause physiological injury to the tissue. The mode of action of CO_2 in inhibiting or reducing effects of ethylene is due to the competition of CO_2 with ethylene for the binding site or by inhibiting ethylene oxidation to CO_2 through a feedback inhibition mechanism.

Increased CO_2 and reduced O_2 slows down the loss of chlorophyll and biosynthesis of carotenoids and anthocyanines. Further, there exist some experimental results that elevated CO_2 can result in detrimental effects on color of some commodities during CA storage and following transfer to air. Despite these factors unwanted changes during storage of fresh produce as; loss of texture due to ripening and softening, loss of flavor due to changes in carbohydrates, organic acids, proteins, lipids and organic compounds and loss of nutritive value are prevented by increased CO_2 and reduced O_2 atmospheres.

II. 3. DIFFUSION OF GASES THROUGH POLYMER FILMS

Molecular transport of small molecules through polymer films has been widely studied. Several theories of diffusion, permeation and solution have been developed to relate the experimental data to polymer film morphology, chemical structure and other physical properties.

Gases and vapors can permeate through materials by macroscopic or microscopic pores and pinholes or they may diffuse by a molecular mechanism, known as "activated diffusion". In activated diffusion the gas is considered to dissolve in the packaging material at one surface, to diffuse through the packaging material by virtue of a concentration gradient and to reevaporate at the other surface of the packaging material (Fennema, 1975).

II. 3.1. Factors Affecting the Diffusion of Gases

II. 3.1.1. Temperature

The polymeric materials are composed of long chains of unit mers in either branched or unbranched form. In the solid state depending on the interaction between the chains, the polymer is either amorphous or crystalline. The crystalline materials are considered to be impermeable to gases and vapors.

By increasing the temperature the polymer mass can deform depending on the ability of the polymer chains to untangle and slip past one another.

II. 3.1.2. Nature of Gas

The important properties of a gas in activated diffusion are molecular size and solubility in the polymer. For the diffusion of larger molecules larger holes need to be formed in the polymer which requires a greater energy. Thus, the activation energy required for diffusion can be said to be proportional with the size of molecules where for solubility this is the reverse.

II. 3.1.3. Nature of Polymer

The free volume theory of diffusion states that the rate of diffusion will be governed by the number and size distribution of pre-existing holes depends on the degree of packing of the chains. The ease of hole formation depend on the segmental chain mobility and on the cohesive energy of the polymer. The introduction of unsaturation into the polymer backbone leads to greater ease of rotation of the chains and higher diffusivity of penetrants. The introduction of side groups decreases the chain flexibility leading to lower diffusion constants and a greater energy of activation for diffusion.

II. 3.1.4. Effect of Glass Transition

Glass transition is the point or a narrow range at which there is a change from glassy or quasi-crystalline state to a liquid-like (rubbery) one. Above glass transition temperature there is greatly increased segmental mobility allowing for a greater zone of activation which leads to an increase in the energy of activation.

II. 3.1.5. Effect of Crosslinking

As the degree of crosslinking increases, the diffusion constants decrease and the magnitude of the change is greater with the larger penetrant molecule. The energy of activation for diffusion increases with increasing crosslinking

II. 3.1.6. Effect of Plasticizers and Relative Humidity

The addition of a plasticizer to a polymer decreases the cohesive forces between the chains resulting in segmental mobility. This results in an increased rate of diffusion and a lower activation energy.

Polymers which swell greatly in water always have increasing diffusivity with increasing relative humidity. However, small decreases in the diffusivity of gases at very high relative humidities were reported.

II. 4. USE OF NATURAL ZEOLITES

In the late 1950's the scientific community become aware of zeolites which constitute more than 90% of many bedded sedimentary rocks of volcanic origin and occuring worldwide.

Zeolites are crystalline hydrated alumino silicates of alkali and alkaline earth cations that possess infinite three dimensional crystal structures. They are further characterized by an ability to lose and gain water reversibly and to exchange some of their constituent cations without major change of structure.

By the words zeolite or zeolitic or the name of a specific zeolite mineral a zeolite rich rock or product that may contain between 50 and 95 % of a specific zeolite phase should be understood.

Based on their high ion-exchange capacity and water retentivity natural zeolites have been used extensively in Japan as amendments for sandy, clay-poor soils. Also for preparation of chemical fertilizers clinoptilolite offers a slower release of large cations such as ammonium and potassium. Coupled with its valuable ion-exchange properties which allow a controlled release of micronutrients, such as Fe, Zn, Cu, Mn and Co, the ability of clinoptilolite to sorb excess moisture makes it an attractive addition to chemical fertilizers to prevent caking and hardening during storage and to animal feedstuffs to inhibit the development of mold.

When clinoptilolite-rich tuff was used as a soil conditioner, significant increases in the yields of wheat (13-15 %), eggplant (19-55 %), apples (13-38 %) and carrots (63 %) was reported when from 4 to 8 tons of zeolite was added per acre.

Natural zeolites are also used as dietary supplements for several types of domestic animals. When chickens were fed with a diet clinoptilolite and mordenite, they needed less food and water and still gained as much weight in a two week trial compared to ones having a normal diet. The use of zeolites in the diets of young and mature pigs resulted that the weight gain of animals of both ages receiving diets containing 5% clinoptilolite was 25 to 29 % greater than that of animals receiving normal diets.

The physical and chemical properties of many natural zeolites lend themselves to a wide variety of applications in the tratment of animal wastes.

In closed or recirculating aquaculture systems oxygen enriched air can be produced by the selective adsorption of nitrogen by activated zeolites.

Based on the dehydration-rehydration properties of the zeolite and the extreme nonlinearity of its water adsorption isoterm, units have been developed that are capable of producing 6 kWh energy per square meter of collector area.

II. 5. MATHEMATICAL MODEL FOR THE PERMEATION OF GAS MIXTURE THROUGH THE POLYMER FILM

The unsteady molar balance written for a transferring species for the low pressure side of a permeation cell by simplification of the conservation equation for non reactional case can be written as,

$$V\frac{dC_A}{dt} = \vec{N}_A S \tag{II.1}$$

where, N_A is the molar flux, S is the cross-sectional area normal to the transfer, C_A is the molar concentration in the low pressure side and V is the volume of low pressure side of the cell.

The one dimensional (1-D) molar flux of CO_2 or O_2 through the polymer film is;

$$\vec{N}_A = -D_A \frac{d\overline{C}_A}{dz} \tag{II.2}$$

Equation of continuity for CO_2 and O_2 is;

$$\frac{\partial \overline{C}_A}{\partial t} + \vec{\nabla}\vec{N}_A = R_A \tag{II.3}$$

When R_A=0 i.e., there is no homogeneous chemical reaction and for

(1-D),

$$\frac{\partial \overline{C}_A}{\partial t} + \frac{\partial(\vec{N}_A)}{\partial z} = 0 \tag{II.3}$$

Substitution of N_A from Equation (II.2) with the assumption of constant diffusivity yields;

$$\frac{\partial \overline{C}_A}{\partial t} - D_A \frac{\partial^2 \overline{C}_A}{\partial z^2} = 0 \tag{II.4}$$

boundry conditions of the system are

$\overline{C}_A = H_A C_{A0}$ at z=0, t>0 (II.5)

$\overline{C}_A = H_A C_A$ at z=L, t>0 (II.6) where, H_A is the solubility constant, C_{A0} is the molar CO_2 or O_2 concentration of the incoming gas and L is the film thickness.

Assuming the change in the $\overline{C}_A$ with respect to time is very small compared with that of z direction, Equation II.4 can be simplified to

$$D_A \frac{d^2\overline{C}_A}{dz^2} = 0 \tag{II.7}$$

After applying the boundary conditions,

$$\overline{C}_A = \frac{H_A}{L}(C_A - C_{A0})z + H_A C_{A0} \tag{II.8}$$

Equation (II.8) is the concentration distribution in the film where flux, $\vec{N}_A$, can be determined from the Equation (II.2). After differentiating Equation (II.8) and substituting into Equation (II.1)

$$-\frac{D_A H_A S}{L}(C_A - C_{A0}) = V\frac{dC_A}{dt} \tag{II.9}$$

and further integration of this expression yields

$$\ln\left\{\frac{C_{A0} - C_A}{C_{A0}}\right\} = -\left\{\frac{D_A H_A S}{LV}\right\}t \tag{II.10}$$

is obtained.

Equation (II.10) shows the variation of CO_2 or O_2 concentrations with time in the low pressure side of the cell.

From Equation (II.10) the permeability of a film for a gas can be evaluated theoretically in terms of diffusivity constants. For the emprical determination of permeability a term B has been defined as the ratio of (amount of gas).(thickness of film) to (area).(time).(pressure difference). The idea is important in packaging science, as polymer films are classified according to their permeabilities to specific gases.

II.6. MATHEMATICAL MODELS FOR ADSORPTION OF GASES ON SOLIDS

The two of the important relations proposed for adsorption phenomena are Langmuir and Brunauer, Emmett and Teller (BET) models (Rosenbaum, 1970). The former predicts the behaviour according to a chemi-sorption character and can simply be given as;

$$n = \frac{fC}{g + C} \qquad \text{(II.11)}$$

where, n is the rate of removal in appropriate units, C is the concentration and f and g are the rate coefficients.

On the other hand, the BET model, based on weaker forces of attachment on the adsorbant surface predicts physi-sorption.

CHAPTER III

EXPERIMENTAL

III.1. MANUFACTURING A NEW POLYMER BASED PACKAGING MATERIAL

A packaging film was tried to be produced by combining natural zeolite with commercial polyethylene either in the form of extruded film or as beads. For this purpose six methods described below were used.

III. 1.1. Materials

III. 1.1.1. Polyethylene

Polyethylene was purchased from the market as polyethylene beads (Petkim, TURKEY) or as films of thickness 0.06mm.

III. 1.1.2. Zeolite

Zeolite was received from Etibank Bigadiç natural mineral resources region in unprocessed form. In the region the yield is quite high containing about 80 % ore and the rocks mainly are composed of clinoptilolite, remaining being erionite, chabazite and analcime.

III. 1.2. Methods

III. 1.2.1. Preparation of Zeolite

The mineral was in the form of large pieces about 20x18x8 cm in dimensions as received from the region. These pieces were first crushed in a jaw crusher (Wedag BOCHUM, 1963, Karl Kolb, Frankfurt, Germany) and then were ground with a hammer mill (Laboratory Mill Model 4, Arthur H. Thomas Company, Philadelphia, P.A., U.S.A.). The ground samples were classified into three size ranges by sieving (Octagon 200 Test Sieve Shaker, Endocotts Limited, London). The three groups were -420μ/+212μ, -212μ/+106μ and -106μ/+53μ.

III. 1.2.2. Methods Used for the Production of Zeolite-Polyethylene Film

In order to obtain a zeolite + polyethylene film with suitable physical properties for packaging several methods were tried. These were i.) hot pressing zeolite particles on to the film, ii.) mixing polyethylene melt with zeolite particles and spreading, iii.) adding zeolite to the polyethylene dissolved in a solvent, iv.) coating polyethylene granules with zeolite particles in a druggie pan, v.) extrusion of zeolite covered polyethylene beads as a film and vi.) extrusion of zeolite covered polyethylene beads as a film and then hot pressing.

The procedure and the parameters used according to these six methods are given below.

III. 1.2.2.1. Hot Pressing

In these trials zeolite was embedded on the surface of the polethylene film confined between two plates where the temperature of the plates and the applied pressure can be adjusted. Zeolite particles with dimensions less than 74μ (200 mesh) were used for the experiments. Pre-weighed amount of polyethylene film was placed on a non-sticking paper and weighed amount of zeolite was spreaded on to the film surface. This was covered with an another non - sticking paper and hot pressed (Paul Weber Stgt. Uhlbach, Germany). The temperature of pressing was measured by means of four thermocouples placed into the press which are adjusted to be as near as possible to the surface of the press. Pressing was carried out at different temperatures and different periods as given in Table III.1.

Table III.1. Experimental parameters used for hot pressing.

Mass of zeolite per mass of polyethylene (kg/kg)	Temperature of Pressing (^{0}C)	Time of Pressing (minutes)
0.2	120	20
0.3	120	20
0.4	120	20
0.5	120	20
0.6	120	20
1.0	120	30
1.0	140	30
1.0	140	45
1.0	145	20
2.35	100	190
2.35	122	30
5.0	120	250
5.0	145	30

As an alternative procedure a similar test was carried out by spreading first large zeolite particles, i.e., -250μ (60 mesh) /+ 177μ (80 mesh) on to the polyethylene film. These were then pressed manually on the polyethylene surface in order to deform the surface. Upon creating sufficient surface rougness, the large particles were cleared from the surface and small particles were spreaded manually to fill the cavities formed. The particles in excess remaining on the surface were gently swept away. Then this film was hot pressed for 30 minutes at 110^0 and 120^{0}C.

III. 1.2.2.2. Mixing Polyethylene Melt with Zeolite and Spreading

As a second means of processing zeolite impregnated polyethylene film, polyethylene was melted and zeolite was added to the melt.

The experiment was started at 65^0C, after 80^0C the film started to soften. In the temperature range 120-145^0C shrinkage of the film took place and then in the range 150-165^0C it started to melt. Between 190^0 C and 205^0C it completely melted and slight mixing with zeolite particles of average size 74μ could be achieved. The mixture was not perfectly homogeneous at this temperature. The total time passed for heating was two hours. In order to obtain a film from this mixture, the mixture was spreaded by an automatic spreading machine (Automatic Film Applicator-133, Sheen Instruments Ltd., England,).

For this procedure several zeolite/polyethylene ratios, 0.5/10, 1/10 and 2/10, for the average zeolite particle sizes of 74μ were studied to determine the optimum ratio and the particle size for spreading.

III. 1.2.2.3. Adding Zeolite to the Polyethylene Dissolved in a Solvent

In the third method polyethylene was dissolved in a solvent and zeolite was added into this solution. The solvent used was xylene (Merck) being the most suitable one for polyethylene.

According to this procedure primarily the most proper polyethylene to xylene ratio was determined by the several combinations tried. These were 1/10, 1/9, 1/8, 1/7 and 1/6 as mass ratio of polyethylene to xylene. The most proper ratio determined was one part polyethylene per ten parts of xylene. Using this ratio polyethylene in the form of sheets was put into xylene and the mixture was kept at 75^0C for one hour while keeping the solution mixed intermediately. When the mixture became completely uniform zeolite with average particle size of 74μ were added. The amount of zeolite added was varied for different batches as 0.05, 0.1, 0.15, 0.2 and 0.25 parts of zeolite per part of polyethylene. For a specific ratio heterogeneous mixture was kept mixed continuously at 75^0C for ten minutes. Then the mixture formed was poured as a thin film in a petri dish and dried in a vacuum oven at 80^0C until all xylene was evaporated leaving a thick and brittle film as residue. Then the obtained film was cut into very small pieces, placed between heat stable and non-sticking papers and hot pressed at 130^0C for five minutes. The block diagram for this process is given in Figure III.1.

II. 1.2.2.4. Coating Polyethylene Granules in a Druggie Pan

In the fourth method, polyethylene beads were coated with zeolite by using a druggie pan (Armfield, FT12 Ball Mill, England). The unit has a stainless steel rotating pan directly mounted onto the output shaft of a geared motor to give variable speed adjustments with the direction of rotation easily reversible. Further, the complete rotation of the pan can be set at different angles with respect to horizontal for satisfactory tumbling of the contents of the pan. Zeolite particles of average size 74μ and polyethylene beads were placed into the pan and heated with the pan bottom immersed in an oil bath at 180^0C. While continuous mixing and heating, zeolite particles were attached on the softened surface of the polyethylene beads.

III. 1.2.2.5. Extrusion of Polyethylene Film with Zeolite

In the first step of this method, zeolite covered polyethylene beads were produced. For this purpose, polyethylene beads together with very excess amount of ground zeolite of sizes +53μ, +106μ and +212μ were mixed, and the mixture was slowly heated for just the surface of the beads should melt and ease the attachment of the zeolite particles to their surface.For this purpose, different temperatures were tested and successful results were obtained when the temperature of the mix was between 140 and 150^0C. The optimum temperature of heating was choosen as 145^0C and the experiments were carried out at that temperature. Then, the samples were placed in an oven for three hours at 145^0C (OV/160 CLAD, England) to recover and determine the amount of zeolites held per mass of the beads. The amount of zeolite held by the beads were calculated

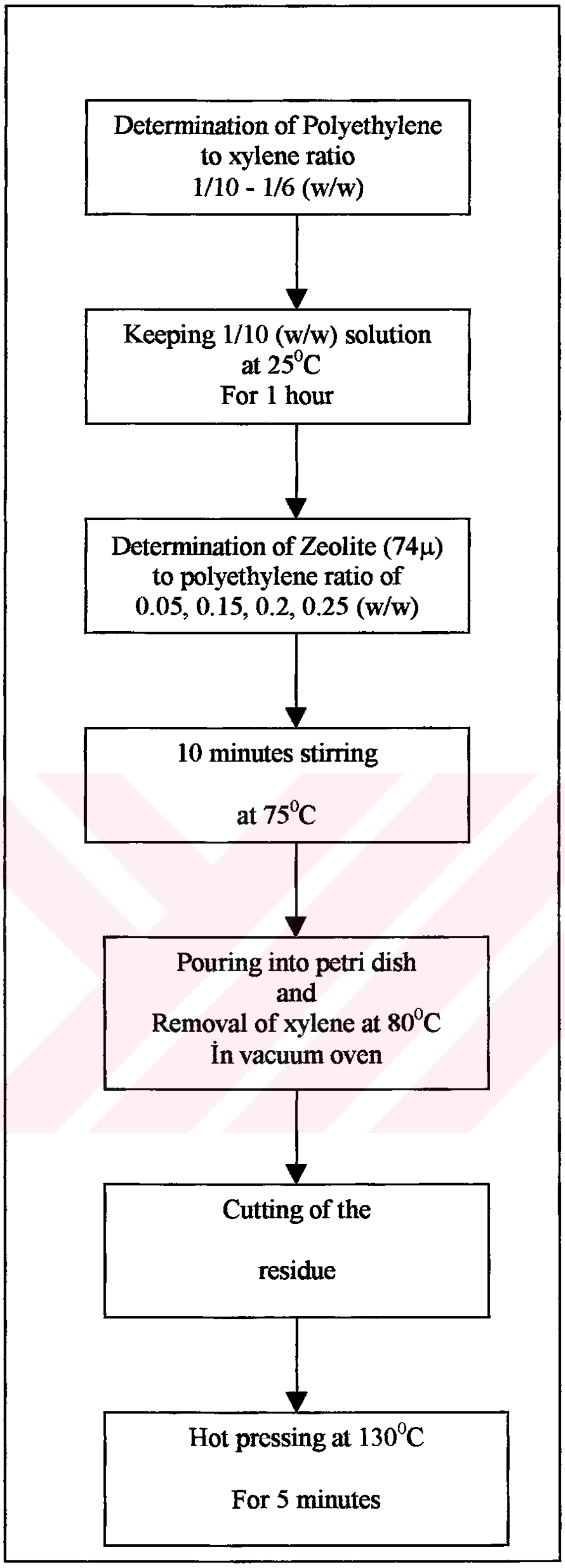

Figure III.1. Experimental steps used in the production of zeolite-polyethylene film by the solution method.

beads were calculated from the weight of the zeolite covered beads and weight of the beads fed. This ratio was checked for different trials and was found to be differing by ± 0.01 kg/kg beads.

Zeolite coated polyethylene beads were hot extruded in an industrial extruder (Heminstone, 1977,Taiwan, in Doğan Plastik, İzmir).The extruder die exit temperature was 110^0C and the extruder temperature was 90^0C which were kept constant by a thermostat. The thickness of the film was adjusted by the feed rate in this case being 30 kg per hour. The flow rate of the air was adjusted so that a blowing tower of 3m height and 0.5m width was provided. The block diagram for this process is given in Figure III.2.

III. 1.2.2.6. Extrusion of Polyethylene Films with Zeolite and Hot Pressing

The films prepared by extrusion as described in Section III.1.2.2.5. contained large amounts of zeolite and their flexibility was very low and some surface defects like holes caused by aggregates of zeolite was observed in some parts. For this reason, the so prepared films were subjected to hot pressing at 120^0C for five minutes to be used for permeability experiments.

III. 2. DETERMINATION OF FILM PERMEABILITY OF THE EXTRUDED-HOT PRESSED FILM TO WATER VAPOR, OXYGEN AND CARBONDIOXIDE

III. 2.1. Determination of Permeability to Water Vapor

In a cup of total volume 180 cm^3, a predetermined amount of water was placed in a cup and the surface was tightly covered with the produced films. The cup was placed in a heater-cooler oven (Nüve ES 500, Turkey). At a set temperature, humidity in the oven was continuously measured with a humidity sensor (NEL RH 1300, Turkey). Prior to the experiments the humidity sensor was taken to the manufacturer for maintanance and calibration.The weight of the cup was measured continuously with respect to time at the oven temperatures of 10, 20, and 30^0C.During the water vapor permeability measurements, the relative humidity of the environment was; 70 % for 10^0C, 40 % for 20^0C and 30 % for 30^0C. There was a ± 5 % fluctuation in the relative humidity values which was due to the fact that the oven used ambient air for cooling purpose.

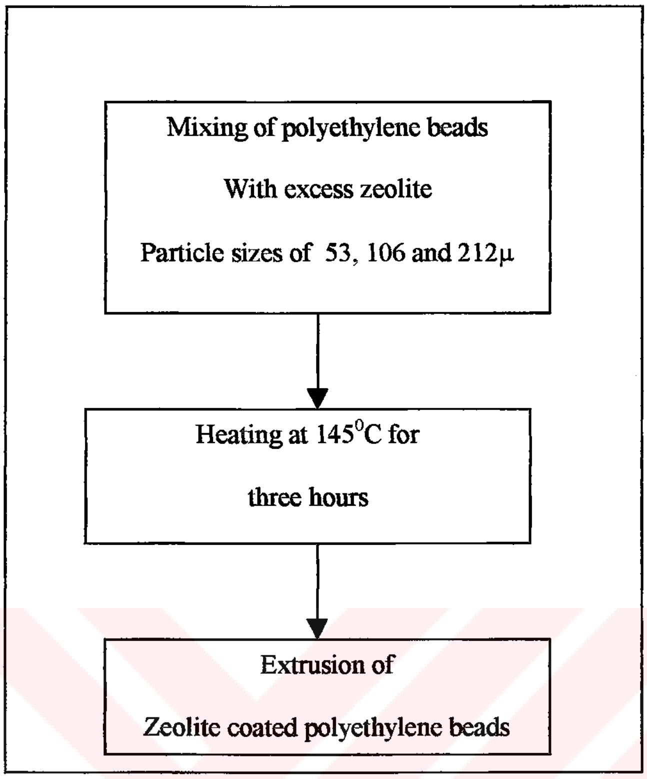

Figure III.2. Experimental steps used in the production of zeolite coated polyethylene beads extrusion.

III. 2.2. Determination of Permeability to Selected Gases

The permeabilities of the prepared films against oxygen-nitrogen and carbondioxide-nitrogen systems were measured. For each zeolite particle size two measurements were performed and the results were averaged.

III. 2.2.1. Materials

Oxygen, carbondioxide and nitrogen gases were supplied from gas cylinders (Oksan Kimya, Ankara).

III. 2.2.2. Permeability Apparatus

A permeability measurement system was set-up to measure the permeation rate of the selected gases. The figure for the experimental set-up is given in Figure III.3.

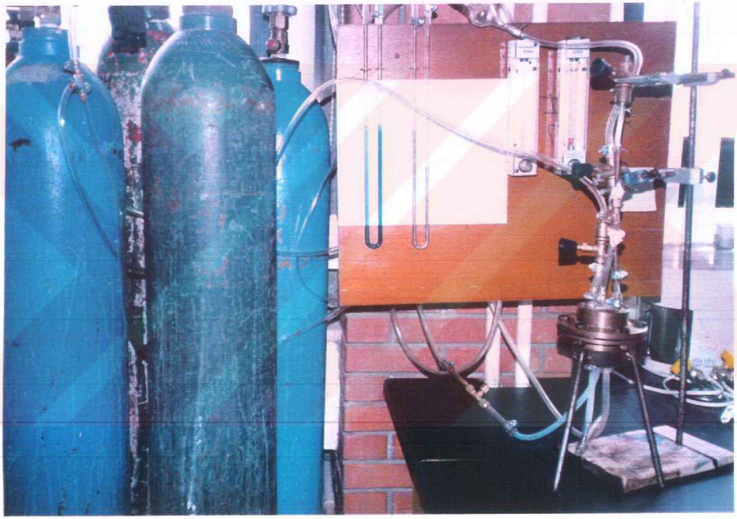

Figure III.3. Experimental set-up.

The schematic representation of the gas permeability system is given in Figure III.4.

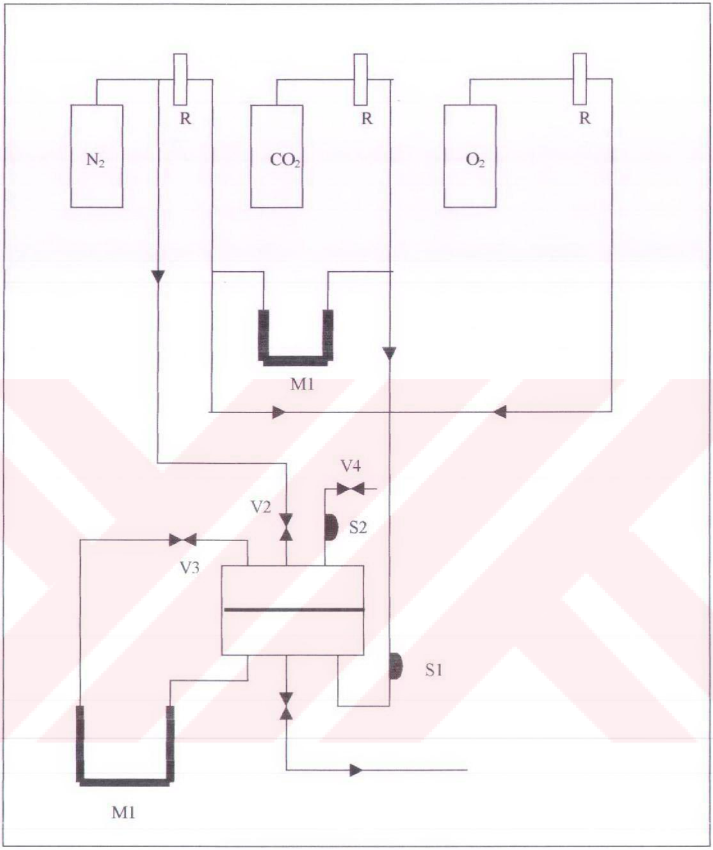

Figure III.4. Schematic representation of the gas permeability system.

Three taps were placed to the base of each compartment of the diffusion cell. On the high pressure side, these were connected to the mixture inlet line, to the U-manometer and to the mixture outlet line. In the mixture inlet line also a sampling port was placed. On the low pressure side, the taps were connected to the nitrogen inlet line, to the manometer and to the outlet line having a sampling port and an adjustment valve on it. This valve was a needle valve to regulate the pressure difference between the upper and the lower compartments of the cell.

The desired flowrates and compositions of the gas mixtures were adjusted by means of the neddle valves and the rotameters (R). Also a U-tube manometer (M1) was used to ensure the equality of the pressures in the lines prior to mixing.

The penetrant gas mixture with the set composition was prepared by adjusting the volumetric flow rates of oxygen or carbondioxide in nitrogen by the rotameters on the gas lines. Then, the feed mixture was kept swept for overnight through the high pressure side of the cell to provide uniform composition of the mixture within the film.

Just before starting the experiment the low pressure side of the cell was purged with nitrogen for ten minutes, to provide an inert gas atmosphere into which the penetrant gas diffuses. After purging, inlet and outlet valves (V2 and V4, respectively) of the low pressure side were turned off simultaneously. Also cell manometer valve (V3) was closed in order to prevent any possible dilution of the low pressure side gas due to large dead volume of the tubing between the cell and the manometer (M2).

The gas mixture was allowed to flow through the high pressure side of the cell. Pressure difference between the two compartments of the cell was adjusted to 8 cm Hg by using the neddle valve at the gas mixture outlet. Samples were taken against time by a gas tight syringe from the high pressure (S1) and the low pressure compartment of the cell (S2).

Main part of the apparatus is the cylidrical diffusion cell (Figure III.5) This was constructed from brass in the form of two seperable compartments connected by flanges. The polymer film to be tested was placed between rubber gaskets and was fixed tightly between the cell compartments by the flanges. The diffusion area was $3.02\text{x}10^{-3}$ m^2.

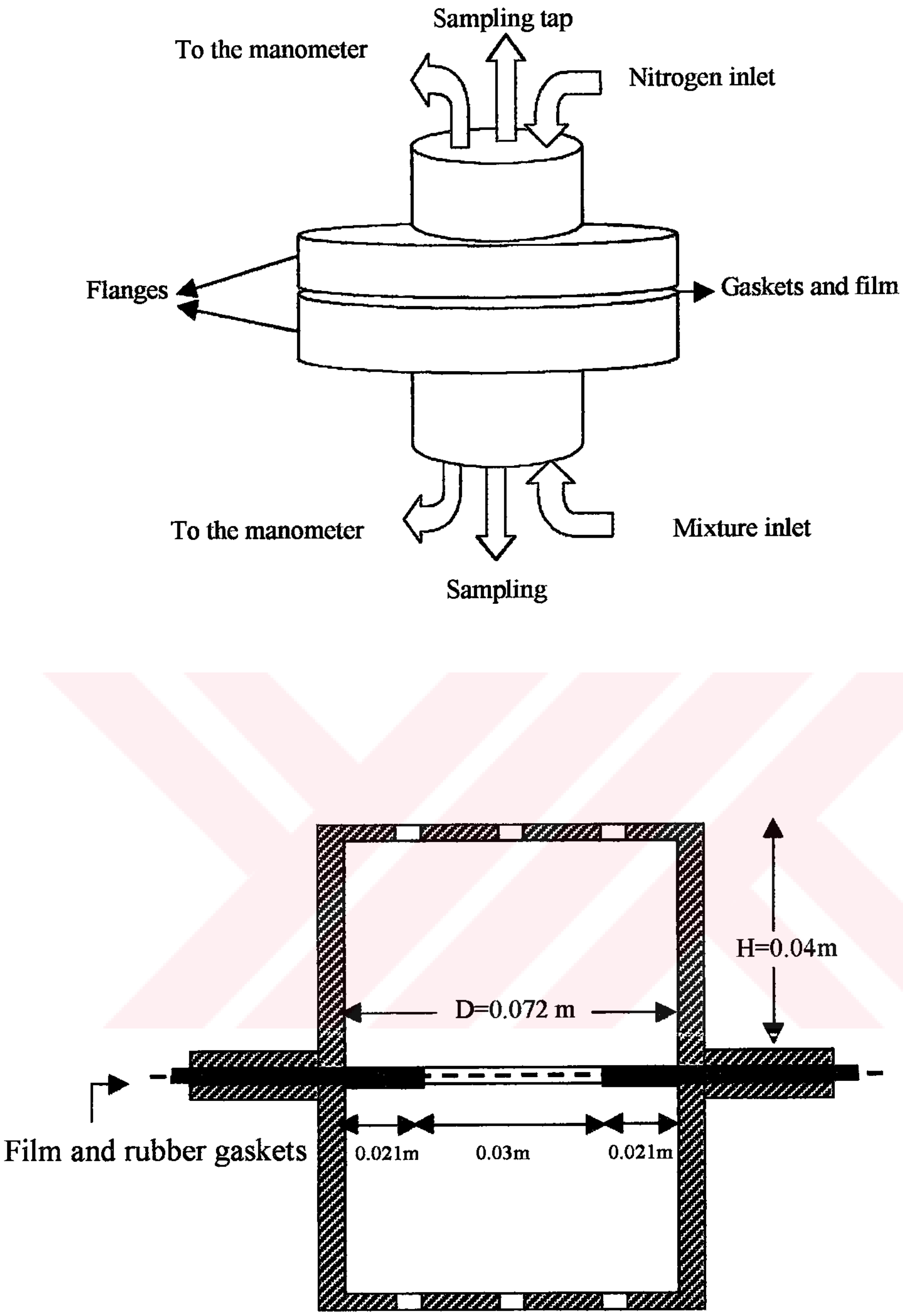

Figure III.5. The cylindrical diffusion cell.

Experiments were conducted at the room temperature, for the high pressure compartment concentrations of 20 ± 2 % (v/v) for carbondioxide and 10 ± 2 % (v/v) for oxygen.

III. 2.2.3. Measurement of the Concentration of the Permeating Gases

The gas samples from the compartments were analyzed by means of a gas chromatoghaph (Shimadzu, Japan). The chromatograph was a dual detector type and Thermal Conductivity Detector (TCD) was used during the measurements. Carrier gas was helium. Two different columns namely Poropak Q for nitrogen - carbondioxide mixture and Molecular sieve 5A for oxygen - nitrogen mixture were used. By use of the analyzer (Chromatopack, Shimadzu, Japan) the sample composition was reported as % by volume.

For the measurement of the concentrations of the nitrogen - carbondioxide mixture in Poropak Q column, the column, injection, column to detector and Thermal Conductivity Detector (TCD) temperatures were adjusted to 40, 50, 60 and 60^0C respectively. Flow rate of the carrier gas was 22 ml/min. The retention time for nitrogen was 0.6 minutes and for carbondioxide was 2.5 minutes.

For the measurement of the concentration of the oxygen - nitrogen mixture in Molecular Sieve 5A, the column, injection, column to detector and TCD temperatures were adjusted to 35, 50, 70 and 70^0C respectively. Flow rate of the carrier gas was 14 ml/min. The retention time for oxygen was 4.7 minutes and that for nitrogen was 10.3 minutes. In Appendix A.2. the chromatographs are given for these measurements.

III. 2.3. Determination of the Film Structure

The image analysis system used for the determination of the film structure consists of three main parts that are connected by several interfaces; a camera (Cohu Inc.), a dual monitor image processing computer equipped with an image grabber (Targa, Truevision) and an image processing software (Mocha, Jandel Inc.). The images were directly taken by the camera using a KOWA vari-focal lens with a maximum aperture ratio of 1:1.8. A standard 100 W light bulb was used for top lighting, while a UV source was used for bottom lighting in order to provide a higher intensity light than the room lighthing.

The analysis is image acquisition and calibration in which an image is captured and grabbed on 256 gray levels and then stored in the hard drive of the computer for further treatment. This stored image has a standart format of 719X511 pixels in which each pixel may have a color or monochrome value. After storing the image, a scale value which is a function of the magnification is entered in order to convert the spatial measurement value in pixels to centimeters.

CHAPTER IV

RESULTS AND DISCUSSION

IV. 1. PREPARATION OF THE ZEOLITE-POLYETHYLENE FILM

The purpose of preparing polyethylene film embedded with zeolite was to combine and increase the individual advantages of both materials for use in food packaging. The results and assessment of the products prepared according to the different methods for the manufacture of such a composite film is given below.

IV. 1.1. Hot Pressing

The films obtained by the process of embedding ground zeolite particles with an average particle size of 74μ on the surface of 60μm and 100μm thick polyethylene films using a hot press at 100-145^{0}C did not yield a satisfactory product. This was primarily because the distribution of zeolite was not uniform and the mechanical strength of the prepared films was low where it resembled a craft paper more than a plastic film. When compared with the FH film which has the zeolite particles on one side of the film indicating that they have been attached to the surface by suitable means, a logical processing seemed to be spreading hot ground rocks on the warm softened film. However, it was not possible to conclude about a the relevant time-temperature combination. This is mainly because with the available manual hot press it was not possible to adjust both of these parameters with sufficient accuracy.

IV. 1.2. Mixing Polyethylene Melt with Zeolite Particles

As a second possible alternative complete mixing of polyethylene and zeolite was tested. According to the trials with different average zeolite particle sizes and zeolite/polyethylene ratios, the optimum for spreading was found to be 74μ and 1/10 (w/w), respectively. When the particle sizes were greater than 74μ, this yielded very heterogenous appearance and were also hard to spread. On the other hand, for smaller particle sizes it was necessary to employ greater amounts of zeolite which severly affected the density of the mix. Further, in determining the optimum zeolite/polyethylene ratio the primary factor which affected the result was found to be the spreadability.

When a sufficient amount of well mixed molten mixture prepared at the optimum conditions, i.e., 1/10 (w/w) zeolite/polyethylene at 190-205^{0}C, it was tried to be spreaded as a thin film. With the available instrument a number of drawbacks were observed. Primarily, the melt was highly viscous and too hot to be used in the automatic spreader. This caused non uniform thickness of the spreaded film and sticking of the material to the spreader blade due to hardening of the material by rapid cooling. Thus, as a means to hastening the process of spreading the melt on the flat surface as a thin film, manual operation of the blade was practiced. However, this was also not successful again owing to the increasing viscosity of the material by cooling. The reason for the failure of this method is because of the comparably high temperature requirement, i.e., around melt temperature during the spreading process, whereas spreading had to be done at room temperature with the existing spreader.

IV. 1.3. Obtaining a Film by Adding Zeolite to a Solution of Polyethylene

To eliminate the spreadability problem associated with the phase change induced by cooling in the previous method, a similar but less temperature affected method was used. In this respect as a suitable solvent to dissolve polyethylene, xylene, was selected. As the necessary preliminary study the solute/solvent ratio and the temperature giving the best solution was determined.This was obtained when a ratio one part polyethylene per ten parts xylene was used at 75^0C. Then, as the other parameter to be decided, zeolite/polyethylene ratio appeared to be the best at 0.1 grams of zeolite per one gram of polyethylene. However, the resulting mixture of the dissolved polyethylene and zeolite was like a jelly which again was not any more a spreadable fluid at the operation temperatures of the spreading machine. This was most probably due to the rapid temperature drop from 75^0C to room temperature and adsorption of some solvent by the zeolite particles to yield a highly concentrated solution of polyethylene in xylene.

The unsuccessful spreading due to solidification of the mixture as a non-uniform layer on a plate by vaporizing the solvent appeared as a suitable procedure by which thick films could be obtained. Then small pieces could be formed from the thick films to be subjected to hot pressing.

The films produced according to the above procedure were quite successful than the previous ones. The distribution of zeolite through the film was quite uniform and the obtained film was more flexible, clear and the thickness of the film could be controlled easily by the amount of the small pieces to be pressed. However, this method was abondened since the film production by this method was not suitable and feasible for industrial purpose owing to utilization of a toxic solvent, time consumption and the need for additional equipments as well as provision for ventilation comperatively giving rise to high cost.

IV. 1.4. Coating Polyethylene Granules in a Druggie Pan

For industrial purposes, the idea of employment of polyethylene beads in place of polyethylene film seemed to be a more applicable processing method. Thus, in the further studies it was planned to first attach zeolite particles on to the surface of polyethylene beads and then have them extruded as a film.

In the preliminary trials it was observed that it was quite hard to have zeolite particles attached to and kept on the surface of polyethylene beads.To accomplish this polyethylene beads were added to a bed of zeolite particles prepared in the druggie pan and heated. Subsequent to several temperature-time studies in the dragee pan, the best result for this method was obtained as one hour at 180^0C using 53, 106 and 212μ average sizes of zeolite. This method was also considered as not suitable primarily because the production rate was very low and further, condensation of the oil vapors generated in the oil bath took place on the material. The latter problem could have been solved by placing a cover on the mouth of the pan. However, then additional manufacturing cost would be introduced as for a special lid with window.

IV. 1.5. Extrusion of Polythylene Film with Zeolite

From the previous trials it was estimated that for a successful coating of polyethylene beads, the beads should be immersed in considerably excess amount of zeolite and heated. The heating trials were done in an oven. For each size group of the zeolite particles used, the best result was obtained as three hours at 145^0C. The mass ratio was high with large particles and quite low with the fine ones. The results as mass of zeolite per mass of polyethylene beads at the end of 3 hours at 145^0C with respect to the average particle sizes of 53, 106 and 212μ were 1.082, 1.133 and 1.256 respectively.

The resulting beads were found to be successfully covered and hence subjected to extrusion in an industrial extruder. However, because the extruder was not a specific one for this composite material, the zeolite particles sedimented at the bottom and formed aggregates which caused surface disorders. In addition they were quite thick because the air pressure used in the extruder was not sufficient to blow the zeolite containing heavy films. However, an intermediate zone in the extruded film was quite promising for improvement.

This method with respect to the loss of material and non-uniformity of the produced films was considered unsuccessful although it was an achievement for industrial application.

IV. 1.6. Extrusion of Polyethylene Films with Zeolite and Hot Pressing

Despite the fact that extrusion of zeolite coated polyethylene beads as a film was considered unsuccessfull, still it was an achievement provided the product can be improved with respect to thickness and uniformity. Therefore, excluding a length of the film at the two ends, the smooth zone having uniform zeolite distribution was removed from the extruded film. Since the film was thick as a final improvement the selected zone of the film was subjected to hot pressing.

The film obtained after pressing offered most of the expected flexibility and uniformity in thickness and the distribution of zeolite particles in the film. Therefore, it was decided to use this film in the gas permeability tests.

In the Table IV. 1. the methods used, optimum values of the parameters employed and the results are summarized.

In the light of the studies performed the following steps can be recommended for the industrial zeolite covered polyethylene film production:

According to the desired production capacity, the ground zeolite particles and polyethylene beads should be placed in a tank of sufficient volume, in a ratio to have all the beads kept buried in the zeolite particles. The amount and the purity of the raw materials are very important. The polyethylene beads should be pure and be of high quality. In the same manner zeolite particles should be composed of only one kind of zeolite so that the physical properties of the film can easily be controlled. In order to obtain a uniform and homogeneous film, the particle size and the size range of the zeolite particles should be very small, i.e., smaller than 53μ and its amount should be excess to have all of the beads kept buried in the zeolite particles bed. By this way, zeolite in powdered form will easily cover the whole surface of the polyethylene beads

Table. IV. 1. The optimum parameters and corresponding results obtained from the different methods of film production.

Methods	Optimum Parameters	Result
Hot Pressing	Zeolite particle size less than 74μ. 100 -150°C of pressing temperature. 0.3-3 hours of pressing	Unsuccessful since no homogeneity achieved.
Mixing polyethylene melt with zeolite	Melting range 190-205°C Zeolite particle sizes of 74μ were used	Unsuccessful due to difficulty in spreading as a film.
Adding zeolite to polyethylene + solvent solution	Dissolving temperature of 75°C zeolite with particle size less than 74μ were added as 0.05, 0.1, 0.15, 0.2 and 0.25 parts of zeolite per parts of polyethylene Hot pressing at 130°C for 5 minutes.	Film was successful but the method was not suitable and feasible for industrial production.
Coating polyethylene beads with zeolite in a druggie pan	Heating temperature of 180°C and time of 0.5-1 hours.	Method was not suitable since the production capacity was very low.
Extrusion of polyethylene film with zeolite	For coating temperature of 145°C and 3 hours required. 0.082 g 53μ / 1.0 g PE 0.133 g 106μ / 1.0 g PE 0.256 g 212μ / 1.0 g PE	Method was suitable however, due to large amounts of zeolite, films were not uniform.
Extrusion and hot pressing	Hot pressing At 120°C for 5 minutes.	Method was successful and the produced films were suitable

Tank should be suitable for continuous mixing and heating. After putting polyethylene beads and the zeolite particles in the tank they should be heated to 145^0C and kept at that temperature for three hours while mixing continuously. Then the combined material should go over a sieve to eliminate the excess of the zeolite particles, which may cause formation of aggregates and hence subsequent disorders. As an alternative design fluidized bed coating can be studied.

When this process is finished zeolite covered polyethylene beads should be extruded through a straight die opening into a thick film. In the extruder air feed rate must be determined for such a material. The produced raw film from the extruder should be pressed between hot rolls at a specified temperature around 130^0C and a convenient pressure depending on the set thickness of the film so that a film with desired thickness can be obtained.

IV. 2. MEASUREMENT OF PERMEABILITY TO WATER VAPOR

Water vapor permeability measurements were carried out at three different temperatures and for five different films. The 212μ, 106μ and 53μ films are produced by extrusion of zeolite coated polyethylene beads and hot pressing. Polyethylene film and FH film was obtained from the market. The experimental data as weight of water plus the film and the cup with respect to time for these films are given in Appendix A.1.

For the 212μ film the zeolite particles are in the size range of 212μm to 420μm, for 106μ film between 212μ and 106μ and for 53μ film between 106μ and 53μ. The 212μ film, 106μ film and 53μ film contained 15± 3 %, 15± 3 % and 5 ± 3 % zeolite by weight, respectively. The film thicknesses for the five films were; 0.35mm, 0.30mm, 0.35mm, 0.08mm and 0.05mm respectively for 212μ film, 106μ film ,53μ film, polyethylene film and FH film.

For these films the fraction of water lost versus time plots are given in Figures IV.1 to IV.3 for 10^0C, 20^0C and 30^0C measurements.

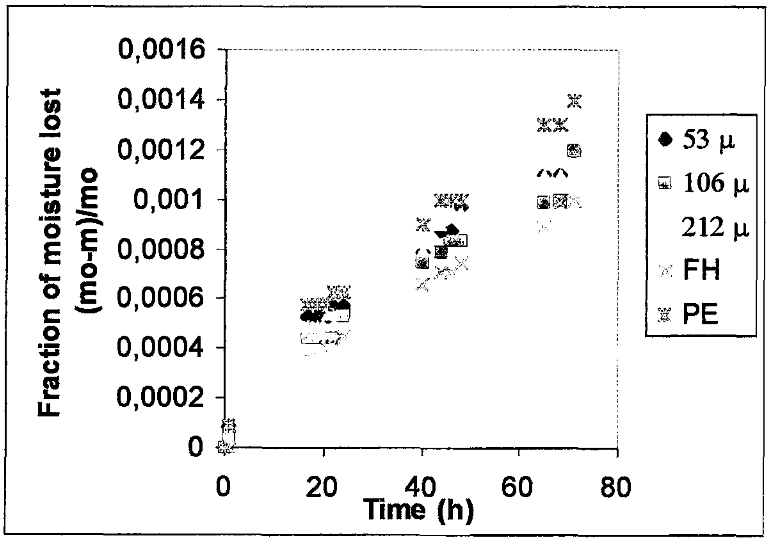

Figure IV.1. The fraction of moisture lost with respect to time at 10^0C.

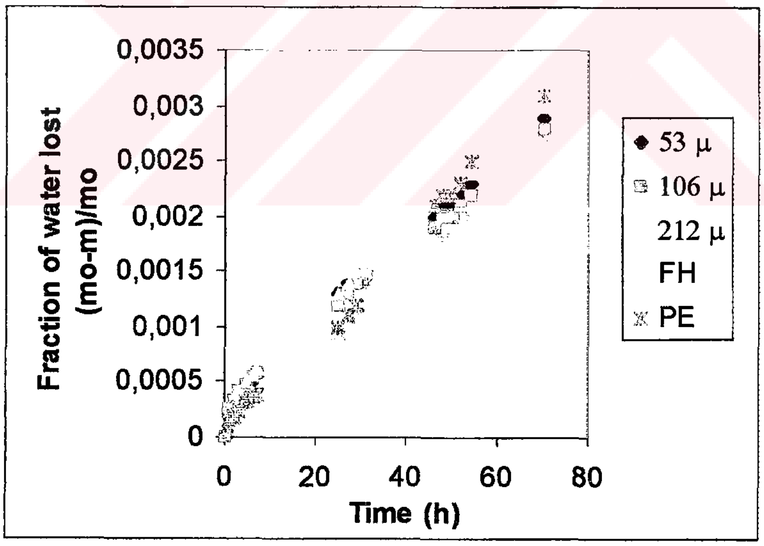

Figure IV.2. The fraction of moisture lost with respect to time at 20^0C.

The trends of the fraction of moisture lost with respect to time, i.e., water permeation with time, curves indicate two distinct zones. For the initial few hours, they exhibit an unsteady behaviour with gradual decrease from high rates to their steady state values. In the second zone, the linear trend implies steady or constant moisture transfer rate.

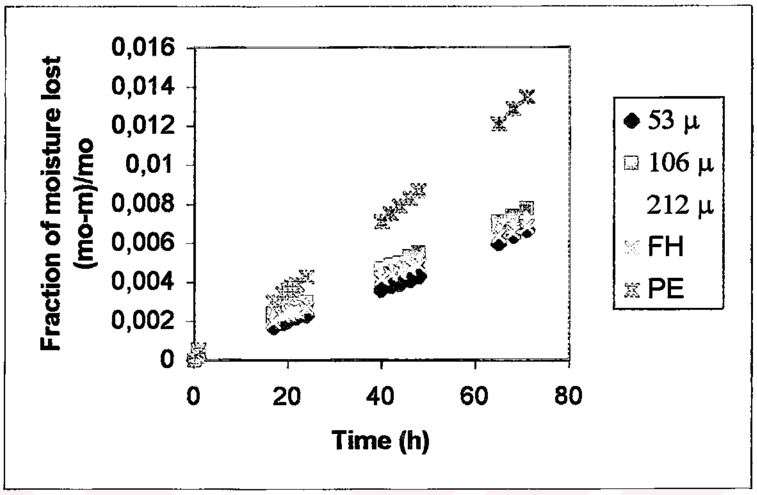

Figure IV.3. The fraction of moisture lost with respect to time at 30^{0}C.

This kind of a trend can be modelled by using the Langmuir isotherm type of equation. This equation can be written including the parameters of the water vapor permeability measurement experiments as follows:

$$m^* = \frac{K_1 t}{K_2 + t} \qquad \text{(IV.1.)}$$

where m^* is the fraction of moisture lost written as $(m_0 - m)/m_0$. The m values are the average of two measurements. The model constants are calculated and given in Table IV.2. The values of the K_1 represents the m^* value at very large times. Which represents the highest possible value for fraction of water lost.

However, in several measurements it was observed that, within the experiment time,i.e., 70 hours, the lost fraction was higher than those values. As previously stated the heater-cooler oven uses air from surroundings for cooling purpose. Therefore, the conditions within the oven changes continuosly. Although the Langmuir isotherm equation represents the data with high regression coefficients, oving to the problems related with the measurement system, use of the model for the given system is restricted to short times i.e., two or three days.

Table IV.2. The rate coefficients for the model equation.

	K_1	K_2	R^2
T = 10^0 C			
53 film	9,68E-04	33,9	0,9979
106 film	1,15E-03	19,3	0,9944
212 film	9,59E-04	22,3	0,9963
PE film	1,12E-03	27,3	0,9974
FH film	2,26E-03	14,6	0,9820
T = 20^0 C			
53 film	1,84E-03	8,9	0,9155
106 film	1,68E-03	6,7	0,8583
212 film	1,88E-03	8,1	0,9004
PE film	1,60E-03	12,5	0,8960
FH film	2,08E-03	23,5	0,9741
T = 30^0 C			
53 film	6,27E-03	10,1	0,9916
106 film	6,27E-03	25,2	0,9985
212 film	6,28E-03	9,7	0,9881
PE film	6,49E-03	11,4	0,9926
FH film	8,21E-03	96,5	0,9888

From Figures IV.1. to IV.3. it can be seen that polyethylene film has the highest permeability to water vapor. Addition of zeolite to this film decreased its permeability. The manufactured film permeabilities were between polyethylene and FH film.

For the water vapor permeability measurement data single factor analysis of varience was applied in order to see if there exists a significant change in the amount of water present in the cup. The results showes that, there is no significant change in the amount both for temperature and film effects. For this analysis the resulting F values were smaller than the critical F values corresponding to α=0.05 indicating insignificant difference as shown in Appendix A.4.

IV. 3. MEASUREMENT OF CARBONDIOXIDE AND OXYGEN PERMEABILITIES

The experimental results pertaining to the permeabilities of the five films separately to carbondioxide and oxygen are given in the Appendix A.3. The data reflect the variation of the concentration of the gas with time for the film used.

The thicknesses of the films named 212μ, 106μ, 53μ, polyethylene and FH were 0.30, 0.30, 0.35, 0.08 and 0.05 mm respectively, as measured by a micrometer. Further, the steady high pressure chamber concentrations for CO_2 as percent by value in the carbondioxide-nitrogen mixture were 20.22, 18.18, 20.26, 17.10 and 18.76 for the films 212μ, 106μ, 53μ, polyethylene and FH films respectively. Similarly, the steady oxygen concentrations were 9.54, 7.78, 11.09, 10.42 and 10.18 in the written order of the films above.

The plots of permeability data for carbondioxide and oxygen for the tested films are shown in Figures IV.4. to IV.8.

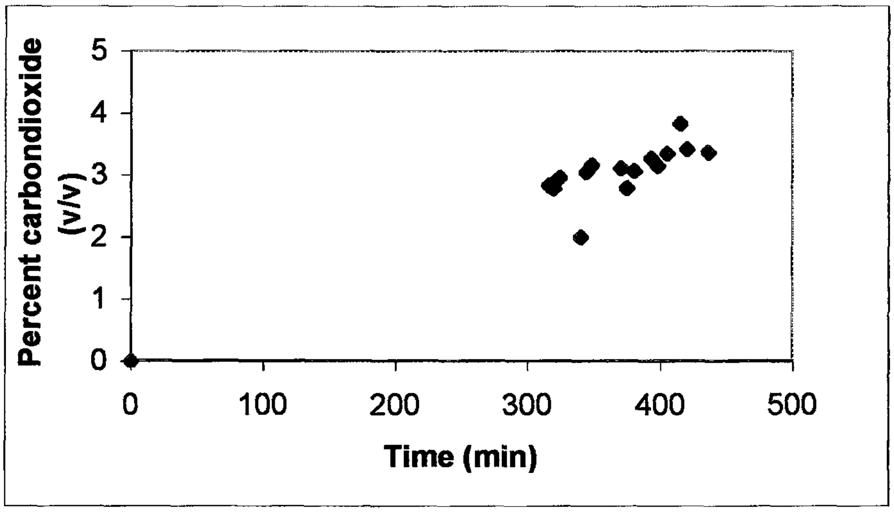

Figure IV.4.(a.) The increase of percent carbondioxide with respect to time for 212μ film.

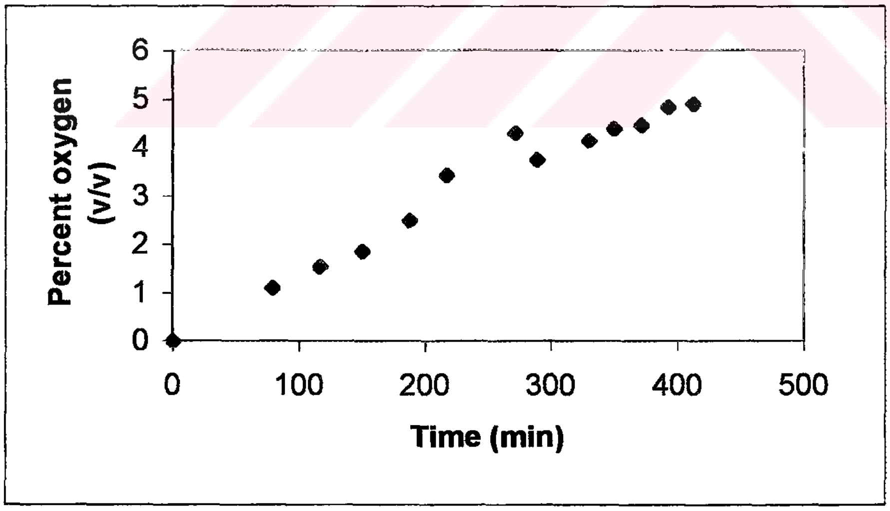

Figure IV.4.(b.) The increase of percent oxygen with respect to time for 212 μ film.

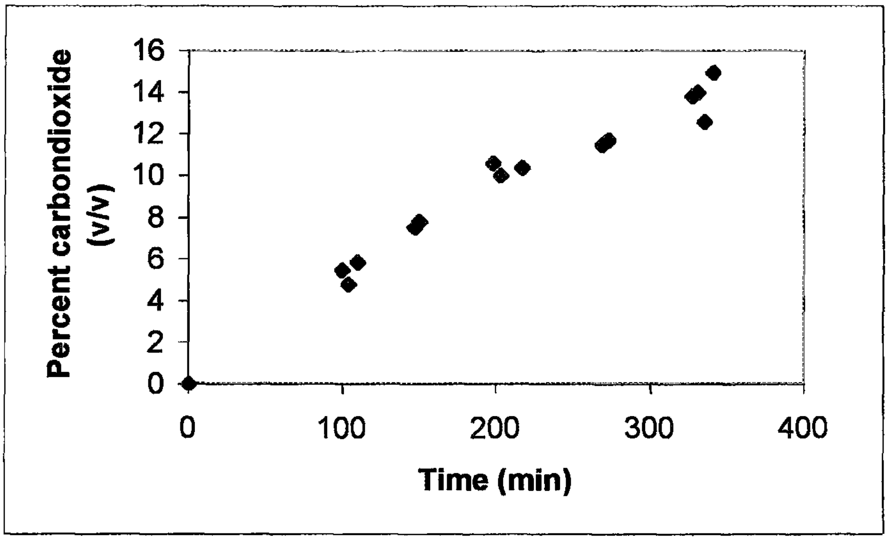

Figure IV.5.(a.) The increase of percent carbondioxide with respect to time for 106µ film.

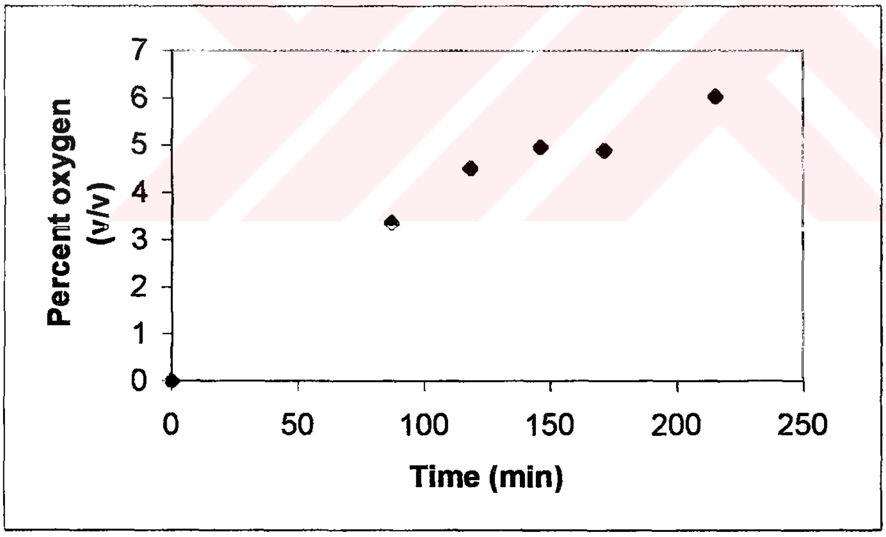

Figure IV.5.(b.) The increase of percent oxygen with respect to time for 106µ film.

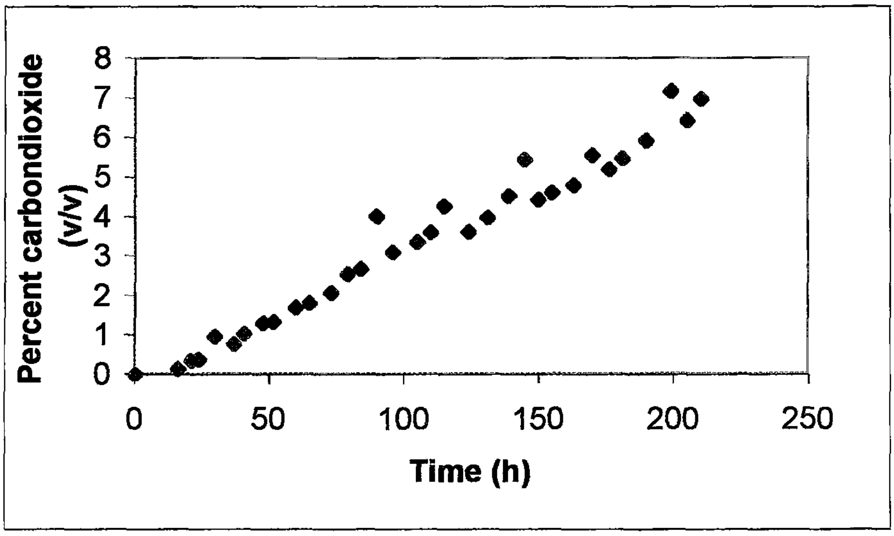

Figure IV.6.(a.) The increase of percent carbondioxide with respect to time for 53μ film.

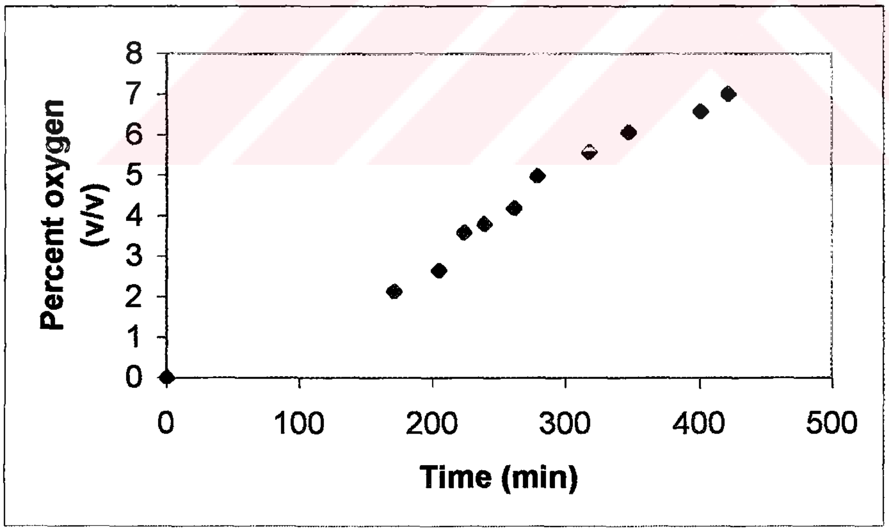

Figure IV.6.(b.) The increase of percent oxygen with respect to time for 53μ film.

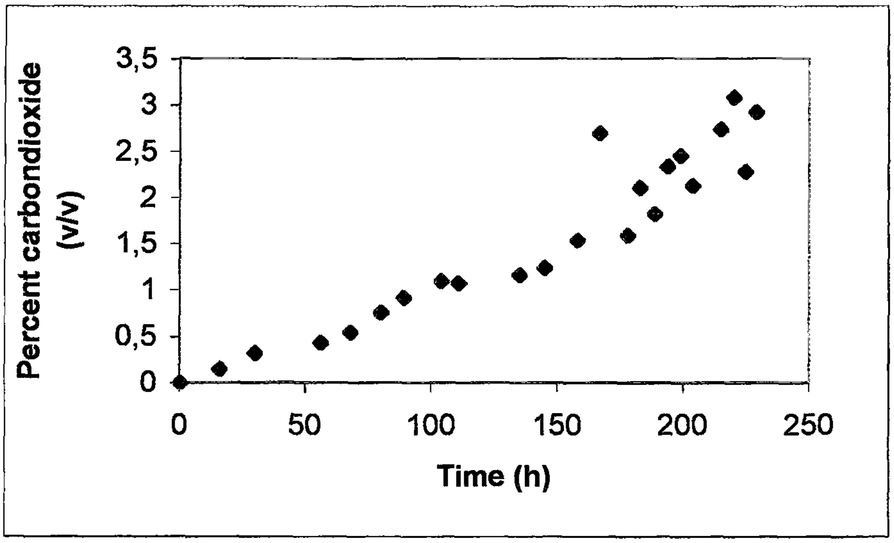

Figure IV.7.(a.) The increase of percent carbondioxide with respect to time for polyethylene film.

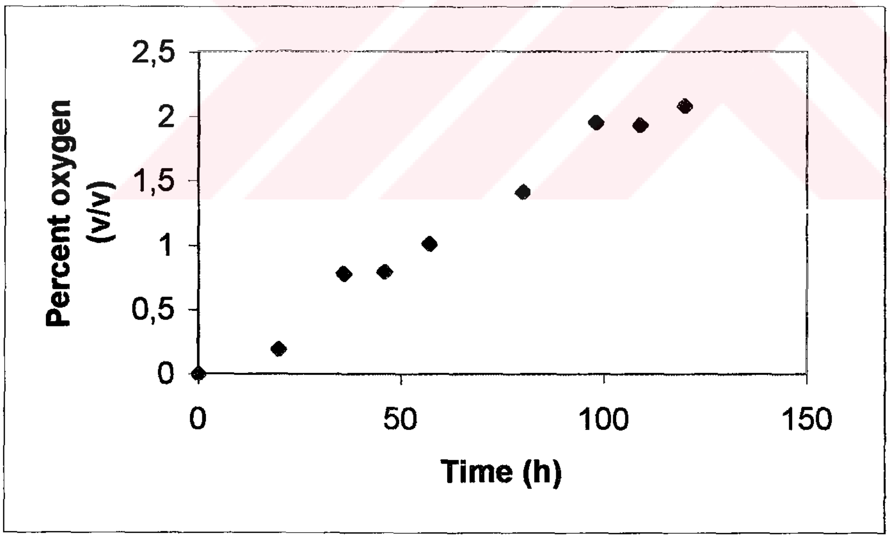

Figure IV.7.(b.) The increase of percent oxygen with respect to time for polyethylene film.

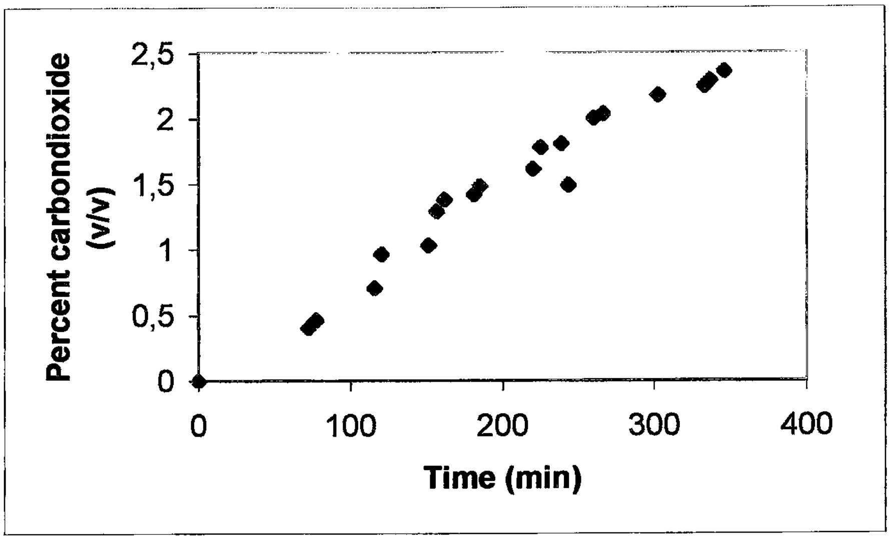

Figure IV.8.(a.) The increase of percent carbondioxide with respect to time for FH film.

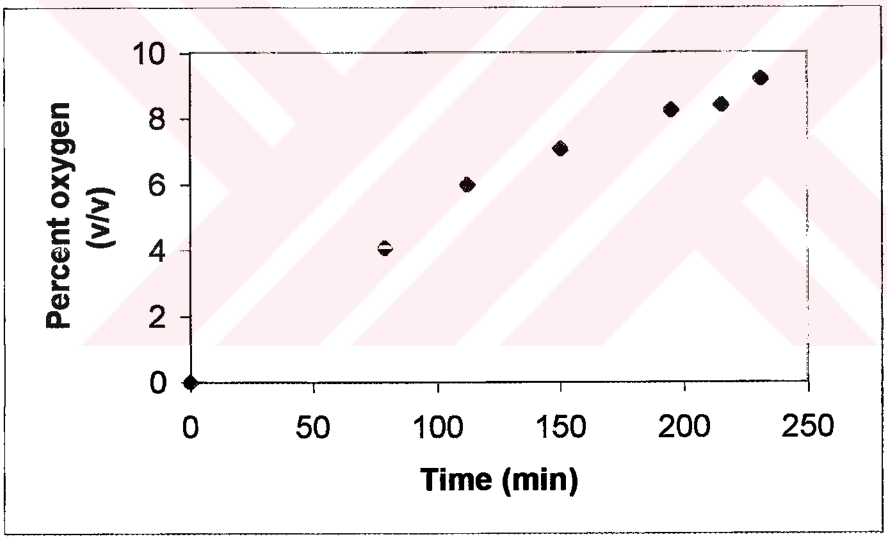

Figure IV.8.(b.) The increase of percent oxygen with respect to time for FH film.

In the measurements the pressure in the high and low pressure sides were kept at 1.033 atm and 0.927 atm respectively. The volume of the low pressure side was 100 cm^3.

The percentage values given by the chromatopack was converted into volumes by multiplying them with the volume of the low pressure side. Using the difference of the two pressures and with the known values of area and the total time the permeability (B) values were calculated as,

B=(amount of gas)(film thickness)/(area)(time)(pressure difference)

The permeability values are given in Table IV.3. As can be seen from this table the ratio of carbondioxide permeability to oxygen permeability increased with increasing particle size of the zeolites.

Table IV. 3. The permeabilities of carbondioxide and oxygen.

Particle size of zeolite	B_{CO2} (cm^3.mil/ m^2.day.atm)	B_{O2} (cm^3.mil/ m^2.day.atm)	B_{CO2}/B_{O2}
Polyethylene	59389	54894	1.082
53μ	135925	116780	1.164
106μ	258549	193395	1.337
212μ	135942	82266	1.655
FH	6509	35084	0.185

To assess the validity of this result, as a second means Equation (II.10) was used for determination of the permeabilities from the plots of ln ((C_{A0} - C_A) / C_{A0}) versus time. The parameter (DHS/LV) was calculated from the slope for each film. Then, from the known values of the diffusion area $3.02*10^{-3}$ m^2, diffusion volume 100 cm^3 and thickness of the films, the permeability of the films were found as the product of D.H with the units with the units m^2/s.

For each film relative permeabilities were calculated for carbondioxide and oxygen by dividing the produced film's permeability for that gas with that of the polyethylene film. Finally, for comparison the ratio of the relative permeabilities of carbondioxide to that of oxygen for the produced films were calculated. Results for this second procedure are given in Table IV.4. From this table it can be seen that, the ratio of relative carbondioxide permeability to relative oxygen permeability increases with increasing particle size of the zeolite, which confirm the findings in Table IV.3.

The reason for using relative permeabilities and their ratios for carbondioxide and oxygen was aimed to minimize the possible multiplicative type material and method errors.

Table. IV.4. The relative permeabilities of CO_2 and O_2 changing with average particle size of zeolite.

Particle size of zeolite	Relative CO_2 Permeability	Relative O_2 Permeability	Ratio of Relative CO_2 Perm. To Relative O_2 Permeability
53μ	34.99	18.93	1.85
106μ	59.87	30.63	1.95
212μ	23.96	9.37	2.56

From the calculated relative permeabilities it is seen that the permeabilities of the produced films are more than the polyethylene. This means that addition of zeolites to polyethylene film increases its permeability to the gases studied.

In membrane science the ratio of gas permeabilities are referred as the selectivity. By examining the results from that point of view, it can be said that the effect of increasing average particle size is more than providing holes for gases to permeate. If such evidence would have been occurred due to the empty spaces between zeolites and polymer molecules, the gas permeabilities would be increased with decreasing selectivity. However, in this case the selectivity is increased although there exist a reduction in permeation rate for 212μ films.

According to the results of the study the ratio of the average of the carbondioxide permeabilities to that of oxygen for polyethylene film was 1.065 at 290K. This value was verified by having the films subjected to measurement also in the set up in Tübitak Marmara Research Institute as 1.0135 at 295K

The permeabilities of FH film for carbondioxide and oxygen was quite low with respect to the polyethylene film used and the manufactured film. As stated before, this film was the only one at hand which contained zeolite, and its zeolite and polymer compositions were not published as it is a patented product. Therefore, this film was used as a sample to compare the manufactured films.

IV. 4. Examination of the Film Structure by Image Analysis Technique

The images of each film well representing the film structure which were magnified by ten times were chosen and stored. The print-outs of those images are given in the Figures IV.11 to 15.

The images of the polyethylene film purchased from the market and that of the produced film appears to be about the same. The zeolite particles are seen on the pictures as embedded within the film structure.

The image of the FH film is quite different from the others, implying different polymer structure, zeolite type and processing.

Figure IV.9. The film structure of 212µ film.

Figure IV.10. The film structure of 106μ film.

Figure IV.11. The film structure of 53μ film.

Figure IV.12. The film structure of polyethylene film.

Figure IV.13. The film structure of FH film.

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

V. 1. CONCLUSIONS

Aim of this study was to manufacture a new polymer based packaging material and test it for the permeabilities of oxygen, carbondioxide and water vapor.

At the stage of film production it can be concluded that polyethylene beads should be first covered with zeolite particles prefarably at around 145^0C and during a suitable time. Then films should be produced by extrusion followed by a hot press treatment. The zeolite particle size to be used for coating the polyethylene beads should be less than 53μ and the pressure and the temperature for the extruder must be determined specifically for the feed.

For desirable mechanical and physical properties of the proposed film according to the recommended process, the zeolite particle size, zeolite/polyethylene ratio, temperature and pressure in both extrusion and finishing rolls should be carefully adjusted. Further, the amount and purity of the raw materials are very important.

The permeabilities of the produced films for water vapor indicate an increase with temperature and the produced films permeability values were between that of polyethylene and FH films.

The permeabilities of the produced films for carbondioxide and oxygen indicate an increase in the ratio of the carbondioxide to oxygen permeability with increasing zeolite particle size. As the reverse is required for MA conditions, smallest possible zeolite particle size should be used for the production of polyethylene based film.

V. 2. RECOMMENDATIONS

For future work it can be recommended that the permeabilities of the produced films for ethylene gas, which, being a plant growth hormone, is very important in storage of the commodity should be measured.

Also, in order to observe the effect of temperature on the film permeabilities, gas permeability measurements in the temperature range 4-40^{0}C can be recommended.

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APPENDIX

A.1 Data for weight of water in the measurement cup.

A.1.1. The weight of water (g) with respect to time for 212µ film at different temperatures.

T = 10^0 C			T = 20^0 C			T = 30^0 C		
t (h)	cup 1 (g)	cup 2 (g)	t (h)	cup 3 (g)	cup 4 (g)	t (g)	cup 5 (g)	cup 6 (g)
0	113,77	111,90	0	111,29	113,76	0	112,63	110,94
1	113,77	111,88	1	111,27	113,74	1	112,59	110,92
17	113,73	111,83	2	111,26	113,74	17	112,37	110,71
19	113,73	111,83	3	111,26	113,73	19	112,35	110,69
21	113,72	111,83	5	111,25	113,72	20	112,34	110,67
22	113,72	111,83	6	111,25	113,72	22	112,32	110,65
24	113,71	111,82	7	111,24	113,71	24	112,30	110,64
40	113,70	111,79	25	111,16	113,64	40	112,12	110,47
44	113,69	111,78	27	111,16	113,63	44	112,09	110,43
46	113,68	111,78	31	111,15	113,62	46	112,06	110,41
48	113,68	111,78	46	111,09	113,56	48	112,04	110,39
65	113,66	111,76	50	111,07	113,55	65	111,87	110,23
68	113,66	111,76	54	111,05	113,53	68	111,83	110,21
71	113,65	111,74	70	110,97	113,46	71	111,80	110,18

A.1.2. The weight of water (g) with respect to time for 106μ film at different temperatures.

T = 10^0 C			T = 20^0 C			T = 30^0 C		
t (h)	cup 1 (g)	cup 2 (g)	t (h)	cup 3 (g)	cup 4 (g)	t (h)	cup 5 (g)	cup 6 (g)
0	113,10	114,44	0	111,05	112,95	0	113,14	113,39
1	113,10	114,44	1	113,78	112,94	1	113,11	113,35
17	116,01	114,38	2	113,77	112,94	17	112,87	113,15
19	116,01	114,38	3	113,76	112,94	19	112,84	113,14
21	116,01	114,38	5	113,75	112,94	20	112,83	113,12
22	116,01	114,38	6	113,75	112,93	22	112,79	113,10
24	116,01	114,37	7	113,75	112,93	24	112,77	113,09
40	115,98	114,34	25	113,68	112,86	40	112,55	112,92
44	115,97	114,34	27	113,67	112,85	44	112,51	112,89
46	115,97	114,33	31	113,66	112,84	46	112,47	112,87
48	115,96	114,33	46	113,61	112,78	48	112,45	112,85
65	115,95	114,31	50	113,59	112,77	65	112,23	112,70
68	115,95	114,31	54	113,57	112,75	68	112,19	112,66
71	115,93	114,29	70	113,51	112,69	71	112,14	112,63

A.1.3. The weight of water (g) with respect to time for 53μ film at different temperatures.

T = 10^0 C			T = 20^0 C			T = 30^0 C		
t (h)	cup 1 (g)	cup 2 (g)	t (h)	cup 3 (g)	cup 4 (g)	t (h)	cup 5 (g)	cup 6 (g)
0	116,07	112,76	0	113,80	112,03	0	114,78	114,03
1	116,06	112,75	1	113,78	112,02	1	114,76	114,01
17	116,01	112,70	2	113,77	112,02	17	114,62	113,81
19	116,01	112,70	3	113,76	112,01	19	114,60	113,79
21	116,01	112,70	5	113,75	111,99	20	114,58	113,77
22	116,01	112,69	6	113,75	111,98	22	114,56	113,75
24	116,01	112,69	7	113,75	111,97	24	114,55	113,74
40	115,98	112,67	25	113,68	111,87	40	114,42	113,56
44	115,97	112,66	27	113,67	111,86	44	114,40	113,54
46	115,97	112,66	31	113,66	111,85	46	114,37	113,51
48	115,96	112,65	46	113,61	111,79	48	114,35	113,49
65	115,95	112,64	50	113,59	111,78	65	114,12	113,33
68	115,95	112,63	54	113,57	111,76	68	114,06	113,30
71	115,93	112,62	70	113,51	111,70	71	114,02	113,26

A.1.4. The weight of water (g) with respect to time for polyethylene film at different temperatures.

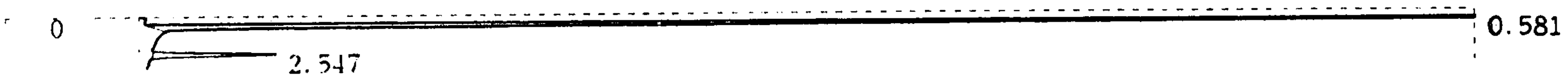
T = 10^0 C			T = 20^0 C			T = 30^0 C		
t (h)	cup 1 (g)	cup 2 (g)	t (h)	cup 3 (g)	cup 4 (g)	t (h)	cup 5 (g)	cup 6 (g)
0	111,44	112,17	0	112,09	110,31	0	111,05	113,70
1	111,44	112,15	1	112,08	110,29	1	111,02	113,60
17	111,38	112,10	2	112,08	110,28	17	110,80	113,27
19	111,38	112,10	3	112,07	110,28	19	110,75	113,24
21	111,38	112,10	5	112,06	110,27	20	110,71	113,23
22	111,38	112,09	6	112,05	110,27	22	110,67	113,19
24	111,38	112,09	7	112,05	110,27	24	110,62	113,17
40	111,35	112,06	25	111,99	110,19	40	110,25	112,91
44	111,34	112,05	27	111,98	110,19	44	110,15	112,84
46	111,34	112,05	31	111,95	110,16	46	110,08	112,80
48	111,34	112,05	46	111,87	110,08	48	110,03	112,77
65	111,32	112,01	50	111,85	110,06	65	109,77	112,51
68	111,32	112,01	54	111,82	110,04	68	109,67	112,45
71	111,31	111,99	70	111,75	109,96	71	109,63	112,40

A.1.5. The weight of water (g) with respect to time for FH film at different temperatures.

T = 10^0 C			T = 20^0 C			T= 30^0 C		
t (h)	cup 1 (g)	cup 2 (g)	t (h)	cup 3 (g)	cup 4 (g)	t (h)	cup 5 (g)	cup 6 (g)
0	114,18	112,37	0	111,75	110,20	0	110,15	112,49
1	114,18	112,37	1	111,74	110,19	1	110,14	112,45
17	114,15	112,32	2	111,74	110,18	17	109,94	112,25
19	114,15	112,32	3	111,72	110,17	19	109,92	112,22
21	114,14	112,32	5	111,72	110,17	20	109,91	112,21
22	114,14	112,32	6	111,72	110,16	22	109,89	112,20
24	114,13	112,29	7	111,71	11015	24	109,87	112,18
40	114,11	112,28	25	111,65	110,09	40	109,71	112,01
44	114,11	112,28	27	111,64	110,08	44	109,67	111,98
46	114,11	112,28	31	111,63	110,06	46	109,65	111,95
48	114,10	112,28	46	111,58	110,01	48	109,64	111,93
65	114,09	112,26	50	111,56	109,99	65	109,48	111,75
68	114,08	112,25	54	111,53	109,98	68	109,45	111,73
71	114,08	112,24	70	111,45	109,90	71	109,42	111,69

A.2. Sample chromatoghraphs for oxygen and carbondioxide.

```
C-R4A CHROMATOPAC    CH=1    REPORT No.=1    CHROMATOGRAM=1:@CHRM1.C00     20 05 99   15:06:08
```



```
** CALCULATION REPORT **
CH PKNO     TIME           AREA        HEIGHT     MK   IDNO        CONC           NAME
 1    1     0.581          83911       21644                        98.568
      2     2.547           1219          93                         1.432
                        -----------  ---------              ----------------
          TOTAL            85130       21737                        100
```

```
C-R4A CHROMATOPAC    CH=1    REPORT No.=2    CHROMATOGRAM=1:@CHRM1.C00     20/05/99   15:10:36
```

```
** CALCULATION REPORT **
CH PKNO     TIME           AREA        HEIGHT     MK   IDNO        CONC           NAME
 1    1     0.579          84404       21891                        98.5351
      2     2.54            1255          96                         1.4649
                        -----------  ---------              ----------------
          TOTAL            85658       21987                        100
```

```
C-R4A CHROMATOPAC    CH=1    REPORT No.=3    CHROMATOGRAM=1:@CHRM1.C00     20/05/99   15:14:47
```

```
** CALCULATION REPORT **
CH PKNO     TIME           AREA        HEIGHT     MK   IDNO        CONC           NAME
 1    1     0.572          74234       19701                        98.5126
      2     2.508           1121          86                         1.4874
                        -----------  ---------              ----------------
          TOTAL            75355       19787                        100
```

A.2. (continued)

```
C-R4A CHROMATOPAC    CH=1    REPORT No.=11    CHROMATOGRAM=1:@CHRM1.C00      31/05/99   12:25:00
```

```
** CALCULATION REPORT **
CH PKNO     TIME         AREA         HEIGHT    MK   IDNO        CONC            NAME
 1    1     4.587          984            59                    8.4317
      2    10.051        10682           257                   91.5683
                       -----------   ---------             --------------
        TOTAL            11666           316                      100
```

```
C-R4A CHROMATOPAC    CH=1    REPORT No.=12    CHROMATOGRAM=1:@CHRM1.C00      31/05/99   12:41:59
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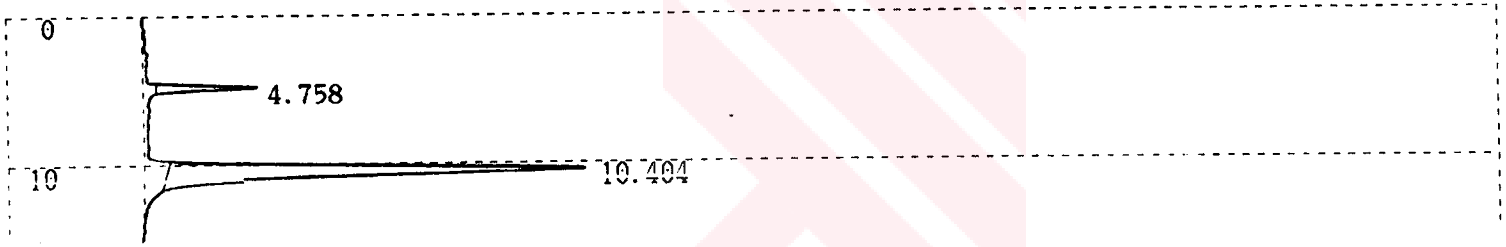

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** CALCULATION REPORT **
CH PKNO     TIME         AREA         HEIGHT    MK   IDNO        CONC            NAME
 1    1     4.758         1373            73                     9.232
      2    10.404        13497           307                    90.768
                       -----------   ---------             --------------
        TOTAL            14870           380                      100
```

A.3. The data for gas concentrations with respect to time.

A.3.1. The permeability data for oxygen and carbondioxide for 212μ film.

Time (min)	% CO2
0	0,0000
316	2,8329
320	2,7860
324	2,9573
340	2,0041
344	3,0528
348	3,1656
370	3,1105
375	2,7916
380	3,0736
393	3,2746
398	3,1528
405	3,3455
415	3,8321
420	3,4177
436	3,3676

Time (min)	% O2
0	0,0000
79	1,1026
117	1,5403
150	1,8559
188	2,4885
217	3,4242
271	4,3045
289	3,7490
330	4,1431
350	4,4004
371	4,4707
392	4,8515
412	4,9138

A.3.2 The permeability data for oxygen and carbondioxide for 106µ film.

Time (min)	%CO2
0	0,0000
100	5,4813
104	4,8000
110	5,8213
147	7,5193
150	7,7861
198	10,6043
203	10,0107
217	10,3792
269	11,4837
273	11,7240
327	13,8178
331	13,9969
335	12,6040
341	14,9418

Time (min)	% O2
0	0,0000
87	3,3550
118	4,5163
146	4,9711
171	4,8966
215	6,0311
234	6,0027

A.3.3. The permeability data for oxygen and carbondioxide for 53µ film.

Time (min)	% CO2
0	0,0000
16	0,1320
21	0,3459
24	0,3692
30	0,9563
37	0,7619
41	1,0297
48	1,3053
52	1,3250
60	1,6921
65	1,7963
73	2,0602
79	2,5285
84	2,6678
90	3,9971
96	3,0778
105	3,3352
110	3,5880
115	4,2452
124	3,5979
131	3,9520
139	4,5054
145	5,4297
150	4,4215
155	4,6004
163	4,7866
170	5,5576
176	5,1900
181	5,4657
190	5,9165
199	7,1757
205	6,4328
210	6,9713

Time (min)	% O2
0	0,0000
171	2,1362
205	2,6525
224	3,5903
239	3,7892
261	4,1888
279	4,9873
318	5,5881
347	6,0683
401	6,6000
422	7,0270

A.3.4. The permeability data for oxygen and carbondioxide for polyethylene film.

Time (min)	% CO2
0	0,0000
16	0,1540
30	0,3247
56	0,4376
68	0,5431
80	0,7602
89	0,9169
104	1,1011
111	1,0825
135	1,1657
145	1,2479
158	1,5455
167	2,7075
178	1,5978
183	2,1134
189	1,8328
194	2,3465
199	2,4599
204	2,1370
215	2,7443
220	3,0912
225	2,2907
229	2,9327

Time (min)	% O2
0	0,0000
20	0,1948
36	0,7788
46	0,7945
57	1,0138
80	1,4159
98	1,9586
109	1,9366
120	2,0883

A.3.5. The permeability data for oxygen and carbondioxide for FH film.

Time (min)	% CO2
0	0,0000
72	0,4036
77	0,4616
116	0,7104
120	0,9676
151	1,0361
156	1,2936
161	1,3799
181	1,4222
185	1,4842
220	1,6164
225	1,7819
239	1,8097
243	1,4943
260	2,0049
266	2,0398
302	2,1837
333	2,2491
337	2,2952
346	2,3640
353	2,3456
381	2,4198

Time (min)	% O2
0	0,0000
79	4,0801
112	6,0083
150	7,0923
195	8,2641
215	8,4317
231	9,2320

A.4. Single Factor ANOVA Tables for Film and Temperature Effects

Anova: Single Factor

Temperature Effect for 212μ Film

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
Row 1	3	337,69	112,5633	1,540933
Row 2	3	337,63	112,5433	1,564133
Row 3	3	337,36	112,4533	1,530433
Row 4	3	337,34	112,4467	1,532233
Row 5	3	337,31	112,4367	1,532233
Row 6	3	337,29	112,43	1,5343
Row 7	3	337,25	112,4167	1,535433
Row 8	3	336,98	112,3267	1,644933
Row 9	3	336,94	112,3133	1,637633
Row 10	3	336,89	112,2967	1,642233
Row 11	3	336,81	112,27	1,7167
Row 12	3	336,6	112,2	1,7587
Row 13	3	336,54	112,18	1,7949
Row 14	3	336,42	112,14	1,8823

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0,680783	13	0,052368	0,032089	1	2,088932
Within Groups	45,6942	28	1,631936			
Total	46,37498	41				

Anova: Single Factor Temperature Effect for 106µ Film

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
Row 1	3	337,29	112,43	1,4287
Row 2	3	339,99	113,33	0,1519
Row 3	3	342,65	114,2167	2,614533
Row 4	3	342,61	114,2033	2,659633
Row 5	3	342,59	114,1967	2,677733
Row 6	3	342,55	114,1833	2,732933
Row 7	3	342,53	114,1767	2,760933
Row 8	3	342,21	114,07	3,0553
Row 9	3	342,15	114,05	3,1012
Row 10	3	342,1	114,0333	3,167033
Row 11	3	342,02	114,0067	3,198033
Row 12	3	341,77	113,9233	3,542933
Row 13	3	341,71	113,9033	3,617733
Row 14	3	341,58	113,86	3,6829

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	9,01684	13	0,693603	0,252932	0,994056	2,088932
Within Groups	76,783	28	2,74225			
Total	85,79984	41				

Anova: Single Factor Temperature Effect for 53μ Film

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
Row 1	3	344,65	114,8833	1,296233
Row 2	3	344,6	114,8667	1,308133
Row 3	3	344,4	114,8	1,2787
Row 4	3	344,37	114,79	1,2927
Row 5	3	344,34	114,78	1,3069
Row 6	3	344,32	114,7733	1,311033
Row 7	3	344,31	114,77	1,3132
Row 8	3	344,08	114,6933	1,378533
Row 9	3	344,04	114,68	1,3813
Row 10	3	344	114,6667	1,400033
Row 11	3	343,92	114,64	1,4437
Row 12	3	343,66	114,5533	1,533233
Row 13	3	343,58	114,5267	1,579433
Row 14	3	343,46	114,4867	1,627433

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0,592574	13	0,045583	0,032809	1	2,088932
Within Groups	38,90113	28	1,389326			
Total	39,49371	41				

Anova: Single Factor Temperature Effect for Polyethylene Film

SUMMARY

Groups	Count	Sum	Average	Variance
Row 1	3	334,58	111,5267	0,276033
Row 2	3	334,54	111,5133	0,284933
Row 3	3	334,26	111,42	0,4108
Row 4	3	334,2	111,4	0,4359
Row 5	3	334,15	111,3833	0,455633
Row 6	3	334,1	111,3667	0,476233
Row 7	3	334,05	111,35	0,5119
Row 8	3	333,59	111,1967	0,774533
Row 9	3	333,47	111,1567	0,862433
Row 10	3	333,37	111,1233	0,909433
Row 11	3	333,24	111,08	0,8971
Row 12	3	332,94	110,98	1,1683
Row 13	3	332,81	110,9367	1,265833
Row 14	3	332,69	110,8967	1,251733

ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	1,767107	13	0,135931	0,19067	0,998507	2,088932
Within Groups	19,9616	28	0,712914			
Total	21,72871	41				

Anova: Single Factor Temperature Effect for FH Film

SUMMARY

Groups	Count	Sum	Average	Variance
Row 1	3	336,08	112,0267	4,117633
Row 2	3	336,06	112,02	4,1392
Row 3	3	335,83	111,9433	4,462033
Row 4	3	335,79	111,93	4,5063
Row 5	3	335,77	111,9233	4,504233
Row 6	3	335,75	111,9167	4,544633
Row 7	3	335,71	111,9033	4,564933
Row 8	3	335,47	111,8233	4,862533
Row 9	3	335,42	111,8067	4,949233
Row 10	3	335,39	111,7967	4,993733
Row 11	3	335,32	111,7733	5,000933
Row 12	3	335,13	111,71	5,3299
Row 13	3	335,06	111,6867	5,377633
Row 14	3	334,95	111,65	5,4589

ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	0,556412	13	0,042801	0,008969	1	2,088932
Within Groups	133,6237	28	4,772274			
Total	134,1801	41				

Anova: Single Factor Film Effect at 10^0 C

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
Row 1	5	568,56	113,712	2,82977
Row 2	5	568,55	113,71	2,818
Row 3	5	571,28	114,256	3,67808
Row 4	5	571,28	114,256	3,67808
Row 5	5	571,26	114,252	3,68127
Row 6	5	571,26	114,252	3,68127
Row 7	5	571,24	114,248	3,68452
Row 8	5	571,12	114,224	3,67863
Row 9	5	571,08	114,216	3,67808
Row 10	5	571,07	114,214	3,68073
Row 11	5	571,04	114,208	3,66372
Row 12	5	570,97	114,194	3,68073
Row 13	5	570,96	114,192	3,68127
Row 14	5	570,9	114,18	3,6632

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	2,30103	13	0,177002	0,049782	1	1,899267
Within Groups	199,1094	56	3,555525			
Total	201,4104	69				

Anova: Single Factor Film Effect at 20^0 C

SUMMARY

Groups	Count	Sum	Average	Variance
Row 1	5	559,98	111,996	1,17928
Row 2	5	562,65	112,53	1,3848
Row 3	5	562,62	112,524	1,37863
Row 4	5	562,57	112,514	1,37628
Row 5	5	562,53	112,506	1,37233
Row 6	5	562,52	112,504	1,37458
Row 7	5	562,5	112,5	1,3848
Row 8	5	562,16	112,432	1,38497
Row 9	5	562,12	112,424	1,37863
Row 10	5	562,05	112,41	1,38315
Row 11	5	561,76	112,352	1,39652
Row 12	5	561,66	112,332	1,39652
Row 13	5	561,54	112,308	1,40282
Row 14	5	561,19	112,238	1,42572

ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	1,419059	13	0,109158	0,079516	0,999992	1,899267
Within Groups	76,87612	56	1,372788			
Total	78,29518	69				

Anova: Single Factor   Film Effect at 30^0 C

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
Row 1	5	561,75	112,35	3,28435
Row 2	5	561,62	112,324	3,27323
Row 3	5	560,6	112,12	3,34245
Row 4	5	560,46	112,092	3,35867
Row 5	5	560,37	112,074	3,36643
Row 6	5	560,23	112,046	3,37263
Row 7	5	560,11	112,022	3,40607
Row 8	5	559,05	111,81	3,57485
Row 9	5	558,82	111,764	3,65028
Row 10	5	558,63	111,726	3,66873
Row 11	5	558,51	111,702	3,68327
Row 12	5	557,47	111,494	3,65183
Row 13	5	557,2	111,44	3,668
Row 14	5	557,01	111,402	3,65632

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	6,253104	13	0,481008	0,137551	0,999816	1,899267
Within Groups	195,8284	56	3,496936			
Total	202,0815	69				

VITA

Safiye Nur (Aktaş) Dirim was born in Ankara on April 3, 1967. She graduated from Food Engineering Department of Middle East Technical University in 1989. Soon after she started the MS Degree program and also started to work as a research assistant in the same department. She received her MS Degree from Food Engineering Department of Middle East Technical University in 1991. She started her Ph.D studies in the same department in 1991.

Her publications are ;

Aktaş,S.N. and Özilgen,M. 1992. Injury of *Escherichia coli* and Degradation of Riboflavin During Pasteurization with Microwaves in a Tubular Flow Reactor. Lebensmittel Wissenshaft und Technologie, 25(3).

Aktaş, S.N.. Kinetics of Microbial Death and Injury and Riboflavin Degradation with Microwave in a Tubular Flow Reactor. M.S. Thesis. M.E.T.U. Food Engineering Department.