
RESEARCH ARTICLES

DEGRADATION OF CASSAVA STARCH - POLYETHYLENE BLENDS

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ABSTRACT

Degradable polyethylene films containing 0-20% w/w of cassava starch, 0-2% w/w of soya oil and 0-0.1% w/w ferric stearate were dispersed with Epolene wax in a dry blend mixer and compounded in a two-roll mill to form sheets. The sheets were cut into small chips that were then extruded in a blown film molding machine to yield polyethylene films. The oxidative degradation of the films was measured by outdoor weathering testing in comparison with indoor testing, and soil burial testing for six months under a natural atmosphere. Biodegradation of the films was determined by measurement of the populations of *Aspergillus niger* and *Penicillium pinophilum* fungi. All degradation processes were followed by monitoring chemical and physical changes of the samples by infrared spectroscopy, average molecular weights by the viscosity method, and tensile properties. FTIR spectroscopy revealed the formation of the carbonyl group as the ketone functionality during degradation. The concentrations of the carbonyl group were high in iron stearate starch-filled PE films. The populations of *Aspergillus niger* and *Penicillium pinophilum* on the samples showed that the latter had a much higher population, indicating that it efficiently promoted biodegradation of the starch-filled PE film in the presence of soya oil and iron stearate. The films were disintegrated into minute pieces containing abundant holes of destroyed starch. The iron stearate starch-PE films lost their physical properties after two months of outdoor exposure. Unlike the outdoor exposure test, the starch containing PE films by a soil burial test took a longer time to degrade. Both physical and mechanical properties of the PE films kept indoors (unexposed) remained unchanged for longer than six months under ambient conditions.

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INTRODUCTION

Plastics are an integral part of everyday life and are used for a multitude of purposes. Polyethylene plastic is among the most dominate packaging materials in today's society. Like other packaging products, when products from polyethylene plastic reach the end of their usage life, most are discarded in open dumps, landfills, or as simple litter. They have the great disadvantage of not being inherently biodegradable, and considerable efforts have been made to accelerate biodegradation. Degradation is a change in the chemical structure of a plastic, involving a deteriorated change in properties. For a polymer to be degradable, a main chain with a hydrolyzable group must be present and accessible. Plastic degradability has been introduced as a method to solve the disposal problem of plastics. One attempt has been made to create degradable plastics by incorporating starch, fatty acids and pro-oxidants into plastic for the production of degradable packaging materials that can be environmentally friendly substances.

Griffin, G.L.S.¹ filed a US patent describing the invention of degradable composites of either polyethylene, styrene-butadiene, or natural rubber with an anti-oxidant, and a latent pro-oxidant. The polymer composition preferably includes biologically sensitive natural fillers. The composites underwent biological breakdown in a natural environment to give molecular fragments created by the onset of oxidative scission of the molecular chains by the presence of such filler particles. Goheen and Wool² investigated the degradation of LLDPE-corn starch blends in soil over 8 months. The effect of starch concentration on weight loss was evidenced by FTIR data. Enhancement of degradation by UV imposed by the $\text{FeOH}(\text{stearate})_2$ was studied in α -olefin thermoplastics.³ Sung and Nikolov⁴ have investigated the degradation of two different starch-polyethylene films under the influence of a pro-oxidant. The accelerated starch biodegradation of the film was investigated by using a buffered *Bacillus* sp. α -amylase solution. The oxidative degradation of the PE was hastened by incubating the film in a forced-air oven at 70°C. The result of the degradation was followed by measurements of physical and chemical changes of tensile properties, molecular weight, and appearance. The extent of PE oxidation was followed by measuring the levels of ketone carbonyl in the PE film. The carbonyl index, defined as the ratio of carbonyl (1715 cm^{-1}) and methylene (1465 cm^{-1}) absorbances, was used to express the measured levels of carbonyl compounds. Defining the carbonyl index (CI), A_{1715}/A_{1465} relative to the invariant methylene (1465 cm^{-1}) absorbance was taken to compensate for the variation on the thickness of the starch-LDPE sample.⁵

The present investigation focuses on the degradation of cassava starch filled polyethylene film by photodegradation and biodegradation.

MATERIALS AND METHODS

Materials

Compounding

Low-density polyethylene resin, a blown film grade with a melt index of 5.50 (JJ4324, TPI, Thailand) was mixed with dried cassava starch (having about 25% amylose, from Thai Wah, Thailand) of 0, 5, 10, 15, and 20 g based on 100 g LDPE, which contained 2% dispersing agent (Epolene wax E-43p, White Group, U.S.A.) in a dry blender at 70°C for 15 min. Soya oil (0 and 2 g based on 100 g LDPE) and iron stearate from BDH, UK (0, and 0.1 g based on 100 g LDPE) were gradually added to the molten plastics on a two-roll mill (Model LRM 110,

Labtech Engineering, Thailand) at 135-140°C for 15 min. A good compatibility between the PE and starch was obtained. A trowel was used during mixing to smoothly spread the material on the rolls. The starch-polyethylene sheet formed was removed from the mill.

METHODS

Dispersibility Measurement of Cassava Starch in PE Sheets

A polarized light microscope (AFXII, Japan) with a Nikon camera was used to observe the dispersibility of cassava starch in the matrix of PE.

Film Preparation

The sheets were cut into small chips by a cutting machine (Labtech Engineering) and the corresponding films of an average thickness of 0.055 ± 0.05 mm were extruded by a film blowing machine (Model PE-142, Numchai Plastic Machinery, Thailand).

Outdoor Weathering Test

The surfaces of the film mounted on racks were exposed to naturally actinic radiation in Bangkok, Thailand at 13°44'N latitude and 100°34'E longitude from September 1994 to February 1995. The average temperature was 27.15 ± 0.50 °C with an average humidity of $71.33 \pm 4.11\%$, and average radiation of 22.18 ± 4.37 mJ m⁻². The variation of rainfall was 375 (Sept.), 156 (Oct.), 4.3 (Nov.), 5.3 (Dec.), 0 (Jan.), and 0.1 (Feb.) mm. A control experiment on similarly prepared films was carried out indoor to compare with those under outdoor exposure, which indicates their service/shelf life.

Outdoor Soil Burial Test

The tests were carried out from September 1994 to February 1995. The film samples of 10 x 2.5 cm² were buried in a perforated plastic box (shown in Figure 1) to allow the samples to be attacked by the micro-organism and moisture. The box was buried in soil at a depth of 15-20 cm below the soil surface. After 6 months, the films were stored in the dark before the mechanical property test was performed.

Cassava Starch-LDPE Degradability by Fungi

A nutrient salt agar without a carbon source using KH₂PO₄, MgSO₄·7H₂O, NH₄NO₃, NaCl, FeSO₄·7H₂O, ZnSO₄·7H₂O, MnSO₄·H₂O, K₂HPO₄, and agar sterilized in an autoclave at 121°C for 20 min was prepared. Two strains of fungi, *Aspergillus niger* and *Penicillium pinophilum* were used for the test. Spore suspensions from the respective stock cultures were prepared to give 1×10^7 to 2×10^7 spores cm⁻³ determined by a counting chamber method. The plastic films of 2.5 x 5 cm were sterilized in 95% ethanol for 10 min and inoculated in the nutrient-salt agar spread with 0.1 cm³ of the fungus spore suspension for 30 days at 30°C. The growth of fungi was recorded after one month. The colors of *Aspergillus niger* and *Penicillium pinophilum* are black and yellowish, respectively. The growth of fungi was estimated by following changes in the number of cells that could be measured by a counting chamber method.

FTIR Measurement

The extent of PE oxidative degradation was followed by measuring the levels of ketone carbonyl absorbances at 1715 cm⁻¹ by FTIR spectroscopy on an FTIR spectrophotometer (Perkin Elmer model 1720, U.S.A.). The carbonyl index was then calculated for the degree of oxidation in the starch-LDPE samples.

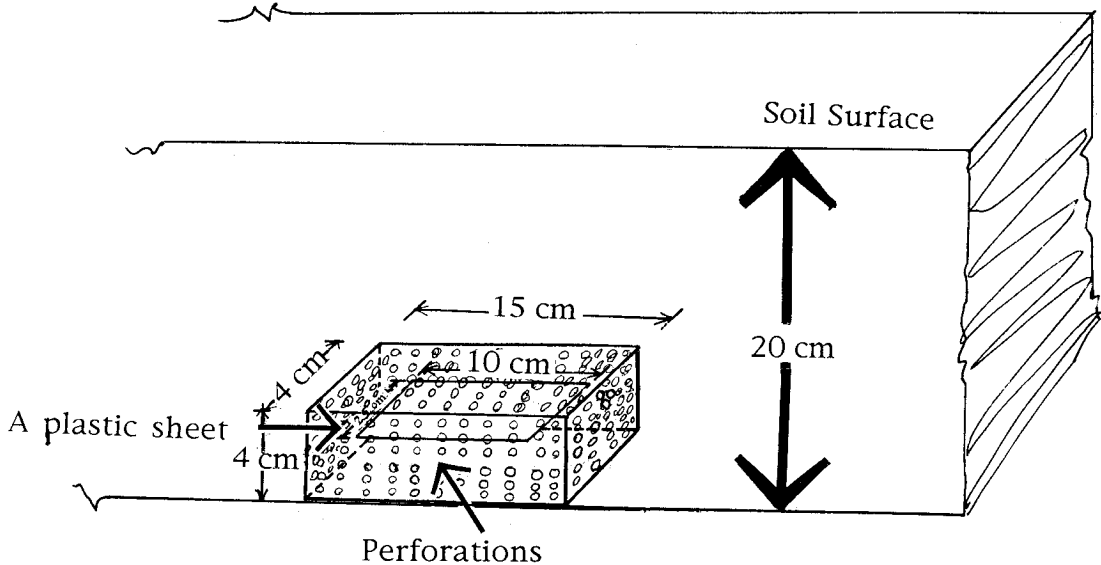


Fig.1 A perforated plastic box buried in soil at the depth of 15-20 cm.

Mechanical Property Measurement

Each sample was subject to mechanical testing by following the ASTM D882 procedure. Tensile strength and the corresponding elongation were measured by an Instron tester (model 1123, U.S.A.) with a cross head speed of 10 mm min^{-1} at $27 \pm 2^\circ\text{C}$ and $65 \pm 2\% \text{ RH}$.

Molecular Weight Measurement

The changes in averaged molecular weights of the LDPE films were determined by a viscosity method, using decahydronaphthalene solution and calculated by the Mark-Houwink-Sakurada equation of $[\eta] = k\bar{M}_v^a$ where $a = 0.738$ and $k = 38.73 \times 10^3$, $[\eta]$ = intrinsic viscosity and \bar{M}_v = viscosity-averaged molecular weight. The a and k values are the constant for a given polymer-solvent system.⁵

Scanning Electron Microscopy

Examination of the surface microstructure of the cassava starch-PE films was performed with a JEOL JSM-35 (Tokyo, Japan) scanning electron microscope.

RESULTS AND DISCUSSION

Dispersibility measurement of cassava starch in PE sheets

For a polymer to be degradable, the main chain with hydrolyzable groups must be present and accessible. Materials that contain an acid, amide, urea, or urethane functional group are susceptible to biodegradation. For starch, both amorphous and crystalline regions exist. With this semicrystalline polymer, the tightly packed crystalline regions are less accessible to degradants, which must diffuse into the region to be effective. Therefore, the amorphous region degrades first, leaving the more crystalline region. Since the amorphous chains tie the crystallites together, when they are hydrolyzed, catastrophic mechanical failure occurs even before weight loss. Since polyethylene does not contain any of the above-mentioned functional groups, and contains mainly C and H atoms, it is therefore inherently non-degradable.

When mixing starch into the matrix polyethylene, a maltase pattern was observed. At the stage of the two-roll milling, the maltase structure of the crystalline region of the starch could not be destroyed. However, the crystalline region was completely destroyed by heat and pressure in a film blown machine. The structure and dispersibility of cassava starch granules in the plastic film are shown in Figure 2. The magnified photomicrographs of the cassava starch and the composite viewed through a polarized light microscope show that the low content starch was fairly well dispersed in the matrix polymer, whereas the granules became agglomerated and randomly dispersed in the LDPE matrix at high contents of starch. In the presence of iron stearate, there is no visual difference in dispersibility in the LDPE. The dispersibility of starch granules at the same content in the presence of iron stearate was almost the same as those containing no iron stearate. The dispersibility degree depends to a larger extent on the wetting property of the dispersing agent between the starch and matrix polymer. Moisture content is another factor that lowers the degree of dispersibility due to that water vapor is absorbed on the starch surface, which protects the molecules of PE from intimately contact with either the dispersant or the matrix polymer. Thomas⁶ also explained the result as the effect of moisture and interfacial loading. The absorbed moisture in the cassava starch was expelled to form water vapor during processing, producing air bubbles in the matrix plastic, and decreasing tensile strength. Due to the weak interfacial bonding, more voids at high contents of starch can possibly reduce the tensile strength.

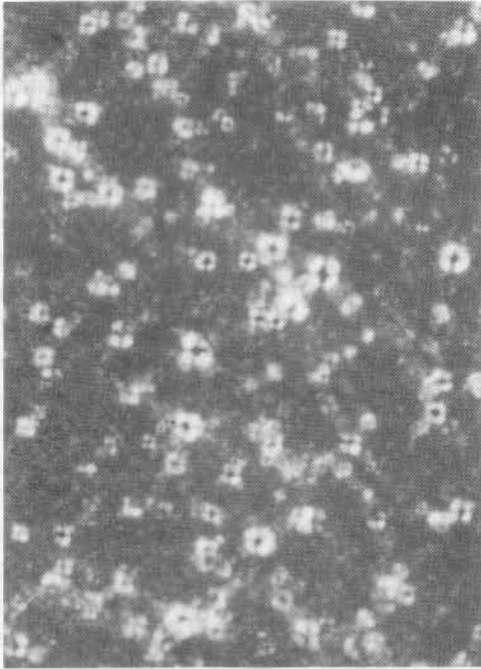
Outdoor weathering test

The IR vibrational modes of unexposed and one-month exposed LDPE films are presented in Figure 3. The peak at 1716.49 cm^{-1} is strong after a one-month exposure, but not for unexposed films. When the films of iron-stearate (0.1 g based on 100 g LDPE) -5% starch-LDPE (PE-S5/F) composites were exposed for one-month, the strength of the peak at 1716.88 cm^{-1} increased significantly. Figure 4 shows the FTIR absorption spectra of the above mentioned virgin and composite films for outdoor exposure of one to three months by the methylene region at 1467.41 cm^{-1} and the carbonyl region at 1713.50 cm^{-1} . The polyethylene band at 1467.41 cm^{-1} serves as an internal standard to which the absorbances of the other bands were related. The band at 1713.50 cm^{-1} corresponds to the carbonyl group in the exposed and degraded polyethylene chain.

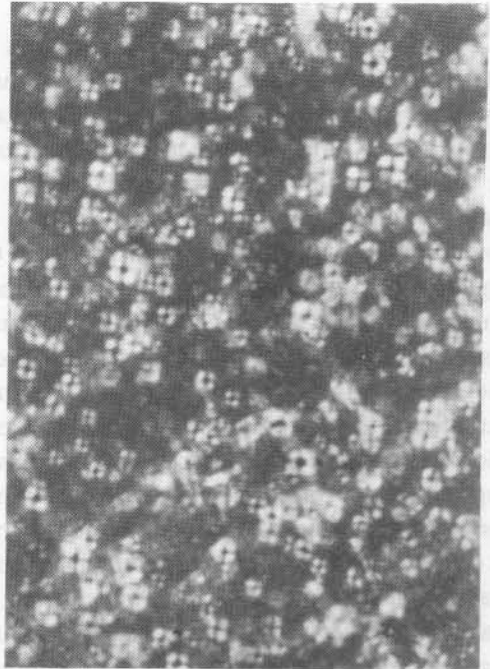
Carbonyl indexes express the extent of oxidation, corresponding to the observed loss in mechanical properties and the averaged molecular weights. Changes in the carbonyl index of LDPE and PE-S5/F films during three-month outdoor exposures are presented in Figure 5 (S stands for starch and F for iron stearate). The conventional LDPE film exhibits the photo-oxidation by an increase of the carbonyl group formation when exposing to sun light. The reaction mechanism of LDPE can be explained as a reasonably radical formation that is the reaction pathway to final products during outdoor exposure.⁷

The chemical transformation for the mechanistic approach and the LDPE oxidative condition is generally understood as the superposition of 3 main sequences:

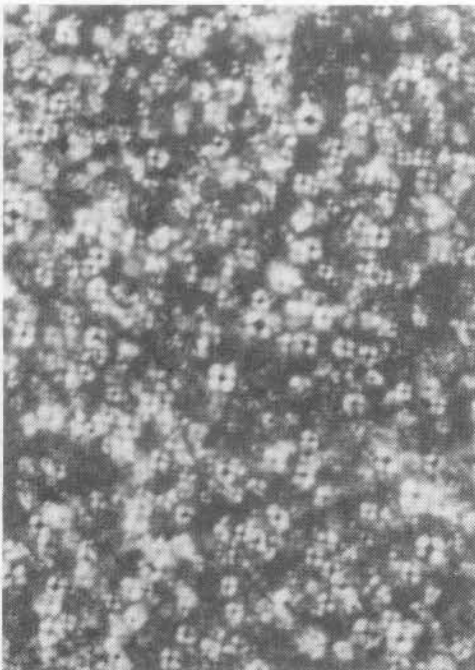
1. primary hydroperoxidation involving usually a short chain reaction, i.e. oxidation taking place at the short chains of LDPE to give hydroperoxide radicals;
2. photochemical and/or thermal homolytic decomposition of hydroperoxidic groups into hydroxylated and carbonylated groups;
3. photoreactions of the groups resulting from the decomposition of hydroperoxides, especially ketonic groups.



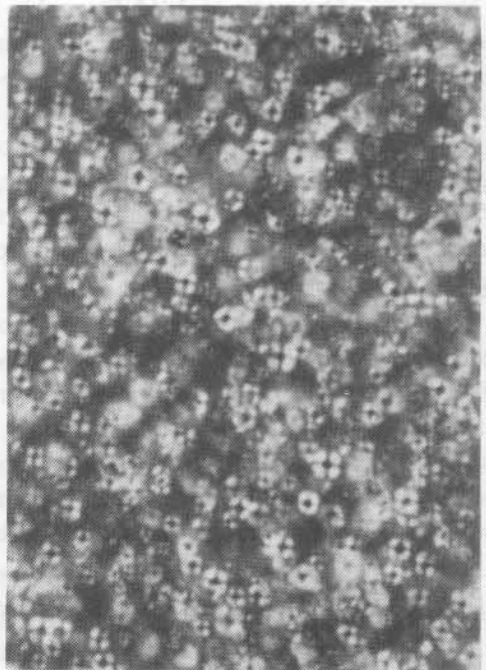
5% starch



10% starch



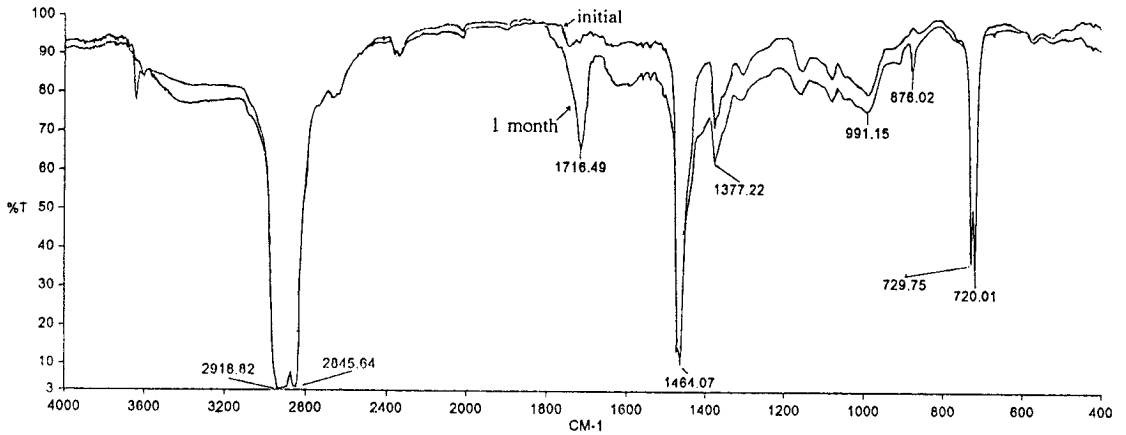
15% starch



20% starch

Fig.2 Dispersibility of cassava starch granules (5, 10, 15 and 20%) in the starch-LDPE films.

Unexposed and one-month exposed PE-5S/0.1F films



Unexposed and one-month exposed LDPE films

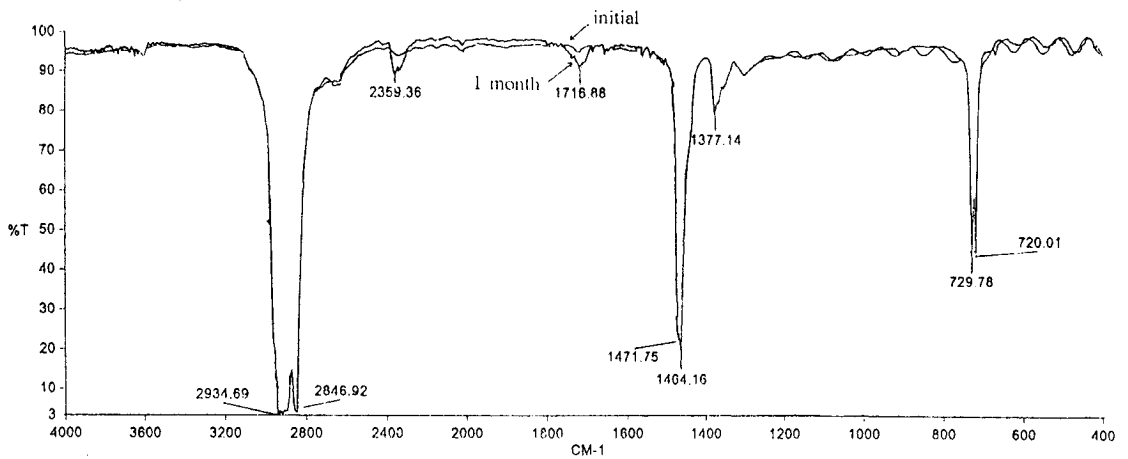


Fig.3 FTIR spectra of unexposed and one-month exposed LDPE films.

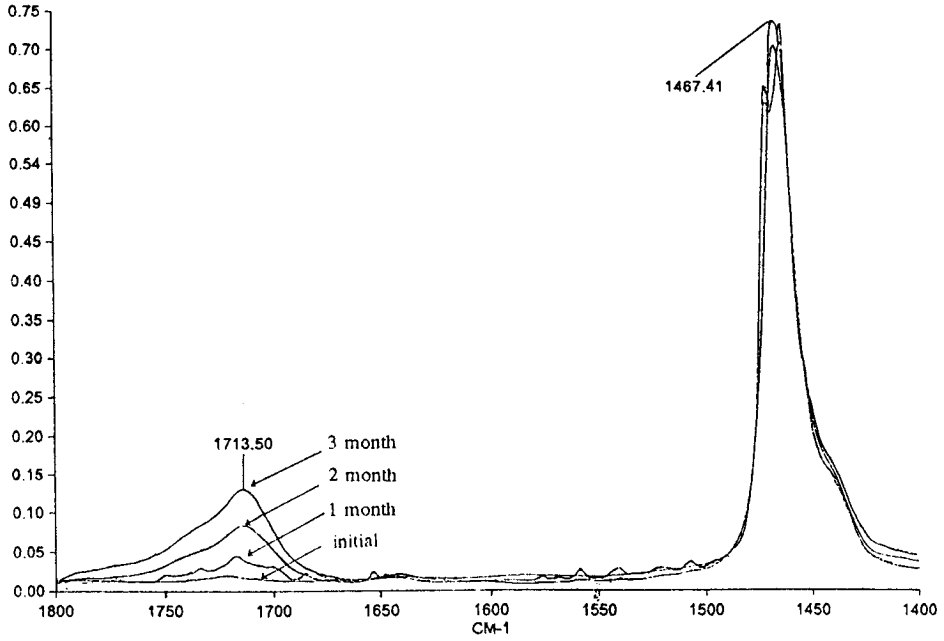


Fig.4 FTIR spectra of outdoor exposure of the iron-stearate-5% starch-LDPE films.

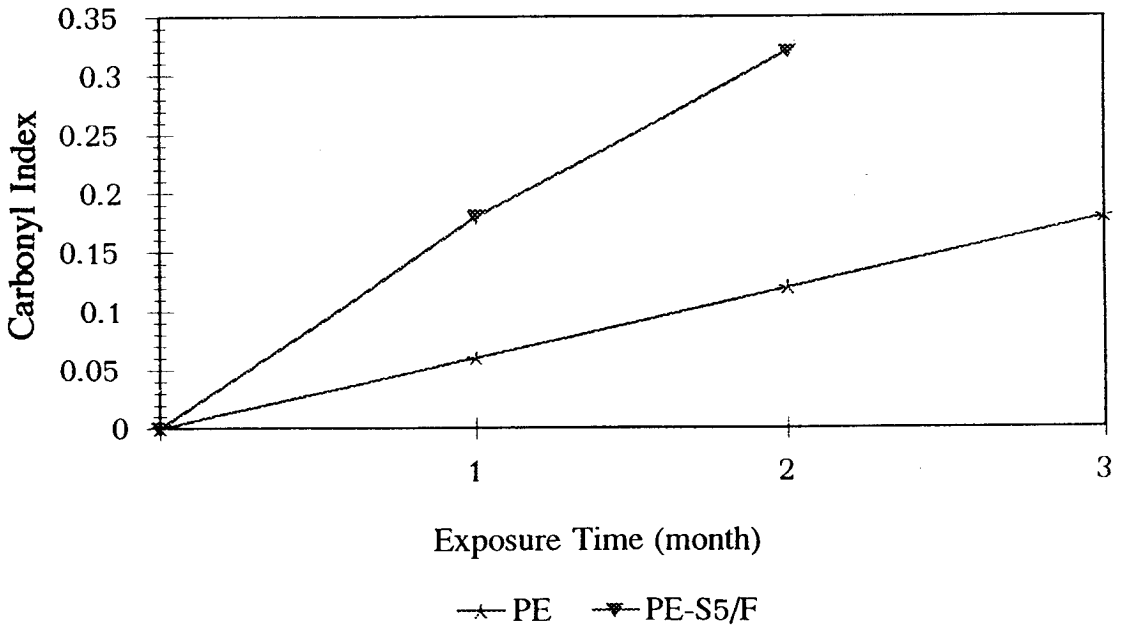
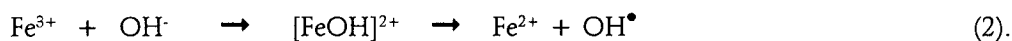
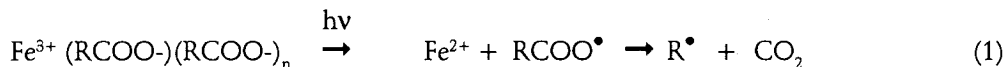


Fig.5 Carbonyl indices of LDPE and iron stearate-5% starch-LDPE films.

Regarding LDPE exposure to long-wavelength radiation, hydroperoxidation occurs essentially on the secondary carbon atoms of the saturated chain and at the α position of vinylidene groups, which can be observed as chemical defects.

Role of iron stearate in the degradation mechanism

According to Griffin¹, the transition metals are capable of initiating electron transitions between their outer shells, and the variable valence states, rendering them capable of inducing oxidation reactions in which the iron stearate, acts as a pro-oxidant in a similar manner, to catalyze the oxidative degradation. Under the action of sun light, the coordination compounds are sources for organic radicals formed in the photo-redox process as in eqs 1 and 2



The free radicals formed can react with the PE polymer, forming the polymer radicals. They are extremely reactive and can further react with oxygen as shown in Figure 6. It is firmly established that the carbonyl groups formed from the decomposition of hydroperoxides are involved in further reactions that greatly contribute to changes in both the chemical composition and the averaged molecular weights of the polymer.⁷ These reactions can also be induced by ultraviolet light absorption, and belong to the well-known type I and II Norrish reactions.

Tensile properties and degradability of various LDPE films during outdoor weathering tests

Figures 7 and 8 illustrate the performance of starch-filled LDPE films and PE-starch-iron stearate films on tensile properties after the outdoor weather tests. For the virgin LDPE films, the tensile strength was 19.7 ± 3.0 N/mm² with an elongation of $619 \pm 2.6\%$. In Figures 7 and 8, tensile strength and elongation at the breaking point decrease with increasing starch content. The presence of iron stearate did not affect the mechanical properties of the films kept at room temperature indoor because the tensile properties of the starch-LDPE and iron stearate-starch-LDPE films were almost the same at the same starch content. Thomas⁶ attributed effect of the cassava starch on tensile properties of the composite LDPE films to the moisture absorbing characteristics and interfacial bonding. The moisture absorbed in the cassava starch was expelled to form water during processing, that producing air bubbles in the matrix plastic. The air bubbles, considered as a defect, decrease the tensile strength of the film. The adhesion of starch and the matrix polymer with a dispersing agent is far weaker than in the virgin plastic, which made the composite break easily under a load. Fresnel voids and other phenomena occurred for a given strain and a particular content of starch, most probably with a high content of starch that reduces the tensile strength.

The mechanical properties of the virgin films change with increasing exposure time, which is a sensitive measure of the heterogeneity of the material. The tensile strength of the LDPE films showed a gradual decrease upon outdoor exposure, while elongation at break in the final period losses about 70% of its original value. For the films with starch content from 5 to 20%, the tensile strength and elongation decrease sharply in the early period of outdoor exposure and approach zero value after one and a-half months of exposure. For the films with both

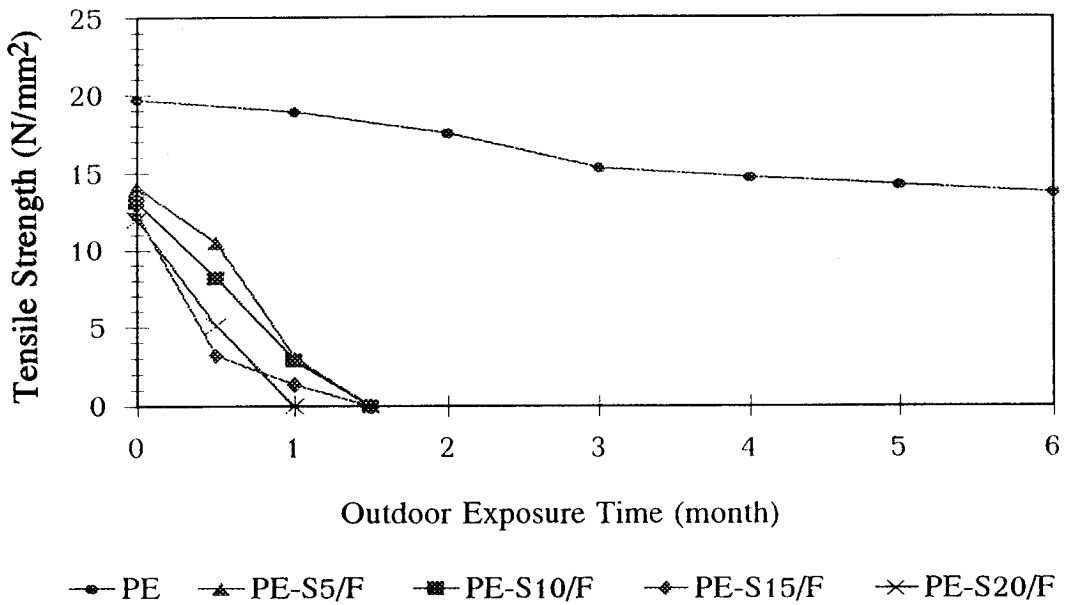
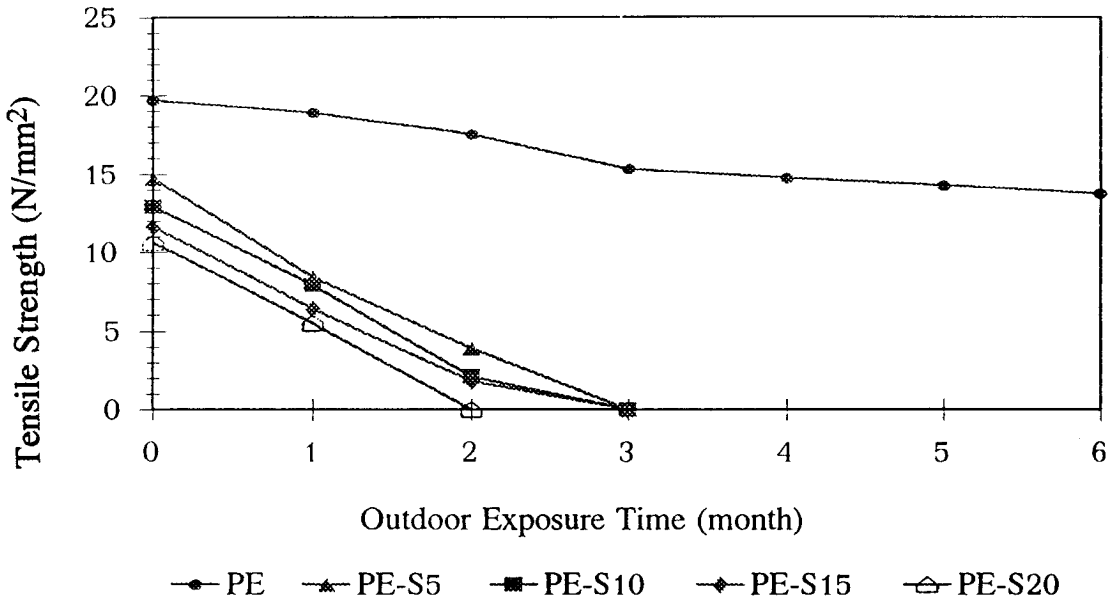


Fig.7 Tensile strength of LDPE and iron stearate (0.1 g)-starch LDPE films during out door exposure. The number after the letter S indicates the percentage of starch.

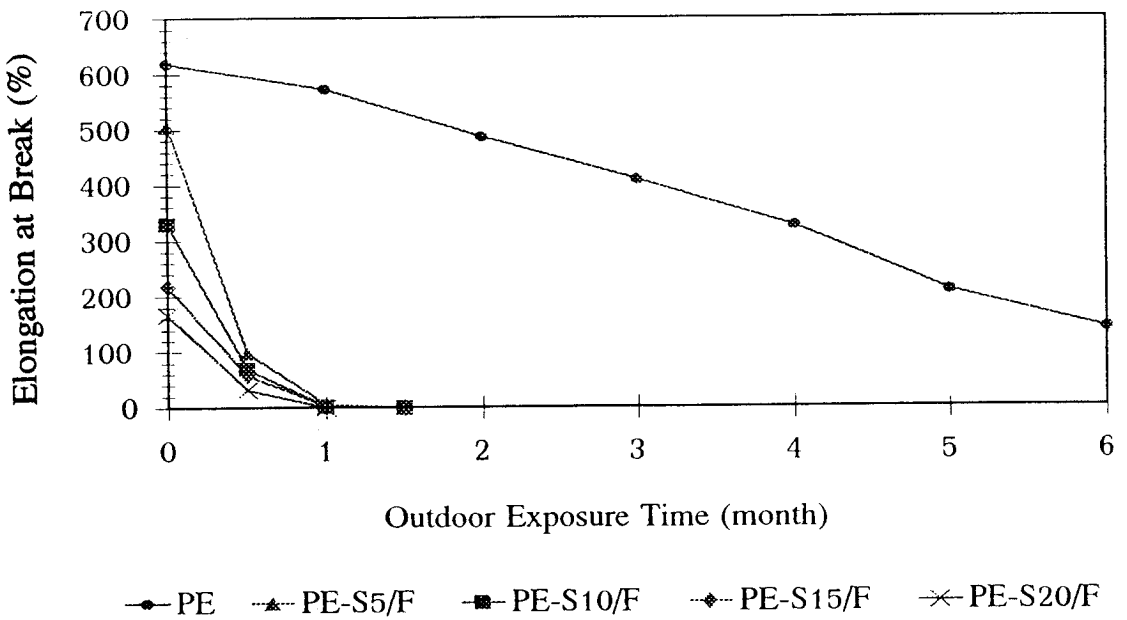
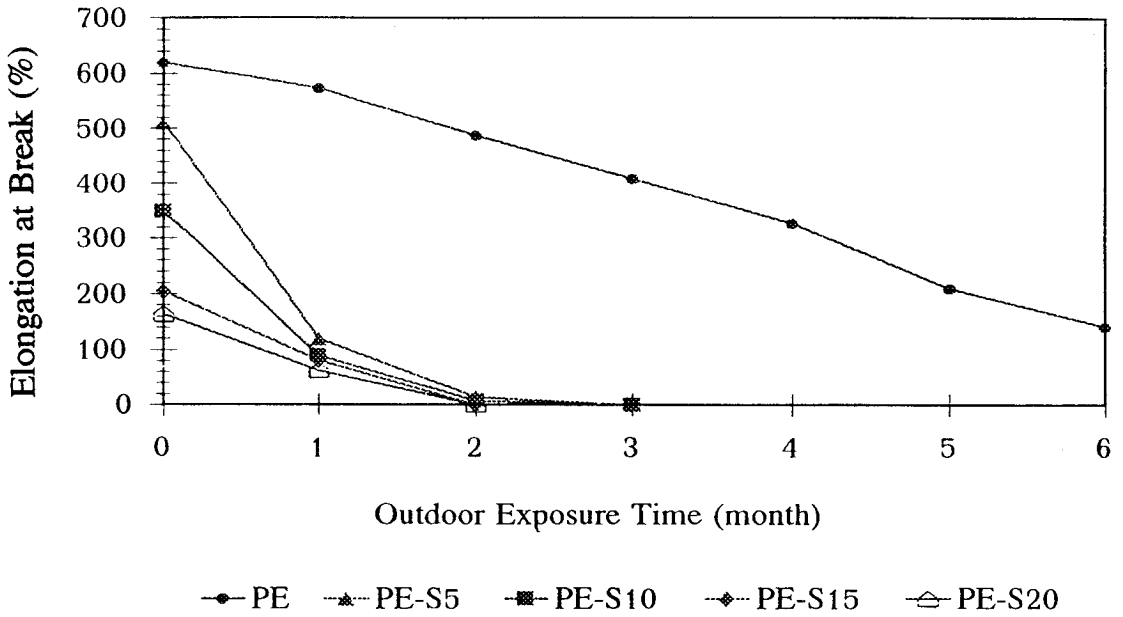


Fig.8 Elongation at break of LDPE and iron stearate (0.1 g) starch LDPE films. The number after the letter S indicates the percentage of starch.

starch and iron compounds shown in Figure 8, a sudden loss in both tensile strength and elongation was observed soon after the outdoor exposure. The values approached the zero value within six weeks. After this time, the films were brittle and crumbled on handling.

Upon indoor exposure of the PE films, the tensile properties of all samples change slightly or are essentially unchanged as shown in Figure 9. Therefore, the degradation of the starch-LDPE films kept indoors require a very long time. The storage time for the starch-LDPE films with or without iron stearate is longer than six months.

Average molecular weight measurement of outdoor exposure test

The changes in molecular weights of PE, PE-S5 and PE-S5/F films at various exposure times are shown in Figure 10. When the exposure proceeds, the reduction in average molecular weight of the PE sample (5.14×10^4) shows an induction period for about two weeks and then it decreases slowly to a slightly lower averaged molecular weight. The presence of iron stearate enhances the decrease in molecular weight manifold: twofold (2.1×10^4) in the presence of starch and about six-fold (9.25×10^3) with both starch and iron stearate.

Tensile properties and degradability of various LDPE films by soil burial test

The effects of soil burial tests on the tensile properties of LDPE, starch-LDPE and iron stearate-starch-LDPE films are shown in Figures 11 and 12. Tensile strength and elongation at break of the LDPE showed an induction period for one month and decreased afterward with a higher rate. The elongation exhibited a stronger reduction than did the tensile strength. For the starch-LDPE films, an induction period was found for both tensile strength and elongation but the elongation showed a significant rate of reduction. The higher rate of reduction in tensile strength was found in the samples containing iron stearate due to the enhanced effect of the pro-oxidant. The decrease in mechanical strength after soil burial can be caused by the starch embedded in the LDPE matrix, which can produce flaws or defects that are a sensitive characteristic feature for mechanical behavior. The higher the starch content, the higher the feebleness in the films.

Average molecular weight determination of the films on soil burial test

Figure 13 shows the molecular weight of the neat PE, PE-S5, and PE-S5/F (0.1 g) as a function of soil burial time. The molecular weights of all samples exhibit an induction period for about 3 months and then they gradually decrease with a lower rate, while the molecular weights of the outdoor exposed films decrease with a higher rate. This can be explained that the starch granules are covered by the polyethylene layer under the soil burial that could not allow sunlight to activate the degradation of LDPE. The starch cannot be attacked easily by the microorganism. It does need a longer time to observe the loss in molecular weight for a burial test comparing with the outdoor exposure test.

Visible biodegradability by fungi

The nutrient-salt selected for this study contains no carbon source, and the microorganism used for this research can survive by utilizing only the nutrient sources from the cassava starch in the plastic samples. Microbial degradation occurs by microorganisms such as fungi or bacteria consuming the material, which leads to increased porosity, void formation and the loss of integrity of the plastic matrix. The visible biodegradability of the starch-LDPE films due to the two fungi is shown in Figures 14 and 15.

The scanning electron micrographs of the starch-iron stearate PE films, shown in Figure 16, reveal the destroyed area of starch that is the starting point of degradation. The primary

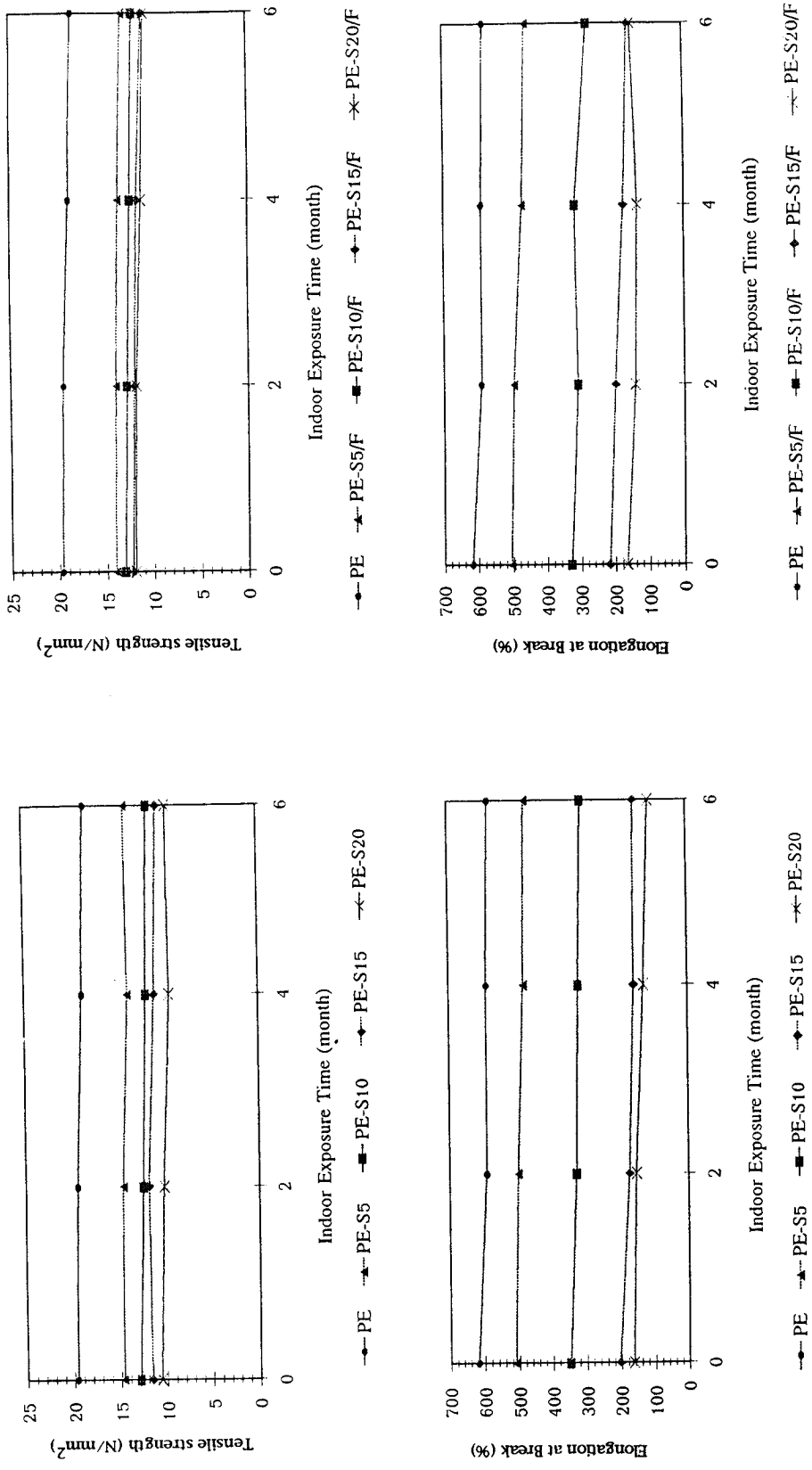


Fig.9 Tensile properties of LDPE and iron stearate (0.1 g) -starch-LDPE films during indoor exposure.

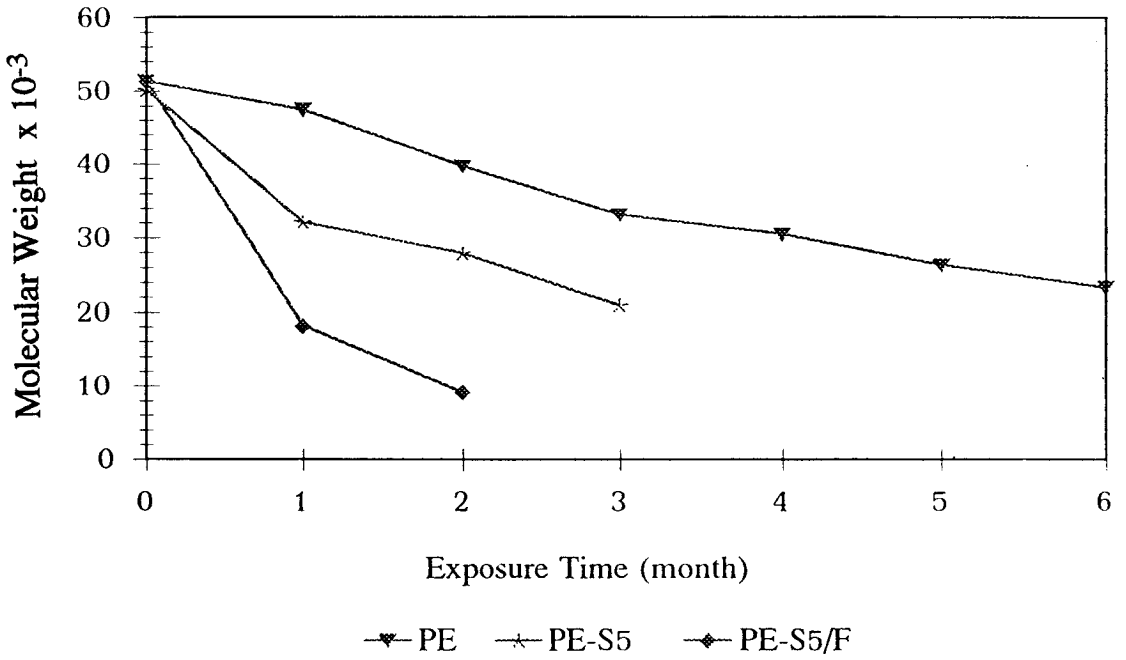


Fig.10 Molecular weight of LDPE, starch-LDPE and iron stearate starch-LDPE films during outdoor exposure.

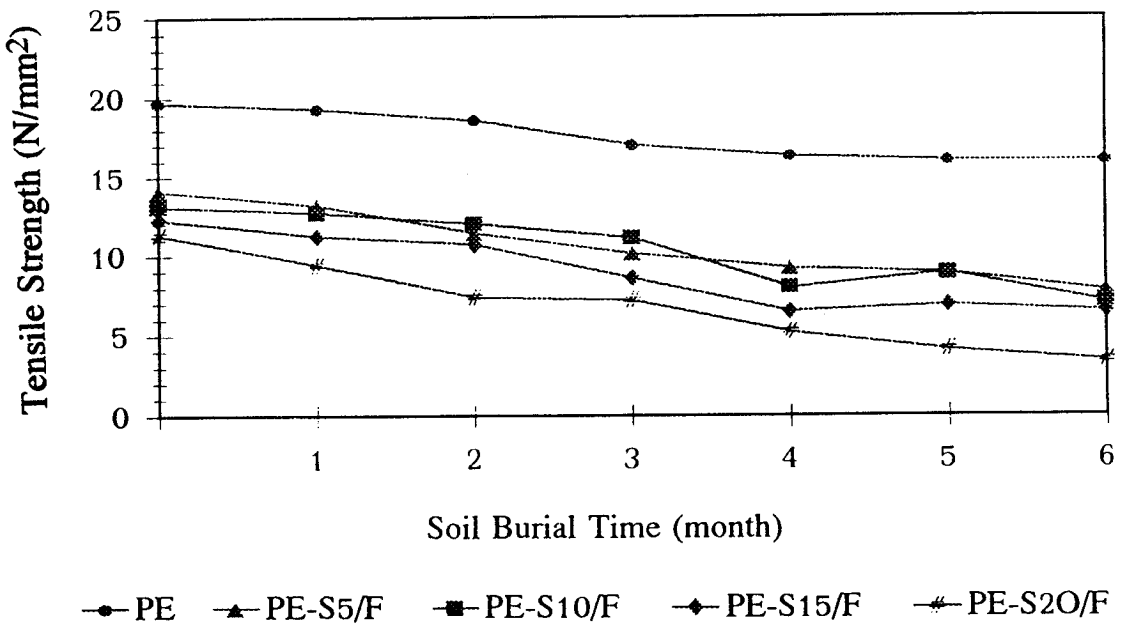
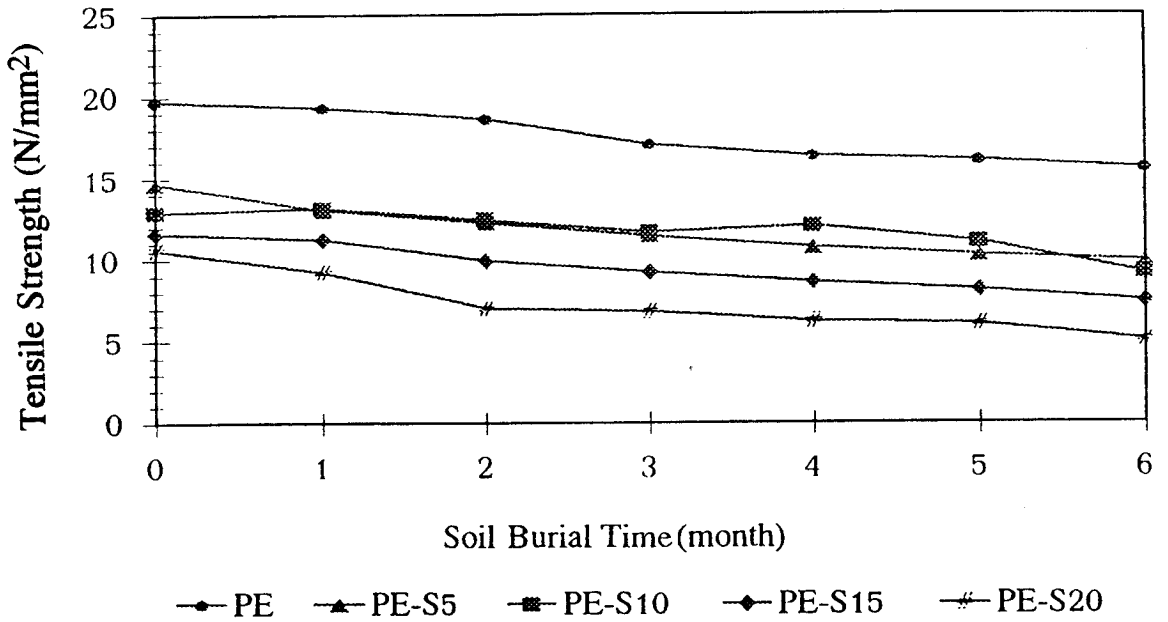


Fig.11 Tensile strength of LDPE, and starch-LDPE film during soil burial test.

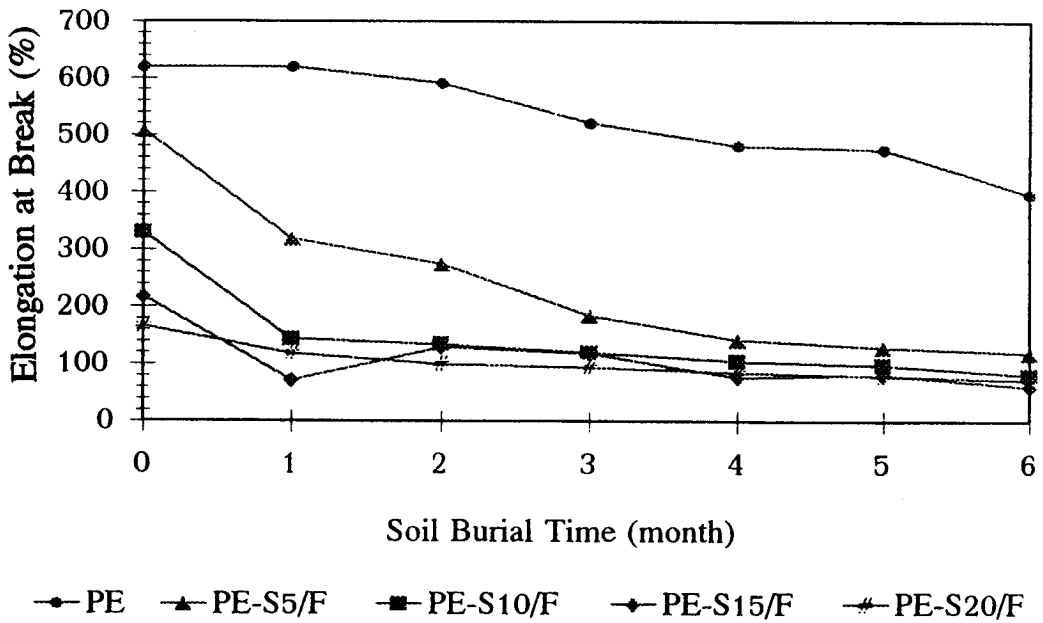
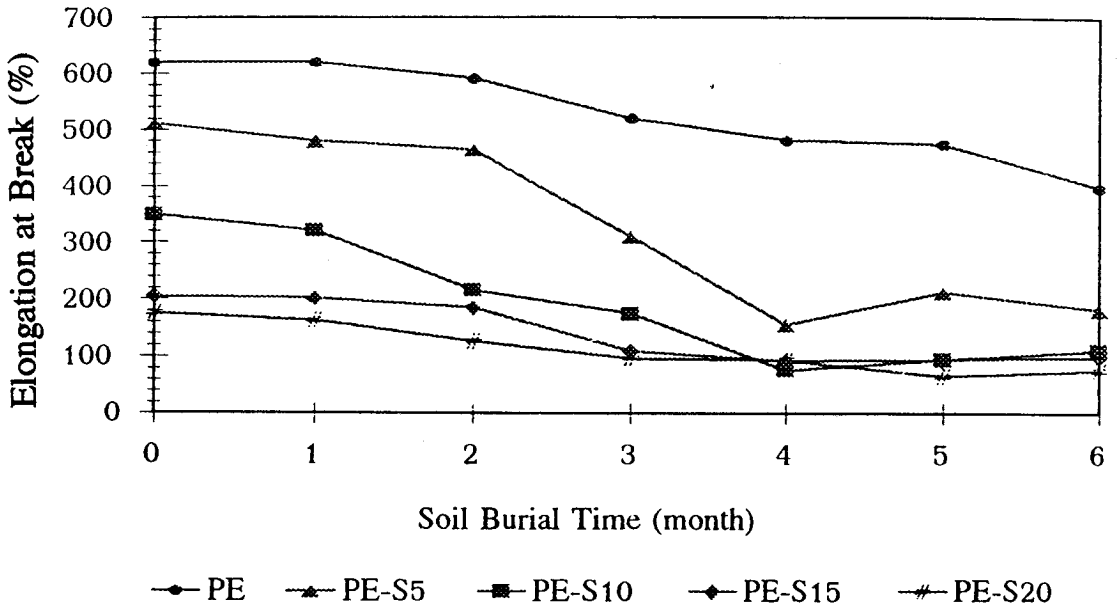


Fig.12 Elongation at break (%) of LDPE and starch-LDPE film during soil burial test.

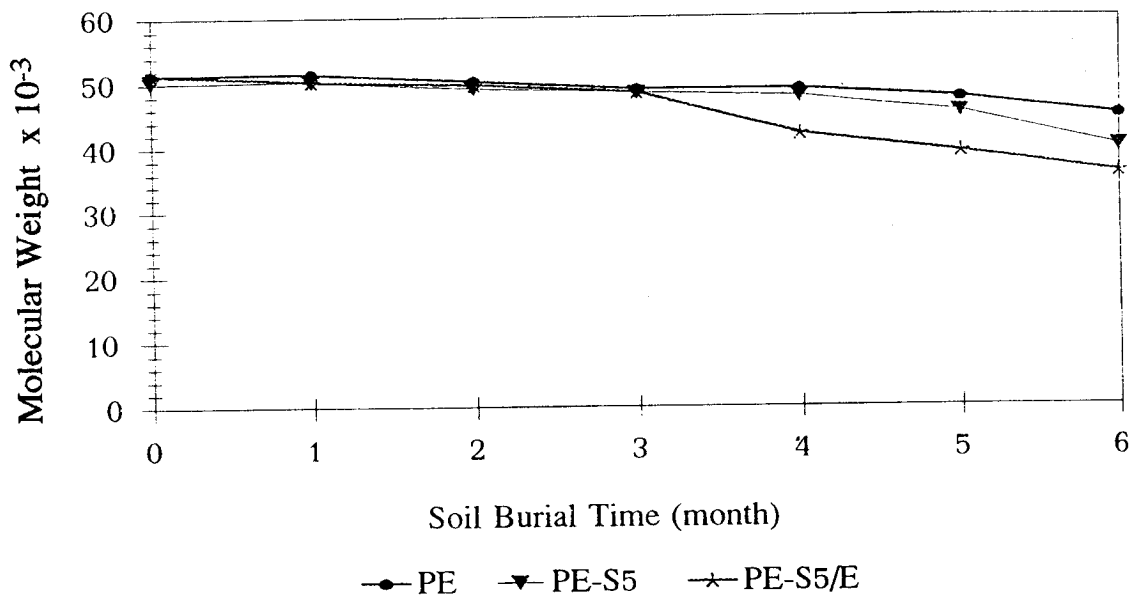


Fig.13 Molecular weight of LDPE, starch-LDPE and iron stearate starch-LDPE films during soil burial test.

mechanism is microbial production of amylase in or near a pore (seen as black spots on the blistering white areas), followed by diffusion of the enzyme into pores and diffusion of soluble digestion products back to the surface where they are metabolized. This mechanism is the only possibility when the pore diameter (depending on the sizes of the microbial cells) is too small to admit a microbial cell. An alternative mechanism could be diffusion of a water-soluble starch to the film surface, at which point degradation would occur. None of the materials lose starch, even when soaked in water for extended periods in the presence of a microbial inhibitor. Therefore, diffusion of amylase to the substrate rather than diffusion of the substrate to the film surface is the more likely mechanism. When the starch is removed from its surface inward, channels are created through, which amylase could diffuse inward and digestion products outwards shown in panels B, D in Figure 17.⁸ In the degraded materials (D), there are a few sites where constrictions occur (arrows), and these sites would control the enzyme and product flux through the entire channel. In contrast, the degraded material (B) does not have the severe constrictions in channels as in A. Therefore, the material A would likely be more repulsively degraded than material C, even though the percentage composition of A and C is identical. In such cases, the decay rate is not governed by the average pore size of the composites, but by the minimum pores, i.e., then the surface and smaller surface pores (at diameters smaller than 0.5 μm) would further hinder the product release from the film interior. Bottlenecks (arrows in Figure 17) may also have a localized effect on concentration on the upstream side of the path, and there may be some compensation for the smaller path dimensions and the influence of path restrictions can be reduced. It should be evident from such considerations that predicting the decay rate of these materials requires more information about the volumetric composition of the blends.⁹ For the present work, the volume composite of the blends cannot be calculated since the experimental technique could not allow the proper measurement of composite volume.

The total population of *Aspergillus niger* and *Penicillium pinophilum* on the surface of the films are shown in Table I. Both the figures (Figures 14 and 15) and Table I indicate that there is very little population of the fungi on the neat LDPE film. For the starch-LDPE and starch-iron stearate-LDPE films, the population of the fungi increases as the starch content increases.

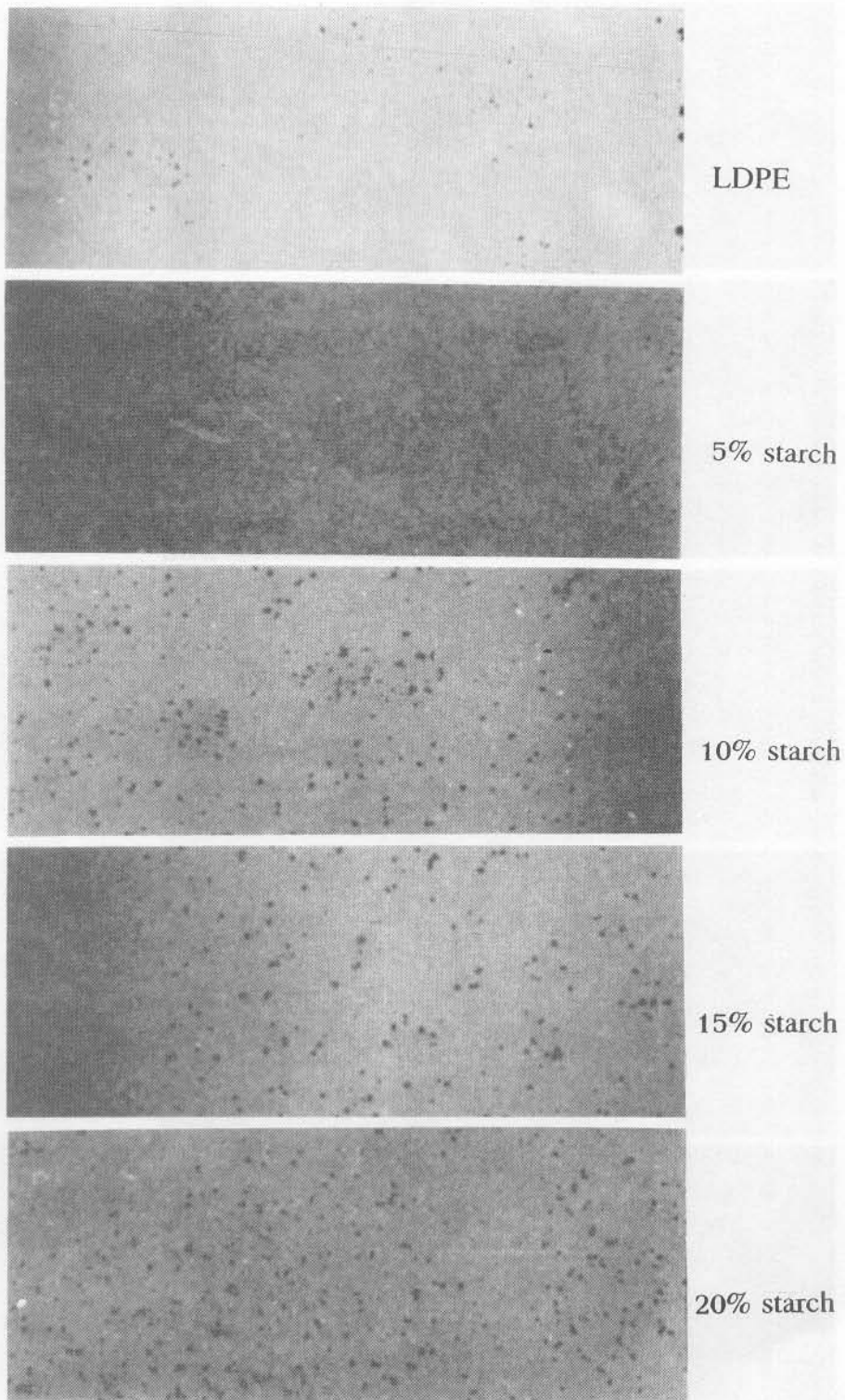


Fig.14 Biodegradability of starch-LDPE films by *Aspergillus niger*.

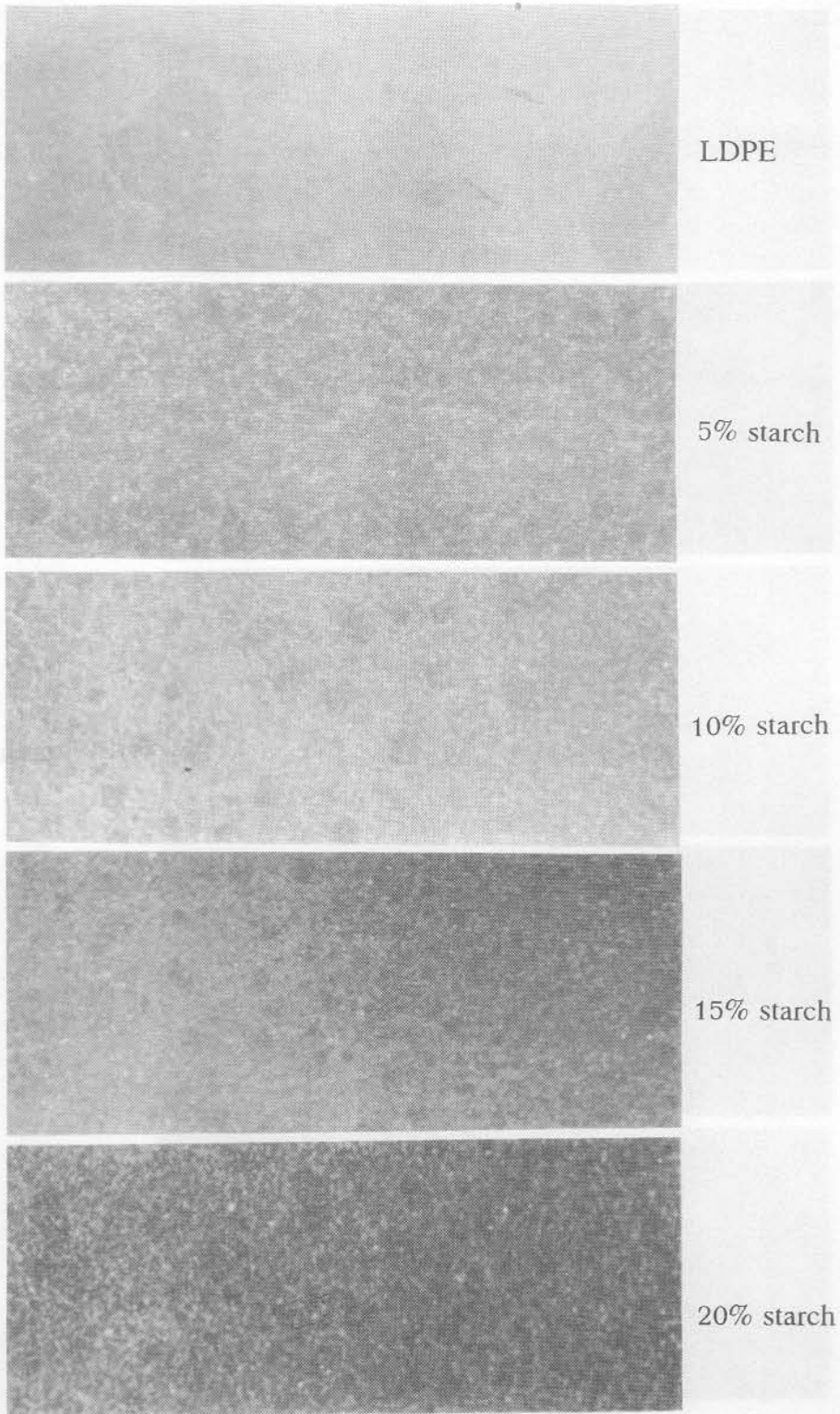


Fig.15 Biodegradability of starch-LDPE films by *Penicillium pinophilum*.

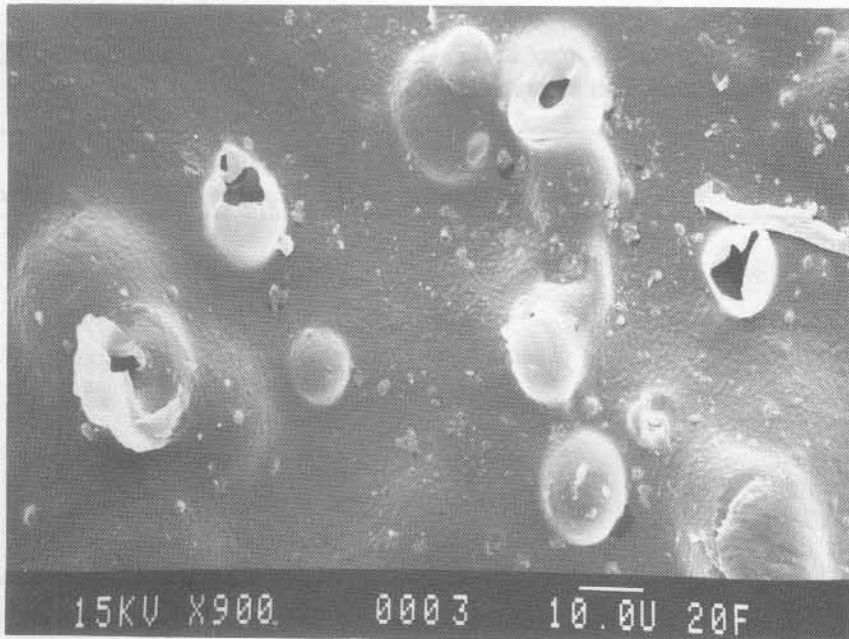
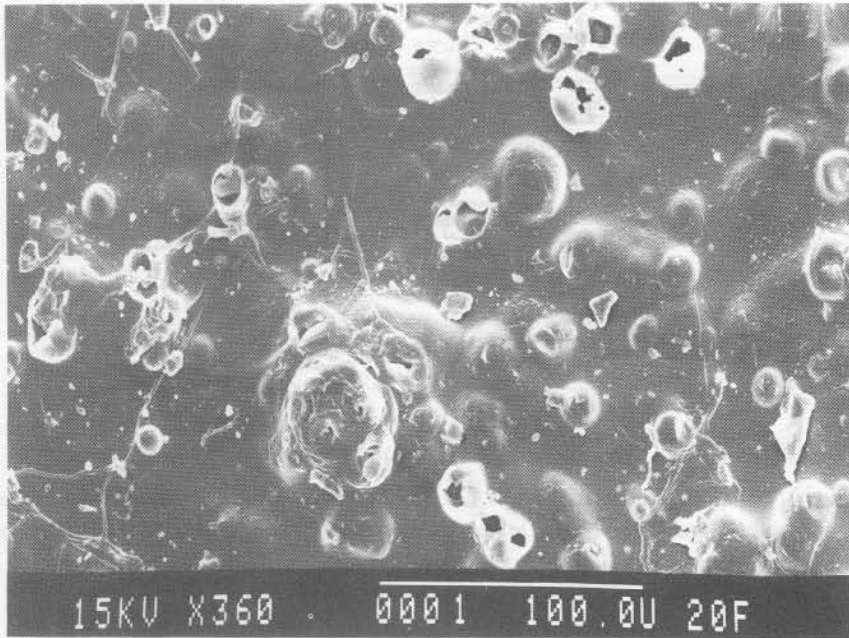


Fig.16 SEM of the starch-iron stearate LDPE film attacked by microorganisms.

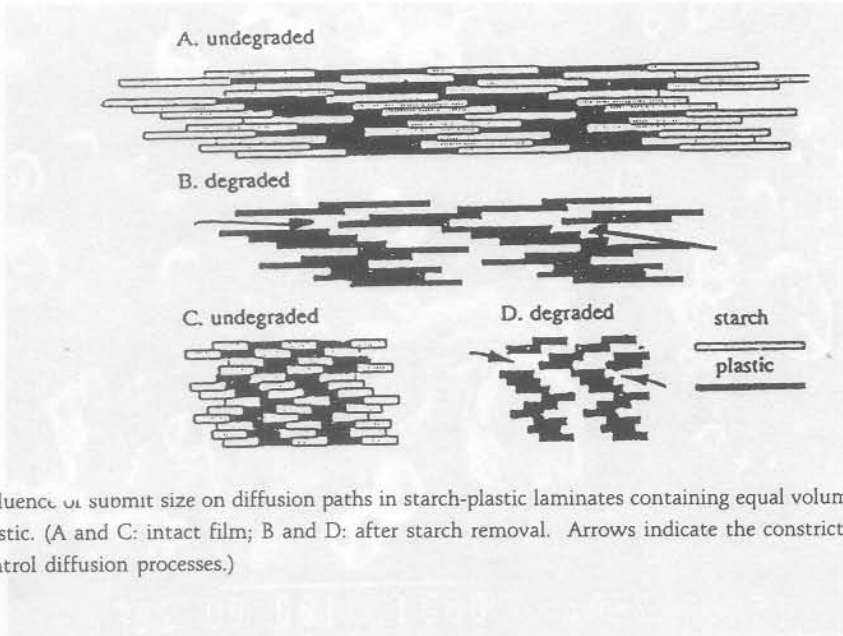


Fig.17 Influence of substrate size on diffusion paths in starch-plastic laminates containing equal volumes of starch and plastic. (A and C: intact film; B and D: after starch removal. Arrows indicate the constrictions that would control diffusion processes.)

Table 1. The size of *Aspergillus niger* and *Penicillium pinophilum* populations in LDPE, starch-LDPE, and starch iron stearate-LDPE films.

Samples	Total population	
	<i>Aspergillus niger</i>	<i>Penicillium pinophilum</i>
PE	40	12
PE-S5	200	3417
PE-S10	476	3901
PE-S15	513	4407
PE-S20	761	7126
PE-S5/F	174	2814
PE-S10/F	414	3196
PE-S15/F	531	3540
PE-S20/F	812	4286

Note: PE = polyethylene film, S = starch, the number followed the S is its related concentration, and F= iron stearate (0.1 g per 100 g of LDPE).

The population of *Penicillium pinophilum* is more effective in promoting biodegradation of the polyethylene film through the incorporation of the cassava starch and iron additive.

With the presence of cassava starch and iron stearate in the LDPE, most samples (except those kept indoor) show a fast decrease in mechanical properties, especially for those under outdoor exposure. The degradable polyethylene may contain the biodegradable substance of starch granules, soya oil that is an oxidizable substance containing double bonds, and iron stearate, which is a pro-oxidant to catalyze the oxidative degradation of polymer chains. Such composites can have simultaneous processes of degradation with a significant synergistic effect. As far as it has been revealed, the degradation proceeds by the following mechanism.³ Under the irradiation of ultraviolet light, heat, and moisture, a decomposition reaction occurs to give free radicals such as OH^\bullet due to the presence of ferrous ions and the radical reacts with the polymer forming the polymer radical or other radicals. These polymer radicals are extremely reactive, and can further react with oxygen shown in Figure 6, with other chains, with the ferrous ions, or with the double bonds of an oxidizable substance. The polymer chains are then split to give small molecules with or without oxygen-containing groups, such as alcohols, ketones, water, etc. During the processing, ferrous ions can act as a reaction promoter, especially as a chain splitter, because the substance has a greater tendency than a saturated polymer chain to form peroxy or hydroperoxy groups. Due to the many hydroxyl groups in the starch's composition, the groups can manifest themselves as promoters and in cooperation with the iron stearate can be considered as co-initiators. At this stage, the plastic becomes brittle and fragile, depending on the prevailing condition. In the subsequent second stage, the microorganisms, if any, in combination with ultraviolet light, heat, or moisture, biodegradation can start to give the small pieces of disintegrated materials of starch. This process can be repeated many times until the smaller particles are obtained. Since the plastic material was buried in soil, the minute particles can penetrate under external influences (for example, rain) into the soil.

CONCLUSION

The present work investigated the degradation techniques of prepared LDPE films containing starch, soya oil and iron stearate by photo-, environmental, and microorganism degradations. Degradation of plastics usually occurs by many degradation pathways. Photodegradation and chemical degradation lead to the oxidation of the plastic to give compounds containing the carbonyl functionality. FTIR can follow the changes in the ketone carbonyl functionality known as the carbonyl index. The intensity of the carbonyl index increases with an increasing amount of starch and iron stearate, which agrees with the decrease in tensile properties. The *Aspergillus niger* and *Penicillium pinophilum* fungi can decompose the starch-containing LDPE while they cannot decompose the virgin LDPE films. *Penicillium pinophilum* is much more effective in degrading the starch-containing LDPE. There was no significantly different decomposing result in the presence of iron stearate compared to those without its presence. Most of the LDPE films in this research can degrade within six months under environmental tests whereas their shelf life is longer than six months. Photodegradation of the PE films is caused by exposure to UV radiation and heat to produce radicals through radical and chain reactions. The present research shows that the presence of iron stearate as a pro-oxidant additive was essential for initiating the LDPE degradation. The rapid disintegration of the plastic in the environment was probably due to the initial biodegradation of starch that provided the greater surface area in the matrix for oxidative breakdown of the polymer, followed by the microbial digestion of the degradation products.

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บทคัดย่อ

ฟิล์มพลาสติกพอลิเอทิลีนชนิดสลายตัวมีส่วนประกอบของแป้งมันสำปะหลังร้อยละ 0-20 โดยน้ำหนัก น้ำมันถั่วเหลืองร้อยละ 0-2 โดยน้ำหนัก และเพอร์ริสเสเดียวเรต ร้อยละ 0-0.1 โดยน้ำหนัก ของผสมได้รับการกระจายตัวด้วยตัวช่วยตัวขี้อิโพรินในเครื่องผสมแห้งและคอมเปาต์ด้วยลูกโม่สองโม่เพื่อทำแผ่นตัดแผ่นเหล่านี้ให้เป็นชิ้นเล็กๆเพื่อนำไปรีดและเป่าในเครื่องเป่าฟิล์มพลาสติก ได้ฟิล์มพลาสติกพอลิเอทิลีน ฟิล์มพลาสติกพอลิเอทิลีนเหล่านี้ ได้ทดสอบการสลายตัวด้วยอากาศภายนอกบ้านเพื่อเปรียบเทียบกับภาวะที่อยู่ในบ้านและการทดสอบแบบฝังดินเป็นระยะเวลาหกเดือนตามบรรยากาศธรรมชาติ การสลายตัวเชิงชีวภาพของฟิล์มพลาสติกวัดได้ด้วยการวัดประชากรของเชื้อรา *Aspergillus niger* และ *Penicilium pinophilum* การสลายตัวทุกกระบวนการติดตามได้โดยดูการเปลี่ยนแปลงทางเคมีและกายภาพด้วยอินฟราเรดสเปกโทรสโกปี วัดค่าน้ำหนักโมเลกุลเฉลี่ยโดยการวัดความหนืด และวัดสมบัติแรงดึง เทคนิคอินฟราเรดสเปกโทรสโกปีสามารถบอกการเกิดของหมู่คาร์บอนิลในนามของหมู่ฟังก์ชันคีโตนระหว่างการสลายตัว ความเข้มข้นของหมู่คาร์บอนิลสูงในฟิล์มที่มีแป้งและเพอร์ริสเสเดียวเรต ปริมาณประชากรของเชื้อรา *Aspergillus niger* และ *Penicilium pinophilum* สูงในกรณีหลังซึ่งแสดงว่าเชื้อราเหล่านี้ส่งเสริมการสลายตัวเชิงชีวภาพของฟิล์มพอลิเอทิลีนเมื่อมีน้ำมันถั่วเหลืองและเพอร์ริสเสเดียวเรตร่วมอยู่โดยแผ่นฟิล์มถูกแยกออกเป็นชิ้นเล็กๆ ซึ่งมีรูเล็กจำนวนมากของแป้งที่ถูกทำลาย ฟิล์มพลาสติกที่มีส่วนประกอบของเพอร์ริสเสเดียวเรตสูญเสียสมบัติกายภาพหลังได้รับแสงนอกรับเป็นเวลานานสองเดือน ซึ่งตรงกันข้ามกับการรับแสงนอกรับ สมบัติทางกายภาพและสมบัติเชิงกลของฟิล์มพอลิเอทิลีนที่เก็บไว้ในบ้านนานกว่าหกเดือน ไม่พบการเปลี่ยนแปลงใดๆ ณ ภาวะปกติ