

CHAPTER 4

RESULTS AND DISCUSSION

Effect of Starch Content on Mechanical Properties of the LDPE Films

The tensile strength and elongation at break of LDPE, starch-LDPE and iron stearate-starch-LDPE films are shown in Table 4.1.

Table 4.1 Tensile properties of starch-LDPE at various contents of cassava starch

Sample	Tensile Strength (N/mm ²)	Elongation at Break (%)
PE	19.7(±3.0)	619(±2.6)
PE-S5	14.7(±2.9)	511(±2.2)
PE-S10	12.9(±3.5)	349(±3.7)
PE-S15	11.6(±3.1)	205(±5.2)
PE-S20	10.6(±4.0)	175(±5.4)
PE-S5/F	14.1(±2.8)	507(±2.3)
PE-S10/F	13.1(±3.4)	330(±5.1)
PE-S15/F	12.3(±3.9)	218(±4.3)
PE-S20/F	11.3(±2.5)	167(±3.2)

For LDPE films without cassava starch, the tensile strength was 19.7 N/mm² and elongation at break was 619%. The tensile strength and elongation of starch-LDPE films are plotted as a function of starch content in Figure 4.1. Tensile strength and elongation at break decrease with increasing starch content. The iron stearate did not affect the mechanical properties. Tensile properties of starch-LDPE and iron stearate-starch-LDPE films were almost the same at the same starch content.

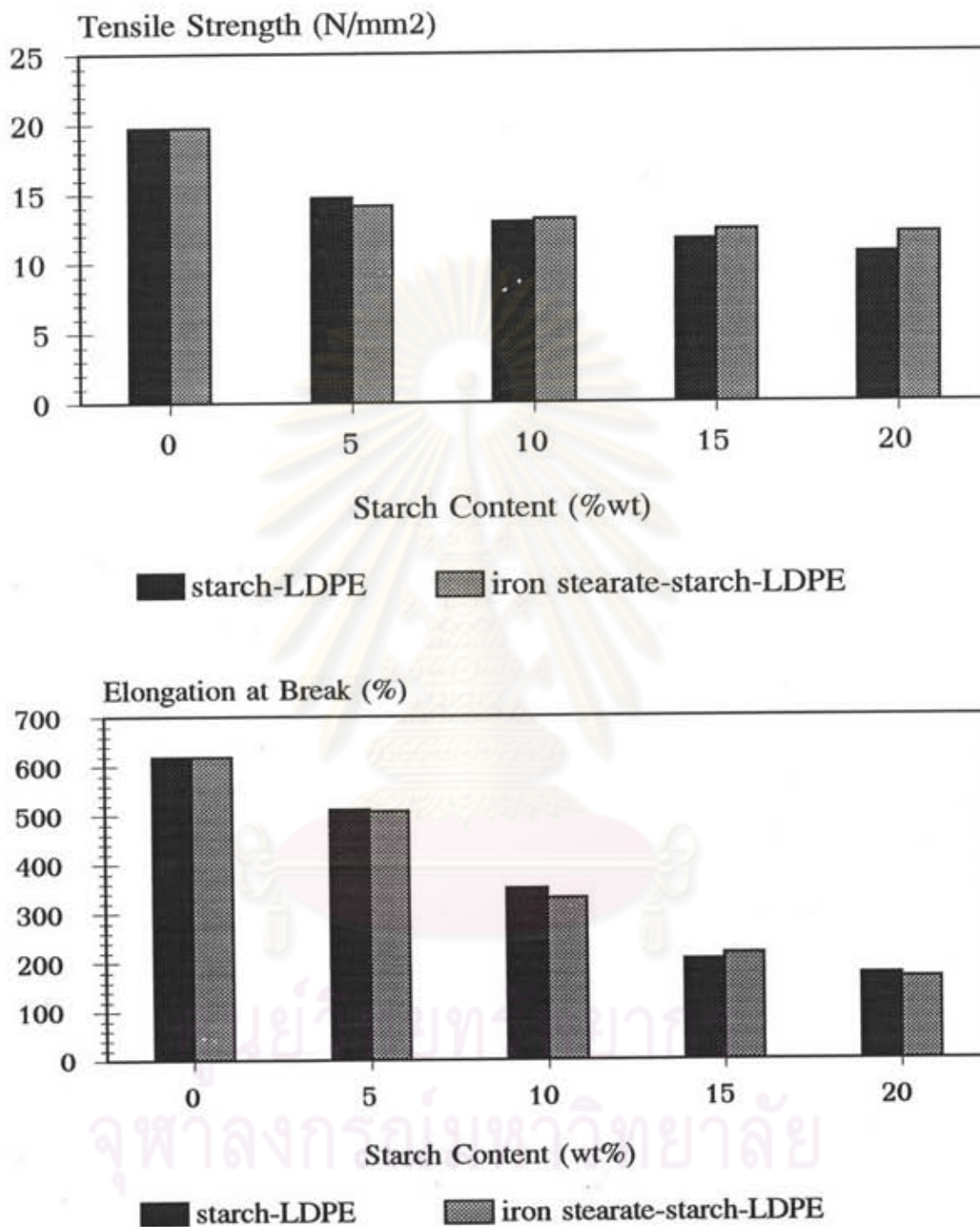


Figure 4.1 Effect of cassava starch content on tensile strength and elongation at break of starch-LDPE films

The Cassava starch affects tensile strength of the composite LDPE films according to their moisture absorbing characteristics and interfacial bonding (Thomas, 1987). The cassava starch can easily absorb moisture in atmosphere. When heat is applied during processing, the water in starch evaporates and causes air bubbles to form within the plastic mixture when it is cooled. The air bubbles decreased the tensile strength of the films. The combination between starch and plastic was only a dispersion of starch granules in the polyethylene matrix. Therefore the adhesion between starch and plastic polymer was not strong, and was broken easily, when a force was applied. The effect of filler to matrix bonding may be more easily understood by referring to stress whitening, which occurs when a tensile specimen is elongated. At a particular stress for the composite, the matrix separates from the filler surface, causing minute voids that reflect light due to refractive index differences between components, called the Fresnel effect. For a given critical strain, the high content of starch particles will cause more voids to form in the matrix than will occur with the low content of starch particles. Therefore the increase of starch content causes a reduction in tensile properties.

Environmental Degradation of Starch-LDPE films

The activity of cassava starch and iron stearate in LDPE degradation was studied by outdoor exposure. The environmental degradation of starch-LDPE film and iron stearate-starch-LDPE film were studied up to 6 months of outdoor exposure. The films were exposed in such a way that the main part of film was free from the obstructions. The average temperature, humidity and solar radiation data are shown in Figures 3.1 and 3.2. The degradation of composite polyethylene were measured by tensile properties, molecular weight and infrared spectra were observed. Table 4.1 shows the mechanical properties of the exposed films.



1. Tensile Properties Measurements

A characteristic feature of the ultimate mechanical properties is their sensitivity to the presence of flaws in the bulk of the material, which facilitates the use of ultimate properties in the detection of processes that occur at localized sites. Stress-strain test is a simple but very sensitive detection method. A typical study of the effect of UV exposure on the tensile strength of unexposed and exposed films of both LDPE and starch-LDPE films is shown in Figure 4.2. It can be seen that the mechanical properties of the films change with exposure time. Based on this observation, the tensile strength and elongation at break is a key of this material property, which decreases as exposure time increases and it is a sensitive measure of the heterogeneity of the material.

From Figure 4.2, tensile strength of the LDPE film shows a gradually decrease after outdoor exposure. Elongation at break at the final period losses about 70% of the original value as a negative linear trend. The behavior of samples containing starch (PE-S5, PE-S10, PE-S15 and PE-S20) differ from that of the neat LDPE ones. Tensile strength and elongation at break decrease sharply in the early period and approach zero value after three months. The PE-S20 film loses all its strength after two months. Elongation at break losses over 38% of the original value in the first month and then approaches zero value within two months.

The properties of iron stearate-starch-LDPE films (PE-S5/F, PE-S10/F, PE-S15/F and PE-S20/F) are plotted as a function of time in Figure 4.3. From this figure, there is a sudden loss on both tensile and elongation of the samples soon after exposure. Tensile decreases and finally approaches zero value within six weeks. Elongation at break losses over 98-100% of their original values in first month. For example, an initial tensile strength of iron stearate-5%starch-LDPE (PE-S5/F) Film was 507%, after 1 month exposure, tensile strength of the film became 6%. After this stage, the films were embrittled and crumbled on handling.

Table 4.2 Tensile properties of LDPE, starch-LDPE and iron stearate-starch-LDPE films during outdoor exposure

(a) Tensile strength

Samples Exposure time	Tensile strength (N/mm ²)								
	PE	PE- S5	PE- S10	PE- S15	PE- S20	PE- S5/F	PE- S10/F	PE- S15/F	PE- S20/F
original	19.7	14.7	12.9	11.6	10.6	14.1	13.1	12.3	12.0
2 weeks	-	-	-	-	-	10.5	8.2	3.2	5.1
1 month	18.9	8.4	7.9	6.4	5.5	3.1	2.9	1.4	0
6 weeks	-	-	-	-	-	0	0	0	0
2 months	17.5	3.9	2.1	1.8	0	-	-	-	-
3 months	15.3	0	0	0	-	-	-	-	-
4 months	14.7	-	-	-	-	-	-	-	-
5 months	14.2	-	-	-	-	-	-	-	-
6 months	13.7	-	-	-	-	-	-	-	-

(b) Elongation at break

Samples Exposure time	Elongation at break (%)								
	PE	PE- S5	PE- S10	PE- S15	PE- S20	PE- S5/F	PE- S10/F	PE- S15/F	PE- S20/F
original	619	511	349	205	164	507	330	218	167
2 weeks	-	-	-	-	-	84	65	58	60
1 months	573	120	90	81	63	6	2	2	0
6 weeks	-	-	-	-	-	0	0	0	0
2 months	487	14	8	3	0	-	-	-	-
3 months	409	0	0	0	-	-	-	-	-
4 months	250	-	-	-	-	-	-	-	-
5 months	210	-	-	-	-	-	-	-	-
6 months	142	-	-	-	-	-	-	-	-

“-” the experiment was not carried out

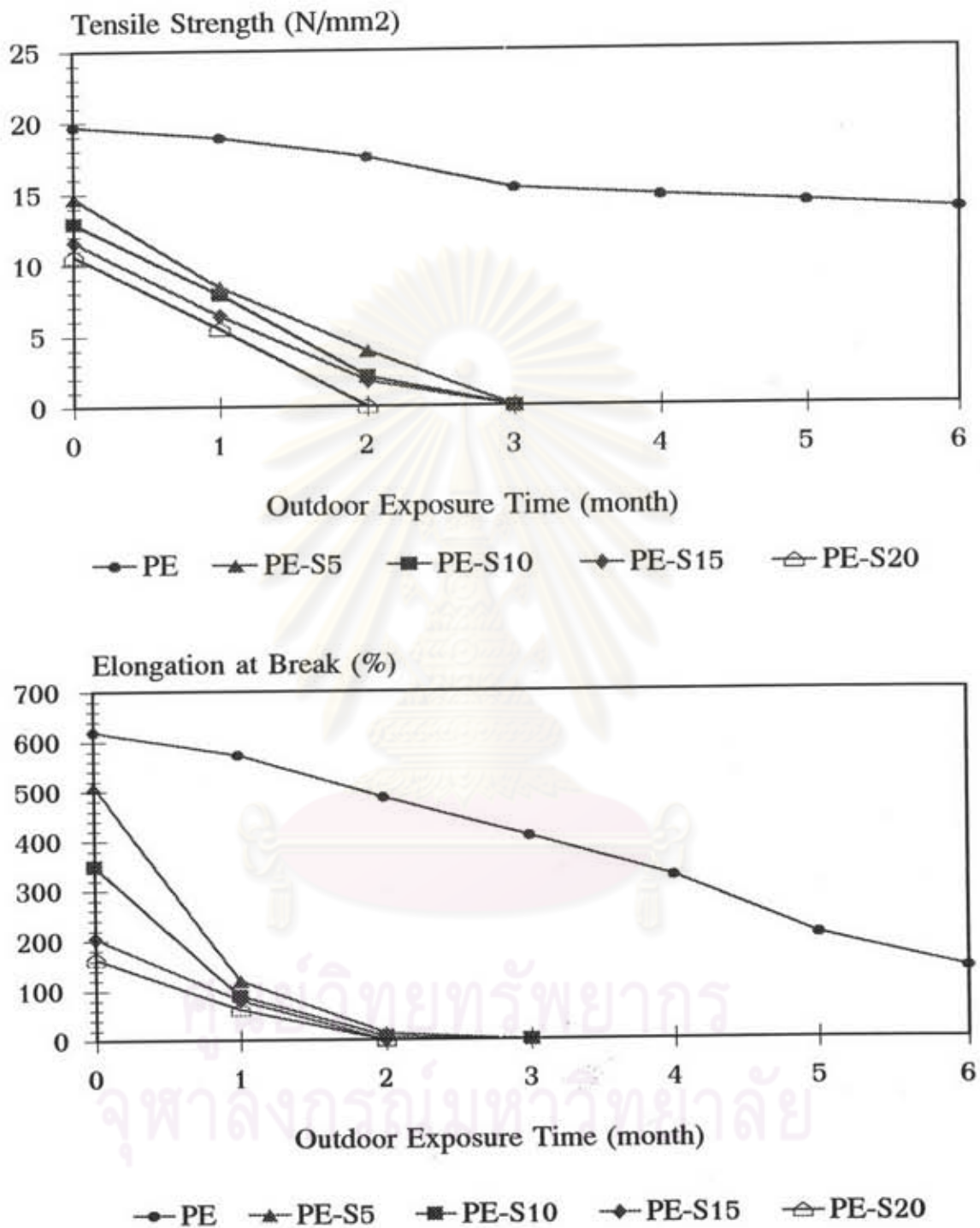


Figure 4.2 Tensile properties of LDPE and starch-LDPE films during outdoor exposure

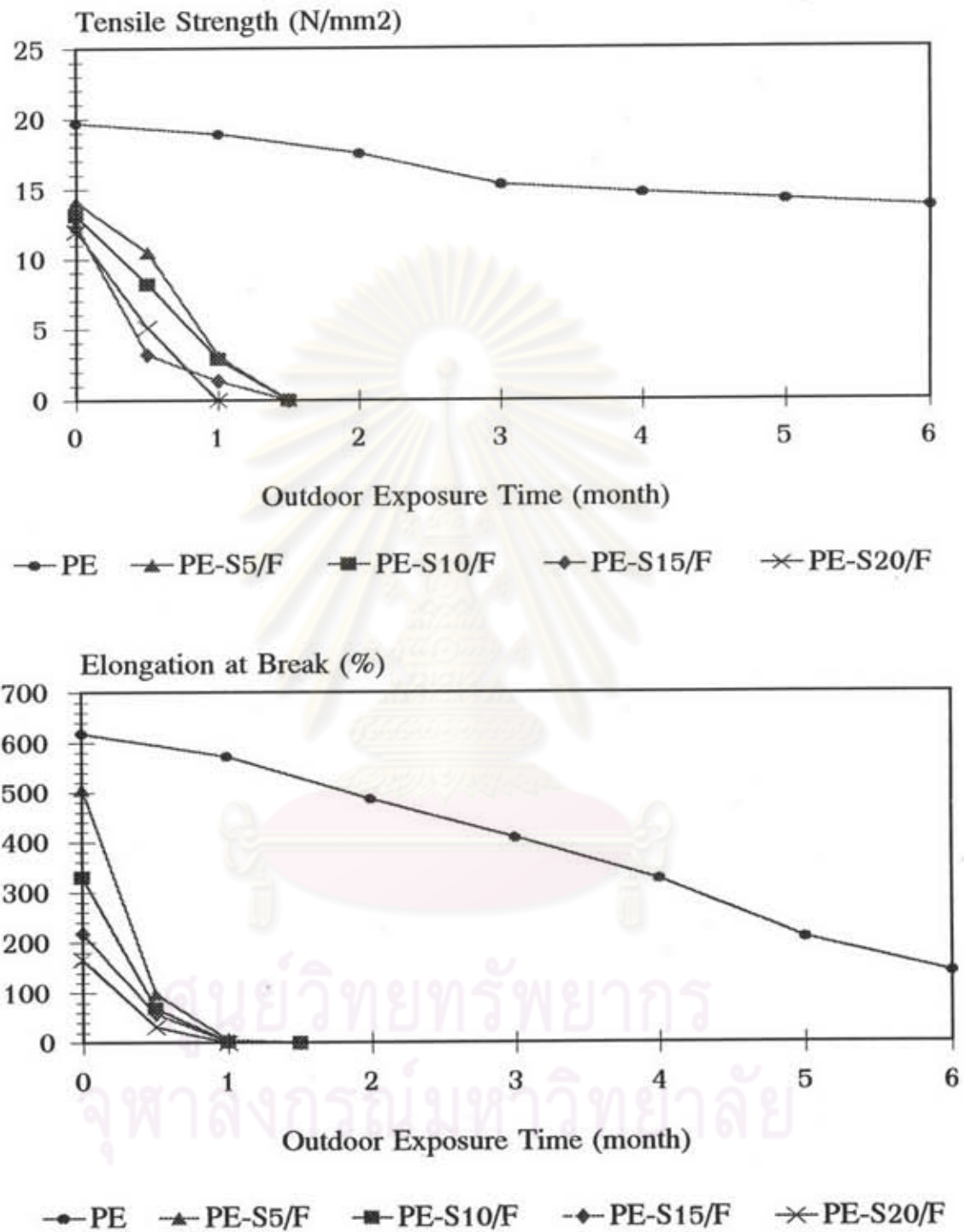


Figure 4.3 Tensile properties of LDPE and iron stearate-starch-LDPE films during outdoor exposure



The indoor exposure of sensitized LDPE and LDPE composite films was also conducted as blank samples for comparison with the outdoor test. The tensile properties of the LDPE, starch-LDPE and iron stearate-starch-LDPE films during indoor exposure are shown in Table 4.3 and Figures 4.4 and 4.5. It can be seen that the tensile properties of all samples change slightly or not change for indoor test. Therefore, it will take a long time for the degradation of starch-LDPE films that are kept indoor. The storage time of starch-LDPE films with/without iron stearate is longer than 6 months.

Table 4.3 Tensile properties LDPE, starch-LDPE and iron stearate-starch-LDPE films during indoor exposure

(a) Tensile strength

Samples Exposure time	Tensile strength (N/mm ²)								
	PE	PE- S5	PE- S10	PE- S15	PE- S20	PE- S5/F	PE- S10/F	PE- S15/F	PE- S20/F
original	19.7	14.7	12.9	11.6	10.6	14.1	13.1	12.3	12.0
2 months	19.5	14.6	12.4	11.8	10.2	14.0	12.8	12.0	11.8
4 months	18.9	14.0	12.0	11.1	9.5	13.7	12.4	11.7	11.2
6 months	18.5	14.2	11.7	10.7	9.7	13.2	12.0	11.0	10.8

(b) Elongation at break

Samples Exposure time	Elongation at break (%)								
	PE	PE- S5	PE- S10	PE- S15	PE- S20	PE- S5/F	PE- S10/F	PE- S15/F	PE- S20/F
original	619	511	349	205	164	507	330	218	167
2 months	592	501	328	174	154	498	310	200	142
4 months	591	483	320	159	130	473	318	175	134
6 months	583	476	309	156	112	461	279	160	151

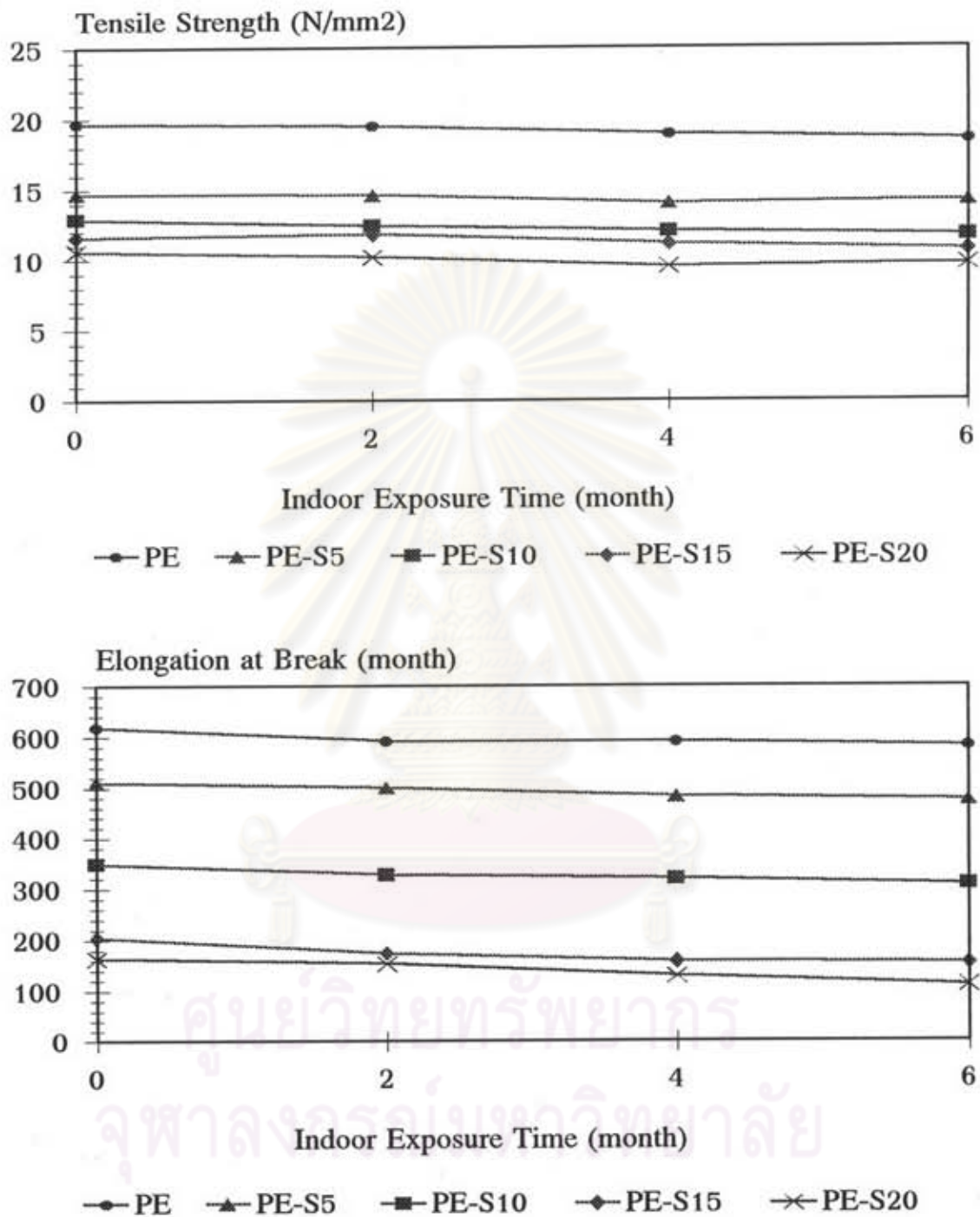


Figure 4.4 Tensile properties of LDPE and starch-LDPE films during indoor exposure

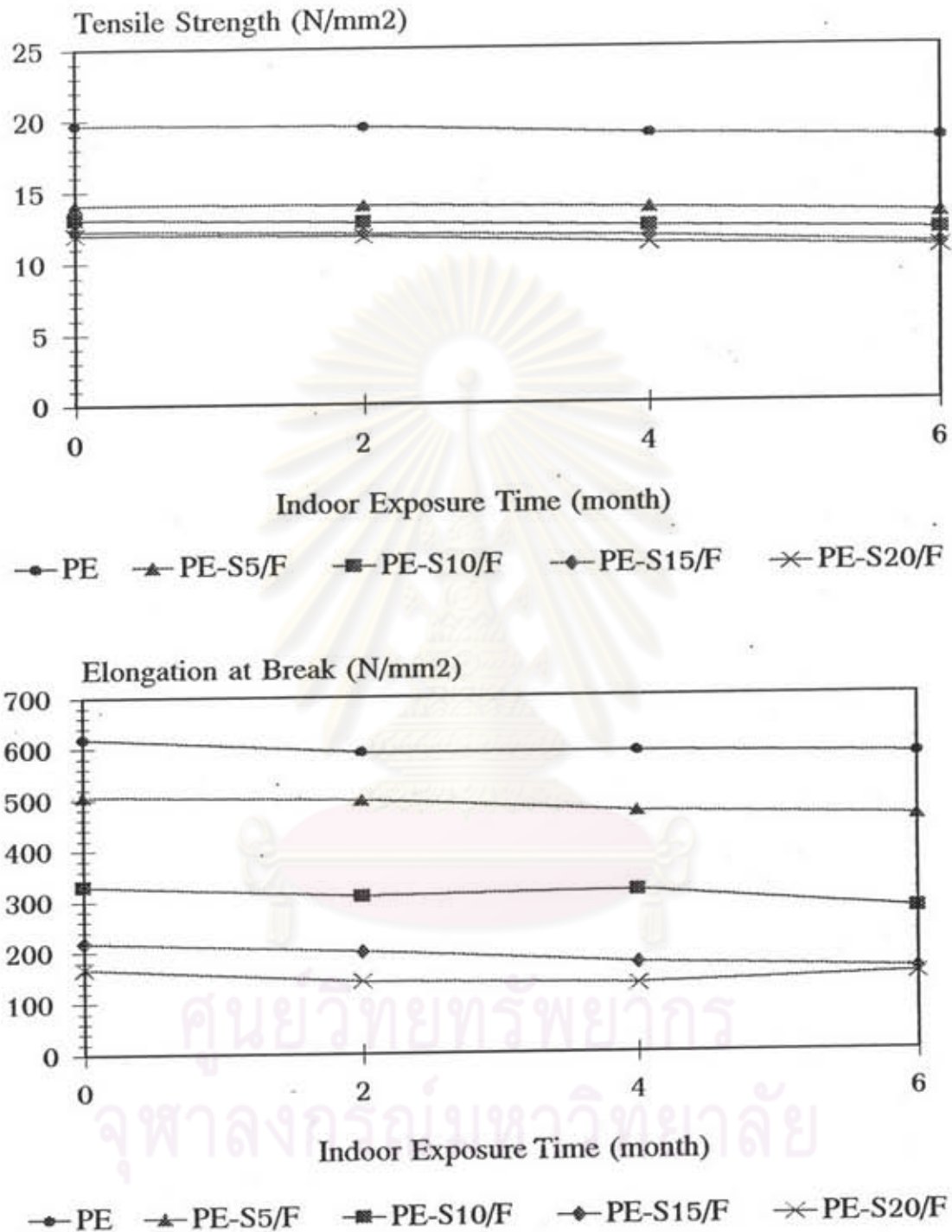


Figure 4.5 Tensile properties of LDPE and iron stearate-starch-LDPE films during indoor exposure

2. Molecular Weight Measurements

The changes of molecular weight of PE, PE-S5 and PE-S5/F films at various exposure times are shown in Figure 4.6. From this figure, when exposure proceeds, the reduction in molecular weight of PE sample shows an induction period for about 1 month and then it slowly decreases to a lower molecular weight. It can be seen that the molecular weight of PE-S5 decreases slower than that of PE-S5/F, corresponding to a sharp drop of tensile strength and elongation at break. The molecular weight of PE-S5/F sample decrease rapidly with time and reaches about 18% of the initial molecular weight after 3 months exposure, i.e. the initial molecular weight of PE-S5/F film was 51360, after 3 months exposure, molecular weight of film became 9250. The decreasing of molecular weight can be described by the oxidative degradation as in FTIR absorption measurements.



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Table 4.4 Intrinsic viscosity and molecular weight of LDPE, starch-LDPE and iron stearate-starch-LDPE films during outdoor exposure

Samples exposure time	Intrinsic viscosity			Molecular weight $\times 10^{-3}$		
	PE	PE-5S	PE-5S/F	PE	PE-5S	PE-5S/F
original	1.16	1.14	11.7	51.36	50.16	51.36
1 months	1.10	0.82	0.54	47.49	32.10	18.22
2 months	0.96	0.74	0.20	39.74	27.93	9.25
3 months	0.84	0.60	-	33.16	21.02	-
4 months	0.79	-	-	30.52	-	-
5 months	0.71	-	-	26.41	-	-
6 months	0.65	-	-	23.43	-	-

"-" the experiment was not carried out.

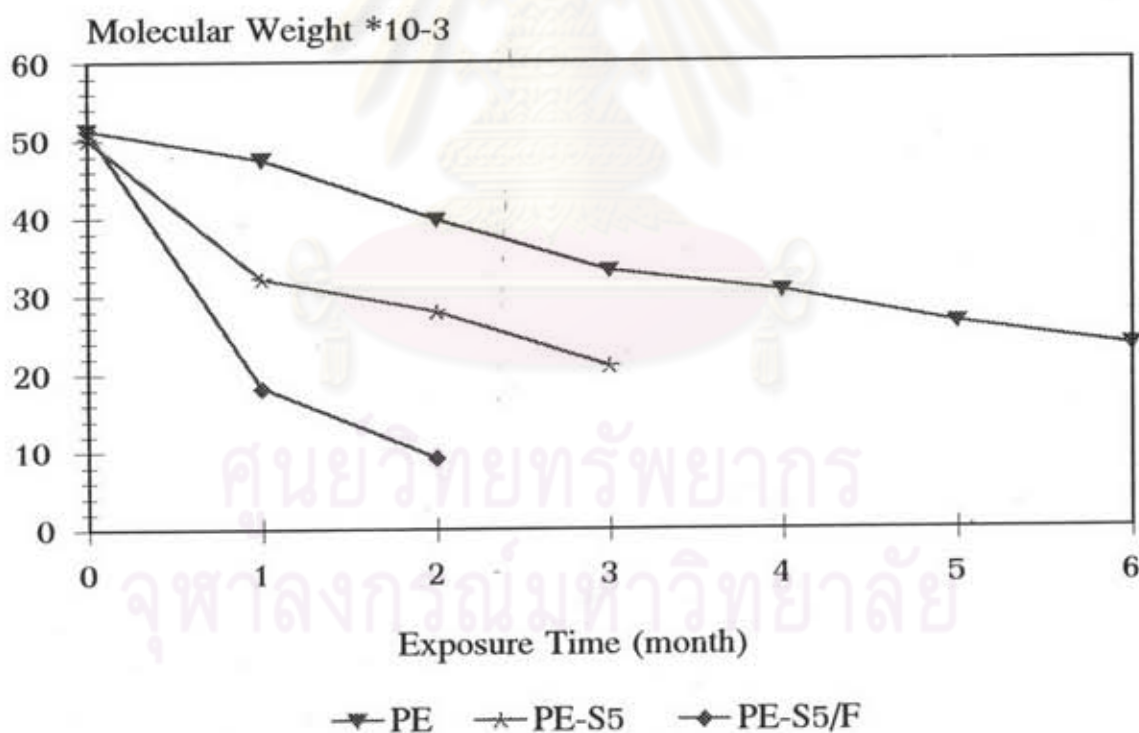


Figure 4.6 Molecular weight of LDPE, starch-LDPE and iron stearate-starch-LDPE films during outdoor exposure

3. Fourier Transform Infrared Absorption Measurements

The FTIR method offers valuable information concerning chemical changes produced in the PE samples. The IR vibrations of polyethylene and starch are shown in Table 4.5. Spectra of the PE and PE-S5/F are shown in Figures 4.7 and 4.8.

Table 4.5 Infrared vibrations and assignments for starch-LDPE films

Major IR bands of Components	
Frequency (cm ⁻¹)	Assignment and Remarks
LDPE	
2850, 2920 (s)	C-H stretching
1460, 1471 (m-s)	CH ₂ scissor and asym bend
1377, 1369, 1352 (w)	C-H bend due to CH ₂ and CH ₃
720, 730 (m-w)	CH ₂ rocking
Starch	
3000-3650 (s, br)	O-H stretching with absorbed water
2850, 2920 (s)	C-H stretching
1640 (w-m)	δ(O-H) bend (absorbed water)
1462 (m, sh)	CH ₂ bending
1445-1325 (m-s)	C-H bending and wagging
1234, 1205 (m-s)	O-H bending
960-1190 (s, br)	C-O stretching (C-O-C and C-O-H)
400-930 (w-m, br)	O-H deformation (broadened by water), C-O-C bend, ring vibration

* w = weak, m = medium, s = strong, sh = shoulder, br = broad



In the FTIR spectra of LDPE and iron stearate-starch-LDPE films, the peaks of importance are:

- (1) The polyethylene band at 1465 cm^{-1} served as an internal standard to which the absorbances of the other bands were related.
- (2) The 1715 cm^{-1} band corresponding to the presence of the carbonyl group in the exposed and degraded polyethylene chain.

FTIR spectroscopy of the samples reveal the formation of carbonyl group, which was identified as ketone (1715 cm^{-1}), in Figures 4.8 and 4.9. The concentrations of carbonyl group in PE-S5/F films increase significantly after outdoor exposure by three times of the PE in the first month. Carbonyl indexes express the extent of oxidation, corresponded to the observed loss in mechanical properties and the molecular weight.

Carbonyl indexes of the samples are plotted as a function of exposure time in Figure 4.12. For PE and PE-S5/F films, the carbonyl indexes increase linearly with increasing exposure time. Particularly, the carbonyl index of iron stearate containing samples are higher than the PE one. These can be explained by the photooxidation reaction of PE.

The conventional LDPE exhibits the photooxidation by an increase of the carbonyl group formation when exposing to sun light. From this result, the reaction mechanism of LDPE (Figure 4.7) can be explained as a reasonably radical formation and the reaction pathway to final products during outdoor exposure (Carvalho, 1992). In the "mechanistic" approach, the chemical transformation of LDPE in oxidative conditions is generally understood as the superposition of 3 main sequences, i.e. :

- primary hydroperoxidation involving usually a short chain reaction ;
- photochemical and/or thermal homolytic decomposition of hydroperoxidic groups into hydroxylated and carbonylated groups ;
- photoreactions of the groups resulting from the decomposition of hydroperoxides, especially ketonic groups.

In LDPE exposed to long wave lengths, hydroperoxidation occurs essentially on the secondary carbon atoms of the saturated chain and in the α position with respect to the vinylidene groups are observed as chemical defects.

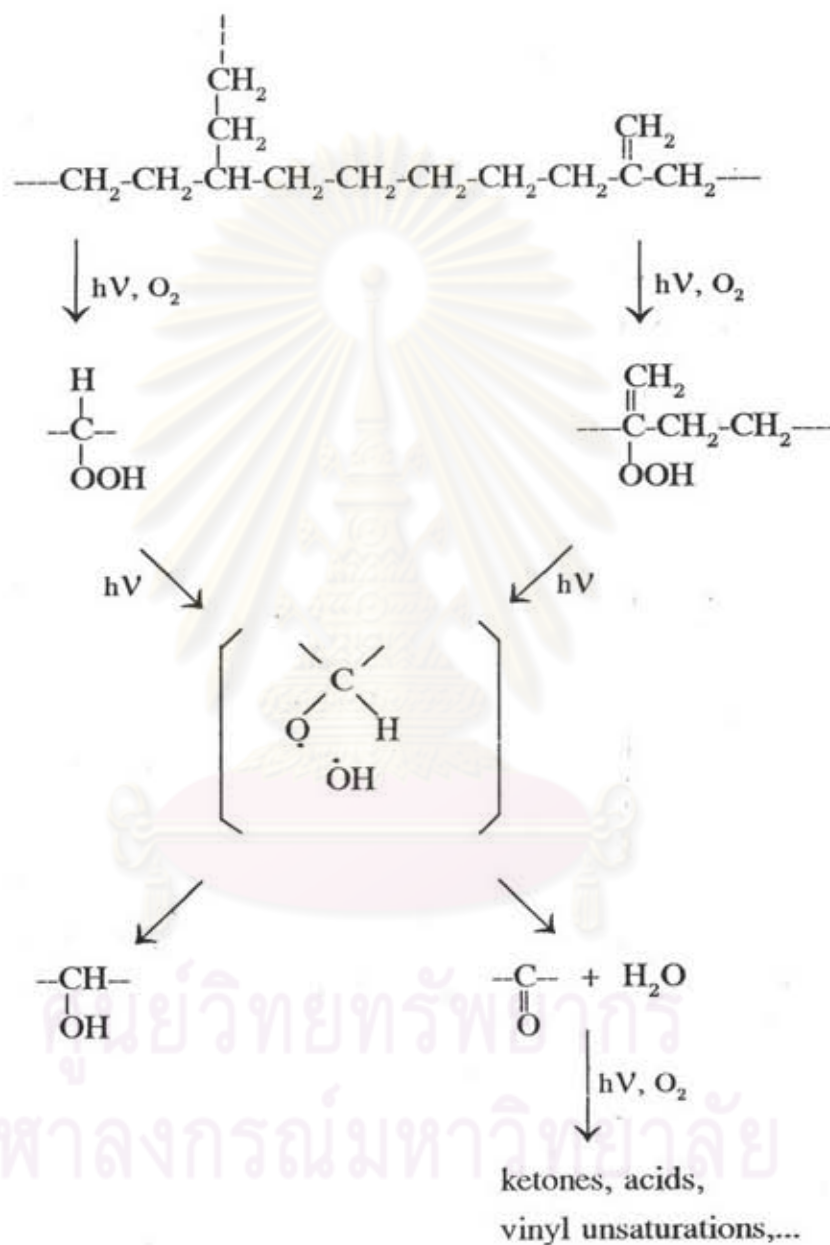
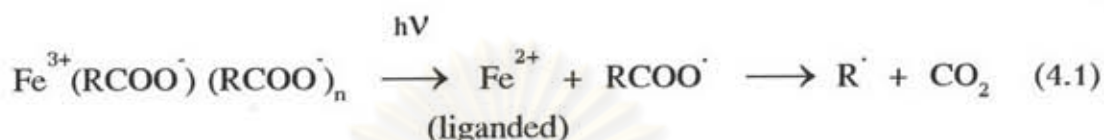


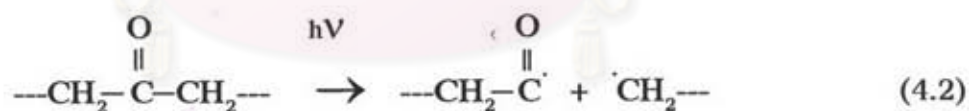
Figure 4.7 Mechanism of degradation reaction of polyethylene film

Since the transition metals are thus usually capable of electron transitions between their outer shells, and the variable valency states resulted render it capable of inducing oxidation reactions in which the iron stearate acts as a prooxidant to catalyze the oxidative degradation (Griffin, 1988). Under the action of sun light, the coordination compounds are sources for organic radicals formed in photoredox process ;

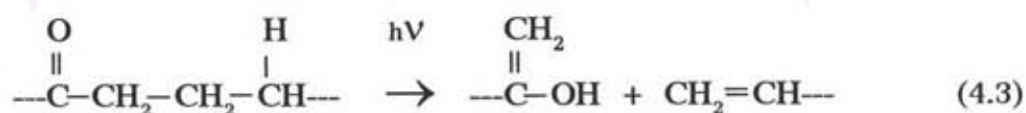


Free radicals are formed and these can react with the polymers, forming the other free radicals. These free polymer radicals are extremely reactive and can react further with oxygen, as shown in the degradation mechanism (Figure 4.7).

It is now 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 molecular weight of the polymer (Carvalho, 1992). These reaction are induced by ultraviolet light absorption, and belong to the well known types I and II Norrish reactions. In type I reactions, chain scission occurs at a bond adjacent to the carbonyl group, i.e.



While in type II reactions, a six-membered cyclic intermediate species is first formed, to result also in chain scission and in the formation of a terminal vinyl group, i.e.



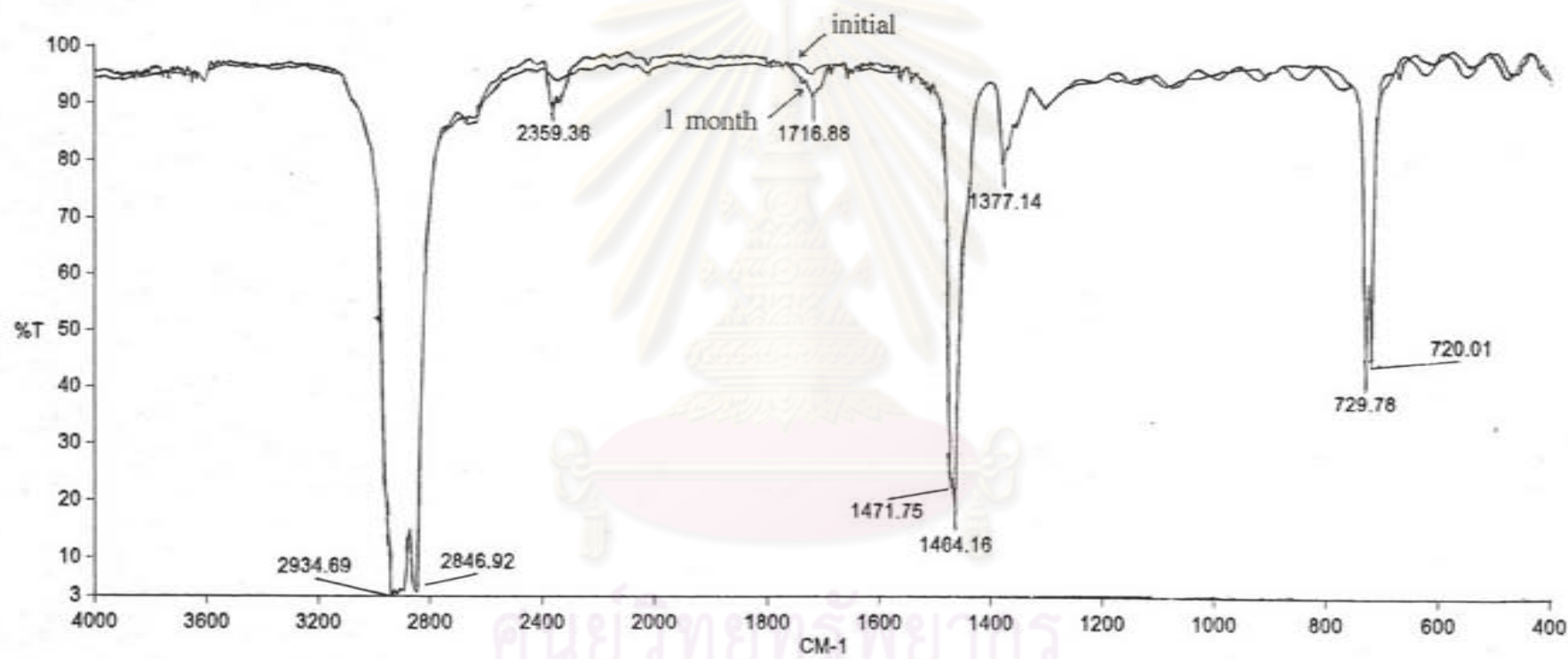


Figure 4.8 FTIR spectra of unexposed and 1 month exposed LDPE

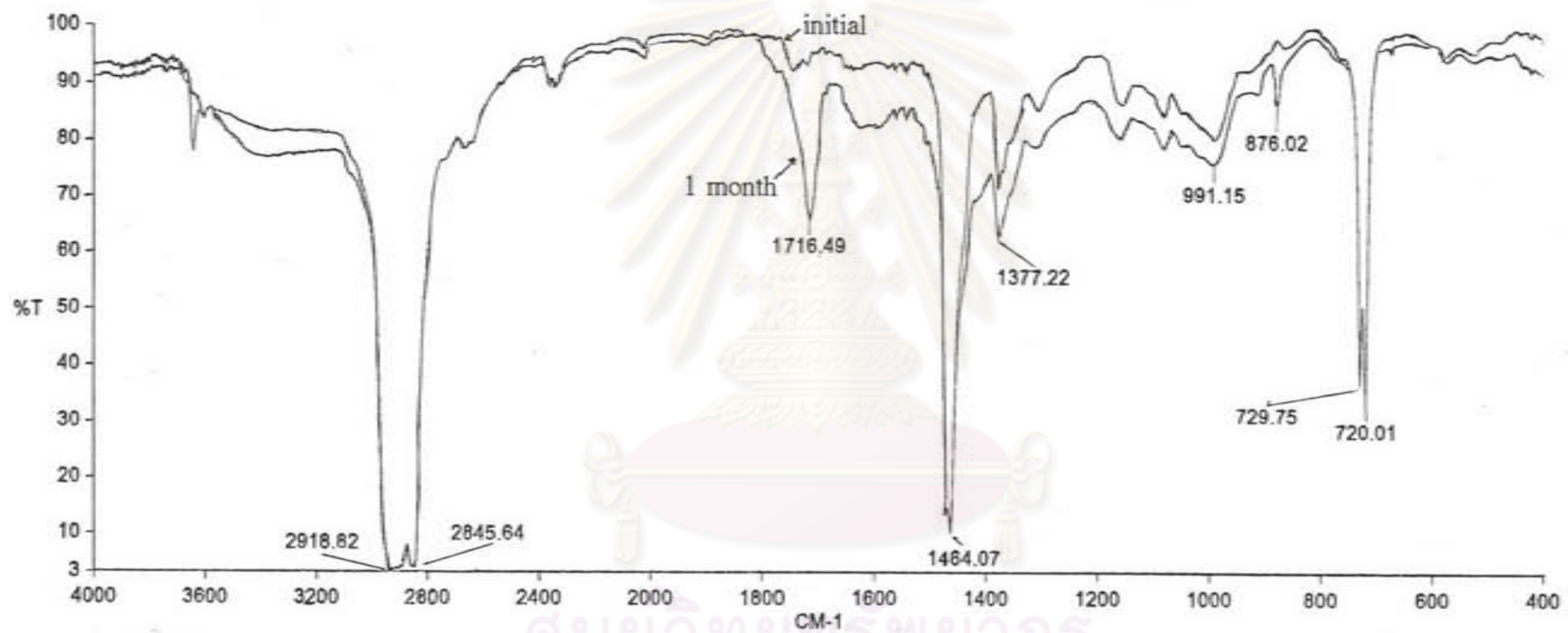


Figure 4.9 FTIR spectra of unexposed and 1 month exposed iron stearate-5%starch-LDPE films

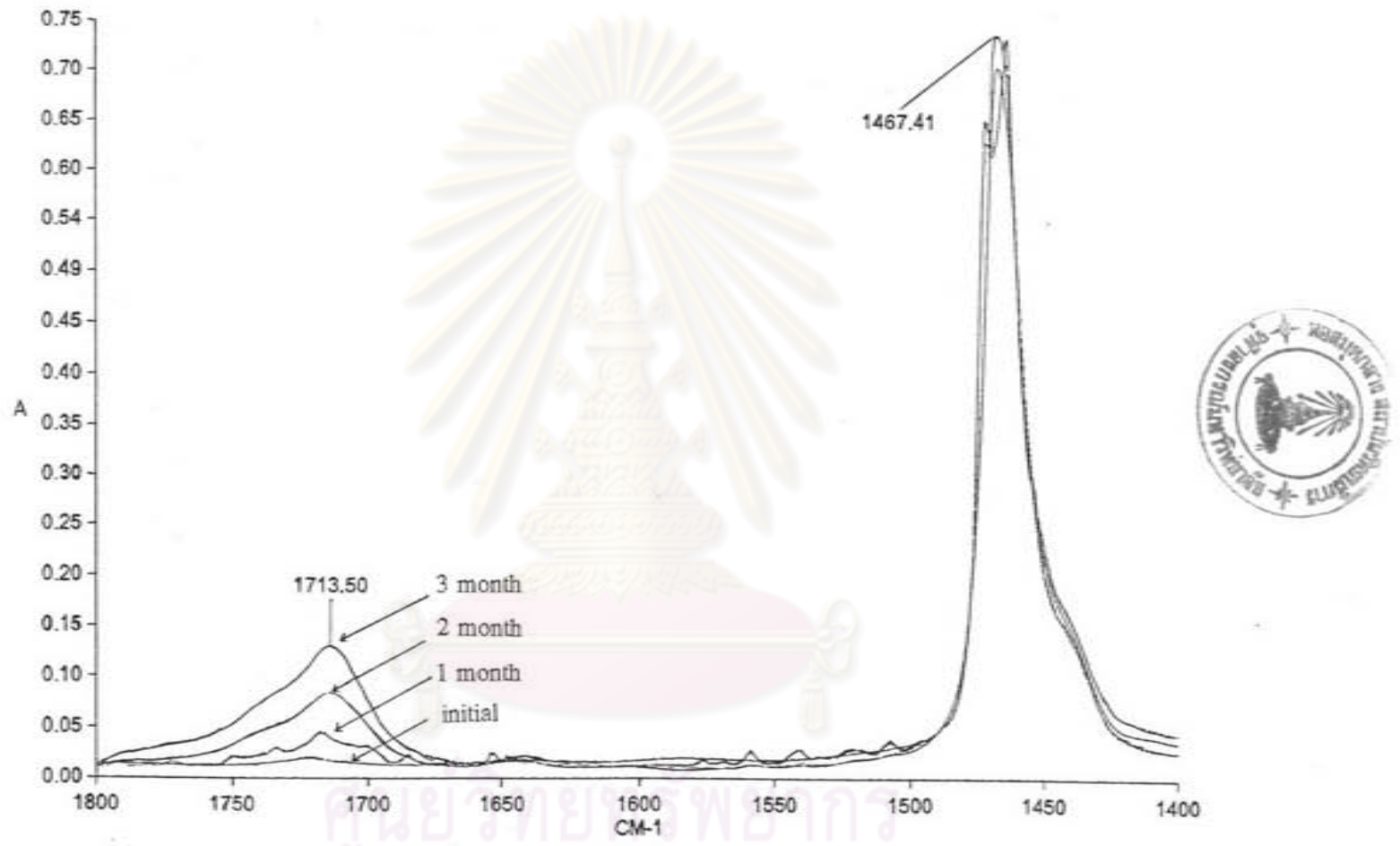


Figure 4.10 FTIR spectra of 0-3 months outdoor exposed LDPE films in the methylene and carbonyl region

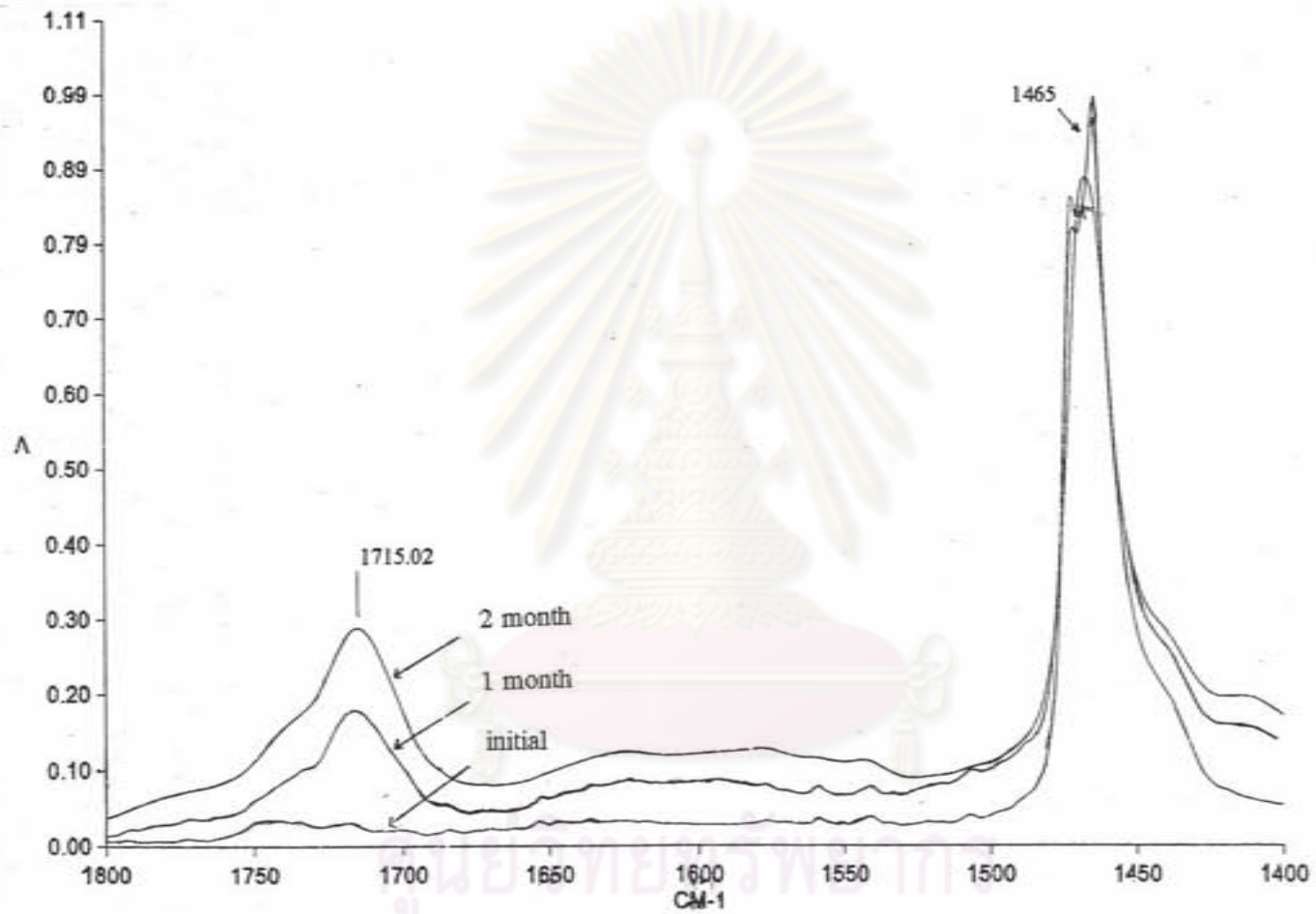


Figure 4.11 FTIR spectra of 0-2 months outdoor exposed iron stearate-5%starch-LDPE films in the methylene and carbonyl region

Table 4.6 Change in the carbonyl indexes of LDPE and iron stearate-starch-LDPE films during 3 months outdoor exposure

Samples Exposure time	Carbonyl Index (I_o)	
	PE	PE- 5S/F
original	0.00	0.00
1 month	0.06	0.18
2 months	0.12	0.32
3 months	0.18	-

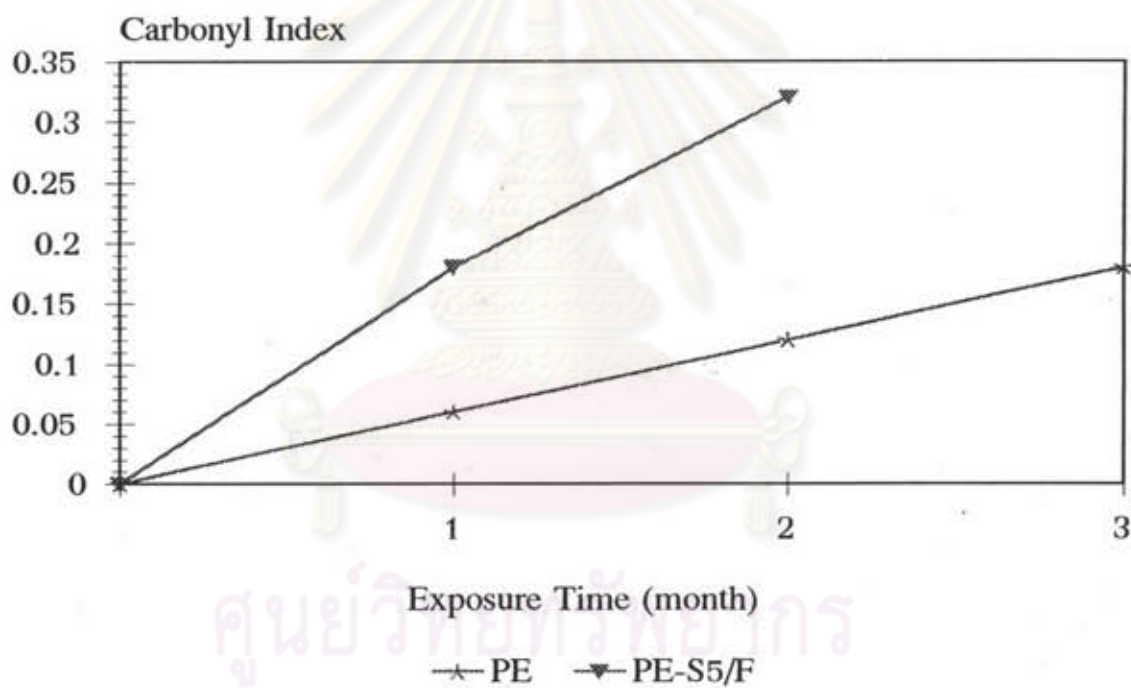


Figure 4.12 The carbonyl indexes of LDPE and iron stearate-5%starch-LDPE films during 3 months outdoor exposure.

Degradation of Starch-LDPE Films by Soil Burial Test

1. Tensile Property Measurements

The typical effect of soil burial on the tensile properties of LDPE, starch-LDPE and iron stearate-starch-LDPE films are shown in Table 4.7, Figures 4.13 and 4.14. Tensile strength and elongation at break of LDPE shows an induction period for 1 month and then decreases afterwards with a higher rate. The effect of soil burial to elongation is stronger than tensile strength. At the final stage, the elongation reaches 65% of the original value.

For the starch-LDPE samples (Figure 4.13), there is an induction period of both properties during the first month. After that, the experiment exhibits a similar trend as the tensile strength of LDPE, but the elongation shows a significantly reducing rate.

For the iron stearate-starch-LDPE films (Figure 4.14), there is no an induction period of elongation but it decreases suddenly soon after the experiment. Tensile strength declines with a higher rate than the samples without iron complex, which can be seen obviously in the final stage.

After the outdoor exposure and soil burial, it can be seen that different starch contents effects the films in the same manner. The more starch content, the higher decline of the mechanical properties with time. The reason for this are based on the characteristic of starch, embedded in the LDPE matrix, that can be degraded under natural condition and then produces the flaws in the bulk of material. A characteristic feature of the mechanical properties is their sensitivity to these defects, so the more starch content causes the more feebleness in the films.

Table 4.7 Tensile properties of LDPE, starch-LDPE and iron stearate-starch-LDPE films during soil burial test

(a) Tensile strength

Samples Exposure time	Tensile strength (N/mm ²)								
	PE	PE- S5	PE- S10	PE- S15	PE- S20	PE-S 5/F	PE-S 10/F	PE-S 15/F	PE-S 20/F
original	19.7	14.7	12.9	11.6	10.6	14.1	13.1	12.3	11.3
1 month	19.3	13.0	13.1	11.2	9.2	13.2	12.7	11.2	9.4
2 months	18.6	12.2	12.4	9.9	7.0	11.4	12.0	10.7	7.4
3 months	17.0	11.4	12.6	9.2	6.8	10.1	11.5	8.6	7.2
4 months	16.3	10.7	12.0	8.6	6.2	9.2	8.0	6.5	5.2
5 months	16.0	10.2	11.2	8.1	6.0	8.9	9.8	6.9	4.1
6 months	16.0	9.8	9.1	7.4	5.9	7.8	7.1	6.5	3.4

(b) Elongation at break

Samples Exposure time	Elongation at break (%)								
	PE	PE- S5	PE- S10	PE- S15	PE- S20	PE-S 5/F	PE-S 10/F	PE-S 15/F	PE-S 20/F
original	620	511	349	205	175	507	330	218	167
1 months	620	480	320	201	162	319	144	72	119
2 months	591	465	216	185	126	275	135	130	100
3 months	521	310	175	110	97	185	121	119	95
4 months	482	159	76	92	96	143	105	78	86
5 months	475	212	95	95	65	130	99	82	80
6 months	398	182	111	99	76	120	82	62	73

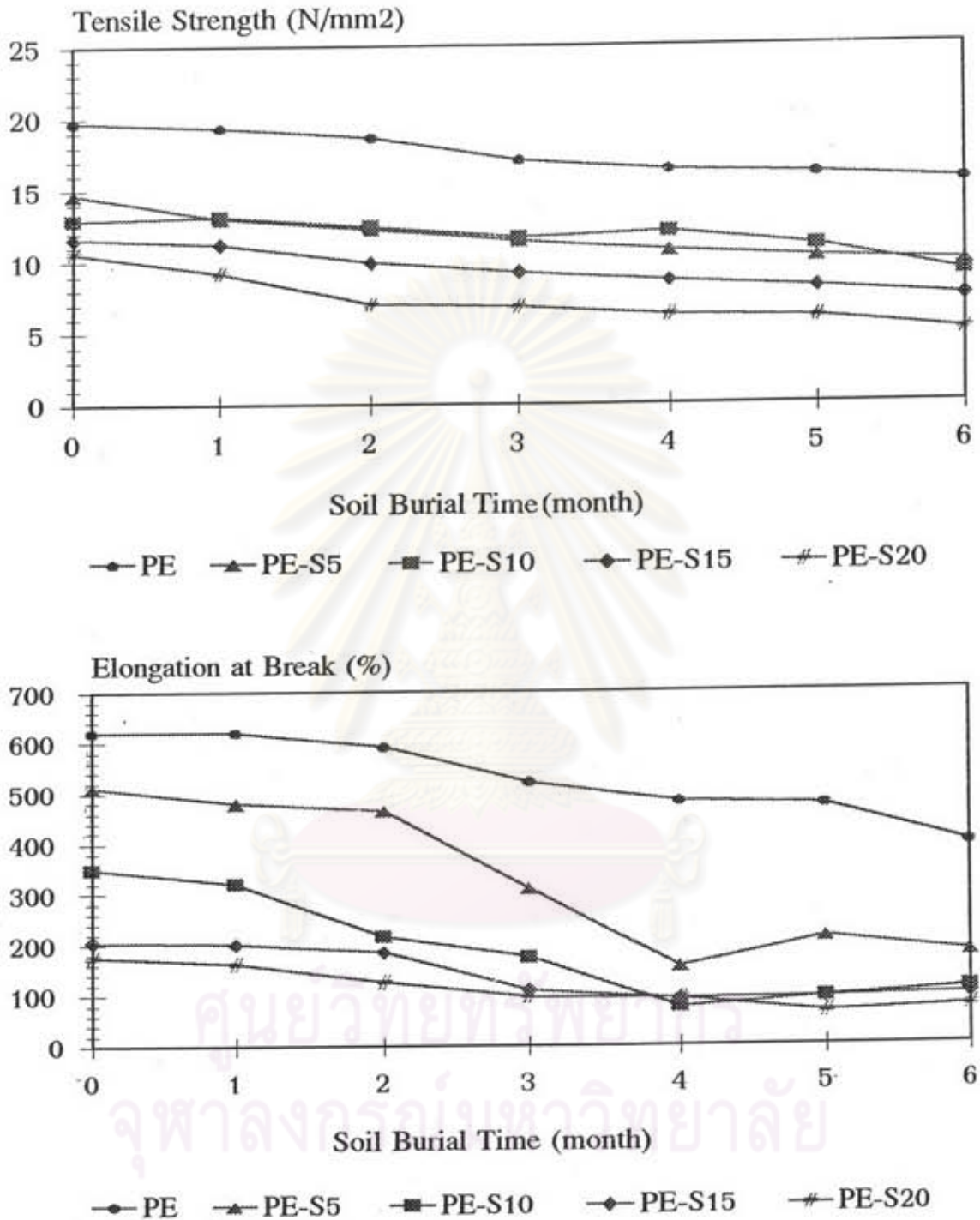


Figure 4.13 Tensile properties of LDPE and starch-LDPE films during soil burial test

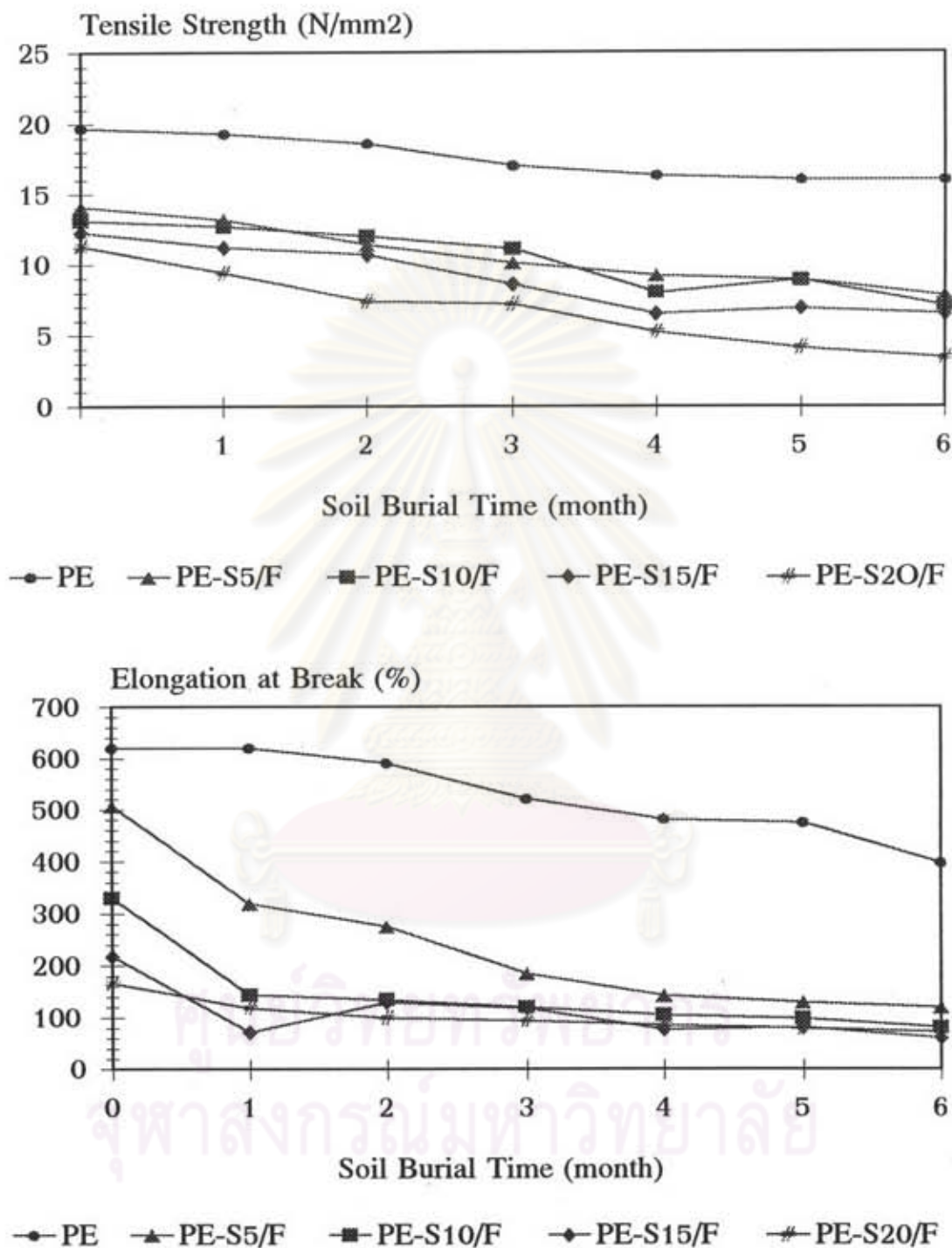


Figure 4.14 Tensile properties of LDPE and iron stearate-starch-LDPE films during soil burial test

From Figure 4.13, tensile strength and elongation at break of the LDPE films show an induction period for 1 month and then decrease linearly with time. The soil burial had a strong effect on elongation but a weak effect on tensile strength. After six months, the tensile strength and elongation reach to 81% and 64%, respectively, of the original values.

For the starch-LDPE samples, there is an induction period of both properties during the first month as shown in Figure 4.13. The tensile strength of the LDPE films exhibits a similar trend as does the LDPE. The elongation decreases sharply with time. After six months the tensile strength and elongation reach 65% and 40%, respectively, of the original values.

In the case of the iron stearate-starch-LDPE films, there is no induction period of elongation, but it decreases suddenly in the first month (see Figure 4.14). Tensile strength of the iron stearate-starch-LDPE films declines with the higher rate than that films without iron complex. After six months the tensile strength and elongation reach 47% and 30%, respectively, of the original values.

2. Molecular Weight Measurements

Figure 4.15 shows the molecular weight traces of the PE, PE-S5 and PE-S5/F films as a function of soil burial time. Molecular weight data are presented in Table 4.8. The molecular weight of all samples exhibit an induction period for about 3 months and then gradually decreases to a lower value. The molecular weight of burial test films decreases with a low rate, while the molecular weight of outdoor exposed films decreases with a high rate. This can be attributed to the fact that, the starch granules are covered by the polyethylene layer under the soil burial and without the sunlight to activate the degradation of LDPE. The starch cannot be attacked by the microorganisms. Therefore, it takes a longer time to observe the loss in molecular weight for burial test compared with the outdoor exposure experiment.

Table 4.8 Intrinsic viscosity and molecular weight of the LDPE, starch-LDPE and iron stearate-starch-LDPE films during soil burial test

Samples Soil burial time	Intrinsic viscosity			Molecular weight $\times 10^{-3}$		
	PE	PE- S5	PE- S5/F	PE	PE- S5	PE- S5/F
original	1.16	1.14	1.17	51.36	50.11	51.36
1 month	1.16	1.14	1.14	51.36	50.11	50.16
2 months	1.14	1.12	1.13	50.16	48.99	49.56
3 months	1.12	1.11	1.11	48.97	48.38	48.38
4 months	1.12	1.10	1.00	48.97	47.79	42.00
5 months	1.10	1.06	0.95	47.79	45.39	39.18
6 months	1.05	0.91	0.89	44.87	36.96	35.86

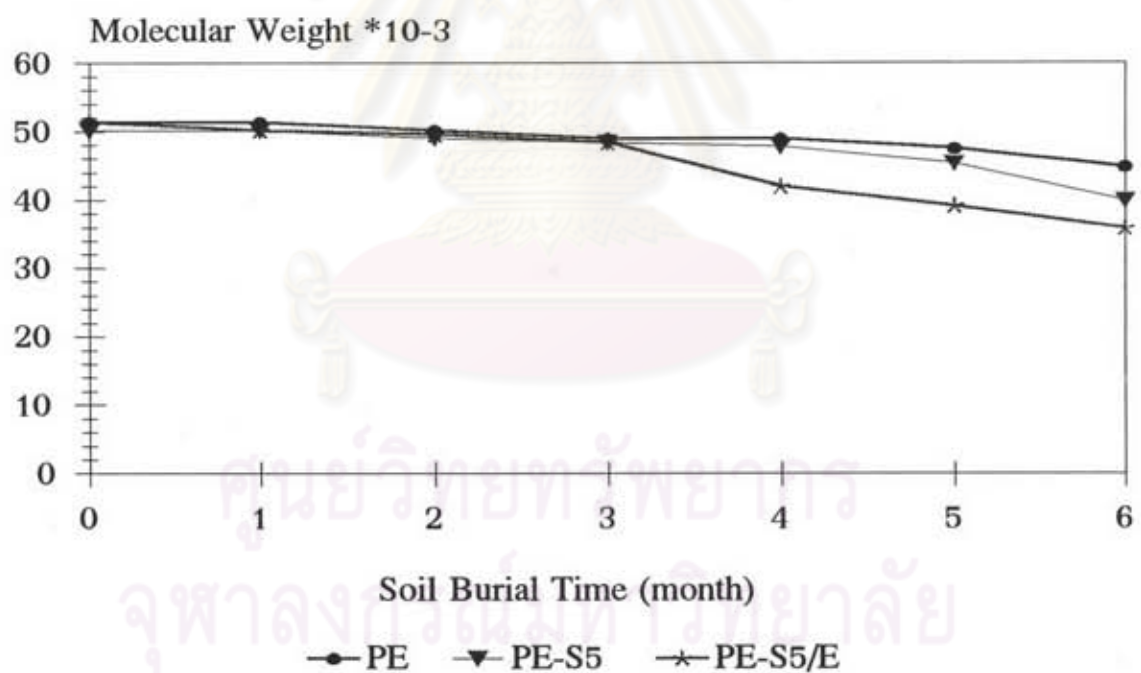


Figure 4.15 Molecular weights of the LDPE, starch-LDPE and iron stearate-starch-LDPE films during soil burial test

Characteristic of the Component and Plastic Mixture on Biodegradability

1. Structure of Cassava Starch Granules

Figure 4.16 illustrated the magnified pictures of the cassava starch granules as seen through a polarized light microscope. All photomicrographs present the polarization cross on the starch granules.

2. Dispersibility of Cassava Starch Granules in the Plastic

Figures 4.17-4.20, as seen through a polarized light microscope, indicate the relationship between the dispersion of starch granules in the LDPE at different starch contents. It can be seen that at high starch content, the starch granules are rather agglomerated and randomly dispersed in the LDPE matrix. For the film with/without iron stearate, the dispersibility of the starch granules in LDPE matrix are almost the same at the same starch content. The degree of dispersibility depends on a large extent, on the wetting property of the dispersing aid and on the starch and matrix polymer. Another important effect on dispersibility is the size of the starch granules and its moisture content. Due to the different nature of the starch and matrix polymer, moisture tends to impair the efficiency of the dispersing aid that lowers the degree of dispersibility.

3. Visible Biodegradability

The nutrient-salt in this study contains no carbon source and the selected microorganisms exhibit that they can survive by utilizing nutrient sources from the starch in plastic samples. The visible biodegradability of the starch-LDPE films with different types of fungi can be seen in Figures 4.21-4.30. The color of *Aspergillus niger* and *Penicillium pinophilum* are black and yellowish, respectively. The growth of fungi was estimated by following changes in number of cells, which can be measured by the counting chamber method (Collin and Lyne, 1989). The total population of *Aspergillus niger* and *Penicillium pinophilum* on surface of the films was shown in Tables 4.9 and 4.10. Figures 4.21 and 4.26 exhibit very little growth of fungi in LDPE films during the experiment. For the starch-LDPE and iron stearate-starch-LDPE films, it can be seen that the population of fungi increases as the starch content increases. The population of *Penicillium pinophilum* is much higher than *Aspergillus niger*. That is, the use of *Penicillium pinophilum* is more effective

to promote biodegradation of the polyethylene film through the incorporation of cassava starch and iron additive.

Table 4.9 The size of *Aspergillus niger* population in LDPE, starch-LDPE and iron stearate-starch-LDPE films

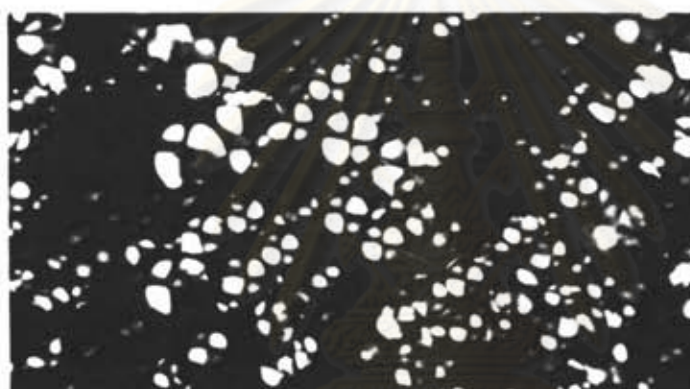
Samples	Total population (spores/ml)
PE	40
PE-S5	200
PE-S10	476
PE-S15	513
PE-S20	761
PE-S5/F	174
PE-S10/F	414
PE-S15/F	531
PE-S20/F	812

Table 4.10 The size of *Penicillium pinophilum* population in LDPE, starch-LDPE and iron stearate-starch-LDPE films

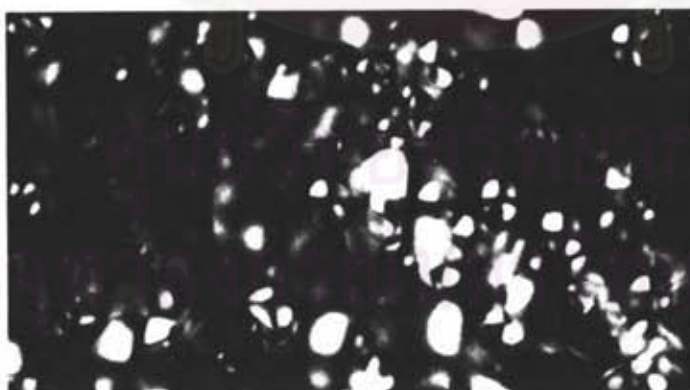
Samples	Total population (spores/ml)
PE	12
PE-S5	3417
PE-S10	3901
PE-S15	4407
PE-S20	7126
PE-S5/F	2814
PE-S10/F	3196
PE-S15/F	3540
PE-S20/F	4286



magnification 100x



magnification 200x



magnification 400x

Figure 4.16 Structure of cassava starch granules, indicating the polarization cross.

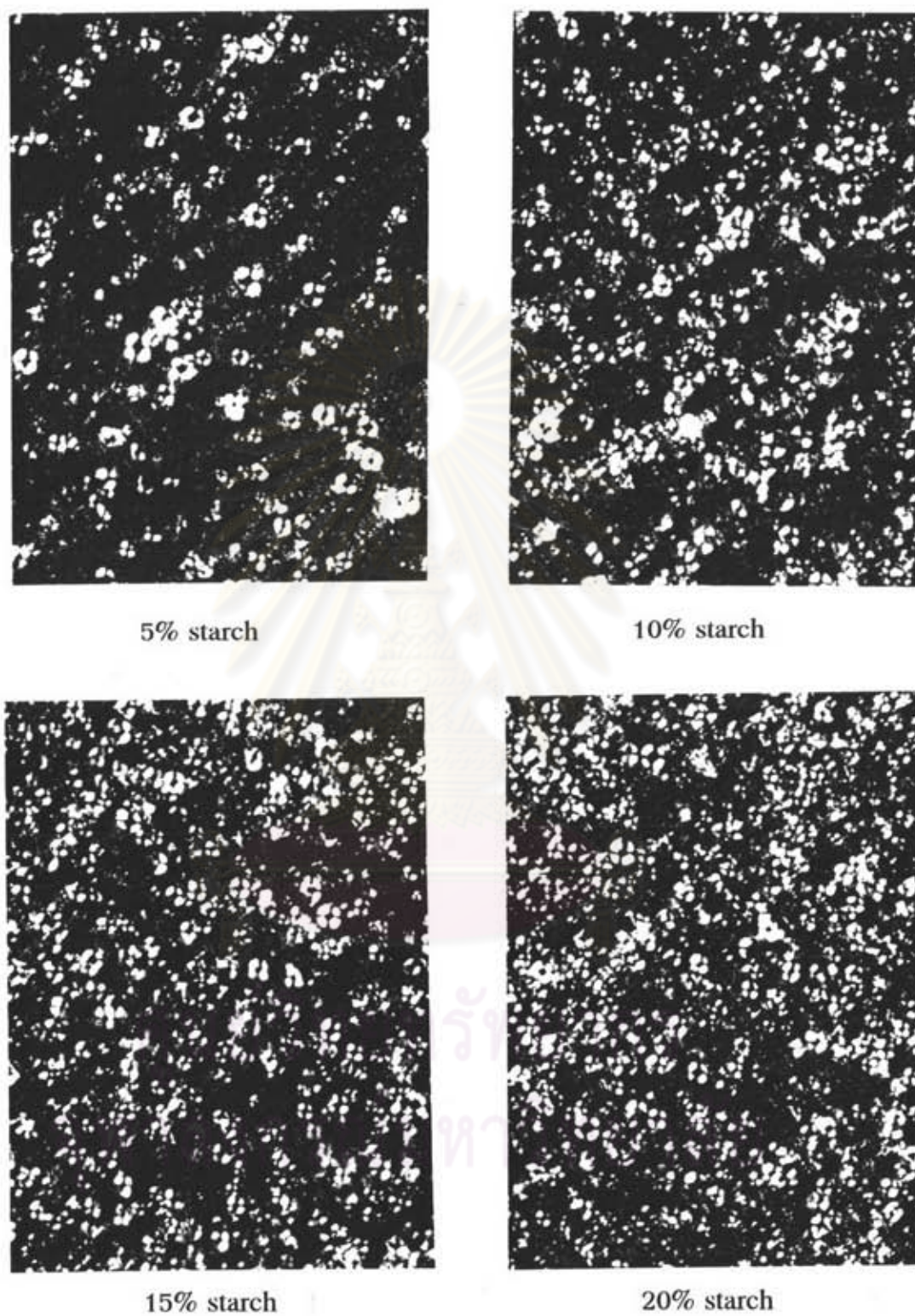
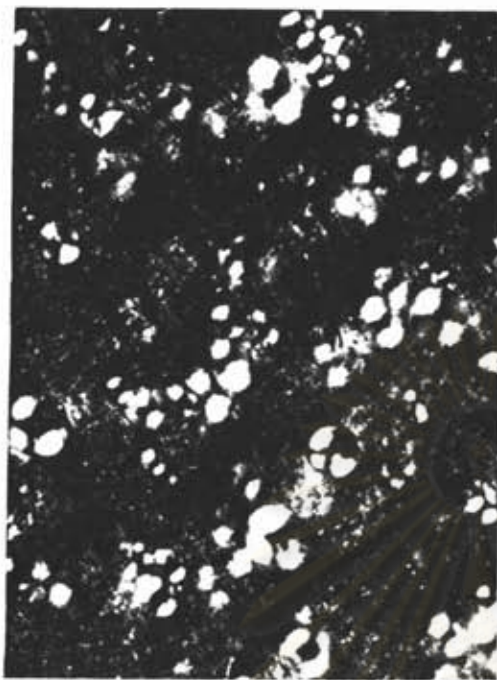
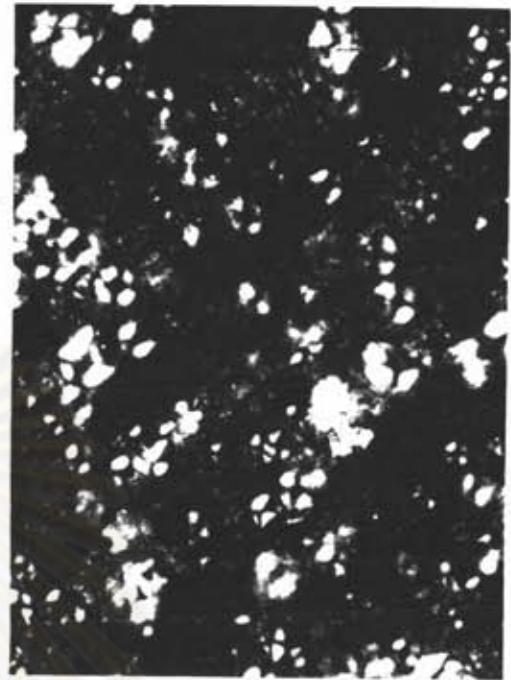


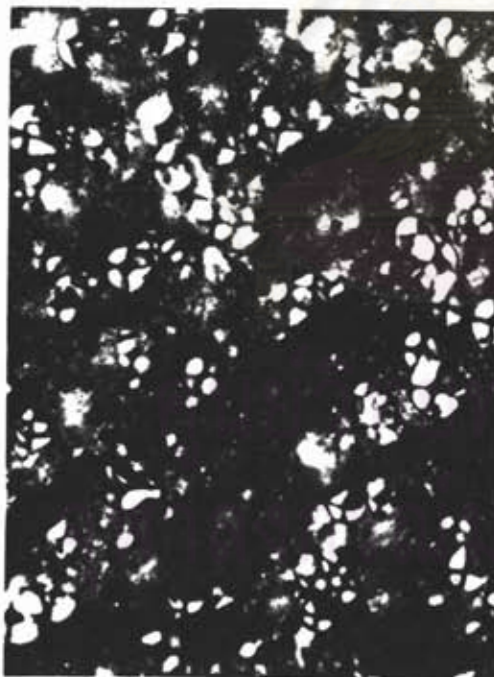
Figure 4.17 Dispersibility of cassava starch granules (5, 10, 15 and 20%) in starch-LDPE films, magnification 100x



5% starch



10% starch



15% starch



20% starch

Figure 4.18 Dispersibility of cassava starch granules (5, 10, 15 and 20%) in starch-LDPE films, magnification 200x

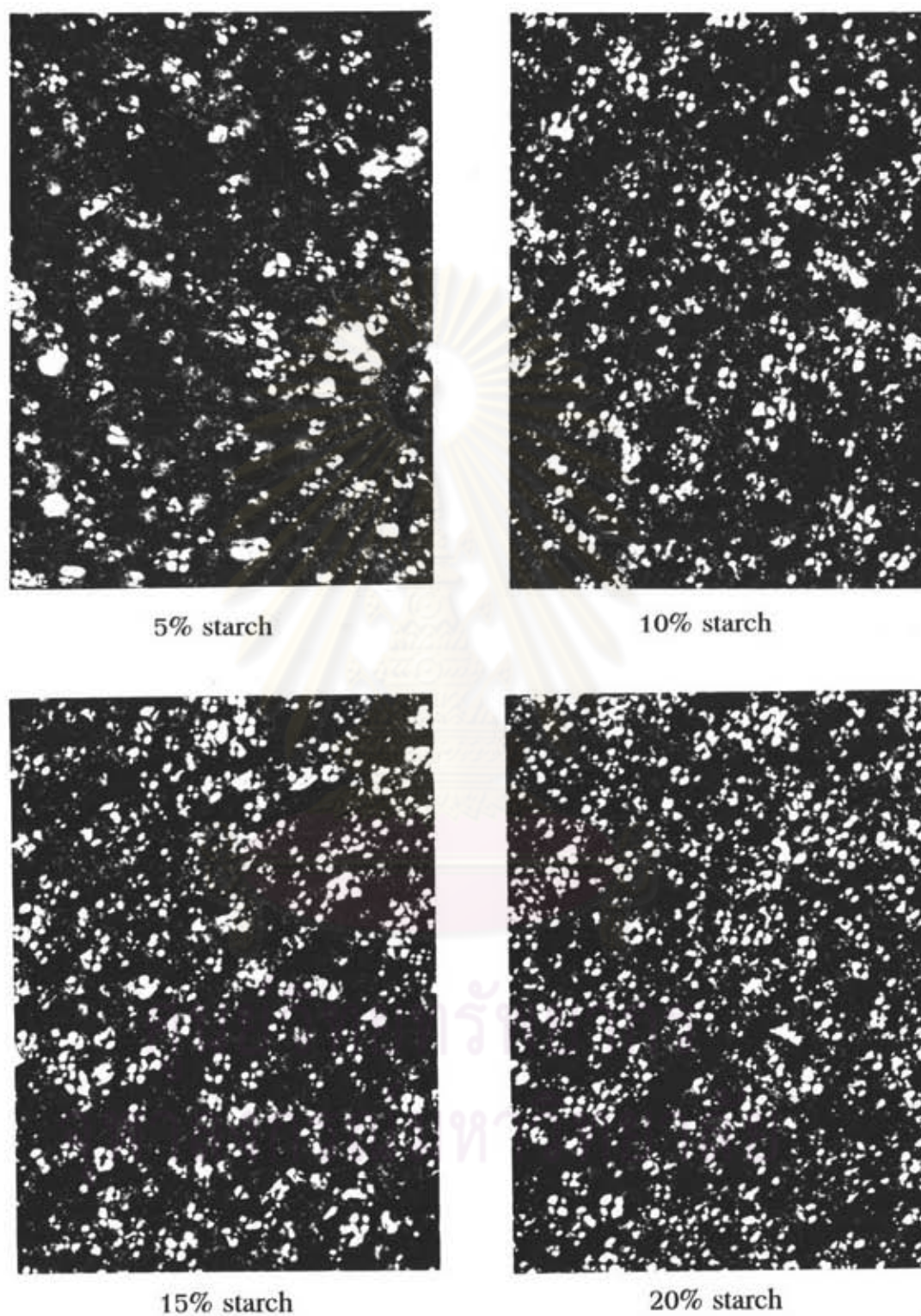


Figure 4.19 Dispersibility of cassava starch granules (5, 10, 15 and 20%) in iron stearate-starch-LDPE films, magnification 100 x

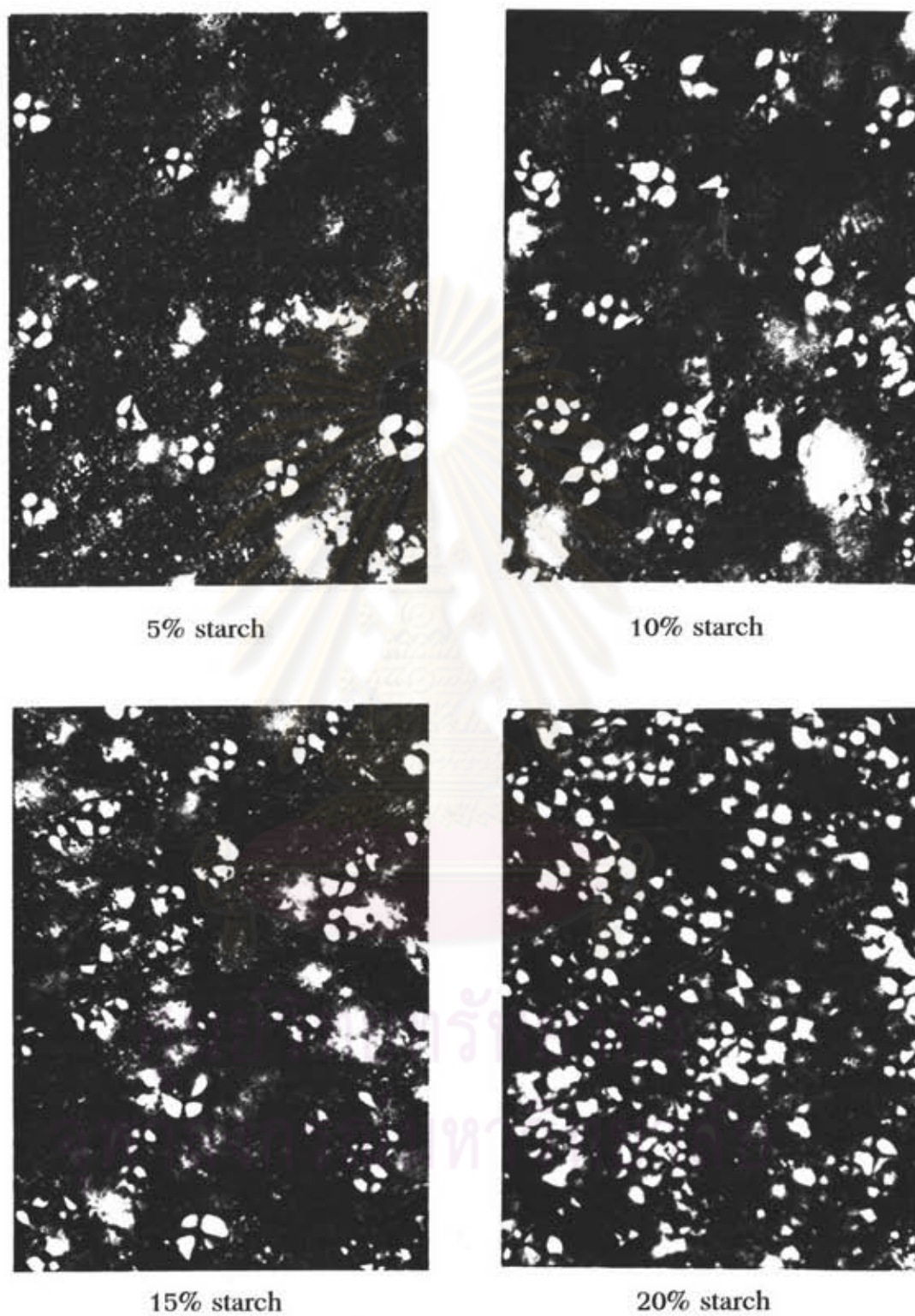


Figure 4.20 Dispersibility of cassava starch granules (5, 10, 15 and 20%) in iron stearate-starch-LDPE films, magnification 200x

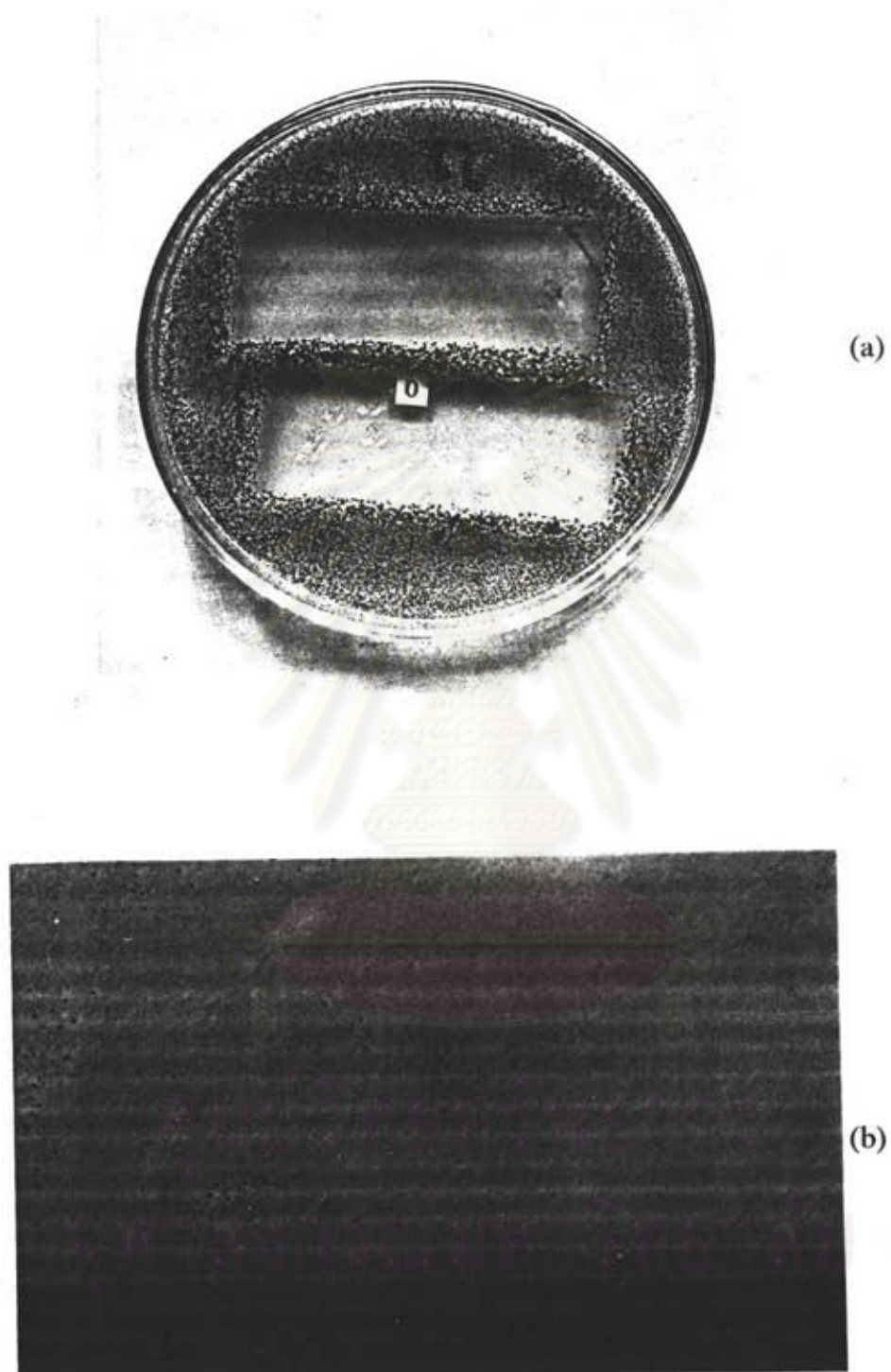


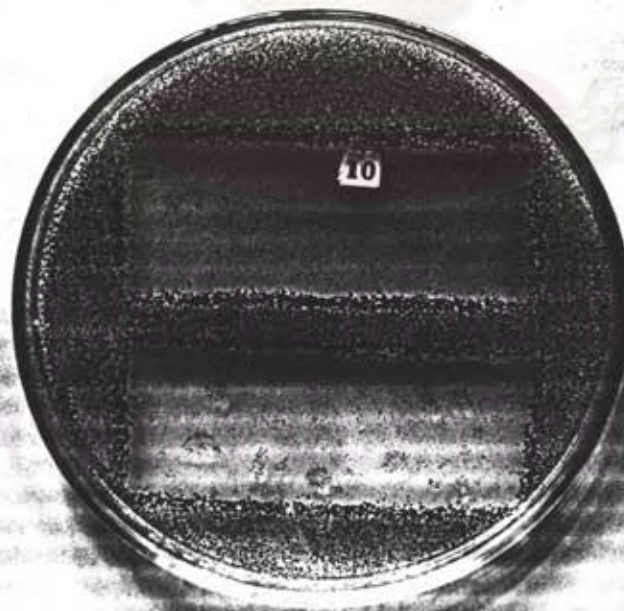
Figure 4.21 Biodegradability of LDPE film by *Aspergillus niger* fungi.

(a) full plate of culture

(b) focus on surface of the film



5% starch



10% starch

Figure 4.22(a) Biodegradability of starch-LDPE films by *Aspergillus niger*

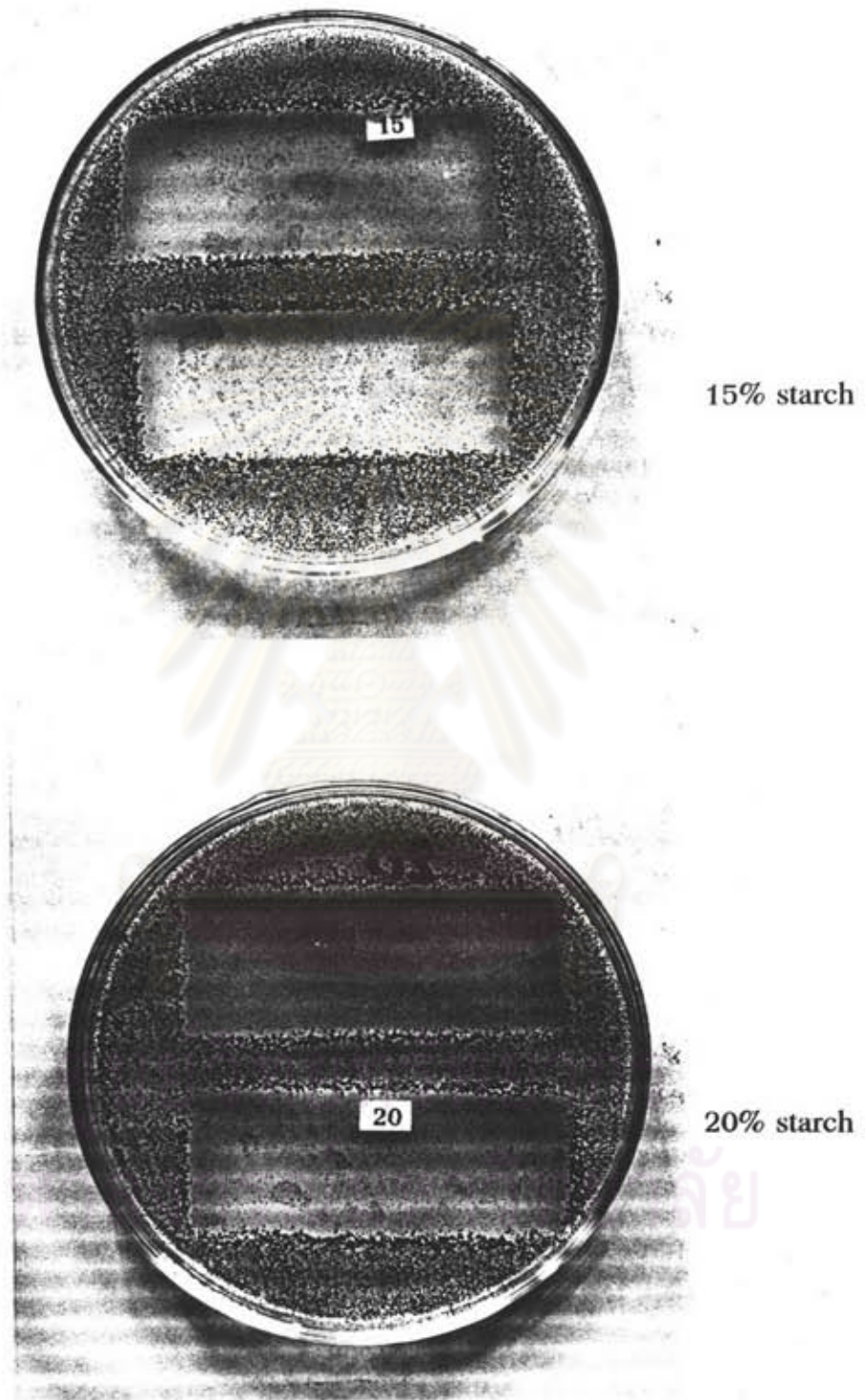


Figure 4.22(b) Biodegradability of starch-LDPE films by *Aspergillus niger*

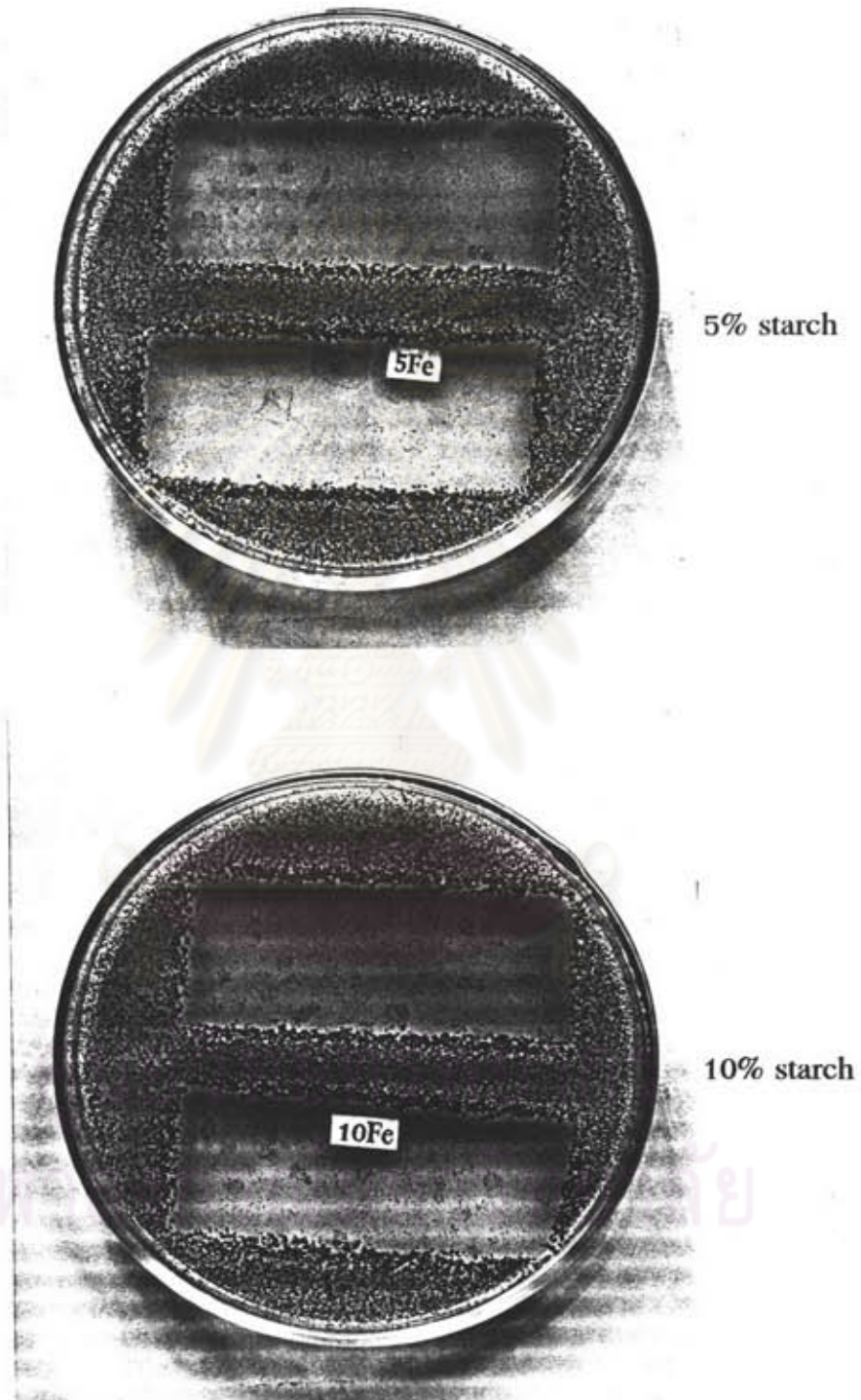


Figure 4.23(a) Biodegradability of iron stearate-starch-LDPE films by *Aspergillus niger* fungi.

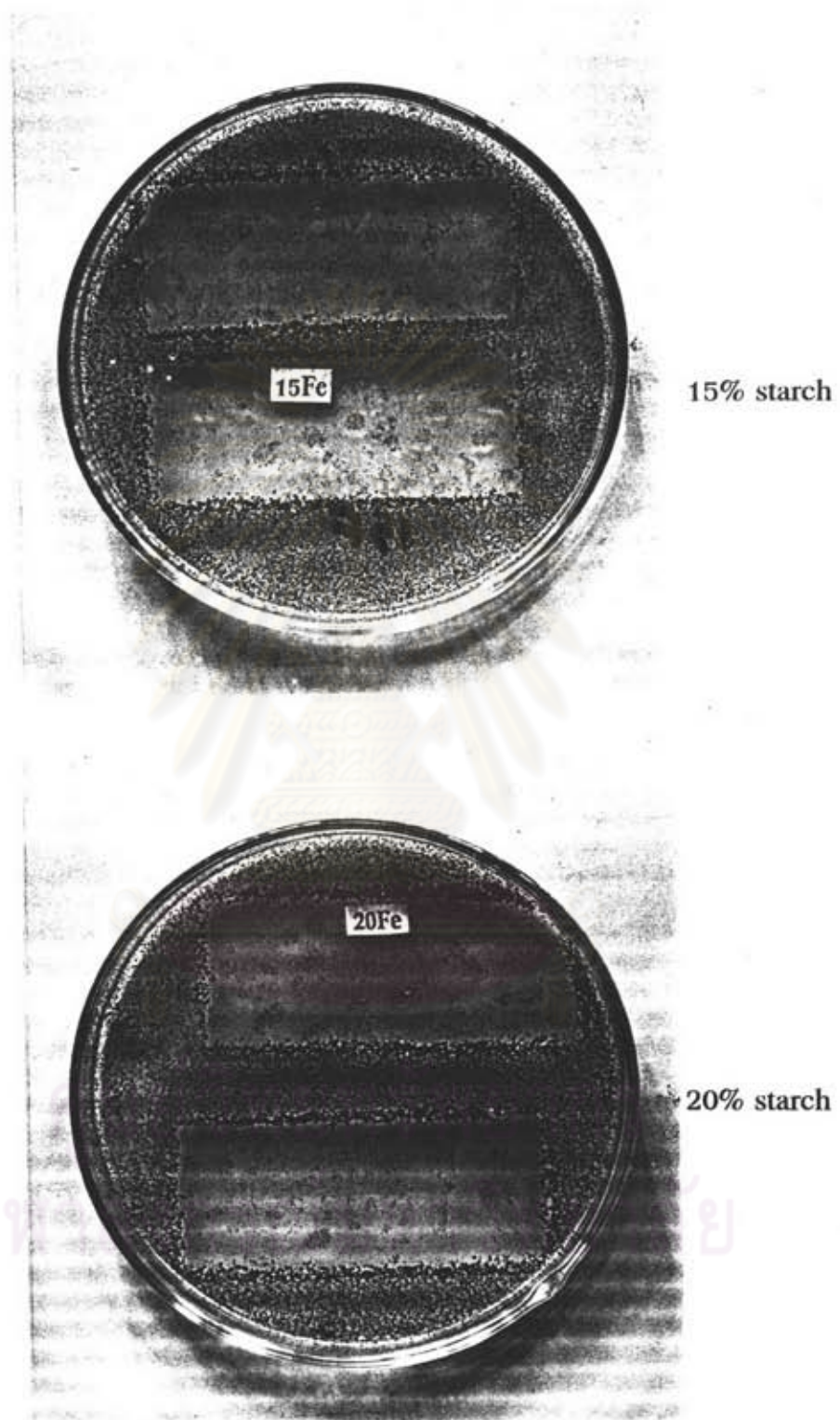


Figure 4.23(b) Biodegradability of iron stearate-starch-LDPE films by *Aspergillus niger* fungi.

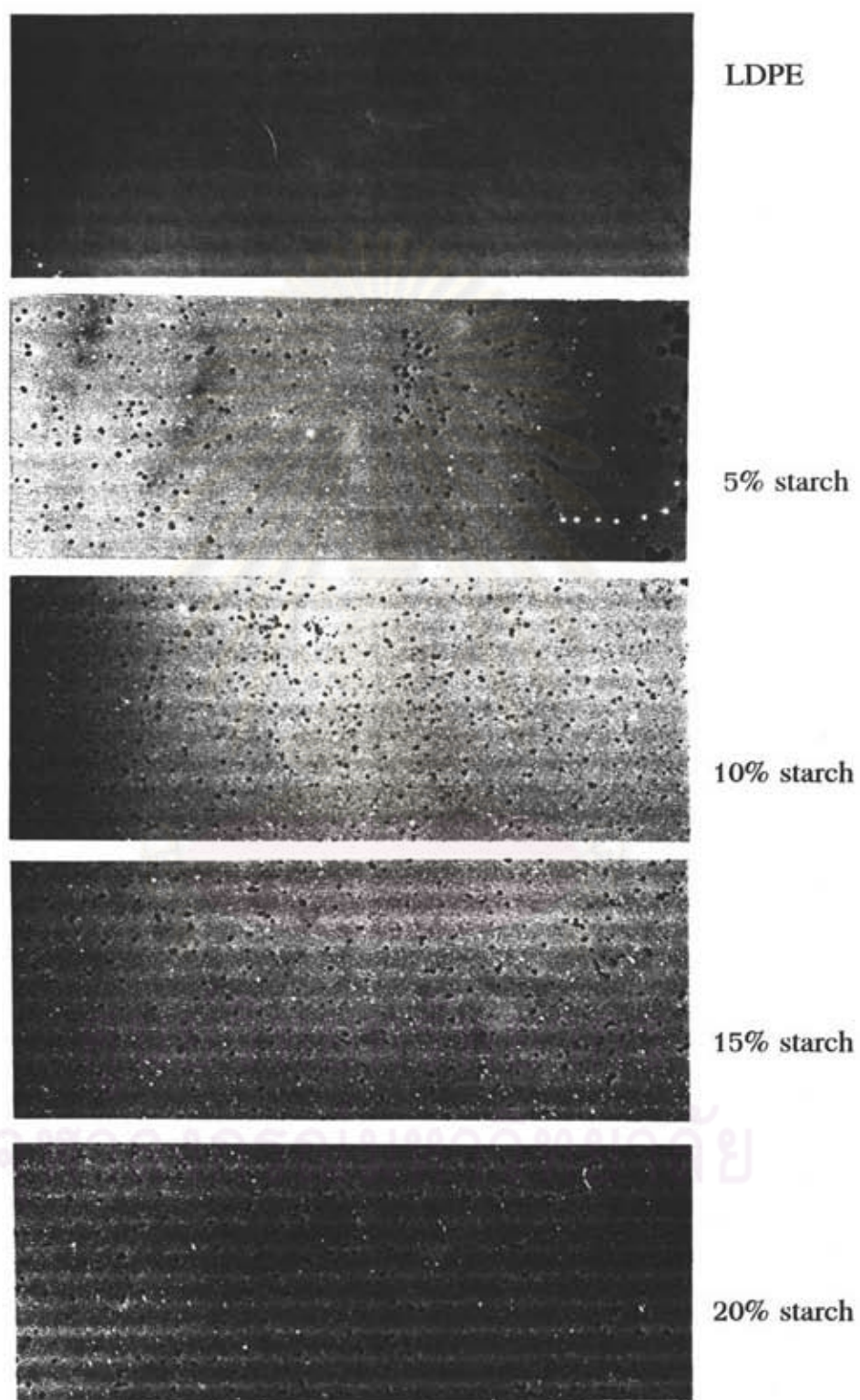


Figure 4.24 Biodegradability of starch-LDPE films by *Aspergillus niger*, focus on surface of the films.

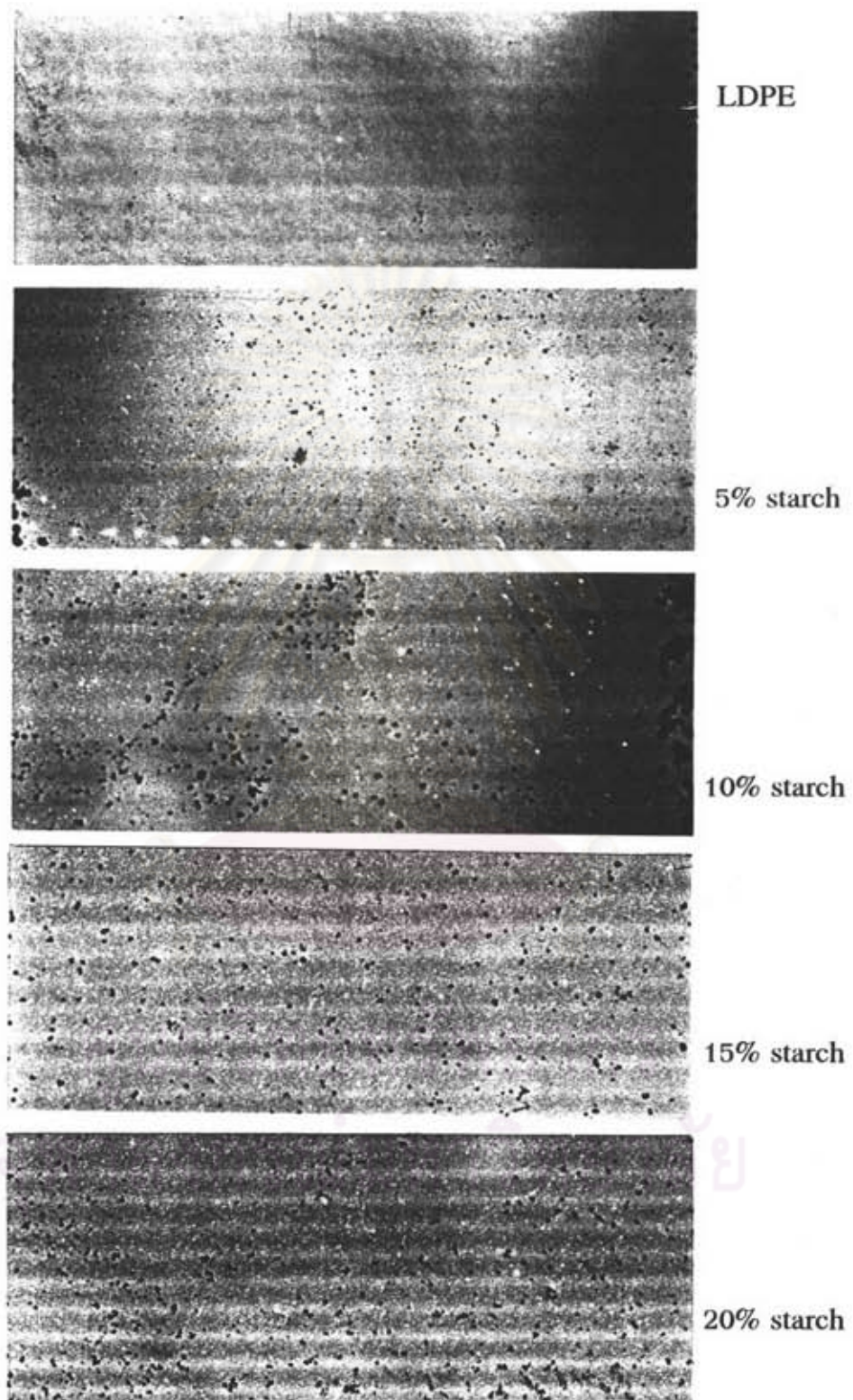


Figure 4.25 Biodegradability of iron stearate-starch-LDPE films by *Aspergillus niger* fungi, focus on surface of the films.

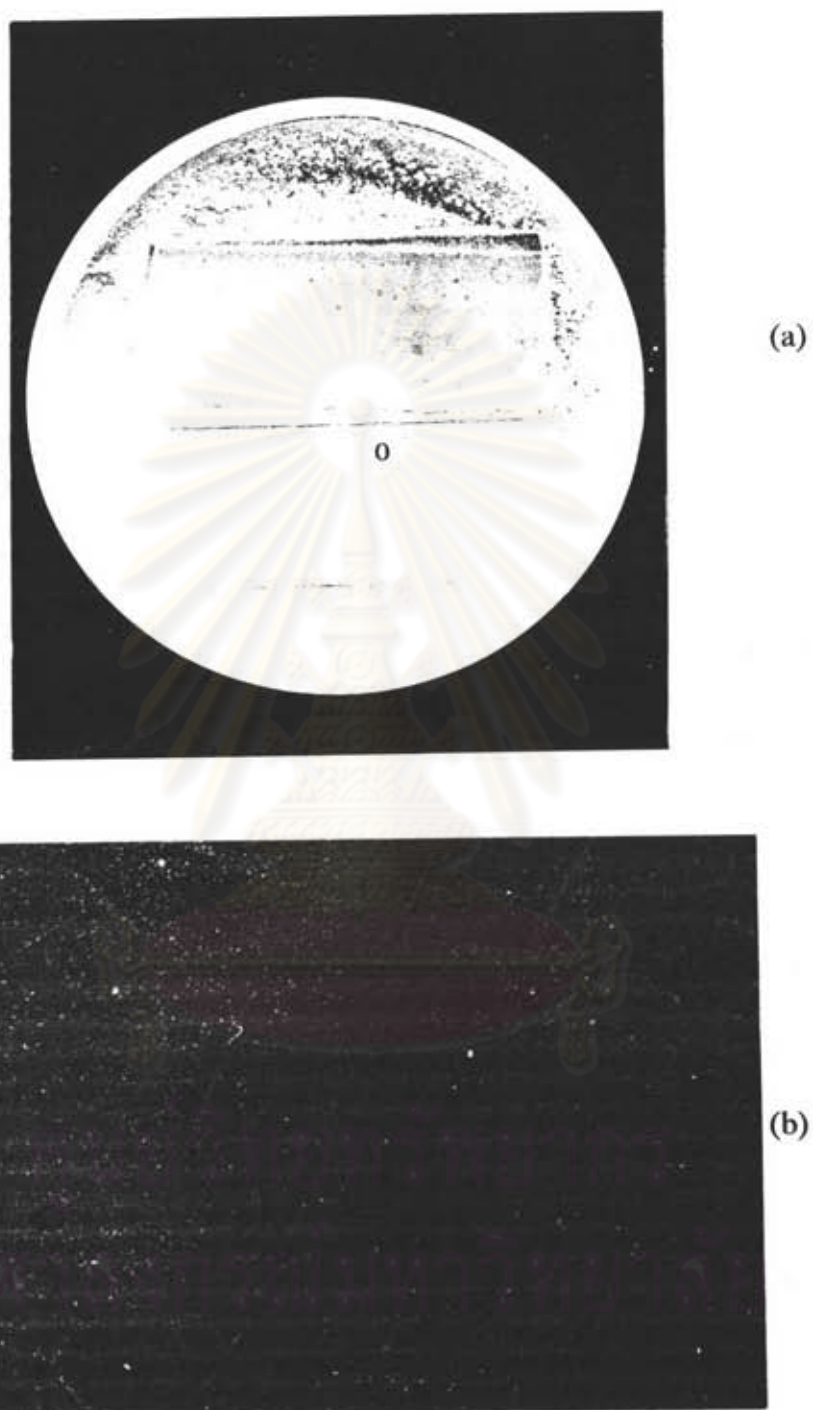
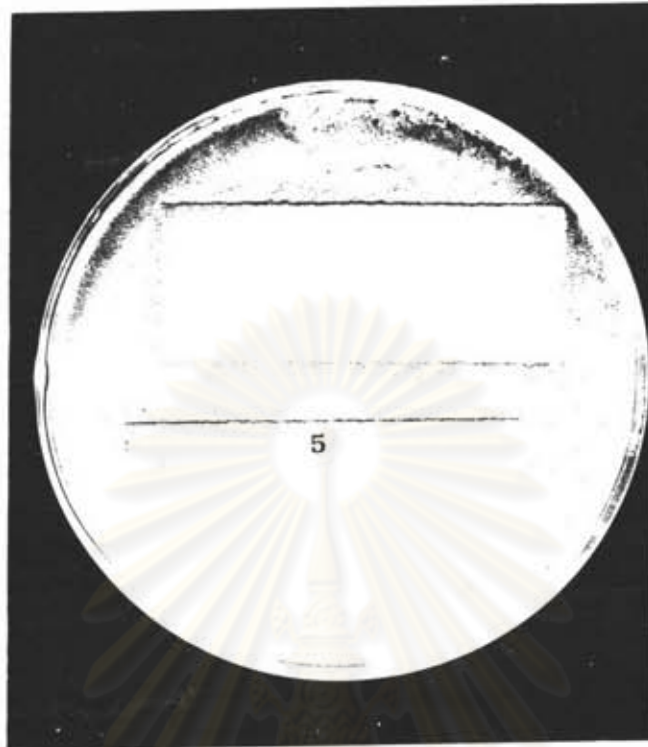


Figure 4.26 Biodegradability of LDPE films by *Penicillium pinophilum*

(a) full plate of culture

(b) focus on surface of the film



5% starch



10% starch

Figure 4.27(a) Biodegradability of starch-LDPE films by *Penicillium pinophilum*

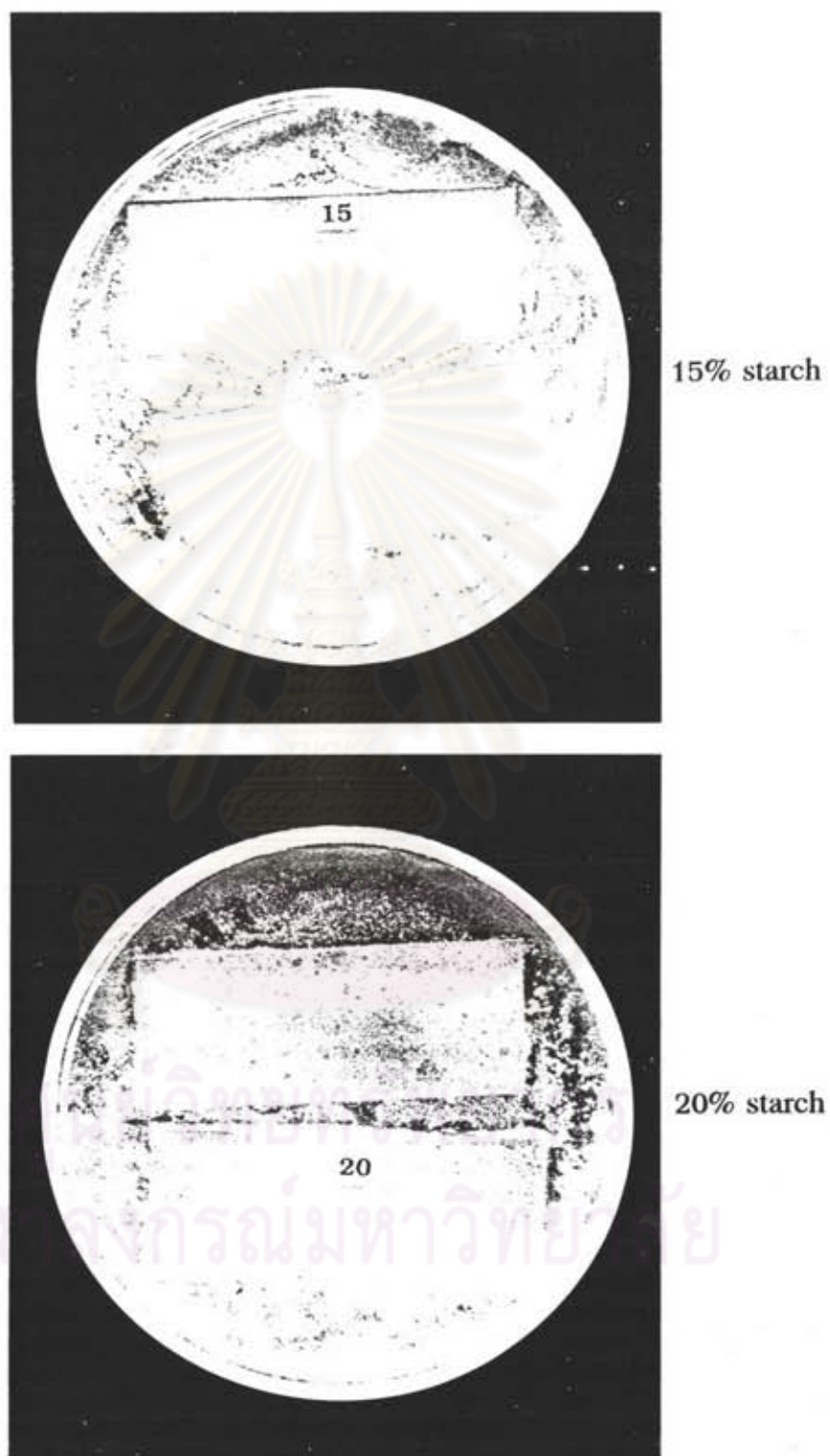


Figure 4.27(b) Biodegradability of starch-LDPE films by *Penicillium pinophilum*

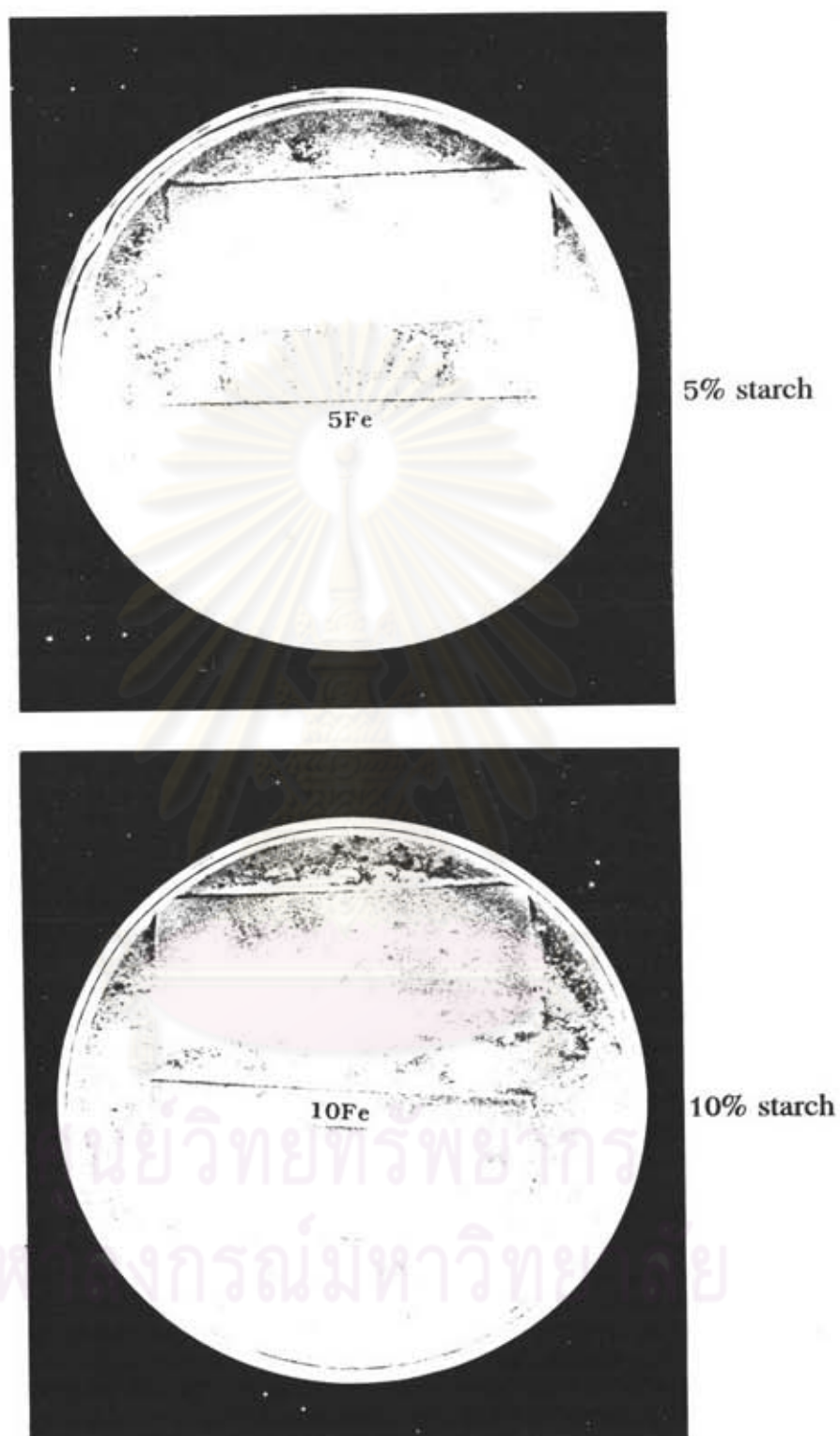


Figure 4.28(a) Biodegradability of iron stearate-starch-LDPE films by *Penicillium pinophilum*

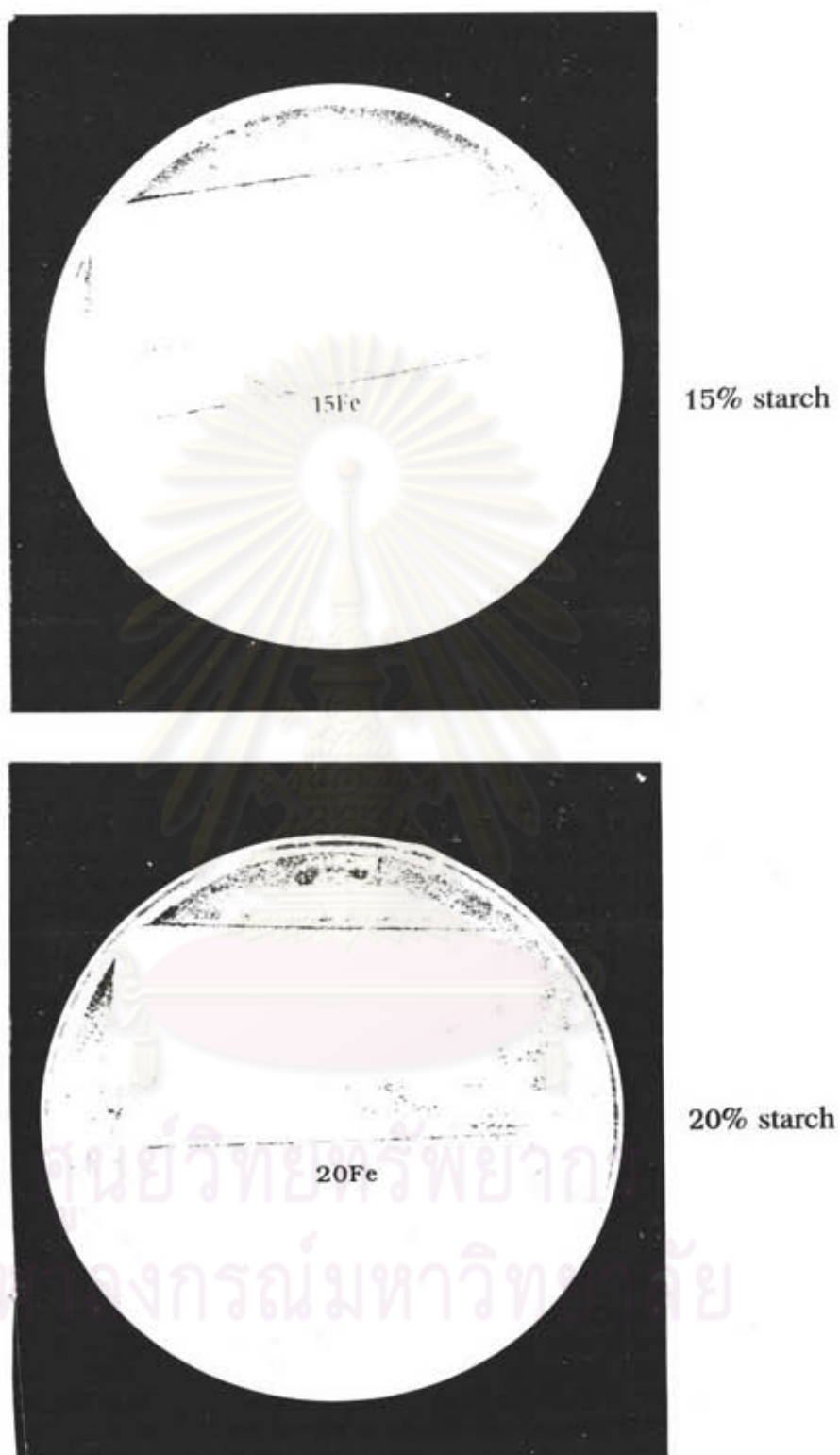


Figure 4.28(b) Biodegradability of iron stearate-starch-LDPE films by *Penicillium pinophilum*

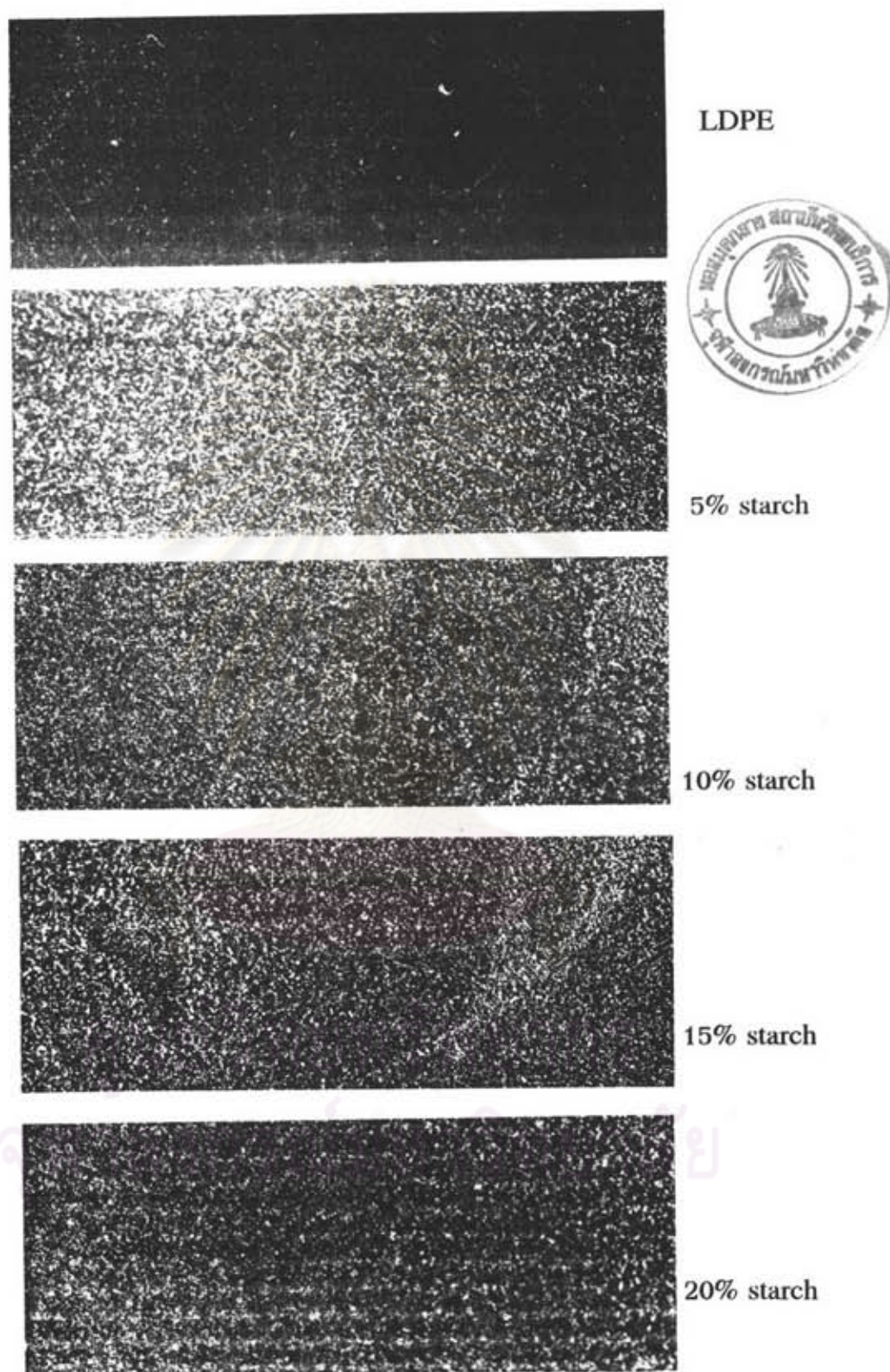


Figure 4.29 Biodegradability of starch-LDPE films by *Penicillium pinophilum* focus on surface of the films.

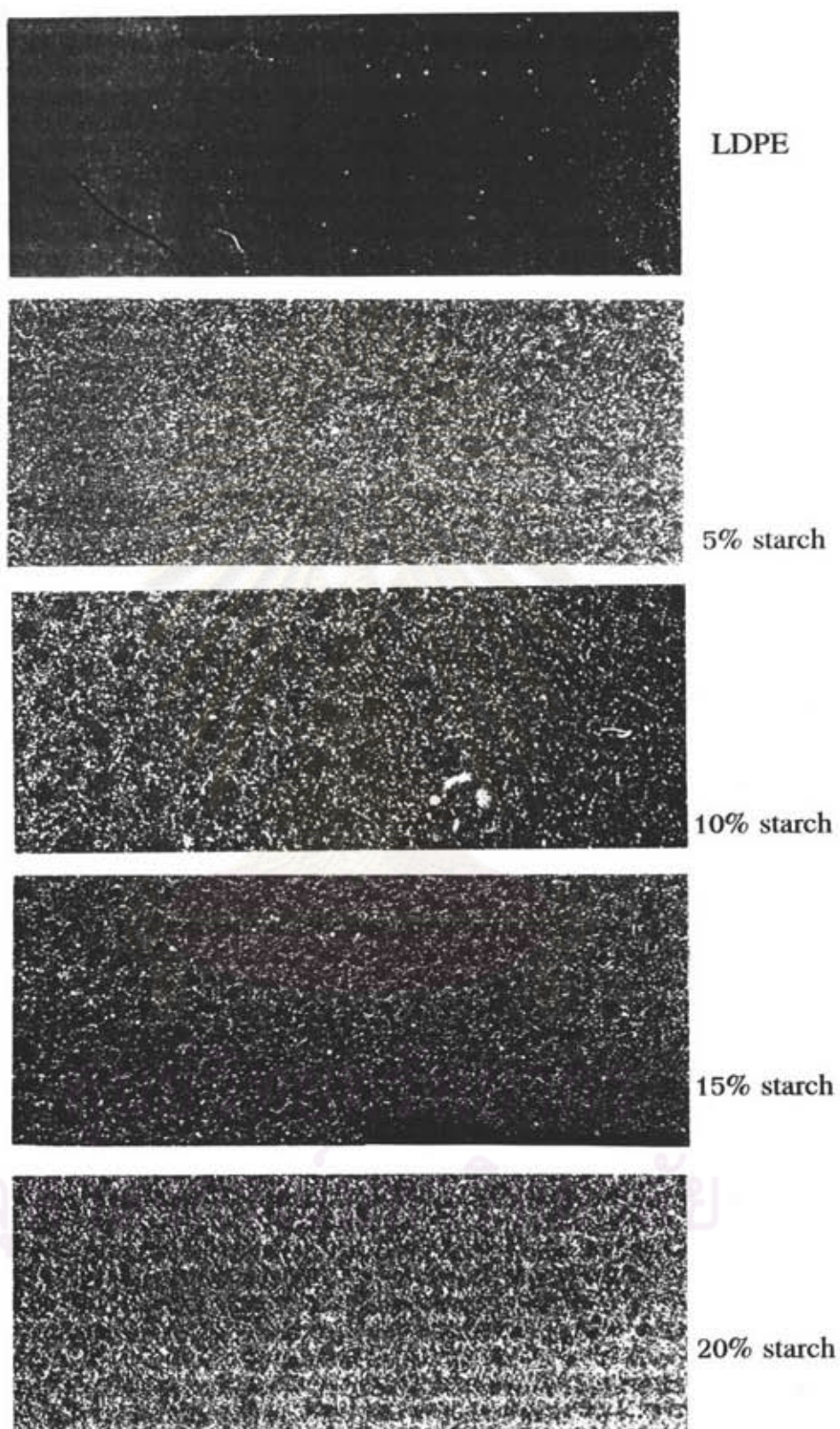


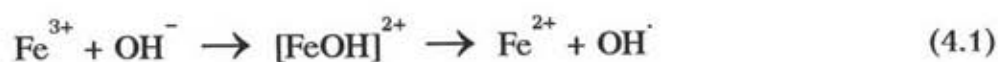
Figure 4.30 Biodegradability of iron stearate-starch-LDPE films by *Penicillium pinophilum*, focus on surface of the films.

Proposed Degradation Phenomena

With the present of starch and iron stearate in LDPE, every samples show the fast deterioration in mechanical properties after experimental test, especially for the outdoor exposure. The results disclose that LDPE with carbon-carbon bonds can be rendered degradable by addition of :

- (a) starch granules, a biodegradable substance
- (b) soya oil, an oxidizable substance which contains double bonds in its molecule and
- (c) an iron stearate, a prooxidant to catalyze the oxidative degradation of polymer chain.

The degradation process is to say that the simultaneous presence of a biodegradable substance, an oxidizable substance and an iron compound leads to a significant synergistic effect. As far as is known so far or can be assumed as probable, the degradation proceeds by the following mechanism(Chiquet, 1990). Under the action of ultraviolet light, sun light or heat or under decomposition conditions, free radicals such as, for example, OH^\cdot are formed due to the presence of the iron ions, and these can react with the polymers, forming other free radicals. These free polymer radicals are extremely reactive and can react further with oxygen, as shown in the degradation mechanism of LDPE (Figure 4.7), with other chains, with iron ions, with a double bond of the oxidizable substance, and the like. Polymer chains are thus split, small chains with or without oxygen-containing groups, such as alcohols, ketones, waters etc. being formed. During this process, the iron ions act both as an initiator and as a reaction promoter, whereas the oxidizable substance acts as a reaction promoter and especially as a chain splitter, since this substance has a greater tendency than a saturated polymer chain to form peroxy or hydroperoxy compounds, and starch, because of the large number of hydroxyl groups in its composition, manifests it self as a promoter and, in conjunction with the iron ions, as a particularly valuable co-initiator, since iron stearate complexes are highly reactive. This can be illustrated by the following equation (4.1):



In this phase, to be described as the first phase, the plastic materials become brittle and fragile into small pieces, depending on the prevailing condition.

In the subsequent second stage, if there are the presence of microorganisms, with the action of ultraviolet light, sunlight or heat, the degradation process continues as in the first stage following can be observed:

[A] Under the mentioned condition the degradation process continues as in the first stage. The small particles disintegrate further into smaller and smaller particles until they disappear.

[B] In the presence of microorganisms, that is to say bacteria, fungi and/or enzymes, such as occur under composting conditions or in contact with the soil, a further degradation stage follows. Due to the disintegration in to small particles, the area of the starch subject to attack by the microorganisms is enlarged several times. The starch is completely biodegraded, whereas the oxygen-containing, split polymer chains are degraded at least partially. Depending on the first stage can still continue, leading to even shorter oxygen-containing polymer chains which, due to the close contact with the microorganisms or enzymes, are in turn partially degraded further. In this way, complete biodegradation at the end of the second stage can be achieved.

Such a two-stage degradation is advisable especially in the case of agricultural sheets which are in contact with the soil, or of scattered wastes. After the first stage, the plastic particles are then so small that they can penetrate under exterior influences, e.g. rain, into the soil. They are then not accessible to light anymore so that a biological degradation of starch and take place which would not occur in the case of conventional photodegradable plastic composition.