

Material Characterization

Porous polyethylene membranes by template-leaching technique: preparation and characterization

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Abstract

Porous polyethylene membranes were successfully prepared by the template-leaching technique. The leachable component was tapioca starch, which was compounded with low-density polyethylene (LDPE) to produce a blend of 2, 4, 6, 8, 10, or 12% by weight of starch. Each blend was melt-extruded to produce an LDPE/starch film of 50, 80, or 100 μm in thickness, respectively. The porous structure of the films was then formed by either acidic or enzymatic leaching of the starch particles from the films. For acidic leaching, the films were immersed in an aqueous solution of HCl, H₂SO₄, or HNO₃ while, for enzymatic leaching, an aqueous solution of α -amylase was used. For acidic leaching, starch particles were best removed by 5 N HNO₃ at 65 °C corresponding to a reduction in the starch content from the initial value of ca. 85%, whereas, for enzymatic leaching, the reduction of the starch content was much lower at ca. 36%. © 2003 Elsevier Ltd. All rights reserved.

Keywords: Porous polyethylene membrane; Template-leaching technique; Mechanical property

1. Introduction

Porous polymeric membranes have received much interest in areas such as filtration (i.e. micro-, macro-, and ultrafiltration), reverse osmosis, gas separation, pervaporation, controlled release, etc. In addition to all of these applications, they can be used as supports for preparing porous ceramic membranes. Four common techniques for preparing porous polymeric membranes are (1) phase separation [1–6], (2) irradiation [7–9], (3) extrusion-stretching [10–15], and (4) template-leaching [16–21]. These techniques have been developed based mainly on the properties of the raw polymeric materials used and perhaps on the targeted applications. Moreover,

each technique gives different membrane characteristics, e.g. average pore size, uniformity of the pore size, porosity, mechanical properties, and even selectivity towards permeate species, which, in turn, dictate the properties and end-uses of the membranes obtained.

Phase separation technique [1–6], also known as phase inversion or solution precipitation technique, is the most important technique by which almost half of all microporous membranes are developed. In this technique, a clear polymer solution is precipitated into two phases: a solid polymer-rich phase that forms the membrane matrix and a liquid polymer-poor phase that forms the membrane pores upon evaporation. The membranes prepared by this technique are usually used in ultrafiltration and reverse osmosis applications. This technique is, however, unsuitable for preparing porous polymeric membranes from polyolefins.

Irradiation or pore-piercing technique [7–9] is composed of two main steps. The first step involves irradiation of a polymer film with high-energy particles

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generated by a nuclear reactor or other type of radiation source. When high-energy particles pass through the film, the polymer chain will break and leave sensitized or damaged tracks. In the second step, the film is submerged in an etching solution, which etches the polymer film along the sensitized tracks in order to form flow-through channels or pores. The number and the diameter of pores can be controlled by adjusting the exposure time in the first step and the etching time in the second step. Even though this technique gives membranes of very uniform pore size, the membrane porosity is usually relatively low.

Extrusion-stretching technique [10–15], usually utilized to prepare porous polymeric membranes from either filled or unfilled semi-crystalline polymers, comprises two consecutive steps. In the first step, an oriented film is produced by melt-extrusion process with a rapid haul-off speed. After solidifying, the film is then stretched in either parallel or perpendicular direction to the original orientation of the polymer crystallites. For unfilled systems, the second stretching deforms the crystalline structure of the film and produces slit-like pores with diameters ranging from ca. 20 to 50 nm [10,12,13]. For filled systems, the second stretching results in partial removal of the solid fillers, yielding a porous structure [11,14,15]. Traditionally, porous membranes prepared by this technique have relatively poor tear strength along the orientation direction and are not widely used as micro-filtration membranes. Instead, they have been used as inert separating porous barriers in batteries and some medical devices.

Lastly, template-leaching [16–21] is the technique suitable for preparing porous membranes from polymers which do not dissolve in common organic solvents. In this technique, a homogeneous film is prepared from a mixture of membrane matrix material and a leachable component. The leachable component can be a soluble low molecular weight substance or even a macromolecular material such as poly(vinyl alcohol) (PVA) or poly(ethylene glycol) (PEG). After the film has been prepared, the leachable component is removed by a suitable chemical treatment. At the right conditions, a porous structure is formed as a result.

Polyolefins, the most abundant and cheapest polymers, are attractive to be used as porous polymeric membranes. Common techniques used to produce porous membranes from polyolefins are irradiation [7], extrusion-stretching [10–15], and sintering [22]. Irradiation and extrusion-stretching techniques are generally similar to those described previously. Sintering, as the name implied, is the technique in which polymer particles are compacted under controlled temperature and pressure to produce a firm, but porous structure [22]. By varying the size distribution and the way the particles are fused, a myriad of pore sizes and structures can be obtained. Some

examples of commercial uses for porous polyolefin membranes can be found on the internet [22,23].

To the best of our knowledge, template-leaching technique has hardly been applied to prepare porous polymeric membranes from polyolefins. It is, therefore, of our interest to prepare porous polyethylene membranes using this technique. This can be achieved by preparing films of low-density polyethylene (LDPE)/tapioca starch blends. The starch particles are considered as the dispersed, leachable component. The porous structure of the film can, therefore, be obtained by either acidic or enzymatic leaching of the starch particles from the films. The as-prepared porous LDPE membranes were characterized for their morphology and mechanical properties.

2. Experimental details

2.1. Materials

LDPE (LD 1905F grade, Cementthai Co., Ltd., Thailand) with a melt-flow index of 5 g/10 min was used as the base material. Tapioca starch (Siam Modified Starch Co., Ltd., Thailand) with an average particle size of 14.8 μm was heated in a hot-air circulating oven for 12 h prior to blending with LDPE. Three inorganic acids, hydrochloric acid (37% HCl, Aldrich), sulfuric acid (97–95% H_2SO_4 , Merck), and nitric acid (65% HNO_3 , Scharlau) were diluted to 5 N for acidic leaching. For enzymatic leaching, α -amylase (Termamyl Supra, 120 KNU/g, East Asiatic Co., Ltd., Thailand) was used.

2.2. Film preparation

LDPE and tapioca starch were compounded in a twin-screw extruder (Collin, ZX-25) using a die temperature of 135 $^\circ\text{C}$ and a screw speed of 50 rpm to obtain an LDPE/starch blend containing 2, 4, 6, 8, 10, or 12% by weight (wt%) of starch. Each blend was later melt-extruded in a chill-roll cast-film extruder (Collin, D8017) using a die temperature, screw speed, and chill-roll temperature of 170 $^\circ\text{C}$, 25 rpm, and ca. 35 $^\circ\text{C}$, respectively, to produce LDPE/starch films. By adjusting the chill-roll speed, an LDPE/starch film of ca. 50, 80, or 100 μm in thickness was produced.

2.3. Formation of porous structure

Porous structure of the LDPE/starch films was formed simply by removal of starch particles using either acidic or enzymatic leaching technique. Before subjecting to a proper leaching solution, specimens (15 \times 15 mm^2), cut from the as-prepared films, were preheated in an oven at 65 $^\circ\text{C}$ for 6 h to remove traces of moisture. In acidic leaching, an aqueous solution of HNO_3 , HCl, or H_2SO_4 was used. The effects of acid type, acid concentration,

leaching temperature, initial starch content, and, finally, film thickness on the amount of starch hydrolyzed were investigated. In enzymatic leaching, only the film specimens with 12 wt% of starch and 50 μm in thickness were immersed in an aqueous solution of 2% by volume of α -amylase in pH 6.5 acetate buffer at 80 $^{\circ}\text{C}$. The percentage of starch removal can be determined by comparing the dry weight of each specimen before and after leaching, using a high-resolution Sartorius digital balance. The porous structure of the as-prepared specimens was visually investigated using a scanning electron microscope (SEM) (JEOL, JSM-6400).

2.4. Mechanical properties and gloss property measurements

Tensile strength and percentage of elongation of the as-prepared porous films were measured based on ASTM D882 using a universal testing machine (Lloyd, LRX). A load cell of 2.5 kN was used along with a 125 mm/min cross-head speed and a 250 mm gauge length. The tensile properties could only be determined in the machine direction because the length of the as-prepared films in the transverse direction was shorter than that of the gauge length. The tear resistance of the films was determined in both machine and transverse directions using a tear tester (Elmendorf, SDL) based on ASTM D1922. The gloss property of the films was determined based on ASTM D532-89 in both machine and transverse directions using a haze/gloss tester (BYK Garder) measuring at a testing angle of 60 $^{\circ}$.

3. Results and discussion

3.1. Formation of porous structure

The formation of porous structure in LDPE/starch films depends essentially on the amount of starch removed from the film matrix. Three methods have been reported to determine the level of starch remaining in/removed from LDPE/starch films: they are (1) chemical analysis, (2) Fourier-transformed infrared spectroscopy (FTIR), and (3) thermo-gravimetric analysis (TGA) [24]. For simplicity, the amount of starch removed from LDPE/starch films can be determined by comparison of the dry weight for each specimen before and after hydrolysis. Mathematically, the percentage of starch removal (% starch removal) can be written as

$$\% \text{ starch removal} = \frac{\% \text{ weight loss}}{\text{initial \% starch}} \times 100, \quad (1)$$

where % starch removal is the percentage of starch hydrolyzed by either acidic or enzymatic solution, % weight loss is the percentage of weight loss after

hydrolysis, and initial % starch is the initial percentage of the starch present in the film specimen.

Fig. 1 shows the percentage of starch removal from 50- μm -thick films containing 12 wt% of starch in solutions of 5 N HNO₃, 5 N HCl, and 5 N H₂SO₄, respectively, at 65 $^{\circ}\text{C}$ as a function of time. It should be noted that the film specimens immersed in water (i.e. control specimens) did not exhibit any weight loss, implying that water did not play a role in removing the starch particles. Comparison of the amount of starch removed by these solutions indicates that starch particles were best removed by the HNO₃ solution, due possibly to its properties as a very strong acid and powerful oxidizer. It is apparent that the percentage of starch removal in both HCl and HNO₃ solutions increased rapidly during the first 6 h of immersion, then leveled off and remained practically constant after 8–10 h. The ultimate percentage of starch removal in HCl and HNO₃ solutions were ca. 80% and 85%, respectively. On the other hand, no rapid increase in weight loss was observed for films immersed in the H₂SO₄ solution. The ultimate percentage of starch removal, for this case, was only ca. 22%.

Fig. 2 illustrates the percentage of starch removal from 50- μm -thick films containing 12 wt% of starch in solutions of 1, 3, and 5 N HNO₃, respectively, at 65 $^{\circ}\text{C}$ as a function of time, in order to elucidate the effect of acid concentration on the amount of starch removed from the films. Apparently, the films hydrolyzed by 1, 3, and 5 N HNO₃ solutions showed the ultimate percentage of starch removal of ca. 33%, 75%, and 85%, respectively. This indicates that the amount of starch removed increased with increasing concentration of HNO₃.

The effect of leaching temperature on the amount of starch removed is shown in Fig. 3. In this figure, the percentage of starch removal from 50- μm -thick films

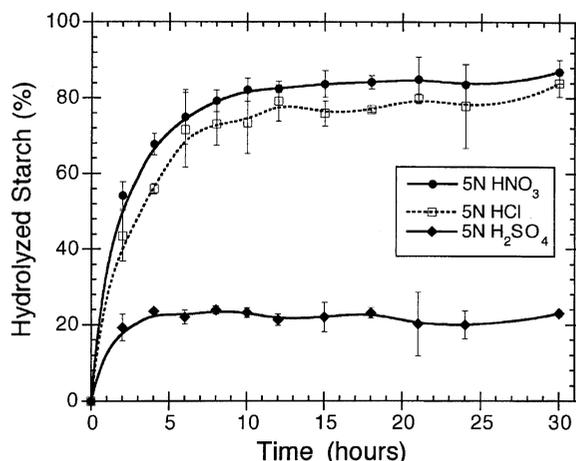


Fig. 1. Percentage of starch removal from 50- μm -thick films containing 12 wt% of starch in aqueous solutions of 5 N HCl, and 5 N H₂SO₄, and 5 N HNO₃ at 65 $^{\circ}\text{C}$ as a function of time.

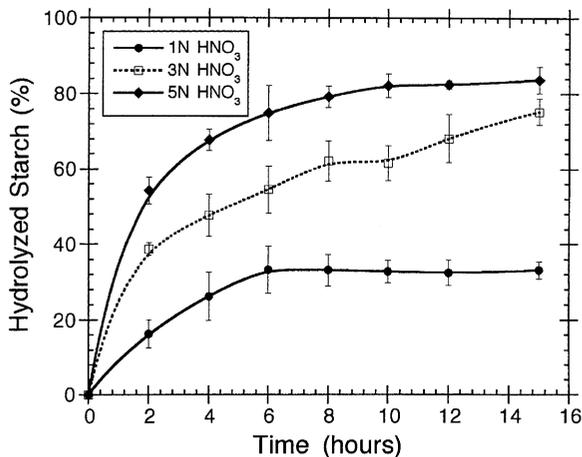


Fig. 2. Percentage of starch removal from 50-µm-thick films containing 12 wt% of starch in aqueous solutions of 1, 3, and 5 N HNO₃ at 65 °C as a function of time.

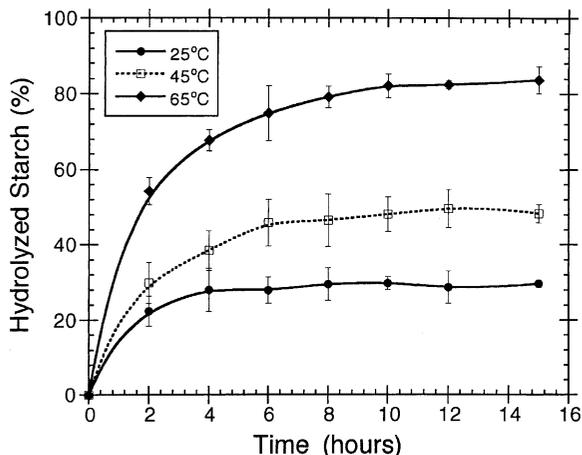


Fig. 3. Percentage of starch removal from 50-µm-thick films containing 12 wt% of starch in 5 N HNO₃ solution at 25, 45, and 65 °C as a function of time.

containing 12 wt% of starch in 5 N HNO₃ solution at three different leaching temperatures of 25, 45, and 65 °C is shown as a function of time. Clearly, the amount of starch removed was much greater at higher leaching temperatures. Specifically, the ultimate percentage of starch removal for 25 and 45 °C was only ca. 28% and 48%, respectively, while the value for 65 °C was as high as ca. 85%. This may be a direct result of the fact that the irreversible swelling temperature (i.e. gelatinization temperature) of tapioca starch lies within 58.5–70 °C. At leaching temperatures well below the gelatinization temperature of the starch, the action of aqueous acid solution causes starch particles to degrade, reducing the leachability of the starch particles. Within the gelatinization temperature range, starch crystallites soften,

resulting in some linear amylose molecules being leached out of the starch granules into the solution.

Fig. 4 illustrates the percentage of starch removal from 50-µm-thick films containing 0, 2, 4, 6, 8, 10, and 12 wt% of starch in 5 N HNO₃ solution at 65 °C for 15 h as a function of initial starch content, in order to exhibit the effect of initial starch content on the amount of starch removed. It is obvious that pure LDPE film (i.e. the film containing 0% by weight of starch) exhibited no weight loss after hydrolytic leaching. This is due mainly to the good chemical resistance of LDPE. At this point, it is safe to say that hydrolytic removal of starch particles was the only factor contributing to the weight loss in LDPE/starch films being observed thus far.

According to Fig. 4, the ultimate percentage of starch removal was found to increase monotonically with increasing initial starch content, especially for films containing the highest amount of initial starch content (i.e. 12 wt%). This may be attributed to the increasing number of pathways formed by the interconnections of starch particles, as they get closer together with increasing starch content. The interconnecting pathways provide for better access to the acid solution in leaching out the starch particles. The above hypothesis was visually verified by SEM micrographs (see Fig. 5a–c). The SEM micrographs evidently showed that the porous structure which was hardly present in specimens of low starch content (i.e. less than 4 wt%) became more interconnected and pierced through the thickness of the film as starch content increased up to 12 wt%. Consequently, it can be recapitulated that, as the starch content increased from 0 to 12 wt%, the microstructure of the films changed from dense, nonporous to porous character.

The effect of film thickness on the amount of starch removed is shown in Fig. 6. In this figure, the percentage

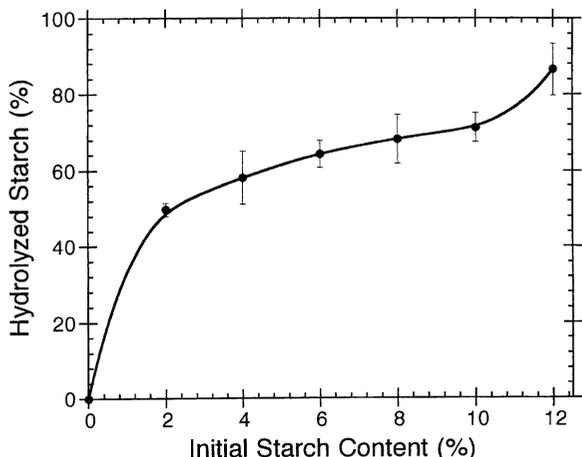


Fig. 4. Percentage of starch removal from 50-µm-thick films containing 0, 2, 4, 6, 8, 10, and 12 wt% of starch in 5 N HNO₃ solution at 65 °C for 15 h as a function of initial starch content.

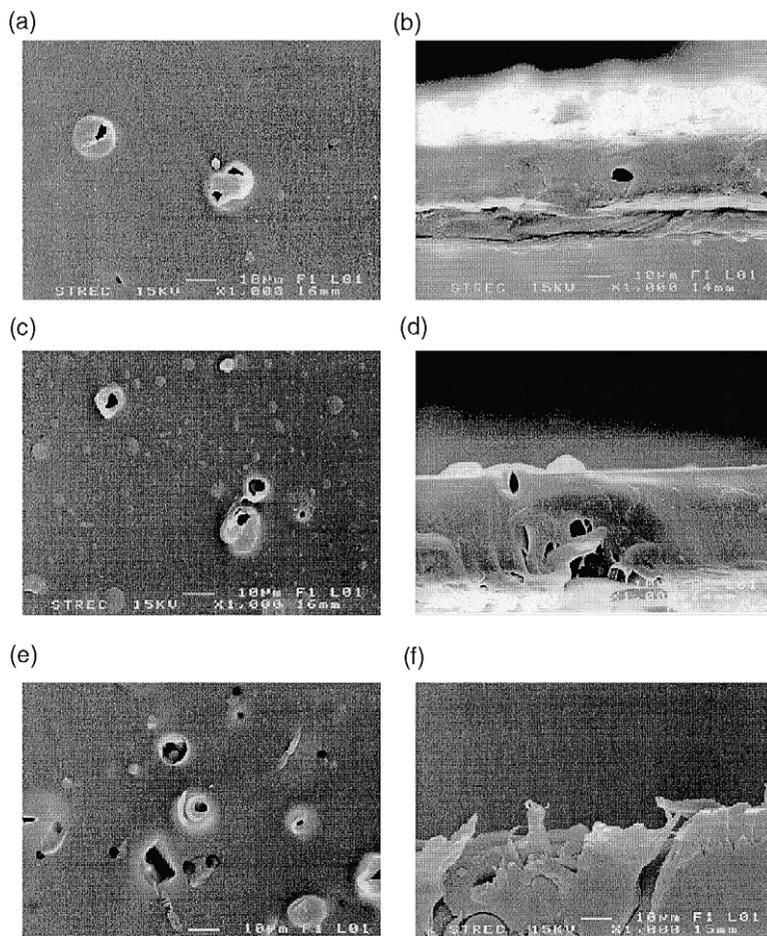


Fig. 5. SEM micrographs of 50- μ m-thick films containing (a) 2 wt%, (b) 6 wt%, and (c) 12 wt% of starch after hydrolyzed in 5 N HNO₃ solution at 65 °C for 15 h. Note that flat-on and edge-on views are shown on the left- and right-hand side, respectively.

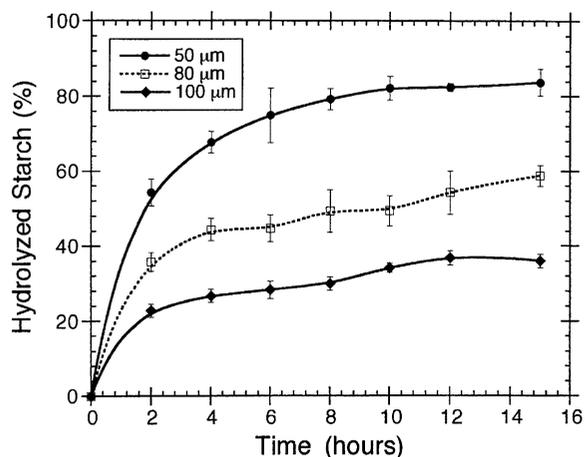


Fig. 6. Percentage of starch removal from 50-, 80-, and 100- μ m-thick films containing 12 wt% of starch in 5 N HNO₃ solution at 65 °C as a function of time.

of starch removal from 50-, 80-, and 100- μ m-thick films containing 12 wt% of starch in 5 N HNO₃ solution at 65 °C is plotted as a function of leaching time. Apparently, the ultimate percentage of starch removal for films of 50, 80, and 100 μ m in thickness was ca. 83%, 58%, and 36%, respectively. The obvious explanation of this observation is that, for a given starch content, the starch particles in the thinner films pack more closely, resulting in the greater number of interconnecting pathways which provide an easier access for the acid solution to penetrate than that in the thicker films. As a result, the percentage of starch removal increased with decreasing film thickness.

In the case of enzymatic leaching, the percentage of starch removal from 50- μ m-thick films containing 12 wt% of starch in the aqueous solution of 2% by volume α -amylase at pH 6.5 and 80 °C is illustrated as a function of time in Fig. 7 in comparison with those in the aqueous solution of 5 N HNO₃ at 65 °C. It is important to note that the percentage of starch removal by the enzyme sol-

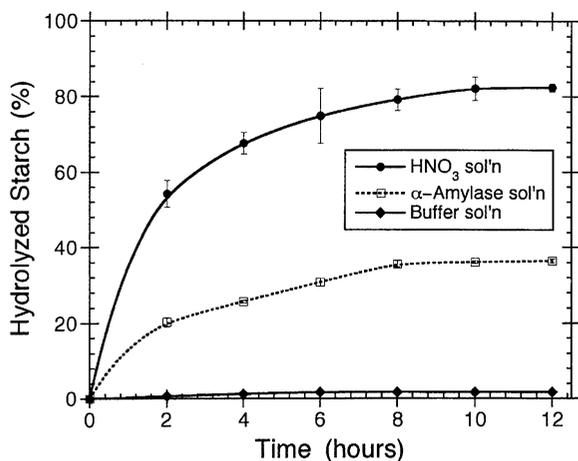


Fig. 7. Percentage of starch removal from 50- μ m-thick films containing 12 wt% of starch in the aqueous solution of 2% by volume of α -amylase at pH 6.5 and 80 °C as a function of time. Percentage of starch removal as a result of the 5 N HNO₃ solution and the acetate buffer solution are also shown for comparison.

ution in Fig. 7 was reported after proper corrections with the amount of starch removed by the acetate buffer solution used to control the pH level (at 6.5) of the enzyme solution (also shown in Fig. 7).

According to Fig. 7, the reduction in starch content by α -amylase increased readily during the first 8 h of the hydrolysis and then remained practically constant at the ultimate percentage of starch removal of ca. 36%. Nakatsuka and Andradý [24] reported that the ultimate percentage of starch removal from 50- μ m-thick LDPE/starch films containing 6 wt% of starch in an aqueous solution of α -amylase at 37 °C was only ca. 10% as determined by the TGA technique, which is obviously lower than that observed in this work. The discrepancy between the results reported in Ref. [24] and this work may be a result of the lower leaching temperature used (i.e. 37 versus 65 °C) and/or the lower initial starch content (i.e. 6 versus 12 wt%). Fig. 7 also shows that the ultimate percentage of starch removal in the α -amylase solution was much lower than that in the HNO₃ solution (i.e. 36% versus 85%). The results correlated extremely well with the SEM micrographs in which the films hydrolyzed in the α -amylase solution (see Fig. 8) exhibited much less porous structure than those hydrolyzed in the HNO₃ solution (see Fig. 6c).

3.2. Mechanical properties

It has been shown that both acidic and enzymatic leaching techniques removed some starch particles from the film matrix, resulting in the formation of a porous structure. In order to observe the effect of porous structure on mechanical properties of the leached films, vari-

ous mechanical tests were performed on both unleached and leached LDPE/starch films. The mechanical properties of interest were tensile strength, percentage of elongation, and tear resistance.

Fig. 9 illustrates values of the tensile strength and percentage of elongation for the unleached, acidically leached (in 5 N HNO₃ solution at 65 °C), and enzymatically leached (in the α -amylase solution at 80 °C and pH 6.5) LDPE/starch films (containing initial starch content of 12 wt%) measured in the machine direction as a function of initial starch content. Apparently, the tensile strength for all of the unleached and leached films showed a slight decrease with increasing starch content, with the discrepancies between the resulting values obtained for leached and unleached films being small (i.e. in the range of ca. 1–5%). Similarly, all of the unleached and leached films exhibited a slight decrease in the percentage of elongation with increasing starch content. In this case, however, the discrepancies between the resulting values obtained for leached and unleached films were quite large (i.e. in the range of ca. 12–16%).

Fig. 10 shows values of tear resistance for the unleached, acidically leached, and enzymatically leached LDPE/starch films measured in both the machine and transverse directions as a function of initial starch content. The tear resistance for the unleached LDPE/starch film exhibited a maximum at ca. 8 wt% of starch in both directions. This can be explained by the formation of crazes, which act as load-bearing entities, before and after the peak values. At low starch contents (i.e. less than 8 wt%), the formation of crazes strengthens the films leading to an increase in tear resistance. Above 8 wt% of starch, the starch particles can pack closely together and the formation of craze overlapping can occur very easily. This results in a decrease in the actual amount of crazes present and, hence, a decrease in the tear resistance.

The aforementioned phenomenon in the LDPE/starch films disappeared after the films were subjected to acidic or enzymatic hydrolysis. Apparently, the tear resistance of the films hydrolyzed by the HNO₃ and the α -amylase solutions showed a monotonous decrease with increasing starch content without the presence of a maximum, most likely a result of the porosity in the films. Therefore, mechanical properties of the films after hydrolysis decreased due to void formation in the film matrix. It should be noted that the films hydrolyzed by the α -amylase solution showed greater tear resistance than those hydrolyzed by the HNO₃ solution, a direct result from the disparity in the porosity levels which were obtained in these films.

3.3. Gloss property

Fig. 11 exhibits gloss values at 60° for the unleached, acidically leached, and enzymatically leached

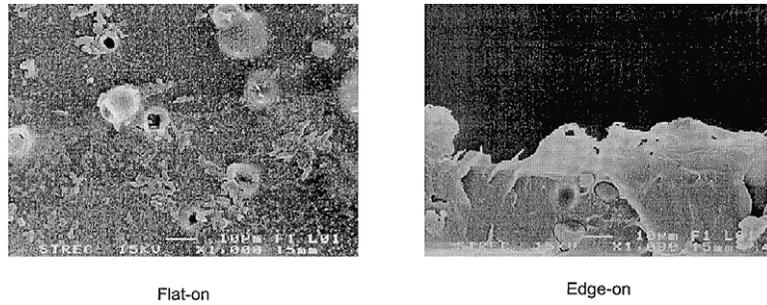


Fig. 8. SEM micrographs of 50- μm -thick films containing 12 wt% of starch after hydrolyzed in the aqueous solution of 2% by volume α -amylase at pH 6.5 and 80 °C for 12 h. Note that flat-on and edge-on views are shown on the left- and right-hand side, respectively.

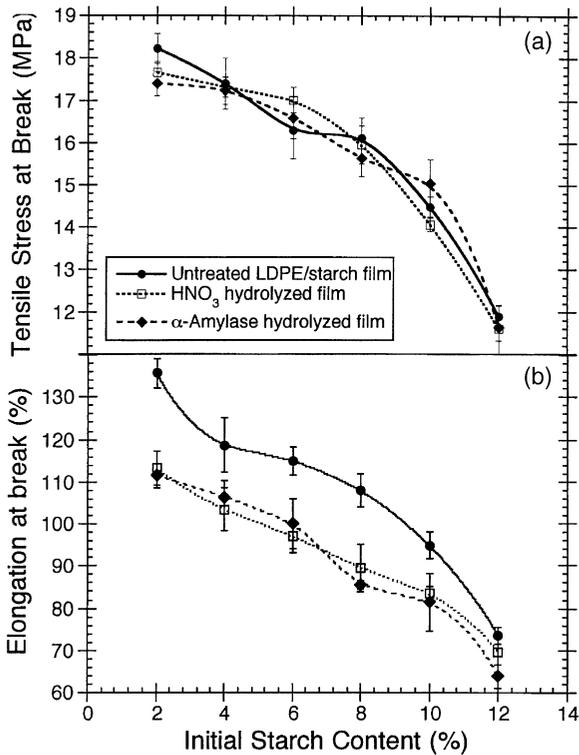


Fig. 9. (a) Tensile strength and (b) percentage of elongation for the unleached, acidically leached, and enzymatically leached films measured in machine direction as a function of initial starch content.

LDPE/starch films measured in both machine and transverse directions as a function of initial starch content. The gloss value for the unleached LDPE/starch film measured in both directions was found to decrease with increasing initial starch content. This was because, at high starch contents, films become more opaque and less light is reflected, while more light is scattered, when comparing with pure LDPE or LDPE/starch films of low starch contents. The gloss values for the acidically

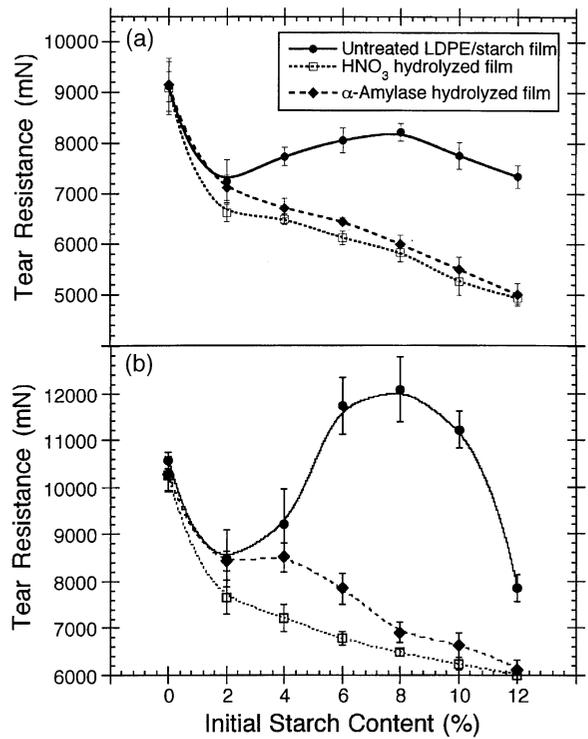


Fig. 10. Tear resistance measured in (a) machine and (b) transverse directions for the unleached, acidically leached, and enzymatically leached films as a function of initial starch content.

leached and enzymatically leached films were greater than those for the unleached films. The most likely explanation is that when some starch particles were removed, less light is scattered. The gloss values also correlated well with the previous results in that starch particles were more effectively removed in the HNO₃ solution than in the α -amylase solution, since it is apparent that the gloss values for the films hydrolyzed in the HNO₃ solution were greater than those for the films hydrolyzed in the α -amylase solution.

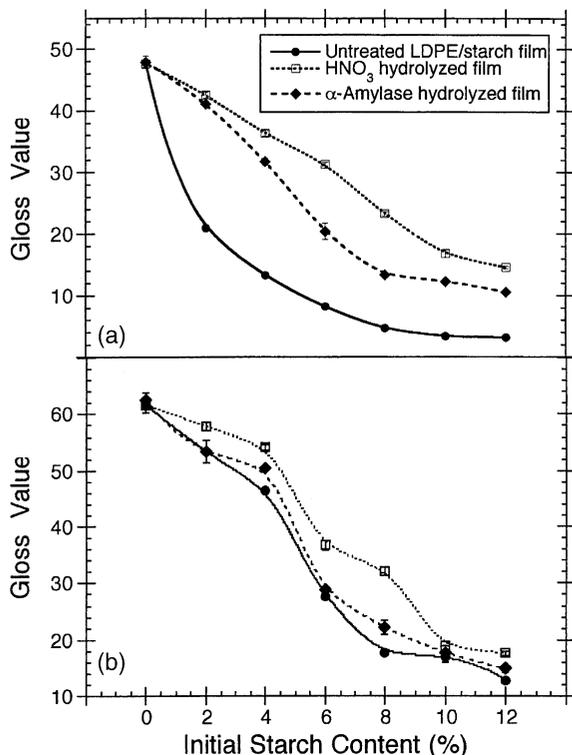


Fig. 11. Gloss values at 60° for the unleached, acidically leached, and enzymatically leached films measured in (a) machine and (b) transverse directions as a function of initial starch content.

4. Conclusions

Porous polyethylene membranes were successfully prepared from LDPE/starch films using acidic and enzymatic leaching techniques. Formation of the porous structure essentially depended on the amount of starch removed from the blend films. Starch particles were most effectively removed by the aqueous solution of 5 N HNO_3 at the leaching temperature of 65°C . The reduction in starch content was found to increase with increasing HNO_3 concentration. The starch particles were most effectively hydrolyzed at temperatures in the vicinity of the gelatinization temperature range of the tapioca starch. As the starch content increased from 0 to 12 wt%, the microstructure of the films changed from dense, nonporous to porous. An increase in the film thickness resulted in a decrease in the amount of starch removed. Starch removal of the blend films in the α -amylase solution at the leaching temperature of 80°C and pH 6.5 was found to be less effective than that in the 5 N HNO_3 solution at the leaching temperature of 65°C . Gravimetric analysis of the acidically leached and enzymatically leached films correlated well with morphological observations obtained by SEM. Both the ten-

sile strength and percentage of elongation for the as-prepared porous membranes were found to decrease slightly with increasing initial starch content. This was most likely due to the increase in the porosity level in the as-prepared porous membranes with increasing initial starch content. Lastly, the gloss value for as-prepared porous membranes was found to decrease with increasing initial starch content.

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