

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Characterization of Banana Starch

4.1.1 Scanning Electron Microscopy (SEM)

The morphological characteristic of extracted starch was determined by SEM. Clearly, Figure 4.1 reveals that the surface of the banana starch granules is very smooth. In fact, it is quite similar to other kinds of starch. The shape of banana starch granules are ranging from oval to irregular. Its granule size varies from 5 μm to 45 μm , however, the average size is in the range of 21 - 24 μm .

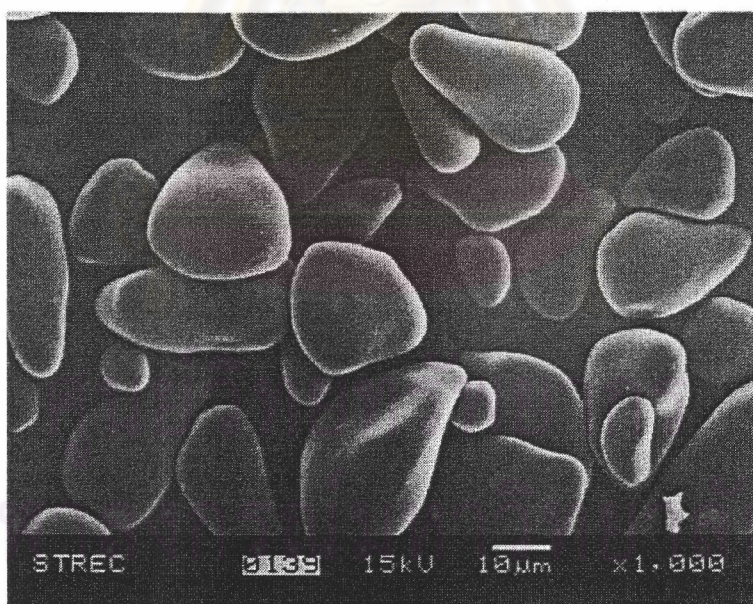


Figure 4.1 SEM micrograph of starch granules of banana.

4.1.2 Compositional Analysis

Since the difference between flour and starch is the existence of protein in the molecule, after extraction, banana starch contain only 0.11% of protein in its molecule. Like any other starches, other compositions including amylose content were analyzed and the proximate analysis is shown in Table 4.1. The amount of amylose in the molecule implies that banana starch consists of both linear and branch molecules at approximately the same quantity.

Table 4.1: Composition of Banana Starch

Component	Amount (%)
Starch	92.87 ± 1.09
Protein	0.11 ± 0.01
Lipid	0.03
Ash	0.044 ± 0.017
Amylose	55.42 ± 0.98

These results are quite similar to the values published by Lii and Chang in 1982 [8]. The only difference, however, is the lipid content in which their result was much higher (0.11 – 0.37%) than that obtained in the present study. The protein and lipid contents of the extracted starch were also different from those reported by Kayisu et al. in 1981 [16]. In their work, the protein and lipid contents are 2 times and 7 times higher than those presented in Table 4.1. The relative composition of these two constituents is very much dependent on the stage of maturity and on the variety of the banana. Therefore, this different finding is in fact the result of the variety in source and stage of maturity of banana used in each study.

4.1.3 Chemical Structure

Figure 4.2 depicts the FTIR spectra of banana starch. From the spectrum, the characteristic broad peak of starch appears at $960 - 1190 \text{ cm}^{-1}$. This peak is attributed to CO bond stretching [27]. The absorption bands at $1350 - 1380 \text{ cm}^{-1}$ is due to CH bending [27,31]. The intense peak at 1640 cm^{-1} belongs to OH bending (absorbed water) [27]. A strong broad band due to hydroxyl bond stretching and a CH stretching peak appears at $3000 - 3650 \text{ cm}^{-1}$ [3,27] and $2800 - 2950 \text{ cm}^{-1}$ [27,31], respectively.

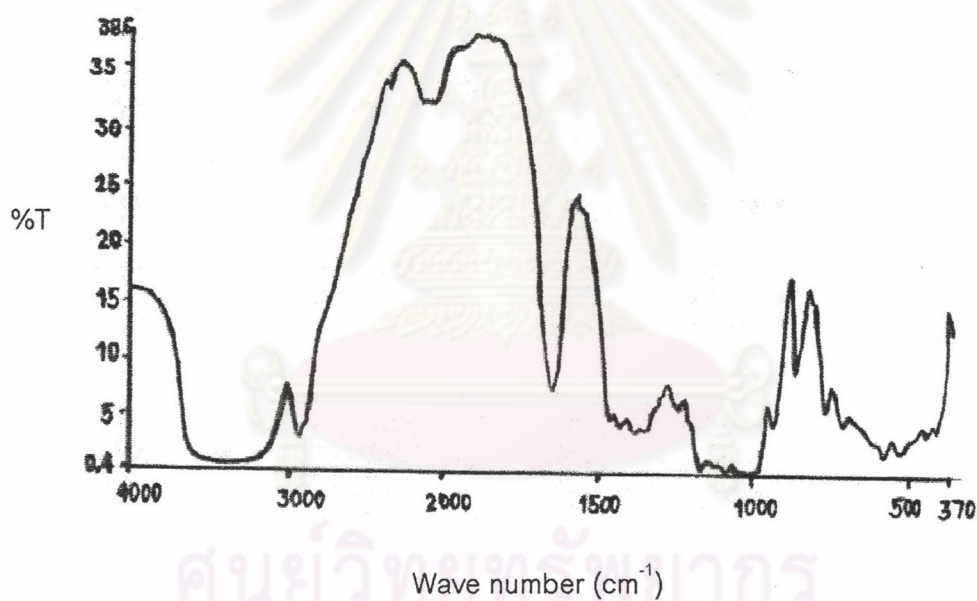


Figure 4.2 Infrared spectrum of banana starch.

4.1.4 Thermal Properties

4.1.4.1 Differential Scanning Calorimetry (DSC)

The gelatinization temperature range obtained from DSC thermograms of banana starch is presented in Figure 4.3. As can be seen, the gelatinization temperature ranges from 72 to 78 °C. From the literature, Lii investigated some properties of banana starch and observed a gelatinization temperature range of 74 – 81°C for green banana and 79 – 83°C for ripening banana [2]. The difference between our data and those published in the literature may be due to the difference in varieties and the degrees of ripening of banana.

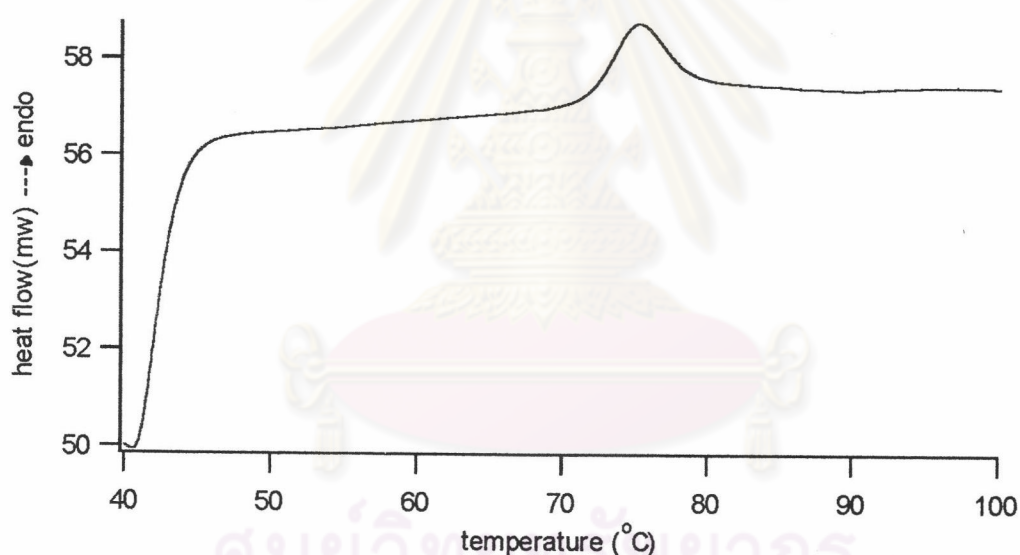


Figure 4.3 DSC heating curve of banana starch.

4.1.4.2 Thermogravimetric Analysis (TGA)

The thermogravimetric analysis (TGA) of banana starch is shown in Figure 4.4. In general, weight losses occur when volatile absorbed by the samples takes place with the formation of volatile products. As seen in Figure 4.4, the initial

weight loss began at approximately 50°C and reached a constant weight plateau after losing 6% of its initial weight. This weight loss corresponds to the loss of the moisture content from the banana starch. Further weight loss occurred at approximately 315°C. At this temperature the banana starch began to degrade. Less than 2% residue was left at 600°C.

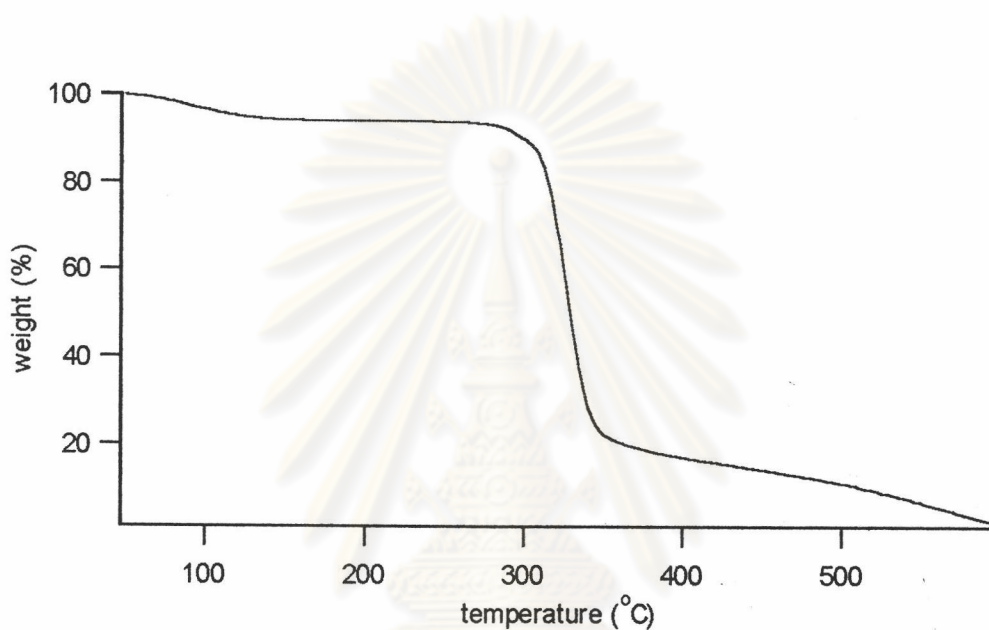


Figure 4.4 TGA curve of pure banana starch.

4.1.5 Starch Density Measurement

Density of banana starch was measured by the picnometric technique as previously described in chapter III. Diethyl ether was used as a non-solvent in this test. It was found that the density of banana starch was 1.74 g/cm³.

4.1.6 Moisture Absorption

The plot of moisture absorption as a function of time for banana starch is exhibited in Figure 4.5. As expected, moisture absorption increased with increasing

time. Because of its hydrophilic nature, banana starch absorbs moisture from the atmosphere. The absorption rate was pretty fast at first and then slowed down a little until it reached equilibrium within a day. Its moisture absorption at equilibrium is almost 20%.

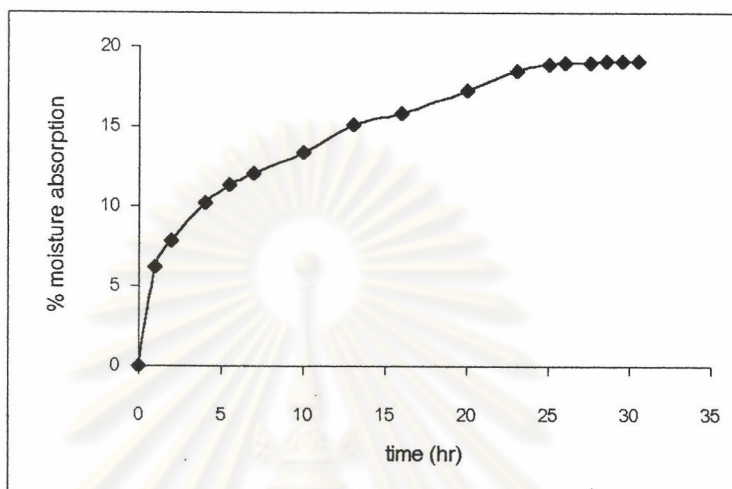


Figure 4.5 Moisture absorption of banana starch.

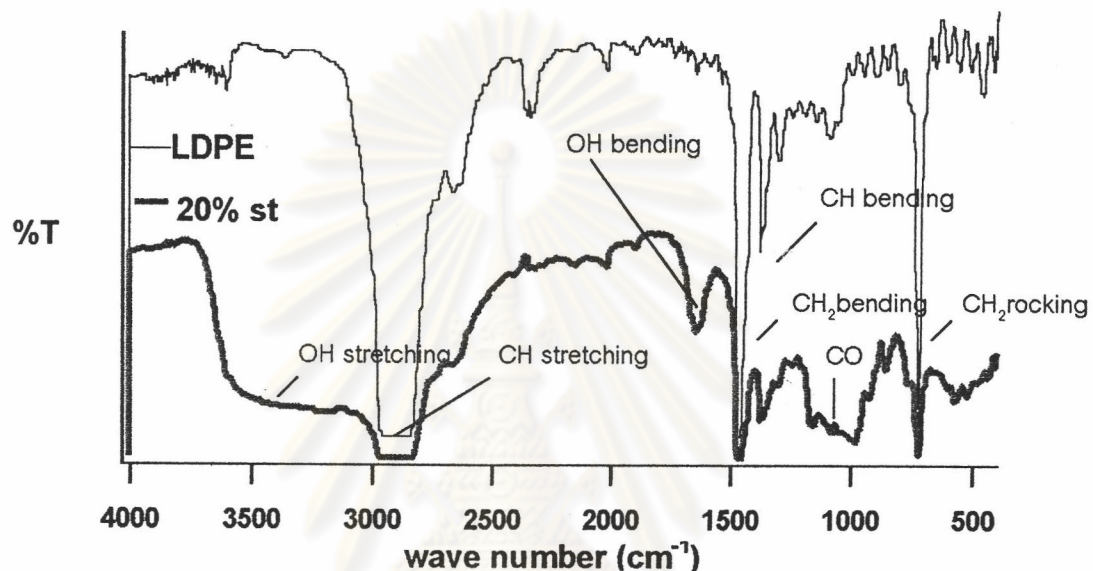
4.2 Characterization of LDPE/Banana Starch Film

4.2.1 Chemical Structure

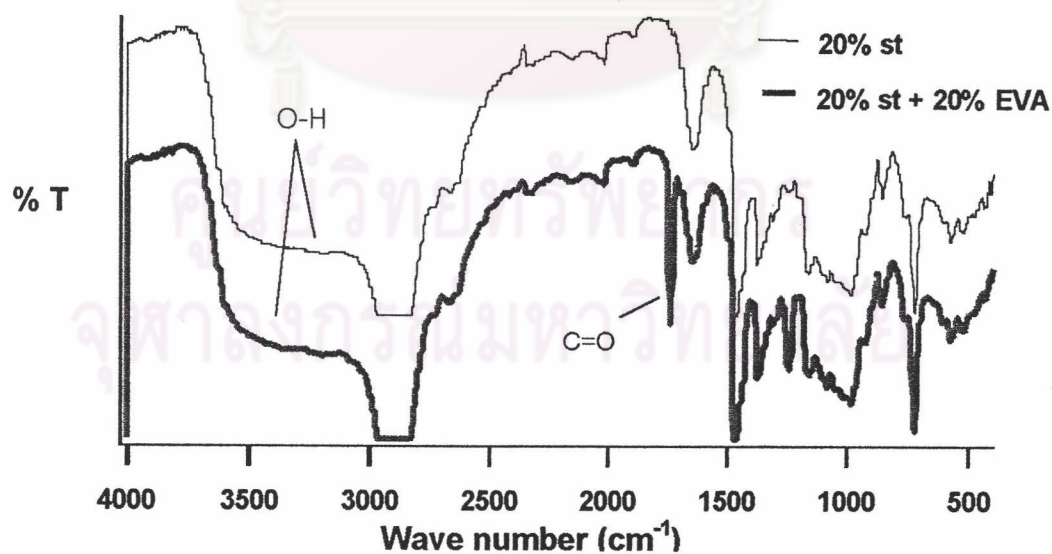
Comparison of the FTIR spectra of the films are illustrated in Figure 4.6. Spectra of LDPE and a 20% starch/LDPE blend are displayed in Figure 4.6(a). The addition bands to those recorded for pure LDPE are CO stretching ($960 - 1190 \text{ cm}^{-1}$) [27], OH bending (absorbed water) at 1640 cm^{-1} [27] and OH stretching ($3000 - 3650 \text{ cm}^{-1}$) [3,27] bands that came from the starch components. Table 4.2 shows IR vibrations of the pure LDPE film. Figure 4.6 (b) shows the comparison of FTIR spectra for the uncompatibilized blend and the compatibilized blend with 20% EVA. The spectrum for compatibilized blend was almost the same as uncompatibilized blend except a sharp peak occurred at 1745 cm^{-1} [3,31]. This new peak in the compatibilized blend is assigned to the carbonyl group ($\text{C}=\text{O}$) from EVA.

Table 4.2: Infrared Vibrations and Assignments for LDPE [3,27,31]

Frequency (cm^{-1})	Assignment and Remarks
2800 – 2950	CH stretching
1462	CH_2 bending
1350 – 1380	CH bending
720, 730	CH_2 rocking



(a)



(b)

Figure 4.6 Infrared spectra of (a) pure LDPE and 20% starch - LDPE films and (b) 20% starch – LDPE films with and without 20% EVA.

4.2.2 Thermal Properties

4.2.2.1 Differential Scanning Calorimetry (DSC)

DSC was employed to discern thermal transitions and to gain some information on the miscibility between banana starch and LDPE. As described in the experimental section, three scans for each samples were performed. Second heating cycles provide more information on the reversible transitions by erasing any prior thermal histories associated with the sample.

The second heating cycles of DSC thermograms for pure LDPE and LDPE/starch/EVA blends are shown in Figure 4.7. Comparing to the DSC thermogram of the pure LDPE film, there was no change in the melting temperature of the LDPE phase at about 103°C.

The percent crystallinity of LDPE phase in the blends determined from the DSC thermograms are given in Table 4.3. A value of ΔH_f° (276 J/g) [32] for purely crystalline PE and the heat of fusion (ΔH_f^*) obtained from the total area of the melting peak including the initial broad region were used to calculate percent crystallinity. The percent crystallinity was then calculated by dividing the measured heat of fusion (ΔH_f^*) by the reference value for perfect PE crystal (ΔH_f°).

Although there is only endothermic transition for the starch/LDPE or starch/LDPE/EVA blend films, this does not mean that the blends are compatible. In fact, like any other starch, banana starch has no melting temperature, but gelatinization and degradation temperatures; therefore, the endothermic transition occurred was solely attributed from the LDPE phase.

Table 4.3 shows the percent crystallinity of the LDPE phase in the blends. Comparing the difference of pure LDPE and 20% starch blends, there is apparent decrease in the heat of fusion as the content of starch increases. However,

when the heat of fusion is corrected by taking into account only the LDPE content in the blend, it is evident that there is no change in the crystallinity of LDPE phase. It can be concluded that LDPE is hardly miscible with starch. For compatibilized blend with EVA, the percent crystallinity of the LDPE phase in the blends decreased as EVA content increased. This decrease is due to the presence of an interaction between LDPE and starch, which hinders the close packing of LDPE chains.

Table 4.3: Percent Crystallinity of LDPE in Various Blends

Film Samples	ΔH_f^* (J/g)	% Crystallinity (total)	% Crystallinity (LDPE phase)
LDPE	54.13	19.61	19.61
20% starch	40.90	14.82	19.60
20% starch + 5% EVA	39.83	14.43	18.22
20% starch + 10% EVA	38.64	14.00	17.86
20% starch + 20% EVA	36.54	13.24	17.21

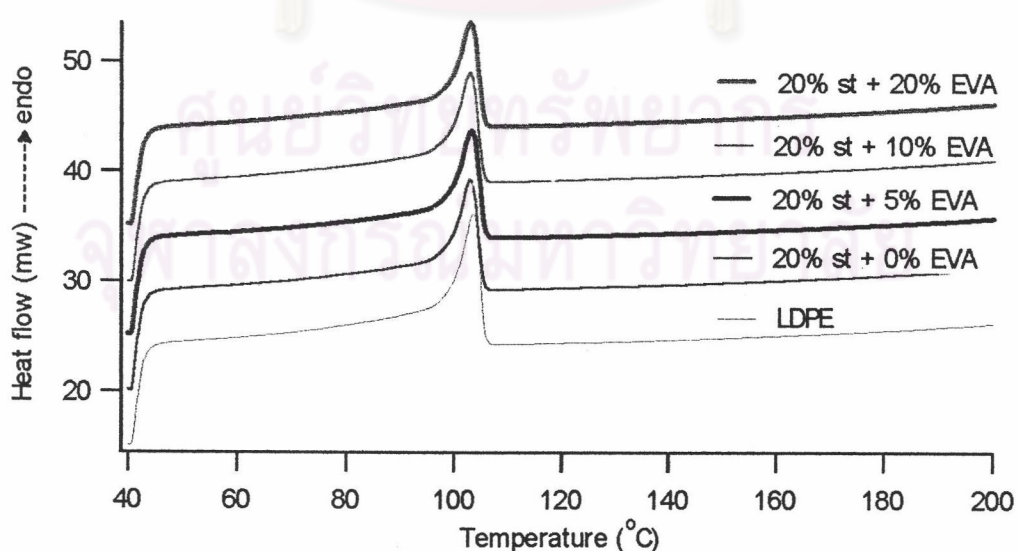


Figure 4.7 DSC thermograms of second heating for the blends.

4.2.2.2 Thermogravimetric Analysis (TGA)

TGA was used to study the degradation temperature of LDPE/starch/EVA blends. The values of the onset of the degradation temperature are very important, since they could indicate the processing and manufacturing temperatures without continuing or initiating a process of decomposition.

The effect of banana starch content on the thermal degradation behavior of the LDPE/starch blends is presented in Figure 4.8. Obviously, the LDPE/starch blends degraded in two stages. The first one around 310 – 340°C is due to starch decomposition as similarly shown in Figure 4.4 for pure starch. With a further rise in temperature to 600°C, all the films exhibited no substantial changes in weight and were stable to 450°C. The second stage of thermal decomposition began near 454°C, with the weight decreasing rapidly to 500°C. This higher thermal decomposition is owing to the LDPE phase. Table 4.4 summarizes the onset of degradation temperature (T_d (onset)) for both stages and also weight loss and residue at specific temperature for all the blends. As listed, less than 2.5% residue was left at 510°C. Clearly, the first T_d (onset) shifted towards low temperature as the amount of banana starch increased. The LDPE film with 5% starch started to degrade at 313.2°C, whereas the film containing 20% starch began to degrade at 308.5°C. Certainly, the banana starch content affected the amount of weight loss of the blend films at this stage. For example, at 330°C, weight loss of the films increased as a function of banana starch content.

However, there was no effect from banana starch content at the second stage of thermal decomposition. The second T_d (onset) was not dependent upon the banana starch content, but the existence of EVA. This is because the degradation temperature of LDPE and EVA is 454°C and 450 - 500°C [33], respectively. Therefore, the shift of thermograms toward higher temperature around 454°C is due to effect of EVA. However, the influence of EVA content on the thermal stability behavior of the LDPE blend films will be explained in the section. These results imply that no matter

how much banana starch was added, the LDPE blend films will absolutely decompose approximately at the same temperature, 500°C.

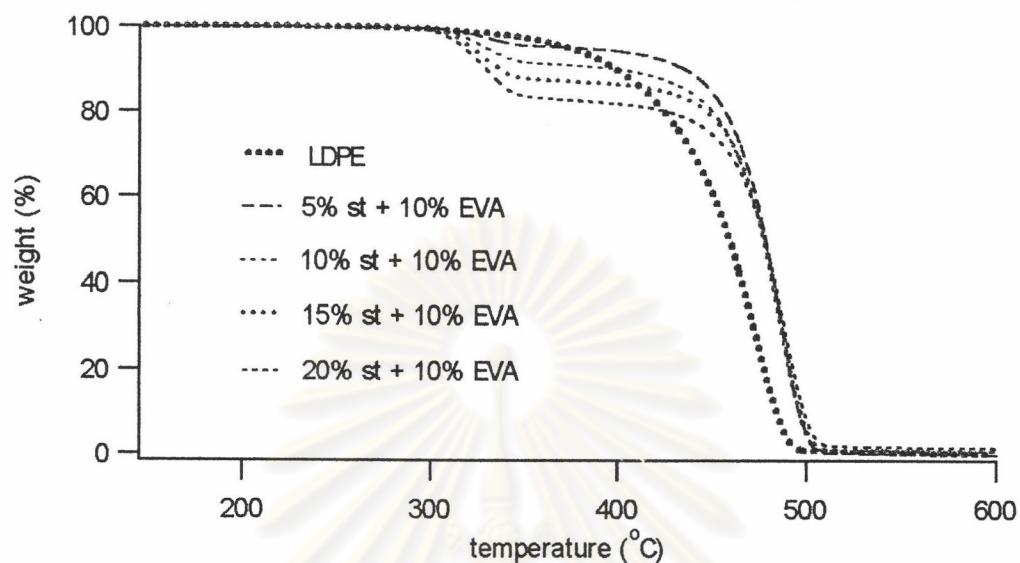


Figure 4.8 TGA curves of compatibilized blends containing 10% EVA and varying banana starch content.

Table 4.4: Onset of Degradation Temperature and Percent Weight Loss for LDPE Blend Films at Various Amount of Banana Starch

Sample	T_d (°C) (onset)		Percent Weight Loss		Residue at 510°C (%)
	First	Second	At 330°C	At 450°C	
LDPE	-	418.9	-	39.17	0.87
5%st + 10% EVA	313.2	454.6	2.58	15.70	0.52
10%st + 10% EVA	311.7	454.2	5.10	20.10	1.11
15%st + 10% EVA	310.0	455.6	7.78	21.25	1.41
20%st + 10% EVA	308.5	454.0	10.13	25.35	2.30

On the other hand, the influence of EVA content is shown in Figure 4.9. Although the blend films show two stages of thermal decomposition as previously described, obviously, the difference exists between these two set of plots (Figure 4.8 and Figure 4.9). From Figure 4.9, as the amount of starch was kept constant, the first period of thermograms for all the blends were completely superimposed up to about 330°C. In fact, the second stage of thermal degradation started right after the first stage, in particular the uncompatibilized blend film (0% EVA). This result confirms the effect of EVA on the thermal stability of the LDPE/banana starch blend films. As shown, thermal stability of the films increased with respect to the amount of EVA. Among them, the LDPE/banana starch compatibilized with 20% EVA had the highest thermal stability. Similar to Figure 4.8, all the blends further degraded up to about 500°C, where the blends almost completely decomposed.

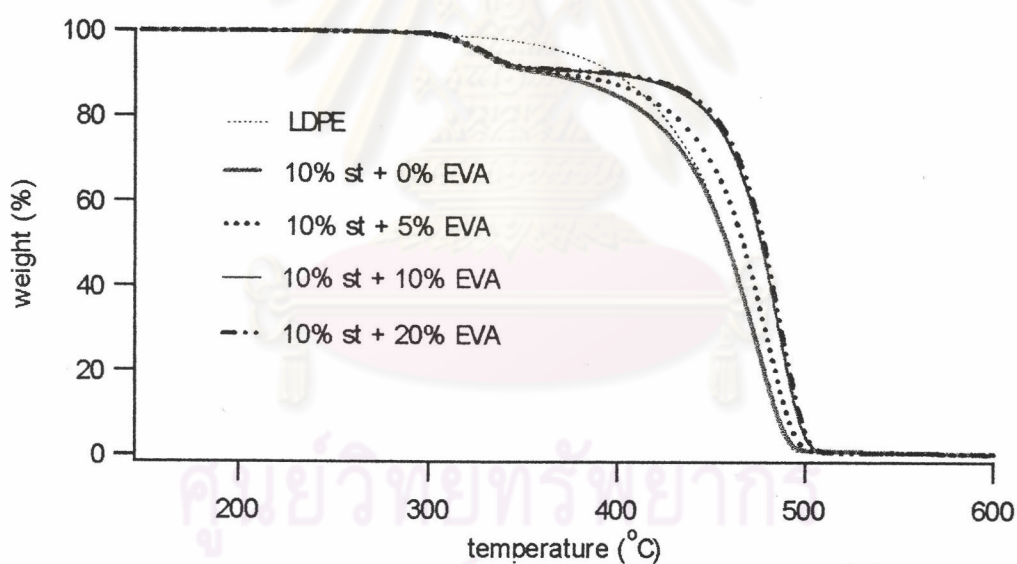


Figure 4.9 TGA curves of LDPE/starch blends with 10% banana starch and different amount of EVA.

Table 4.5: Onset of Degradation Temperature and Percent Weight Loss for LDPE Blend Films at Various Amount of EVA

Sample	T _d (°C) (onset)		Percent Weight Loss		Residue at 510°C (%)
	First	Second	At 330°C	At 450°C	
LDPE	-	418.9	-	39.17	0.87
10%st + 0% EVA	308.2	431.4	4.93	40.39	1.32
10%st + 5% EVA	309.0	438.8	5.08	30.72	1.12
10%st + 10% EVA	311.7	454.2	5.10	20.10	1.11
10%st + 20% EVA	313.1	459.9	5.09	18.98	1.05

From these two Figures it then can be concluded that the blends of LDPE with starch showed two decomposition stages. As the amount of banana starch increased, the first T_d (onset) shifted towards low temperature indicating that the first stage of degradation at 310°C is due to starch decomposition. However, there was no effect from banana starch at the second stage of thermal degradation. As the content of banana starch was kept constant, the first stage of thermograms for all the blends are identical; however, the second T_d (onset) increased as a function of EVA content. Also weight loss at 450°C decreased as the amount of EVA increased. This result confirms that the second stage started to degrade at about 419°C is due to LDPE decomposition. And the thermal stability of the blend films increased upon increasing EVA content as indicated by the shift toward higher temperature of the second stage of thermal decomposition of the compatibilized LDPE blend films. The first stage started to degrade at 310°C is due to starch decomposition, whereas the second stage started to degrade at 454°C is due to LDPE and EVA decomposition. As the amount of banana starch increased, the first T_d (onset) shifted towards low temperature. However, there was no effect from banana starch at the second stage of thermal decomposition. As the amount of banana starch was kept constant, the first stage of thermograms for all the blends are identical. This result confirms that the compatibilized blend with EVA have the higher thermal stability than pure LDPE.

4.2.3 Moisture Absorption of Film

Figure 4.10 illustrates moisture absorption as a function of time for pure LDPE and LDPE blends at various banana starch content. All the blend films were uncompatibilized. As can be seen, the moisture absorption in the uncompatibilized blends depends on the exposure time and the starch content of the blends. Unlike the pure LDPE film with almost 0% of moisture absorption, the LDPE blend films absorbed more and more moisture as the amount of banana starch increased. The LDPE film with 20% starch had highest moisture absorption compared to others. The rate of moisture absorption also depended on the starch content. At 5% starch, the blend film absorbed moisture gradually until it reached equilibrium. However, at high volume fraction of starch, the moisture absorption isotherm is slightly different. The absorption rate was very fast, although every blend films reached their own equilibrium within the same period of time, i.e., at 26 hour. These results ensure that banana starch is more hydrophilic than LDPE, leading to an enhancement of hydrogen bond formation between hydroxyl groups in the starch and moisture; as a result, the moisture uptake of the LDPE films increased as a function of banana starch content.

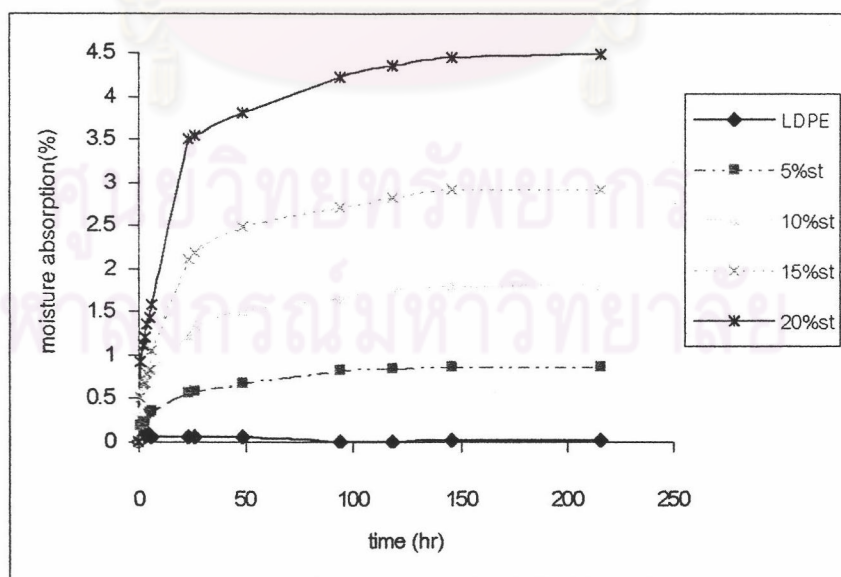


Figure 4.10 Moisture absorption of uncompatibilized films with different amounts of banana starch.

The plot of moisture absorption as a function of time for compatibilized blends with EVA is shown in Figure 4.11. Although the uncompatibilized blends absorbed more moisture than compatibilized blends. Their absorption decreased with increasing compatibilizer content. For uncompatibilized blends, starch granules are merely encapsulated within the LDPE matrix without any bonding. As seen in Figure 4.12(a), there is a gap between starch particle and the LDPE matrix. As opposed to the compatibilized blend film there is a co-continuous phase between the two phases as shown in Figure 4.12(b). This is because EVA helps promoting the interfacial adhesion between the LDPE phase and banana starch phase. In other words, uncompatibilized blends have more surface area between starch and moisture than compatibilized blends; as a result, they can absorb more moisture.

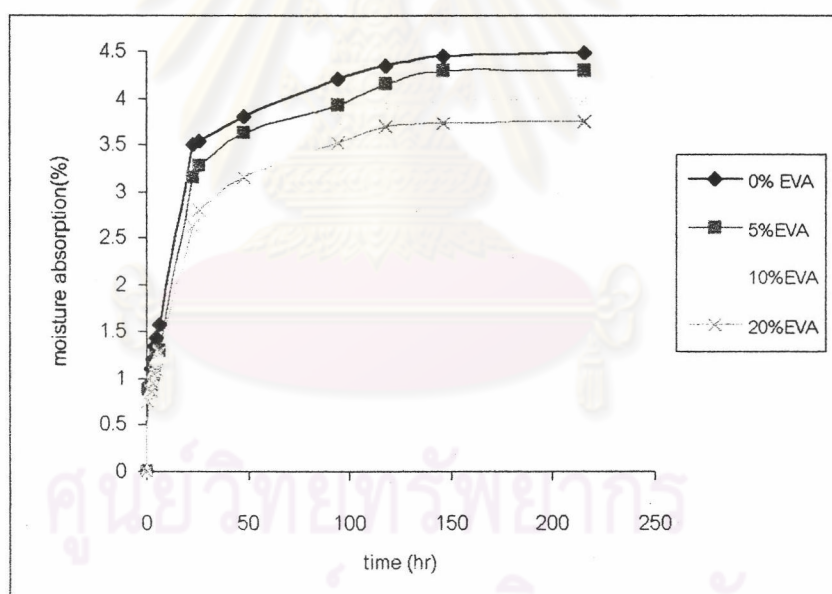
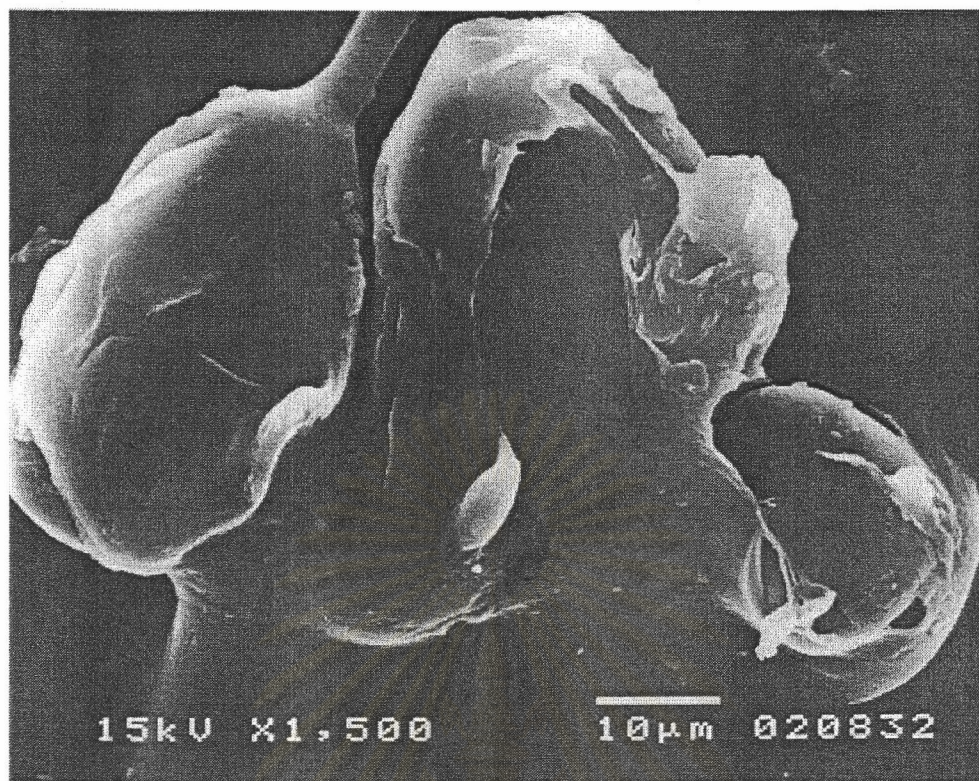
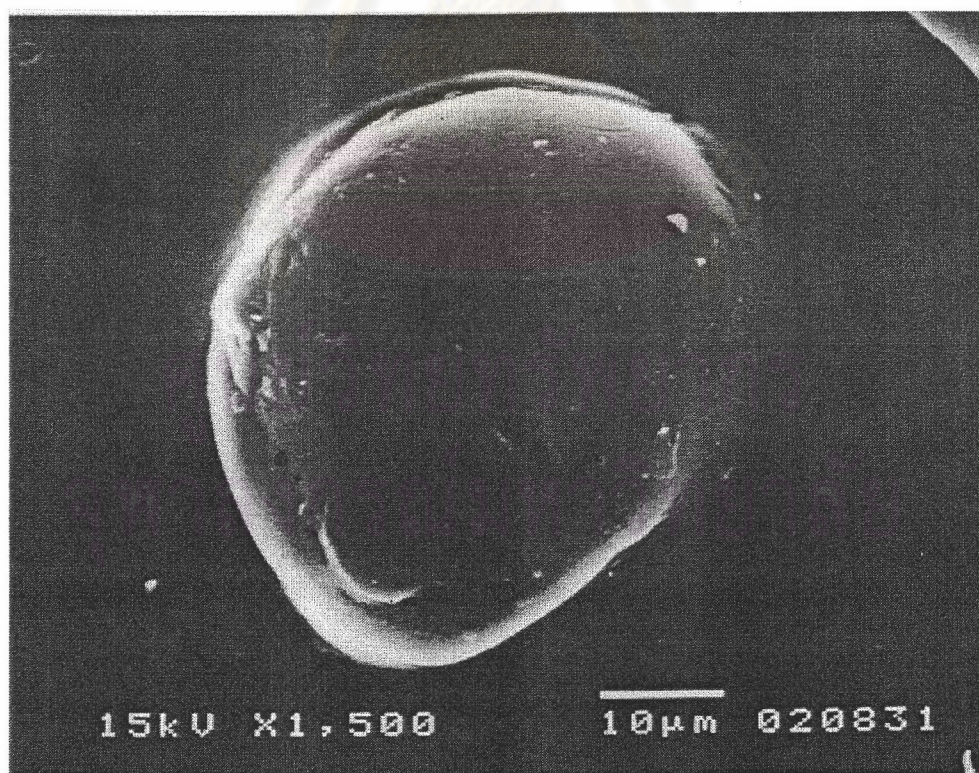


Figure 4.11 Effect of compatibilizer on moisture absorption of 20% banana starch/LDPE films.



(a)



(b)

Figure 4.12 SEM micrographs of the surface of film containing (a) 0% EVA and (b) 20% EVA.

4.3 Tensile Properties

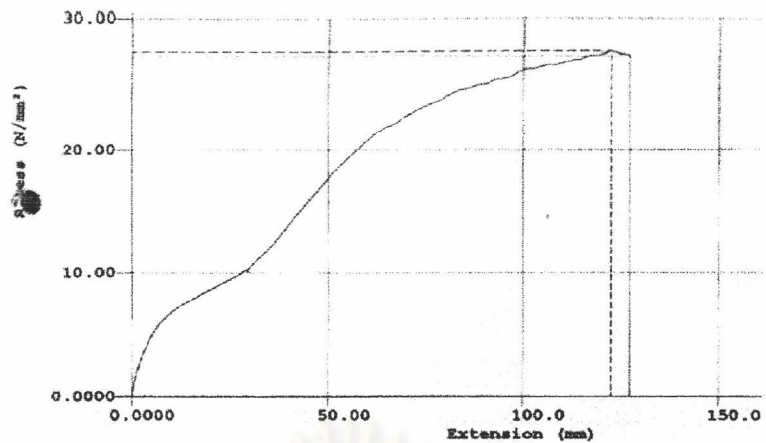
Starch – based LDPE films were prepared using the chill roll cast film. Specimens were cut from these films and the tensile properties were tested.

Effect of Starch on Stress-Strain Relationship

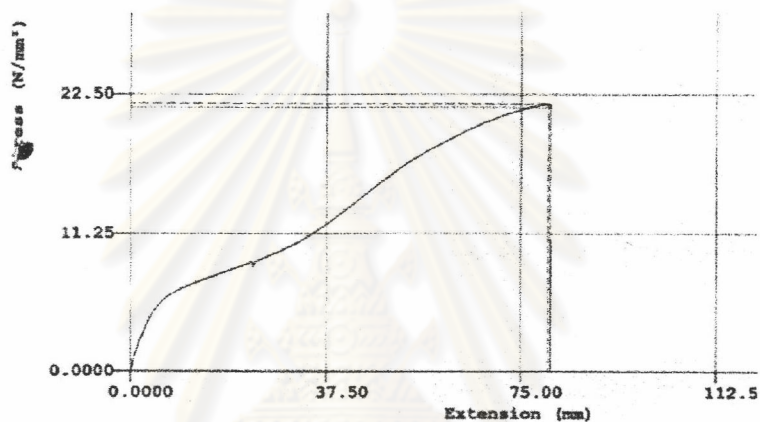
The effect of banana starch on the tensile properties of pure LDPE and LDPE/starch films is shown in Figure 4.13. It is very clear that the tensile properties are highly dependent on starch content. As the starch content increased, the tensile strength and elongation at break decreased. Although the specimen is part filler and part matrix, all of the elongation will come from the polymer if the filler is rigid and there is no adhesion between the two phases.

Since there was no apparent adhesion between starch particles and the LDPE matrix, poor stress transfer at the starch particle-polymer interface occurred. The starch particles can not bear any load, which then behave as a weak point in the LDPE blend film. Stress concentrations was generated around the starch particles, causing the reduction in the tensile strength of the blends.

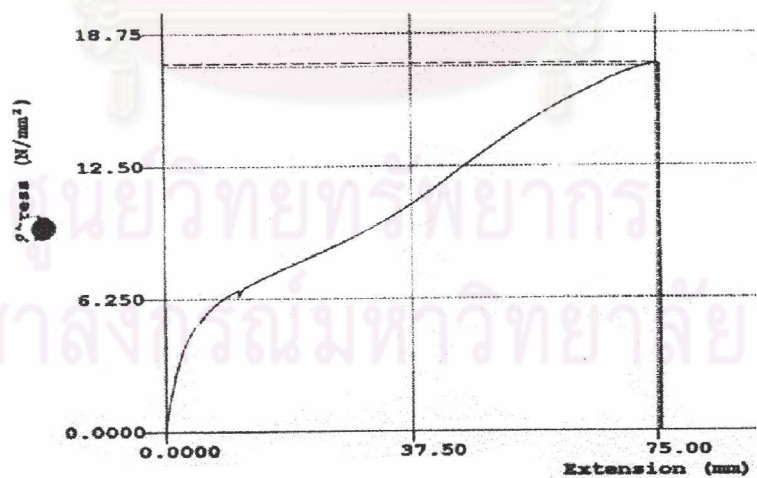
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(a)



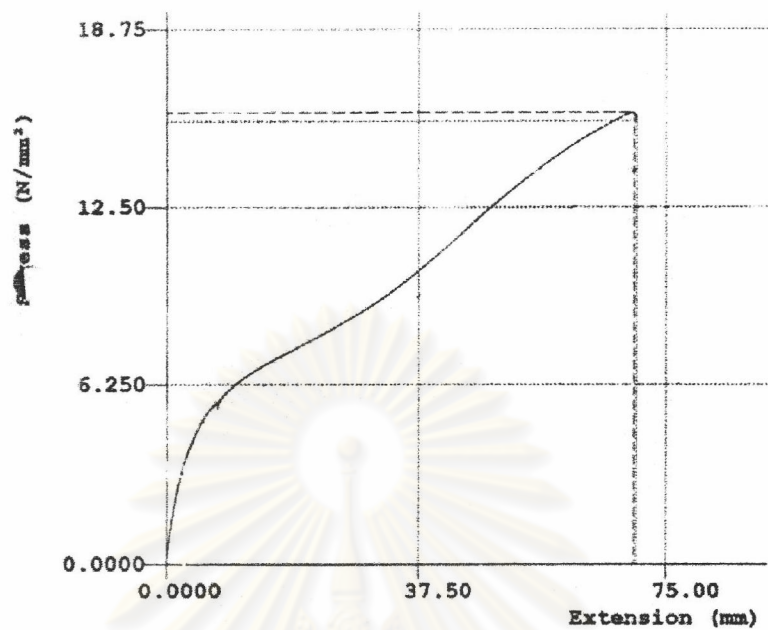
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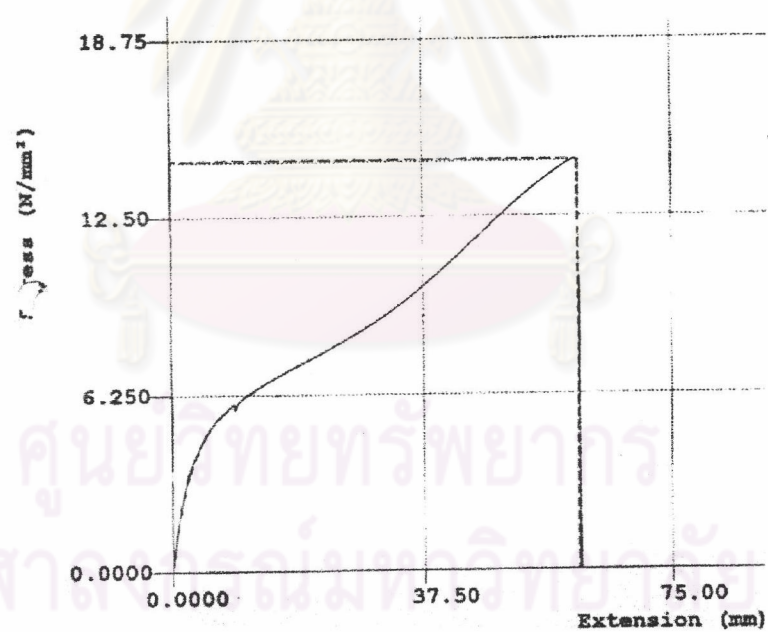
(c)

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Figure 4.13 Stress – Strain curve of LDPE blend films without EVA at different amount of starch (a) 0%, (b) 5%, (c) 10%, (d) 15% and (e) 20% banana starch.



(c)



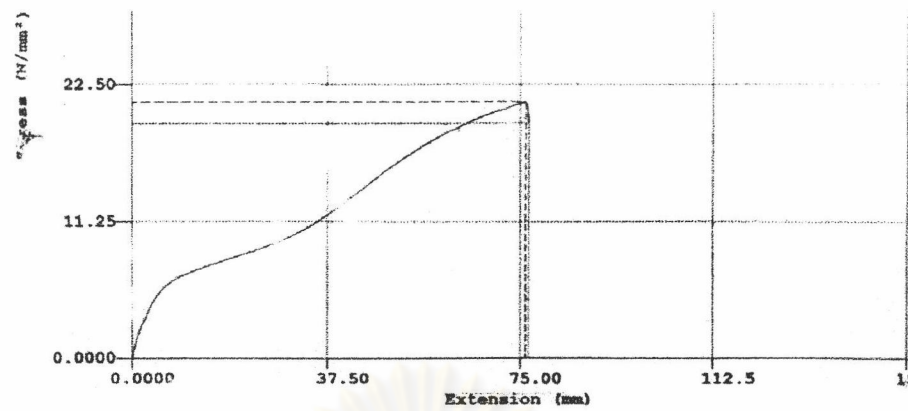
(d)

Figure 4.13 (continued)

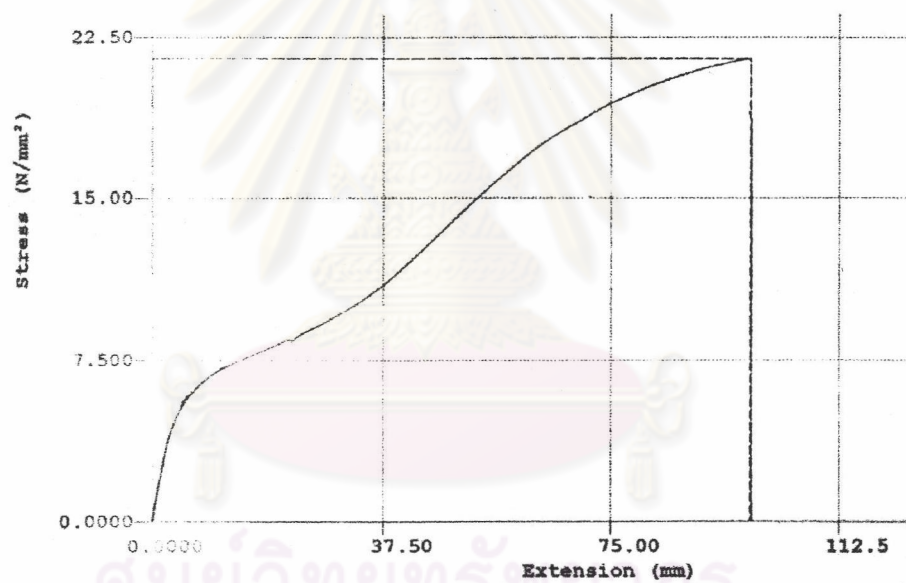
Figure 4.14 presents the effect of compatibilizer on the tensile properties of LDPE/starch films at various EVA contents. The blends with EVA exhibited better tensile properties than those without EVA. For instance, their elongation at break increased from approximately 77% for uncompatibilized blends to 110% for blends containing 20% EVA. The elongation at break slightly increased as increasing EVA content. Similar trend also happened in the case of tensile strength. All data will be compared graphically in the next section. This is due to the improvement in the compatibility between the two phases. The addition of granular starch to LDPE leads to a reduction in tensile properties because of totally different polar character of both components. In contrast with hydrophobic LDPE, banana starch is a hydrophilic polymer due to the presence of hydroxyl groups in starch molecules. As a result of this immiscibility, the tensile properties in the blends decreased. The granular starch leads to stress concentration points in blends that resulting in low tensile strength and elongation at break. There are several methods to enhance the compatibility between two immiscible polymers, including addition of compatibilizer that has functional groups capable of reacting with both the starch and the LDPE.



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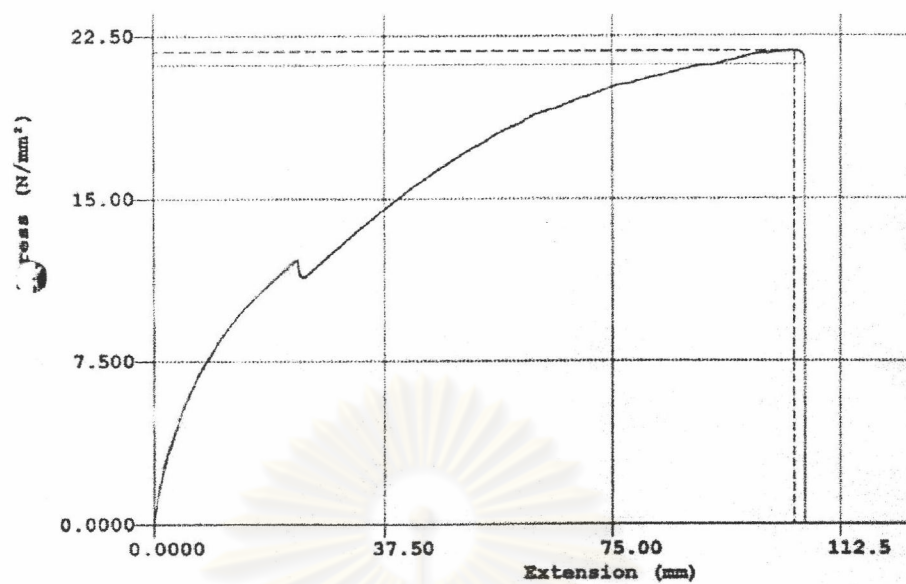
(a)



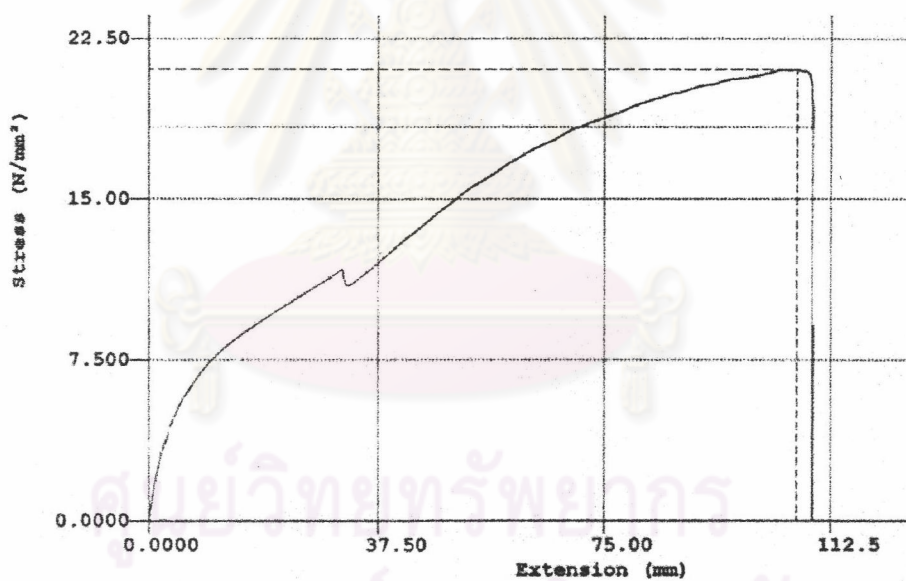
(b)

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Figure 4.14 Stress – Strain curve of 5% starch/LDPE blend films at different amount of compatibilizer (a) 0%, (b) 5%, (c) 10% and (d) 20%.



(c)



(d)

Figure 4.14 (continued)

4.3.1 Effect of Direction

From the chill roll cast film, the LDPE films were biaxial stretched simultaneously. Thus, like other biaxial stretching films such as PET, the LDPE blend films should have preferred orientation so called biaxial oriented film. Figure 4.15 shows the effect of different percentage of starch and direction on the tensile strength of uncompatibilized LDPE blend films.

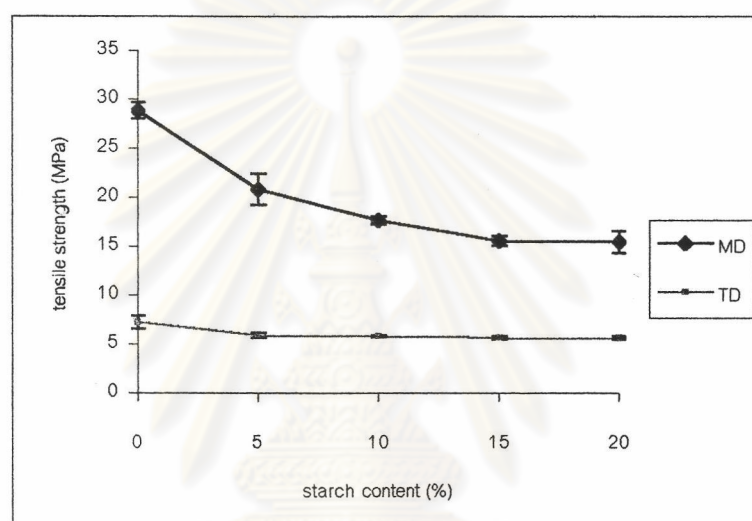


Figure 4.15 Tensile strength of LDPE/starch blends at different direction.

Obviously, as would be expected, the tensile strength in the machine direction (MD) was higher than that in the transverse direction (TD). This result suggests that the LDPE/starch blends have higher orientation in the MD thus making the film stronger in this direction. Also, as mentioned earlier, the tensile strength of blends decreased with increasing starch content in particular in the machine direction. For the transverse direction, starch content seems to have no effect on the tensile strength except at 5% starch, where the tensile strength decreased slightly and remained constant afterwards.

Figure 4.16 shows the comparison of the elongation at break of the LDPE blend films as a function of starch content in both directions.

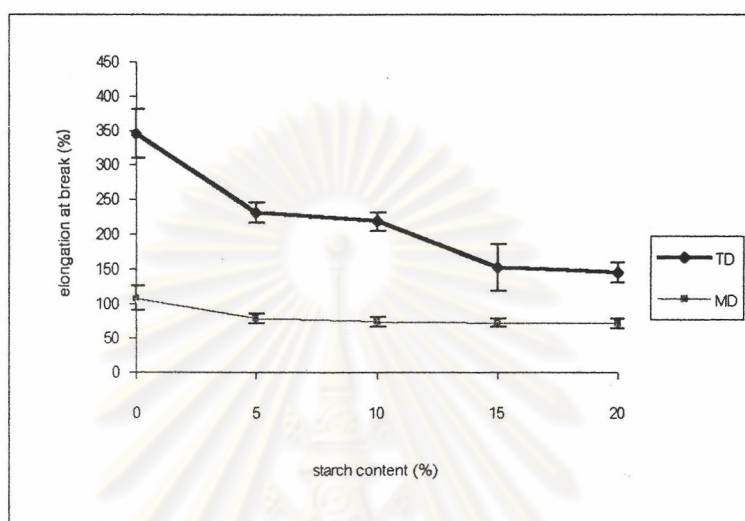


Figure 4.16 Elongation at break of LDPE/starch blends film at different direction.

Opposite to the tensile strength, the elongation at break of films in TD decreased significantly as the starch content increased. There is however no effect from the amount of starch in the MD. All the blend films had lower extension than the pure LDPE film. This decrease in TD is due to the weak interfacial bonding between the starch particles and the LDPE matrix. This poor interfacial adhesion causes almost immediate separation of the matrix from the particles.

The elongation at break in the TD was higher than in the MD at the same amount of starch confirming that the orientation is parallel to the MD direction.

4.3.2 Effect of Compatibilizer

Starch contains hydroxyl groups in its molecules and as a consequence it is a polar hydrophilic polymer. On the contrary, LDPE is a non – polar hydrophobic polymer. Because of the different polar character of the two polymers, they are immiscible. As a result, LDPE/starch blends have low tensile properties. To increase the interfacial adhesion between the two polymers, the use of a compatibilizer is necessary.

The effect of compatibilizer on tensile strength of blends is presented in Figure 4.17.

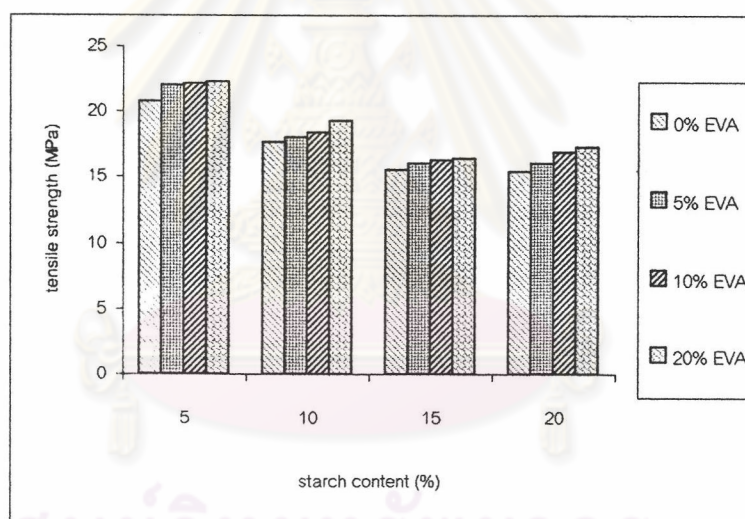


Figure 4.17 Tensile strength of the compatibilized blends with different amounts of EVA.

As expected, the introduction of the compatibilizer into the blends increases the tensile strength compared with the uncompatibilized blends. Among them, the LDPE/banana starch films containing 20% EVA gave the highest tensile strength. This result is the same for every blend compositions. As discussed earlier, it is well known that the tensile properties in polymer blends are partly affected by the interfacial adhesion between the polymers. LDPE and starch are incompatible and their

interfacial adhesion is very poor. The addition of EVA into the blends is expected to reduce the interfacial energy and thereby increase the interfacial adhesion. As a result, these compatible blends showed improved tensile strength compared to those containing no compatibilizer.

Similarly, as clearly shown in Figure 4.18, the elongation at break of blends increases with increasing amount of EVA. It is remarkable that all the blends with 20% of EVA had higher elongation at break than starch blends containing no compatibilizer. This behavior might be due to the higher elongation at break of EVA (700%) [34] and the interfacial adhesion improvement between two phases caused by EVA.

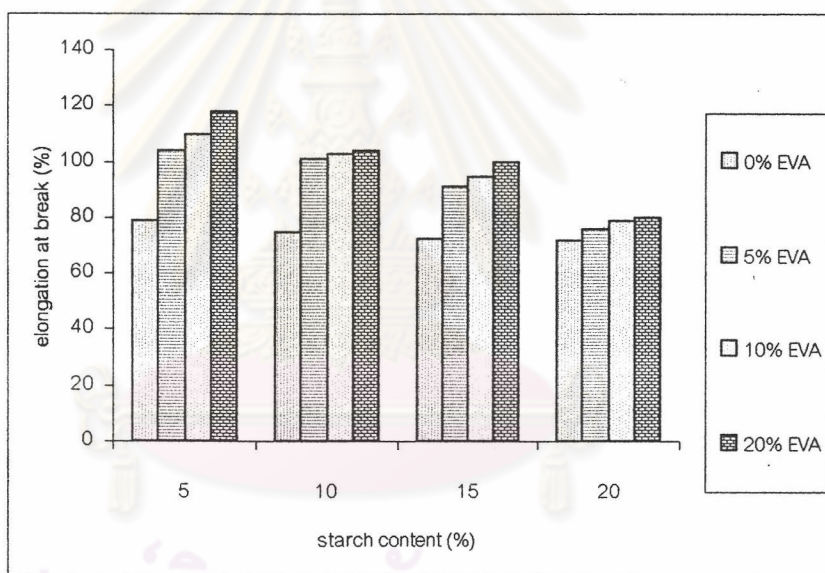


Figure 4.18 Elongation at break of the compatibilized blends with different amounts of EVA.

4.4 Evaluation of the Degradation

Biodegradation of LDPE/banana starch blends was performed by activated sludge and enzymatic treatment. The samples in the form of thin film were cut into the size of 1.5cm x 20cm. The dried samples were weighed and then placed in the activated

sludge and enzyme solution for 8 weeks and 8 hours, respectively. The biodegradation processes were followed by periodically measuring the changes in physical appearance, tensile properties and weight loss as follow:

4.4.1 Activated Sludge Degradation

After being subjected to the activated sludge, samples were removed for testing every 2 weeks. Visual inspection and SEM were used to observe the changes in physical appearance of the film surface. In addition, biodegradation rate was also evaluated by measuring weight loss and tensile properties of the films.

4.4.1.1 Scanning Electron Microscopy (SEM)

In starch/synthetic polymer, it is essential to study the morphology of the final product because most of their properties, especially their mechanical properties, depend on their morphology (phase structure) and the interfacial adhesion between starch and synthetic polymers. In this work, SEM was employed to study the blend morphology of the film surface. In addition, it was used to examine the interfacial adhesion between banana starch and LDPE by observing the fractured surface of the films. Electron micrographs were obtained from samples collected before and after biodegradation testing in activated sludge. The effect of filler loading and compatibilizer was then investigated.

Before Treatment

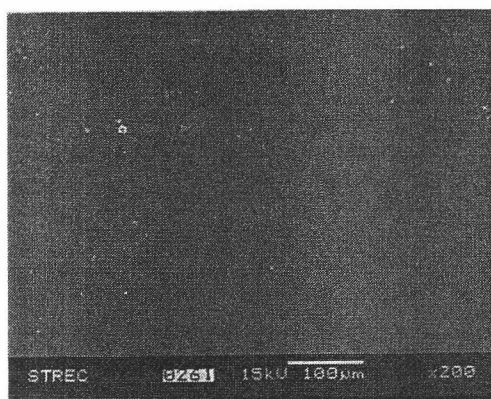
4.4.1.1.1 Effect of Filler Loading

Figure 4.19 shows the surface morphology of pure LDPE and LDPE blend films. Obviously, pure LDPE film had a smooth surface, whereas the presence of starch granules made the blend films surface rougher. As starch content increased, there was more starch on the surface of films. Since the film thickness is about 0.09 mm. and the size of banana starch granules varies from 5 μm to 45 μm in diameter. The closer in the thickness of film and diameter of starch, there is a chance for starch granules to be on the surface.

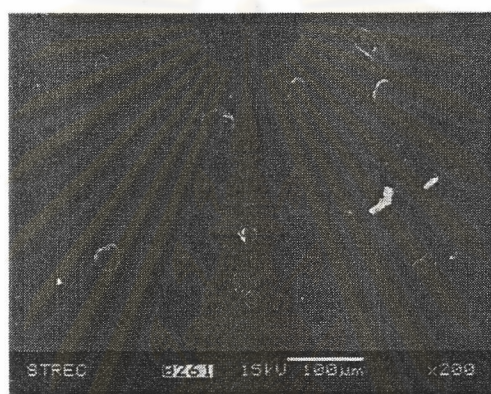
4.4.1.1.2 Effect of Compatibilizer

The effect of compatibilizer on the compatibility of LDPE/starch blends was examined by SEM, as shown in Figure 4.20. However, the compatibility of the blends is difficult to be detected; there is no significant difference among the blends. Thus, fractured surface of the blend films, with and without a compatibilizer, was further investigated, in order to clarify the effect of the compatibilizer. The morphology of the fractured surfaces of 20% starch blends containing no EVA and 20% EVA is presented in Figure 4.21.

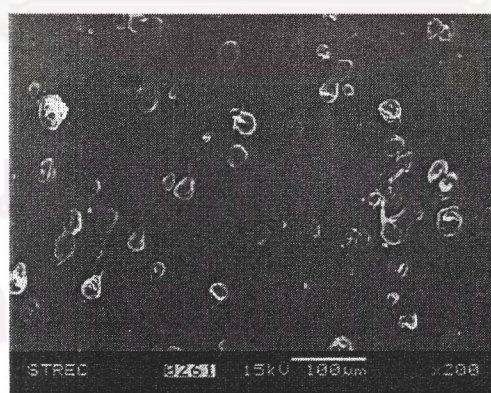
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(a)



(b)



(c)

Figure 4.19 SEM micrographs of LDPE/starch (a) 100/0, (b) 95/5 and (c) 80/20.

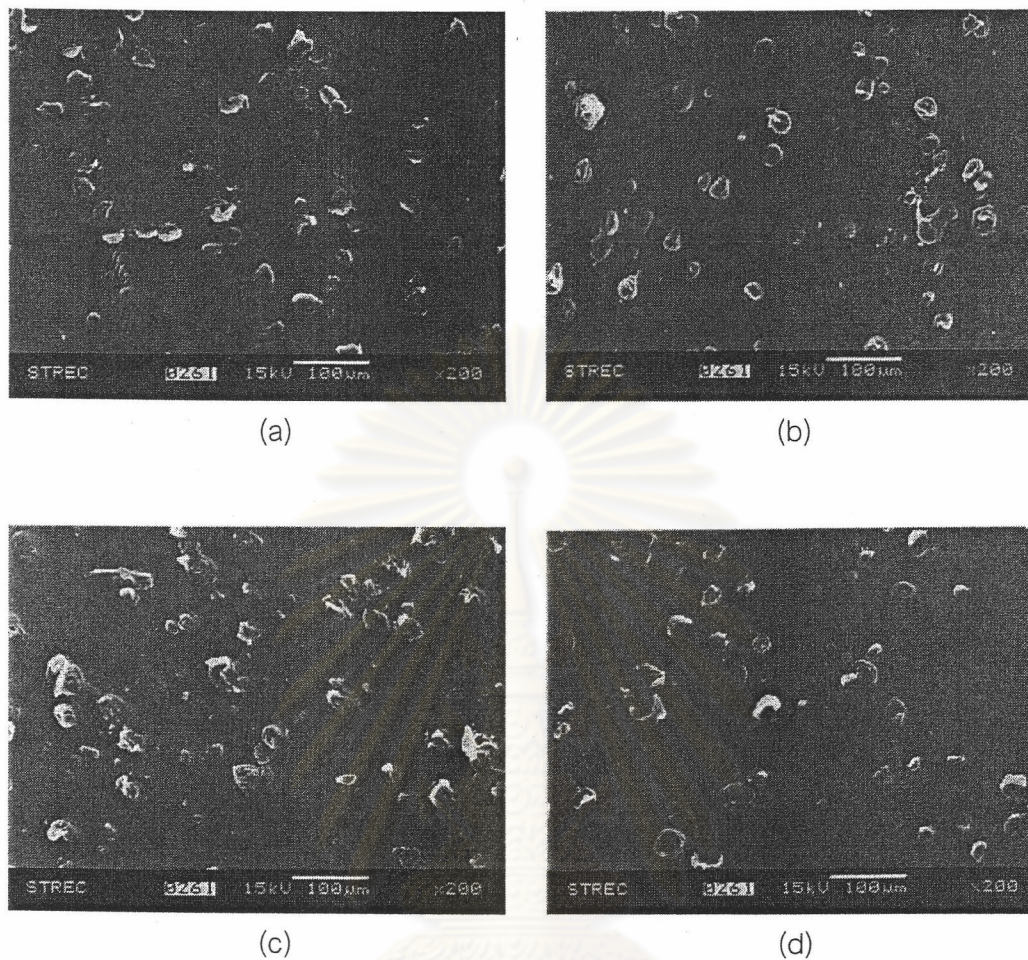
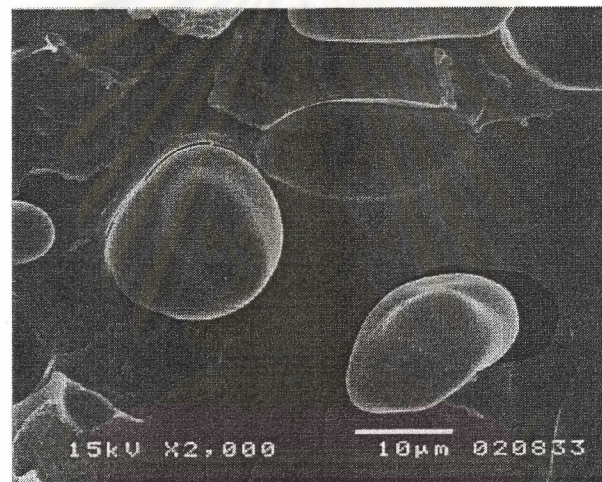


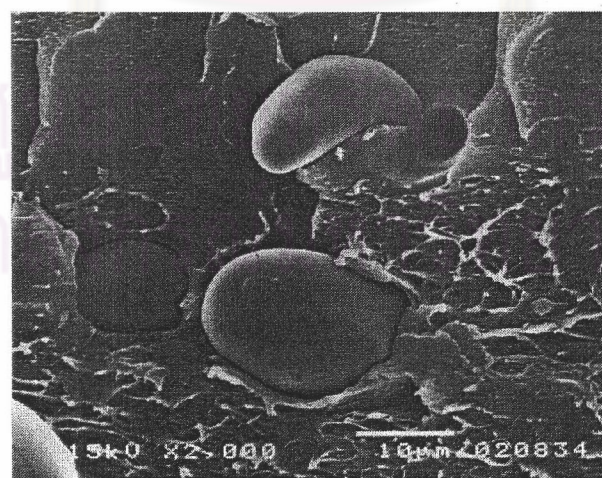
Figure 4.20 SEM micrographs of 20% starch blends of (a) uncompatibilized blend and blends compatibilized with (b) 5% wt, (c) 10% wt and (d) 20% wt EVA.

As the concentration of EVA increased, the dispersion of starch particles became more uniform and showed improved adherence to LDPE. For LDPE/starch blends containing no EVA, the dispersion of the starch particles was observed to be without an adherence to the matrix. However, with increasing EVA content, the particles were dispersed within the matrix with improved adhesion for the LDPE. Hence, the higher the percentage of EVA, the better the compatibility of the two phases. Blends with 20% EVA showed more firmly embedded particles that cannot be pulled out easily during the fracture process. In contrast, the 0% EVA blend is seen that the cavities were created because of the easy pulling of particles. In other words, there was poor

adhesion between the starch and LDPE in uncompatibilized blends, as demonstrated by the sharp interface between starch granules and the continuous phase. Whereas in the case of compatibilized blends, there is more diffused interface or a co-continuous phase formation. Another distinct difference is that the uncompatibilized blend showed a clear-cut fractured surface, while the compatibilized blend exhibited rough fractured surfaces. These results implies that the interfacial bond strength of the starch/LDPE blends was improved by the addition of EVA as evidenced by the enhanced tensile properties compared to those containing no compatibilizer. This indicates that the role of a compatibilizer is primarily to reduce the interfacial energy and therefore increase the interfacial adhesion.



(a)



(b)

Figure 4.21 SEM micrographs of banana starch/LDPE of (a) uncompatibilized blend and (b) compatibilized blend with 20%wt EVA.

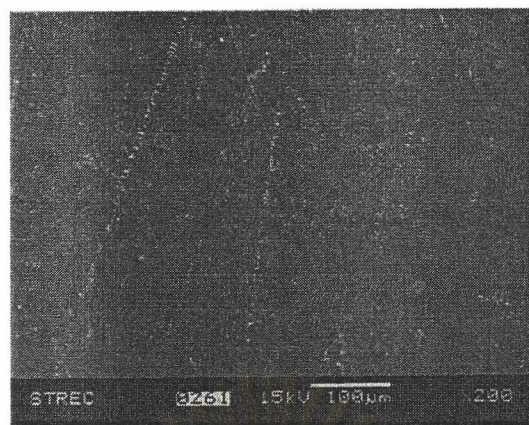
After Treatment

The change in surface morphology and physical appearance of LDPE/starch blends after being exposed to the activated sludge for 2 months was investigated in terms of the amount of starch, the effect of EVA and the duration time for biodegradation test.

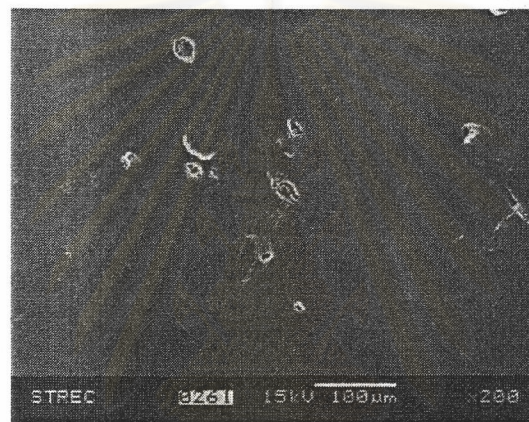
4.4.1.1.3 Effect of Filler Loading

As the starch content increased in the system, more starch granules were viewed on the surface, as seen in Figure 4.22. After 2 months of exposure, pure LDPE film showed no sign of biodegradation. In contrast, the LDPE films containing 5% and 20% starch were obviously degraded as evidenced by the existence of very tiny holes in the LDPE matrix.

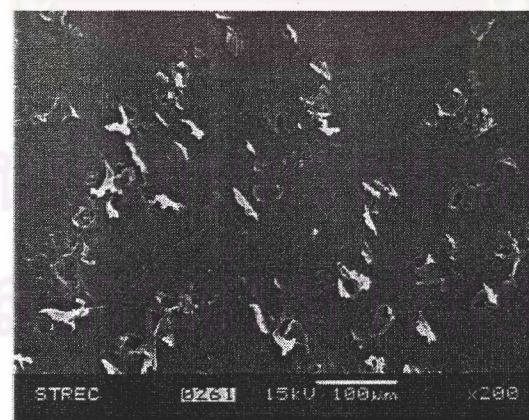
The presence of many minute holes confirmed the result that banana starch was removed from the LDPE matrix after biodegradation. This starch removal was probably due to the loss of partially exposed starch granules near the surface of the films that were not completely covered with LDPE. In other words, these destroyed areas are the result of the initial biodegradation of starch. Obviously, as the amount of starch increased, the number of holes increased. This is because there are more sites on the film surface that can be attacked by microorganisms. Thus, these starting points of degradation, provide greater surface areas for oxidative breakdown of the polymer, followed by the microbial digestion of the degradation products.



(a)



(b)



(c)

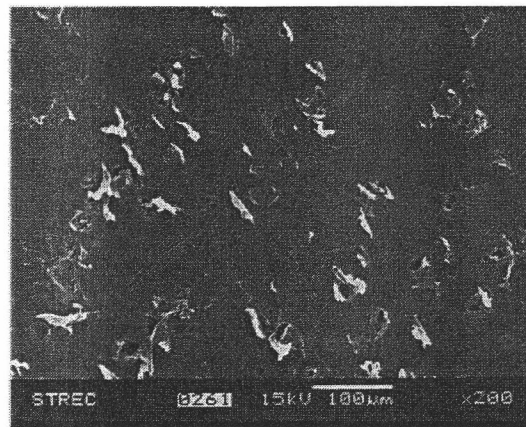
Figure 4.22 SEM micrographs of (a) pure LDPE and LDPE blends with (b) 5% starch and (c) 20% starch after 2 months of exposure in activated sludge.

4.4.1.1.4 Effect of Compatibilizer

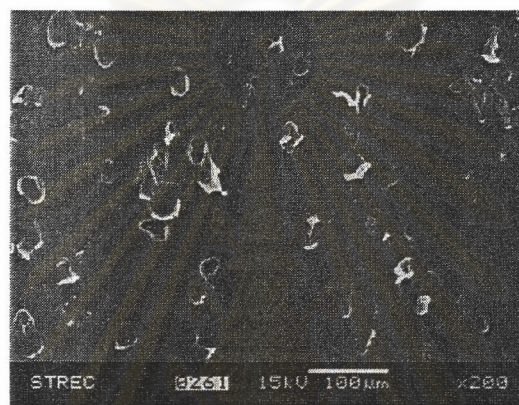
As shown in Figure 4.23, it is very difficult to distinguish the difference between uncompatibilized and compatibilized LDPE blend films. This effect can be investigated by examining the fractured surface of the films, as previously explained. In uncompatibilized blends, starch granules are merely encapsulated within the LDPE matrix without any bonding. Therefore, there is a gap between a starch particle and the LDPE matrix. This gap results in an increase in porosity of the LDPE matrix, which can then easily allow the microorganism attacking throughout the inner part of the LDPE. For compatibilized blends, the interfacial adhesion between two phases causes the difficulty in removing starch granules from the films. As a result, smaller size and less number of holes are expected, leading to greater tensile properties even after biodegradation test, as will be explained in the next section (4.4.1.2).

4.4.1.1.5 Effect of Exposure Time

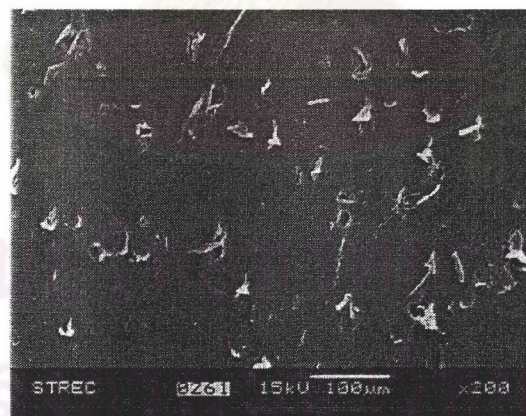
Figure 4.24 shows the progress of biodegradation rate as a function of exposure time. Before treatment, starch granules can be seen on the film surface. However, after only 2 weeks of exposure these granules started to disappear because microorganisms consumed them. This left a film with a surface full of cavities, which became more abundant as the time increased. After 2 months, there were numerous holes in the film corresponding in size to that of the starch granules. These film imperfections led to deterioration in mechanical properties and made the film fragile, as will be discussed shortly.



(a)

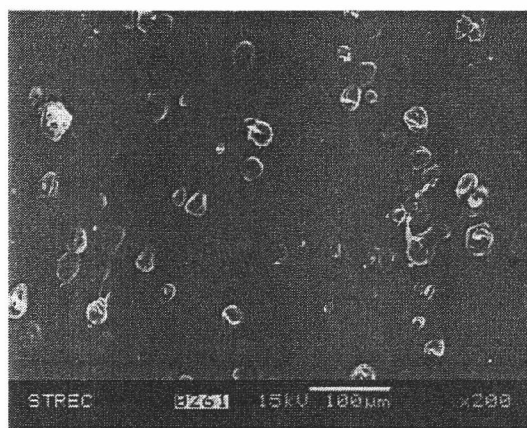


(b)

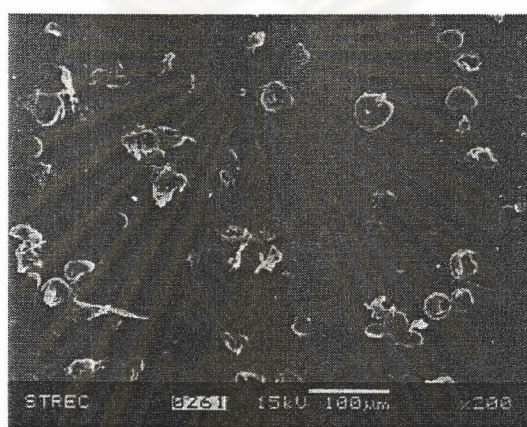


(c)

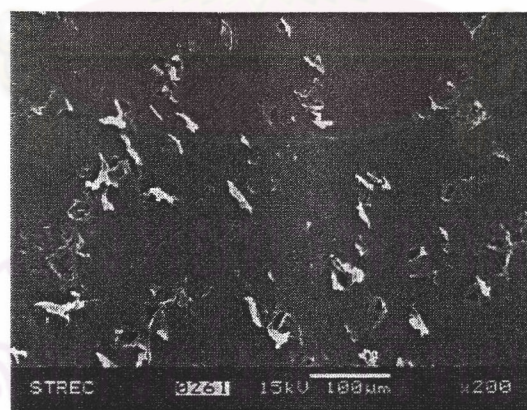
Figure 4.23 SEM micrographs of LDPE/starch blends (80:20 w/w) after being subjected to activated sludge for 2 months: (a) uncompatibilized blends and blends compatibilized with (b) 10wt% and (c) 20wt% EVA.



(a)



(b)



(c)

Figure 4.24 SEM micrographs of LDPE/starch blends with 20wt% starch during exposure in activated sludge for (a) 0 week, (b) 2 weeks and (c) 8 weeks.

4.4.1.2 Tensile Properties

One of the most common methods for assessing the degradation of plastic materials is by measuring change in their tensile properties. The tensile properties of the LDPE/starch blends prior to subjecting in the activated sludge has already presented in section 4.3. Thus, the following results are of the tensile properties after biodegradation test in activated sludge.

4.4.1.2.1 Effect of Filler Loading

Because of the holes created on the surface of the films by starch consumption, Figure 4.25 shows that the tensile properties of the LDPE/starch films decreased with the biodegradation time. This was true for every blend compositions. The increase in starch content decreased the tensile properties as a function of time as well. Indeed, such a decrease was observed in the tensile strength as well as in the elongation at break. As can be seen, there is a continuous reduction in tensile strength and elongation at break as the time of exposure increases. This behavior supports the results from SEM analysis. As mentioned earlier in Figure 4.22, the number of holes or voids increased as a function of starch loading. It is well known that voids, holes, or cracks, even at the microscopic scale are defects and the main reasons for failure of the films. In addition, starch granules cannot bear any load, which then behave as a weak point. As a result, the tensile strength and elongation at break of LDPE/starch blend films decreased as increasing starch content.

4.4.1.2.2 Effect of Compatibilizer

Figure 4.26 shows the plot of tensile strength and elongation at break as a function of time and compatibilizer content. Similar to the films before being subjected to activated sludge, the compatibilized blends also exhibited an increase in the tensile strength compared to the uncompatibilized ones. But as the exposure time

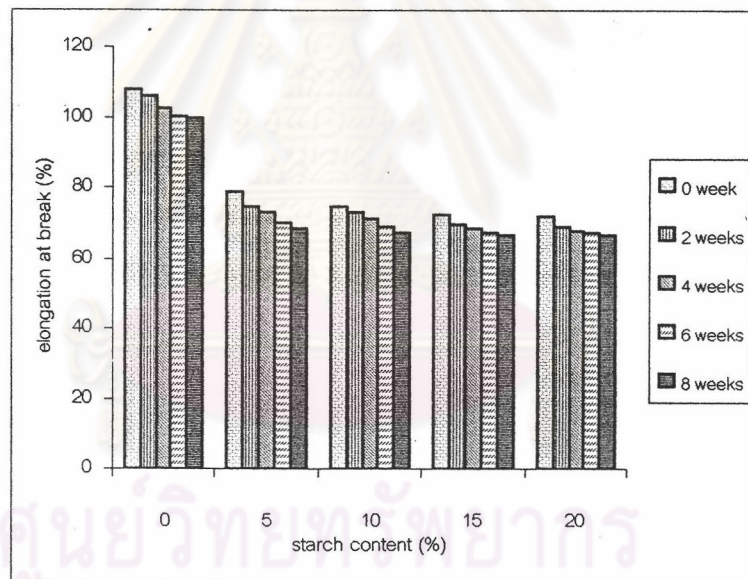
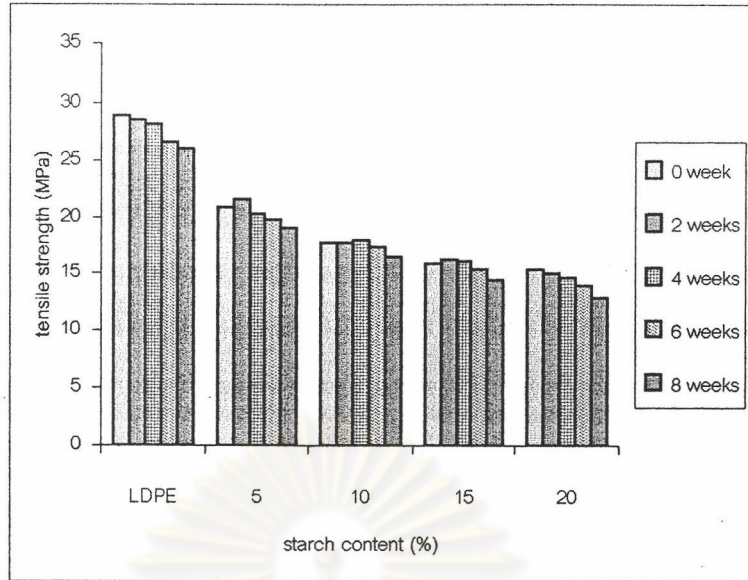


Figure 4.25 Tensile strength and elongation at break of uncompatibilized blend during exposure in activated sludge.

increased, the tensile strength decreased gradually. The trend is similar to that of the elongation at break.

These results are in good agreement with the SEM micrographs shown in Figure 4.21 and Figure 4.24. Because starch granules of the uncompatibilized blend had no interfacial adhesion with LDPE with respect to the compatibilized blends, the uncompatibilized blends had more surface area of starch to be attacked by microorganisms than the compatibilized blends. Therefore, the uncompatibilized blends have more microscopic holes randomly scattering in the film than the compatibilized blends, as the time of exposure increases (Figure 4.24). Consequently, the tensile strength and elongation at break of uncompatibilized blends were lower than the compatibilized blends. For example, from Figure 4.26, after 8 weeks of exposure, the tensile strength of 20% starch/LDPE blend film without EVA is about 13 MPa, whereas that of the compatibilized LDPE blend film with 20% EVA is 14.5 MPa. Similarly, at the same amount of starch and time of exposure (8 weeks), the elongation at break of the films containing no EVA and with 20% EVA is about 66% and 74%, respectively.



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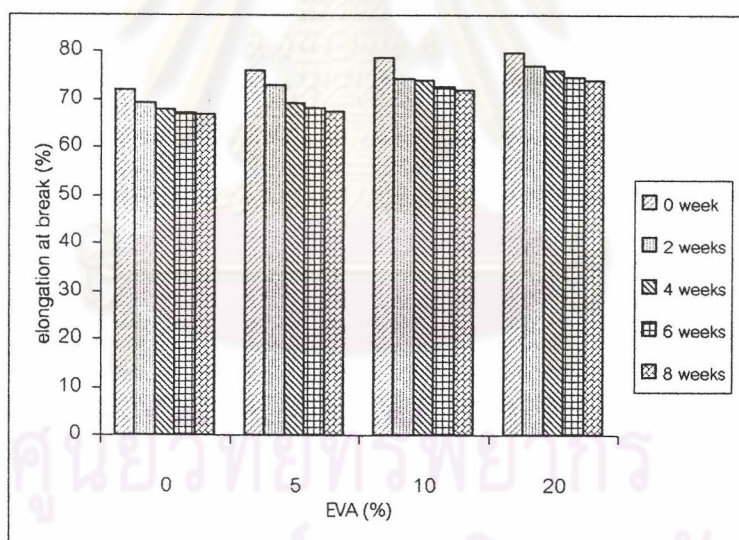
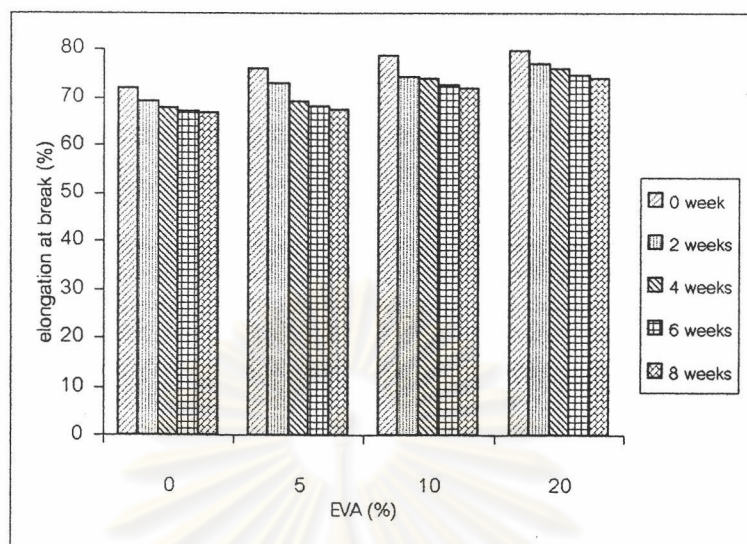


Figure 4.26 Tensile strength and elongation at break of 20% starch films compatibilized with various amount of EVA during exposure in activated sludge.

4.4.1.3 Weight Loss

The most common and direct method to determine the biodegradability of biodegradable films is the weight loss measurement. Although it is quite tedious, its easy and simple make this technique widely used.

4.4.1.3.1 Effect of Filler Loading

Biodegradation of LDPE/starch blends has shown that microbes consume starch, creating pores in the plastic that increase the surface area of the LDPE matrix and provide opportunities for the degradation. Starch consumption by microorganisms results in weight loss of the blends during activated sludge exposure with different amounts of starch and 0% EVA, as seen in Figure 4.27.

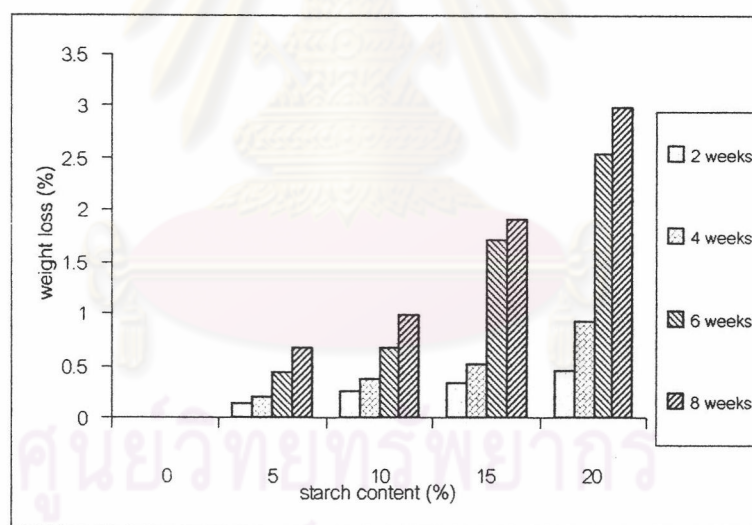


Figure 4.27 Effect of starch content and exposure time on the weight loss of uncompatibilized LDPE blend films in activated sludge.

It can be seen that the LDPE showed no biodegradation during treatment in activated sludge. Thus the weight loss in LDPE/starch film was contributed by starch reduction only. For the blends with low amount of starch e.g. 5% and 10% wt,

the weight loss was very small and even after 2 months of activated sludge their weight loss did not exceed 0.66% and 1.0%, respectively. The biodegradation rate increased for the blend with 15% starch, whereas in the blend with 20% starch there was a rapid weight loss even after the first month. These results indicate that the destruction of the surface depends on the content of starch.

For blends containing low amount of starch, the starch was apparently almost completely covered by LDPE and thus not accessible to microorganism. It must be noted that the starch diameter is about one-fourth of the film thickness and hence microorganisms will consume only the starch that is located at the surface of film. On the contrary, in blends with higher starch content, starch is more exposed and as result, a greater portion of it is consumed by microbes.

4.4.1.3.2 Effect of Compatibilizer

In blends containing the same amount of starch but different amounts of compatibilizer, when the content of EVA increased, the weight loss of the blends exhibited an inverse relation to EVA content, as can be seen in Figure 4.28. This inhibiting effect of EVA copolymer may be due to the hydrogen bonding between the carbonyl groups of EVA and hydroxyl groups of starch. However, as the degradation time increased, percentage of weight loss increased significantly. For example, at 5% EVA content, weight loss increased up to 2.5% from its initial weight after being exposed in activated sludge for 2 months. In fact, this is 5 times higher than that of the same sample at 2 weeks of exposure. These results are in good agreement with the tensile properties and SEM micrographs as already explained.

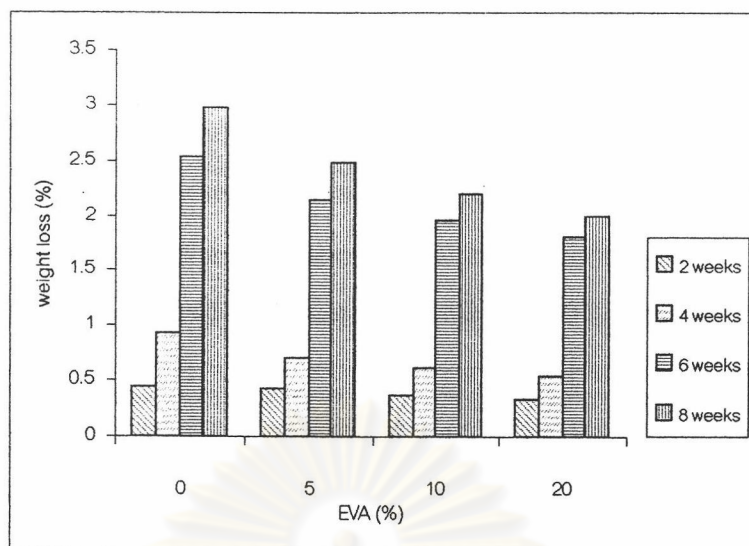


Figure 4.28 Effect of compatibilizer and exposure time on the weight loss of 20% starch/LDPE films in activated sludge.

4.4.2 Enzymatic Degradation

Samples were cut into 1.5 cm x 20 cm and placed in enzyme solution. This study used Termamyl which is an enzyme α -amylase solution. Samples were removed for testing at every 2 hours for 8 hours. After removal, samples were then weighed to determine the weight loss and observed the changes in film surfaces using SEM.

4.4.2.1 Weight Loss

The percentage of weight loss was evaluated as a function of banana starch and EVA contents. The rate of biodegradation of films in enzyme solution and activated sludge was also compared as follow:

4.4.2.1.1 Effect of Filler Loading

Figure 4.29 shows the weight loss of the uncompatibilized blends at various amounts of starch with the exposure time in enzyme. It shows that the percentage of weight loss increased as time and starch content increased. Indeed, such an increase was observed in both enzyme treatment as well as in the activated sludge.

These data clearly indicates that the biodegradability of the blends was enhanced by incorporation of the higher starch content since starch giving rise to an increase in the surface area and a concomitant increase in the rate of degradation.

Comparing between these two methods of biodegradation, surely as would be expected the degradation rate of the LDPE/starch films in enzyme was much faster than that in activated sludge. For instance, it took only 4 hours for the film containing 20% starch to loss about 1% of it initial weight in enzyme solution, whereas it lasted about a month for the film in activated sludge to loss about the same weight. These results can be explained that the enzyme α - amylase is the specific kind of enzyme that can be used to degrade the starch. However, there are many kinds of enzymes, not only enzyme α - amylase, producing from bacteria or microorganisms in activated sludge. Therefore, the concentration of enzyme α - amylase in activated sludge should be less than that in enzyme solution. As a result, it took longer time for the LDPE/banana films to be degraded in activated sludge.

4.4.2.1.2 Effect of Compatibilizer

The weight loss of blends is plotted in Figure 4.30 as a function of EVA content. The weight loss measurements suggest that the compatibilized blends have slightly lower degradation rates than those of the uncompatibilized ones. Furthermore, in compatibilized blends, the biodegradation rate decreases as the

content of EVA increases. These results were in the same trend as of the activated sludge degradation.

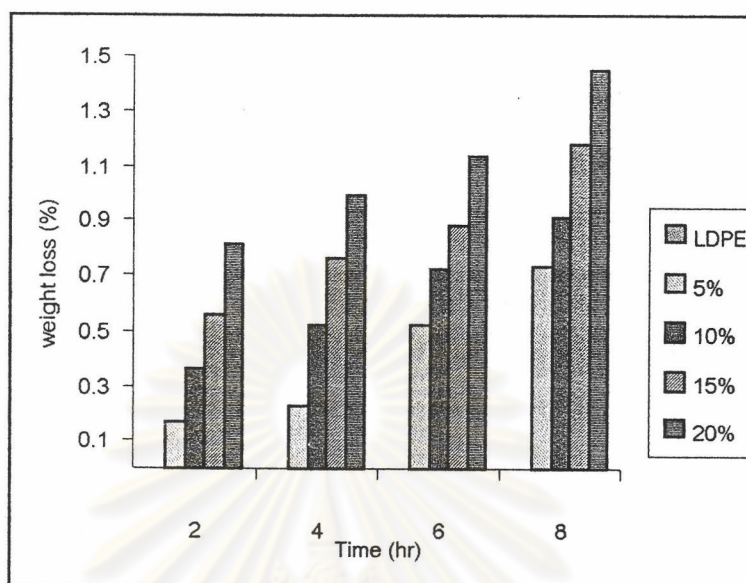


Figure 4.29 Effect of starch content and exposure time on the weight loss of uncompatibilized LDPE blend films in enzyme solution.

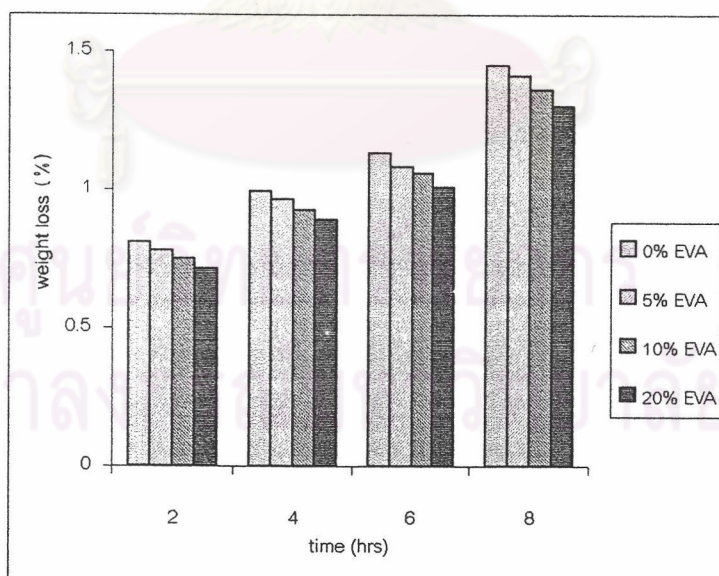
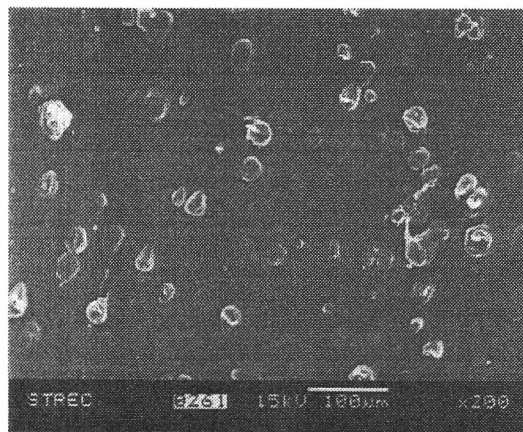


Figure 4.30 Effect of compatibilizer on rate of biodegradation of 20% starch/LDPE films in enzyme solution.

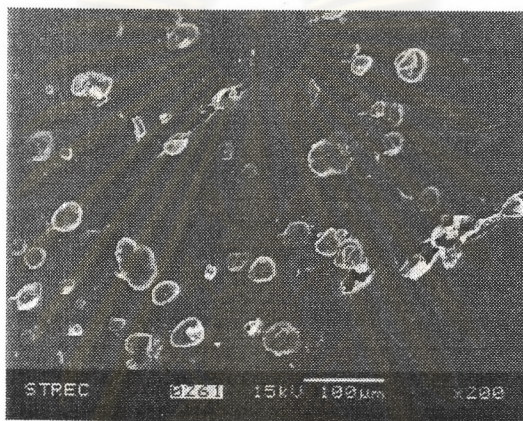
4.4.2.2 Scanning Electron Microscope (SEM)

To confirm the result of the weight loss, the biodegraded samples were also studied by SEM. The micrographs for the uncompatibilized blend containing 20% starch took before and after enzyme treatment are presented in Figure 4.31. The undegraded film is characterized by a surface incorporating the starch granules. The empty craters resulted from the removal of starch granules that were accessible to α - amylase activity were seen in the biodegraded films, i.e., after 2 or 8 hours of exposure. After exposure in enzyme, the starch that is covered with LDPE remains intact. However, the film was already beginning to show signs of degradation after enzyme exposure of only 2 hours. After 2 hours, the surface of film exhibit voids left from the preferential degradation of the starch granules. The consumption of the starch is continued until the 8th hour, relatively large holes appear, suggesting extensive starch consumption. The SEM micrograph evidence suggests that degradation of the blend occurred gradually over the surface.

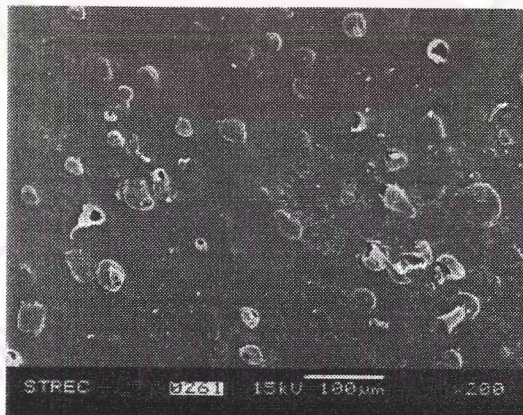
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(a)



(b)



(c)

Figure 4.31 SEM micrographs of the surface of 20% starch/LDPE films (a) before, (b) 2 hours and (c) 8 hours enzyme treatment.