

## A New Protective Polyethylene Based Film Containing Zeolites for the Packaging of Fruits and Vegetables: Film Preparation

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### Abstract

To manufacture a polyethylene film containing zeolite particles for the packaging of foods six manufacturing methods were tried: hot pressing, addition of zeolite to molten polyethylene and dissolved polyethylene solution, coating polyethylene beads with zeolite in a revolving heating pan, extrusion of polyethylene beads with zeolite and hot pressing of the extruded mix film. The experiments were repeated with three different particle sizes of zeolites received from the Bigadiç mine belonging to Etibank. The film produced by the hot pressing of co-extruded zeolite-polyethylene film was found to be quite satisfactory as a packaging material.

**Key words:** Packaging film, Polyethylene, Zeolite

### Introduction

Fresh fruits and vegetables harvested seasonally in large quantities from different areas are mostly stored in suitable environments until marketed and consumed. During storage and transportation, the appropriate maintenance conditions should be practiced since fresh fruit and vegetables are living systems and very sensitive to deteriorative effects (Kader, 1989). 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 (Mathlouthi and Leiris, 1990). As a feature of proper packaging in a sealed package a fresh product creates a modified atmosphere by respiration and gas permeation through the packaging material. Thus, suitable films for packaging should have desired levels of selective permeabilities to oxygen, carbon dioxide and ethy-

lene gases which necessitates commodity diffusion resistance and their effects on quality parameters to be established together with the effect of temperature on these. Such knowledge will enable the selection of a suitable packaging material.

Polyethylene is the most commonly used polymer film for packaging with its advantages of being inert, permeable to gases and impermeable to water vapor (Rooney, 1995). However, due to the large variety and variable properties of produce no single packaging material can be said to be ideal for use with all produce. In order to achieve satisfactory performance with many produce-film combinations, highly permeable porous patches were introduced. Among these a commercial product FH<sup>TM</sup> film containing natural zeolites embedded into polyethylene (Evert-Fresh Co. Inc., Japan) was reported to be extremely suitable for extending the shelf life of produce. Although zeolites have unlimited uses in planting, animal feeding, waste treatment and solar heat collectors (Mumpton, 1983), in Turkey they are unfortunately being wasted in unrelated areas, e.g., as filling

material in cement. With regard to these and the above facts considering the large amount of zeolite deposits of Turkey, in this study we aimed to produce a packaging material using polyethylene and natural zeolites.

## Materials and Methods

In the production of the composite film, finely ground natural zeolite was combined with commercial polyethylene either in the form of extruded film or as beads. Polyethylene was purchased from the market as polyethylene beads (Petkim, Turkey) or as film with a thickness of 0.06 mm. Zeolite was received from Etibank's Bigadiç natural mineral resources region in an unprocessed form. In the region the purity is quite high, containing about 80% ore and the rocks are mainly composed of clinoptilolite + heulandite with the remaining being erionite, chabazite and analcime as determined by X-ray diffraction analysis (Dokuz Eylül University). The zeolite mineral was in the form of large pieces about 20 x 18 x 8 cm in dimension as received from the region. These 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, USA). The ground samples were classified into three size ranges by sieving (Octagon 200 Test Sieve Shaker, Endocotts Limited, London). The three ranges selected were  $-420 \mu/+212 \mu$ ,  $-212 \mu/+106 \mu$  and  $-106 \mu/+53 \mu$ , which shall from now on be referred to as  $+212 \mu$ ,  $+106 \mu$  and  $+53 \mu$  respectively. The natural zeolite samples were analyzed in an X-ray diffractometer (Jeol JSDX-100 S4) and diffraction diagrams were obtained. For the analysis a  $\text{CuK}\alpha$  lamp, a 30 kV working voltage and a 22 mA working current were used. In order to obtain a zeolite + polyethylene film with suitable physical properties for packaging several methods were tried, which can be grouped into three.

In the first group of trials, hot pressing zeolite particles on a polyethylene surface was attempted. In this method zeolite was embedded on the surface of the polyethylene film confined between two plates where the temperature of the plates and the applied pressure could be adjusted. Zeolite particles with dimensions less than  $74 \mu$  (200 mesh) were used for the experiments. A pre-weighed amount of polyethylene film was placed on a non-sticking paper and a weighed amount of zeolite was spread onto the film

surface. This was covered with another non-sticking paper and hot pressed (Paul Weber Stgt. Uhlbach, Germany). The pressing temperature was measured by means of four thermocouples placed into the press located as close as possible to the surface of the press. Pressing was carried out at different temperatures and different periods as given in Table.

**Table.** Experimental parameters used for hot pressing.

Mass of zeolite per mass of polyethylene (kg/kg)	Temperature of Pressing (°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
2.4	100	190
2.4	122	30
5.0	120	250
5.0	145	30

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

In the second group of trials, zeolite was added to either melted or dissolved solutions of polyethylene. In the first part, polyethylene was melted and zeolite was added to the melt. The experiment was started at 65°C, whereafter about 80°C the film started to soften. In the temperature range 120-145°C shrinkage of the film took place and then in the range 150-165°C it started to melt. Between 190°C and 205°C it completely melted and slight mixing with zeolite particles of an average size  $74 \mu$  could be achieved. The mixture was not perfectly homogeneous at this temperature. The total time for heat-

ing was 2 h. 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 (w/w), for the average zeolite particle sizes of 74  $\mu$  were studied to determine the optimum ratio and particle size for spreading.

In the second part polyethylene was dissolved in a solvent and zeolite was added to this solution. The solvent used was xylene (Merck) as it is the most suitable for polyethylene. According to this procedure, the most proper polyethylene to xylene ratio was primarily determined by the several combinations tried. These were 1/10, 1/9, 1/8, 1/7 and 1/6 as mass ratios of polyethylene to xylene among which 1 part polyethylene per 10 parts of xylene proved to be the best. Using this ratio polyethylene in the form of sheets was put into xylene and the mixture was kept at 75°C for 1 h while mixing the solution intermittently. Upon obtaining a homogeneous solution, zeolite with an average particle size of 74  $\mu$  was 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 1 part of polyethylene. For a specific ratio, the heterogeneous mixture was mixed continuously at 75°C for 10 min. Then the mixture formed was poured as a thin film in a petri dish and dried in a vacuum oven at 80°C until all xylene evaporated leaving a thick and brittle film as a residue. Finally, the obtained film was cut into very small pieces, i.e., 0.02 m x 0.05 m rectangular strips, placed between heat stable and non-sticking papers and hot pressed at 130°C for 5 min.

In the third group of trials, polyethylene beads were coated with zeolite. To achieve this we used a revolving heated pan (Armfield, FT12 Ball Mill, England) with 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. Furthermore the complete rotation of the pan could be set at different angles to the horizontal for satisfactory tumbling of the contents of the pan. Zeolite particles of average size 74  $\mu$  to form the bed and enough polyethylene beads were placed into the pan and heated with the pan bottom immersed in an oil bath at 180°C. With the action of continuous mixing and heating, zeolite particles were attached to the softened surface of the polyethylene beads.

The positive result achieved in coating the beads

with zeolite gave rise to the second method, 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 a large amount of ground zeolite of sizes +53  $\mu$ , +106  $\mu$  and +212  $\mu$  were mixed, and the mixture was slowly heated so that just the surface of the beads melted and ease the attachment of the zeolite particles to their surface. For this purpose, different temperatures in the range 140-150°C were tested. The optimum temperature of heating was chosen as 145°C and further experiments were carried out at this temperature. Then the coated bead samples were placed in an oven for 3 h at 145°C (OV/160 CLAD, England) to ensure the attachment. The amount of zeolite held by the beads was calculated from the weight of the zeolite covered beads and the weight of the beads fed. This ratio was checked for different trials and was found to differ by  $\pm 0.01$  kg/kg beads.

Zeolite coated polyethylene beads were hot extruded in an industrial extruder (Heminstone, 1977, Taiwan, Doğan Plastik, İzmir). The extruder die exit temperature was 110°C and the extruder temperature was 90°C, which were kept constant by a thermostat. The thickness of the film was adjusted by the feed rate, in this case being 30 kg/h. The flow rate of the air was adjusted so that a blown column 3 m height and 0.5 m width was formed at the extruder exit.

The films prepared by extrusion as described above 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 films prepared thus were subjected to a curing process by hot pressing at 120°C for 5 min.

After deciding on the method of film production, the film structures of the films produced by this procedure were examined by image analysis (IA) and scanning electron microscope (SEM). The set-up used for this purpose consisted of three main parts that were connected by several interfaces: a camera (Cohu Inc.), a dual monitor image processing computer equipped with 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 lighting.

Analysis was performed by image acquisition and calibration in which an image captured and grabbed on 256 gray levels is stored in the hard drive of a computer with a standard format of 719 x 511 pixels either as a color or monochrome value. After storing the image, a scale value that is a function of the magnification is entered in order to convert the spatial measurement value in pixels to centimeters.

For the same films, film structures were also examined by scanning electron microscope (SEM) (Met. Eng. Dept., METU). For SEM analysis, fine representative samples from the three products of this study plus PE and FH films was used. Each film was observed with x100 and x300 magnification.

## Results and Discussion

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. According to X-ray analysis with a diffractometer, natural zeolite samples contain more than 80% clinoptilolite + heulandite type zeolites. This figure represents both types as the peaks given by these two types coincide. The resolution needs more detailed study, which is beyond the scope of this work. The results and assessment of the products prepared according to the different methods for the manufacture of such a composite film are given below.

### a. Hot Pressing

The films obtained by the process of embedding ground zeolite particles with an average particle size of 74  $\mu$  on the surface of 60  $\mu$ m and 100  $\mu$ m thick polyethylene films using a hot press at 100-145°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 kraft paper more than a plastic film. When compared with the FH film, which appears to have the zeolite particles attached to the surface by suitable means from one side of the film, a logical processing seemed to be spreading hot particles on the warm softened film. However uniform spreading of the hot particles seemed to be a problem. In addition, it was not possible to arrive at the relevant time-temperature combination. This was mainly because with the available manual hot press it was not possible to adjust both of these parameters with sufficient accuracy.

### b. Mixing Zeolite Particles with Polyethylene Melt and Polyethylene Solution

We also investigated the second possible alternative for composite film production, complete mixing of polyethylene and zeolite. According to trials with different average zeolite particle sizes and zeolite/polyethylene ratios, the optimum particle size and the mixing ratio for spreading was found to be 74  $\mu$  and 1/10 (w/w), respectively. When the particle sizes were greater than 74  $\mu$ , they yielded a very heterogeneous 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 severely affected the density of the mix. Further, in determining the optimum zeolite/polyethylene ratio the primary factor that affected the result was found to be spreadability.

When a sufficient amount of well mixed molten mixture was prepared at optimum conditions, i.e., 1/10 (w/w) zeolite/polyethylene at 190-205°C, we tried to spread it as a thin film. With the instrument available 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 spread film and a sticking of the material to the spreader blade due to the 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 main reason for the failure of this method was the comparably high temperature requirement of the process, i.e., around melt temperature, whereas spreading had to be done at room temperature with the existing spreader.

To eliminate the spreadability problem associated with the phase change induced by cooling in the previous method, a similar method less affected by temperature was tried. In this respect, as a suitable solvent to dissolve polyethylene, xylene was selected. For the necessary preliminary study the solute/solvent ratio and the temperature giving the best solution was determined. This was obtained when a ratio of 1 part polyethylene per 10 parts xylene was used at 75°C. The reason for the selection of this ratio was due to toxic nature of xylene and the necessity that it be removed from the system. Therefore, when a homogeneous solution was obtained this ratio was chosen. Then, the other parameter zeolite/polyethylene ratio appeared to be

the best when 0.1 of zeolite per gram of polyethylene was used since zeolite amounts higher than this value resulted in nonhomogeneous distribution. However, the resulting mixture of the dissolved polyethylene and zeolite was like a jelly, which again was not a spreadable fluid at the operation temperatures of the spreading machine. This was most probably due to the rapid temperature drop from 75°C to room temperature and adsorption of some solvent by the zeolite particles to yield a highly concentrated solution of polyethylene in xylene.

Unsuccessful spreading due to solidification of the mixture as a non-uniform layer on a plate by vaporizing the solvent appeared to be a suitable procedure by which thick films, the could be obtained. To process these thick films into thin films hot pressing of small strips cut from them seemed a possible solution.

The films produced according to the above procedure were relatively more successful than the previous ones. The distribution of zeolite through the film was quite uniform and the obtained film was more flexible and clear, and the thickness of the film could be controlled easily by the amount of small pieces to be pressed. However, because of the drawbacks of the utilization of a toxic solvent, time consumption and the need for additional equipment as well as provision for ventilation in the area comparatively giving rise to higher costs, industrial production by this method was not suitable feasible.

### c. Coating Polyethylene Beads and Extrusion

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

We observed in the preliminary trials that it was quite difficult 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 a revolving pan and heated. Subsequent to several temperature-time studies in the pan, the best result for this method was obtained as 1 h at 180°C using 53, 106 and 212  $\mu$  average sizes of the zeolite. This method was also found to be unsuitable primarily because the production rate was very low.

From the previous trials we estimated that for a

successful coating of polyethylene beads, the beads should be immersed in a large amount of zeolite and heated. The heating trials were done in an oven. For each size group of zeolite particles used, the best result was obtained as 3 h at 145°C. 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 h at 145°C with respect to the average particle sizes of 53, 106 and 212  $\mu$  were 1.082, 1.133 and 1.256 respectively.

The resulting beads were found to be successfully covered and hence were subjected to extrusion in an industrial extruder. However, because the extruder was not specific for this composite material, the zeolite particles sedimented at the bottom and formed aggregates that caused surface disorders. In addition, the film was comparatively heavy for the extruders' designed air pressure, which was not sufficient to blow the zeolite containing heavy films. However, an intermediate zone in the extruded film showed promise.

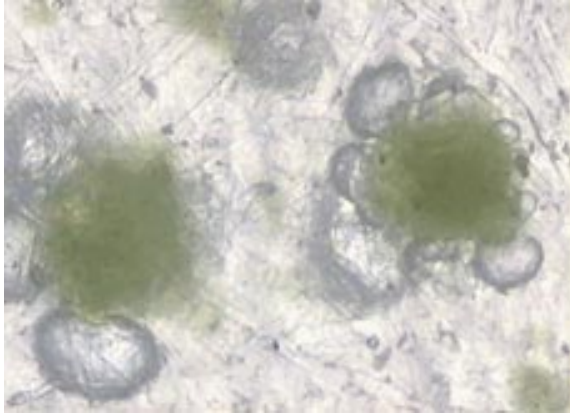
This method was unsuccessful in terms of the loss of material and non-uniformity of the produced films although it was an achievement in industrial application.

Although the extrusion of zeolite coated polyethylene beads as a film was unsuccessful, it still was an achievement promising an improvement with respect to thickness and uniformity. Therefore, after discarding part of the film from both ends, the smooth intermediate zone of the extruded film having uniform zeolite distribution was removed for improvement by hot pressing.

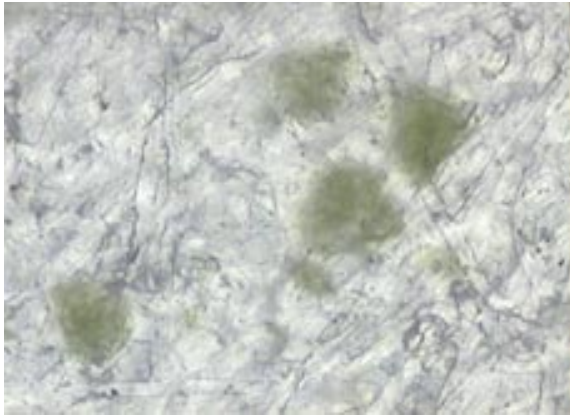
The film obtained after pressing at 120°C for 5 min with the available equipment offered most of the expected structural properties, especially flexibility and uniformity in thickness and the distribution of zeolite particles in the film.

As a means to compare the films produced by the last method with the alternatives, image analysis and SEM photographs were used. The images of the films +212  $\mu$ , +106  $\mu$ , +53  $\mu$ , FH and polyethylene were magnified x10 and stored. The images of the polyethylene film purchased from the market and that of the produced films given in Figures 1-4 appear to be about the same. The zeolite particles can be seen on the pictures as embedded within the film structure. The image of the FH film (Figure 5) is quite different from the others, implying a different polymer structure, zeolite type and processing. The same results were obtained from the examination of

SEM photographs (Figures 6-10). In addition, it can be seen from the SEM photographs that there are no holes between the zeolite particles and the polymer film.



**Figure 1.** Film structure of 212  $\mu$  film.



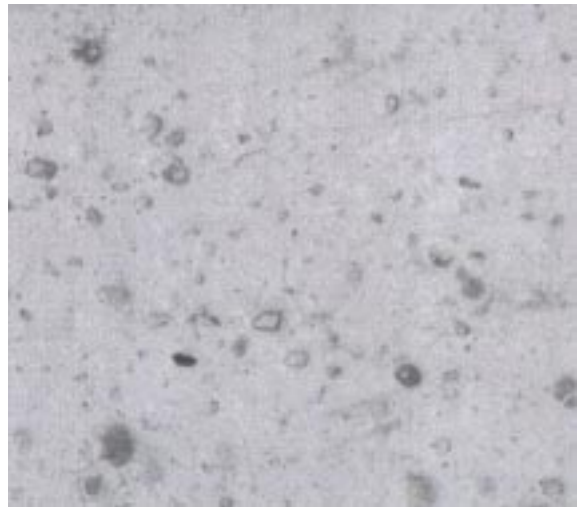
**Figure 2.** Film structure of 106  $\mu$  film.



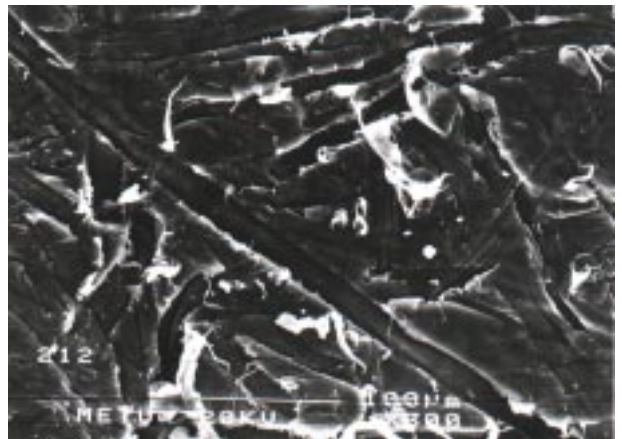
**Figure 3.** Film structure of 53  $\mu$  film.



**Figure 4.** Film structure of polyethylene film.



**Figure 5.** Film structure of FH film.





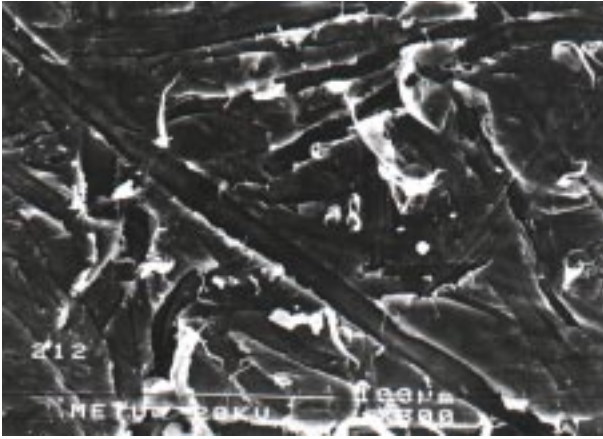


Figure 6. SEM photograph of 212  $\mu$  film.

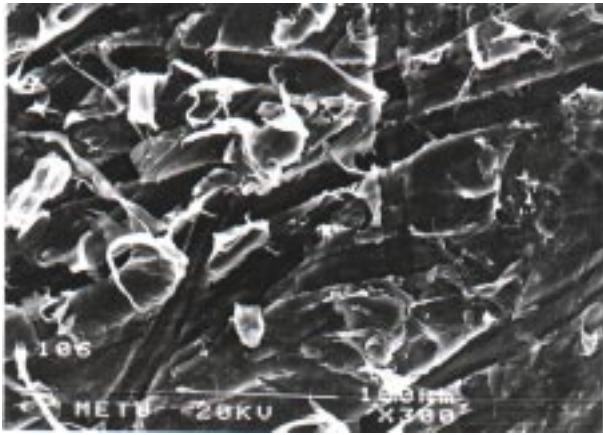


Figure 7. SEM photograph of 106  $\mu$  film.

In the light of the studies performed the following steps can be recommended for an industrial zeolite containing polyethylene film production, which is schematically shown in Figure 11.

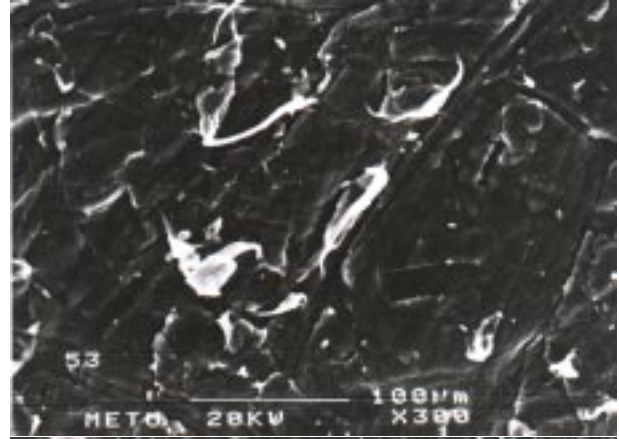
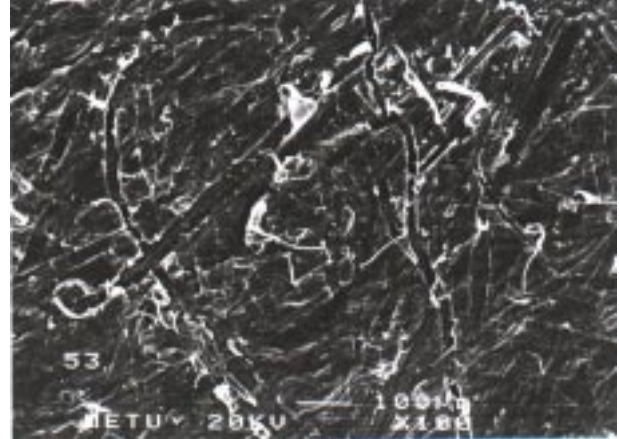


Figure 8. SEM photograph of 53  $\mu$  film.



### 1. Zeolite Coated Polyethylene Beads Production

Industrially it is possible to produce such composite films by using a twin-screw extruder. However, such equipment is costly to employ in research work unless it is already available. Therefore, as an alternative an equally effective method was determined in this study.

According to the desired production capacity, an excess amount of ground zeolite particles of a size smaller than 53  $\mu$  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 tank should be suitable for continuous mixing and indirect heating so that its contents can be heated to 145°C and kept at that temperature for 3 h while mixing continuously. The amount and purity of the raw materials are very important. The polyethylene beads should be pure and 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 be easily controlled. As

an alternative design, a fluidized bed coating could be studied.

### 2. Separation of the Coated Beads

The coated beads plus the excess zeolites should go over a sieve to eliminate excess zeolite particles for recycling.

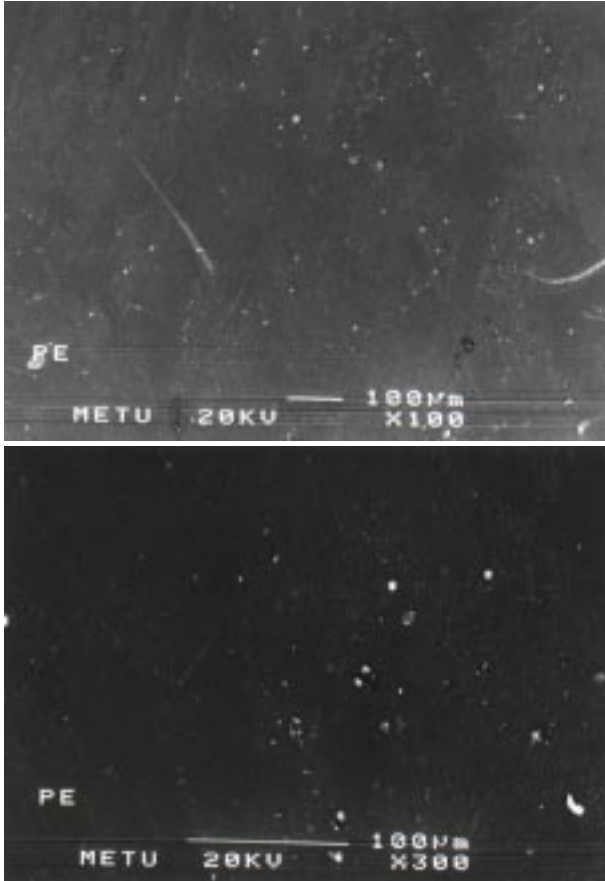


Figure 9. SEM photograph of PE film.

### 3. Extrusion into Film

The zeolite covered polyethylene beads should be extruded through a straight die opening into a thick film. In the extruder, the air feed rate must be adjusted for such a material.

### 4. Annealing Press

The raw film produced from the extruder should be annealed by pressing at a specified temperature around 130°C and a convenient pressure depending on the set thickness of the film so that a film with desired thickness and properties can be obtained. For this purpose, hot rolls are recommended.

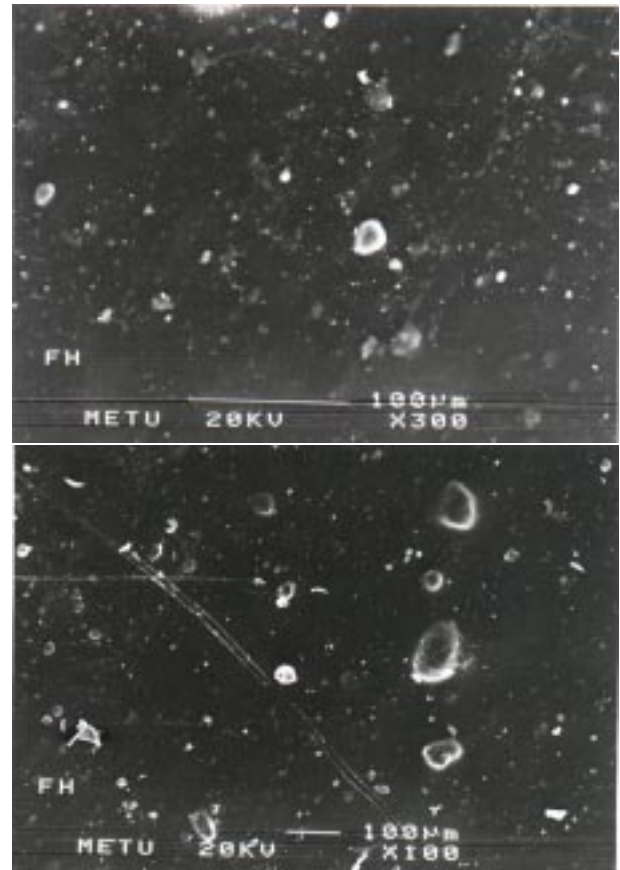


Figure 10. SEM photograph of FH film.

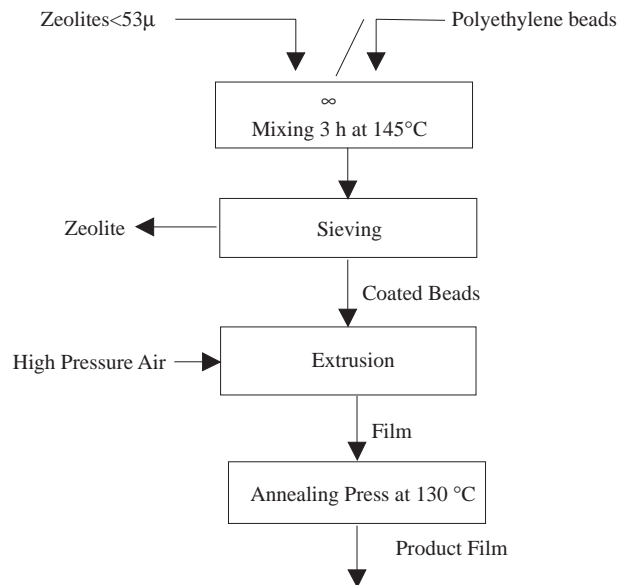


Figure 11. Schematic representation of the recommended process.



## Conclusions

The present study aimed to find a suitable manufacturing process to produce a zeolite polyethylene composite packaging film of acceptable properties, which also makes use of natural Turkish zeolites. We found that such a film can be produced by extrusion and then annealing of zeolite-coated polyethylene beads prepared under specific conditions. However, for such a film to be acceptable in fruit and vegetable packaging, additional properties increasing the shelf and storage life of the commodities are required. Thus, as a film combining the gas adsorptive property of zeolites with a very common food packaging material, polyethylene shall be studied for its permeability to gases of interest that affect storage

life.

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