CHAPTER IV

RESULTS AND DISCUSSION

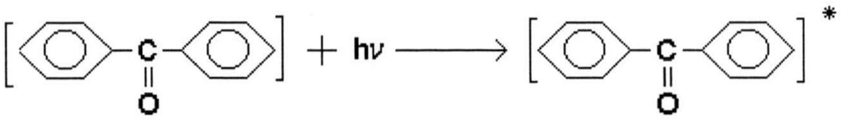
4.1 Selection of Photosensitizer

Photosensitizer was used to accelerate the photodegradation of starch – based LDPE films. Two kinds of photosensitizers, benzophenone and ZnO, were blended with pure LDPE using a twin screw extruder. The blended films were then prepared by a chill roll cast film. Specimens were cut from these films and tested for their photodegradability by outdoor exposure for 4 months. Evaluation of photodegradation was followed by measuring the changes in carbonyl index and tensile properties of the samples. The most potential photosensitizer was selected to further study in terms of the effects of its concentration on the photodegradability of the pure and blended LDPE films by both outdoor exposure and accelerated exposure.

4.1.1 Carbonyl Index

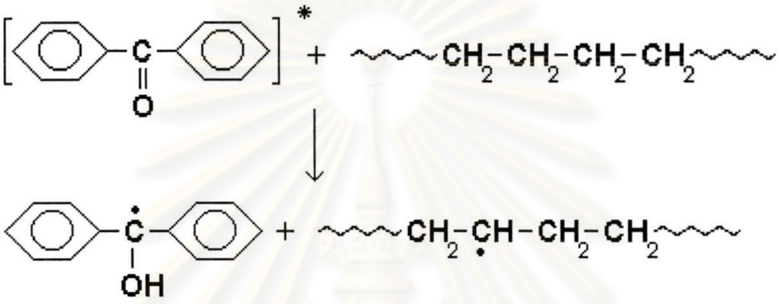
Figure 4.1 shows the IR spectra of LDPE, LDPE/1%benzophenone and LDPE/1%ZnO after 3 months outdoor exposure. For the LDPE films containing two different kinds of photosensitizer, the effect of photosensitizer on carbonyl index as a function of exposure time is demonstrated in Figure 4.2. The data show that the carbonyl index increased as a function of exposure time. The LDPE film containing 1%benzophenone shows highest in photosensitizing activity on photodegradation. In contrast to LDPE/1%ZnO blend film, there is small change in carbonyl index compared to pure LDPE film. The addition of benzophenone can increase the carbonyl index due to the following mechanism:

1. Benzophenone absorbs UV light and is excited into the excited state

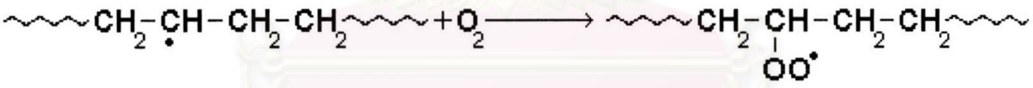


benzophenone　　benzophenone in excited state

2. Benzophenone in excited state abstracts H-atom from PE and forms PE free radical.

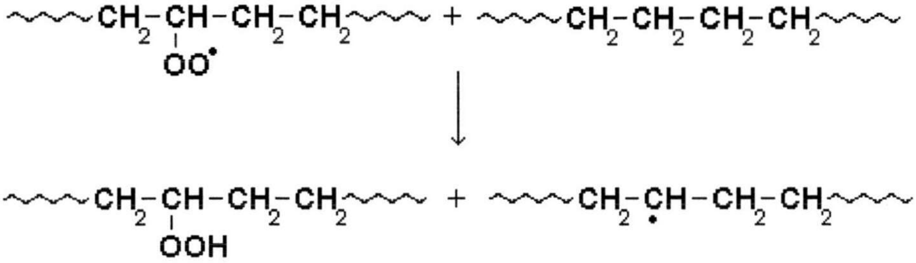


3. LDPE free radical reacts with oxygen and then forms peroxide radical (ROO$^\bullet$).



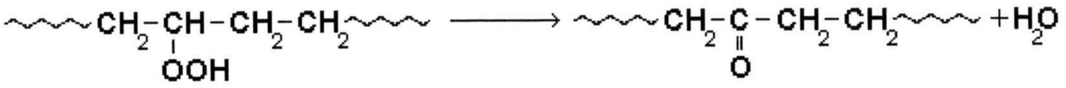
LDPE free radical　　peroxide radical

4. Peroxide radical abstracts H-atom from another polymer molecule and forms hydroperoxide (ROOH)



hydroperoxide

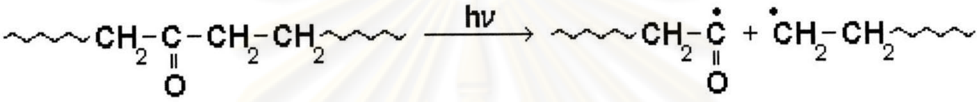
5. Hydroperoxide decomposes to PE molecule with carbonyl group



$$\sim\sim CH_2-\underset{OOH}{CH}-CH_2-CH_2\sim\sim \longrightarrow \sim\sim CH_2-\underset{O}{\overset{}{C}}-CH_2-CH_2\sim\sim + H_2O$$

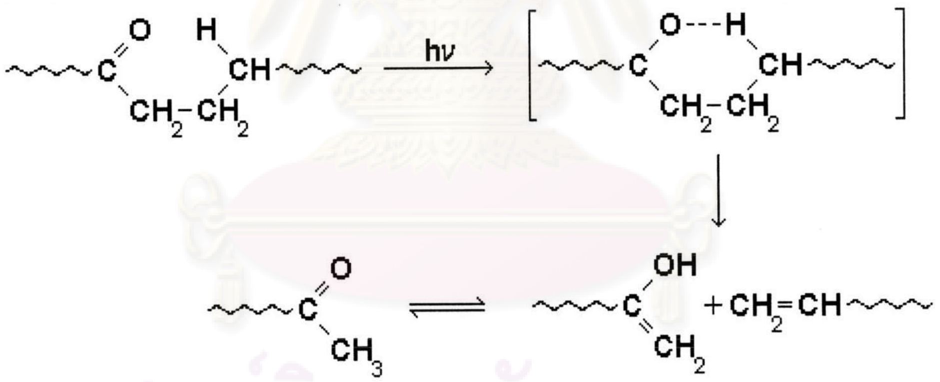
6. Then, the PE molecule with carbonyl group decomposes by Norrish type I or Norrish type II process.

Norrish type I



$$\sim\sim CH_2-\underset{O}{C}-CH_2-CH_2\sim\sim \xrightarrow{h\nu} \sim\sim CH_2-\underset{O}{\dot{C}} + \dot{C}H_2-CH_2\sim\sim$$

Norrish type II



Thus, as clearly seen from the above mechanism, the increase in carbonyl index in PE chain is resulted from the increase in the amount of small fragments of PE chains with carbonyl group. This mechanism makes polymer chain shorten and at the same time decreases molecular weight and tensile properties of polymer.

The results are in the same trend as those reported by Ferguson et al [7]. In their work, carbonyl index was found to increase in LDPE films containing 0.1 wt% ferric stearate and 0.25 wt% TiO_2. After 1 month of accelerated exposure with medium pressure mercury fluorescent lamp, the carbonyl index of LDPE/0.1%ferric stearate and LDPE/0.25%TiO_2 was 0.62 and 0.33, respectively. Similarly these result indicated that ferric stearate was more effective as a photosensitizer than TiO_2. Only 0.1% ferric sterate even resulted in greater value of carbonyl index than the film with 0.25% TiO_2.

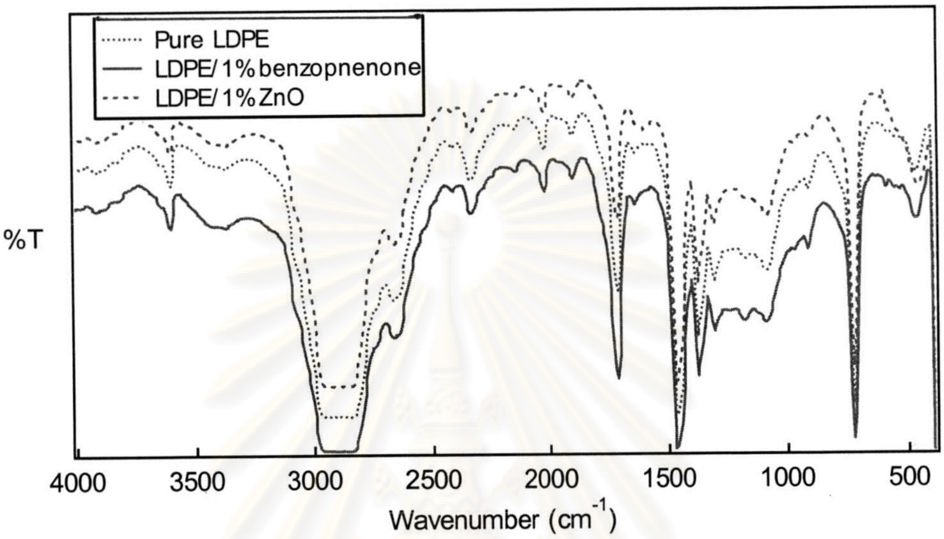


Figure 4.1 Infrared spectra of pure LDPE, LDPE/1%benzophenone, and LDPE/1%ZnO after 3 months outdoor exposure

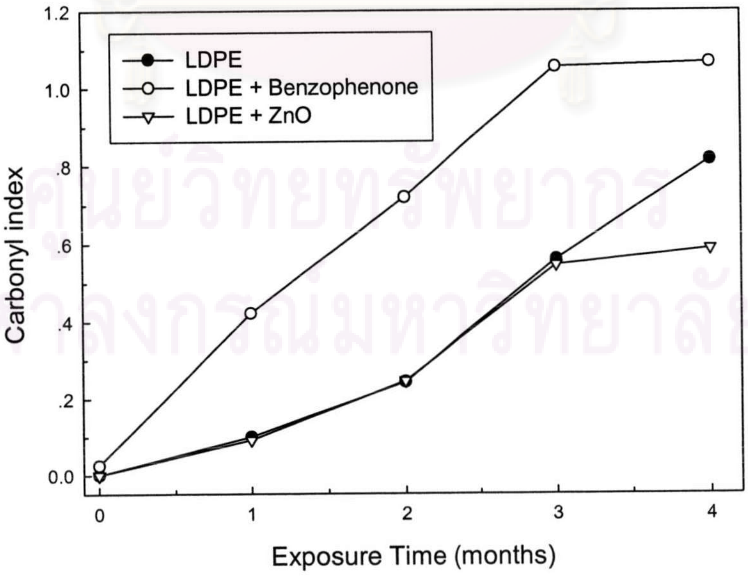
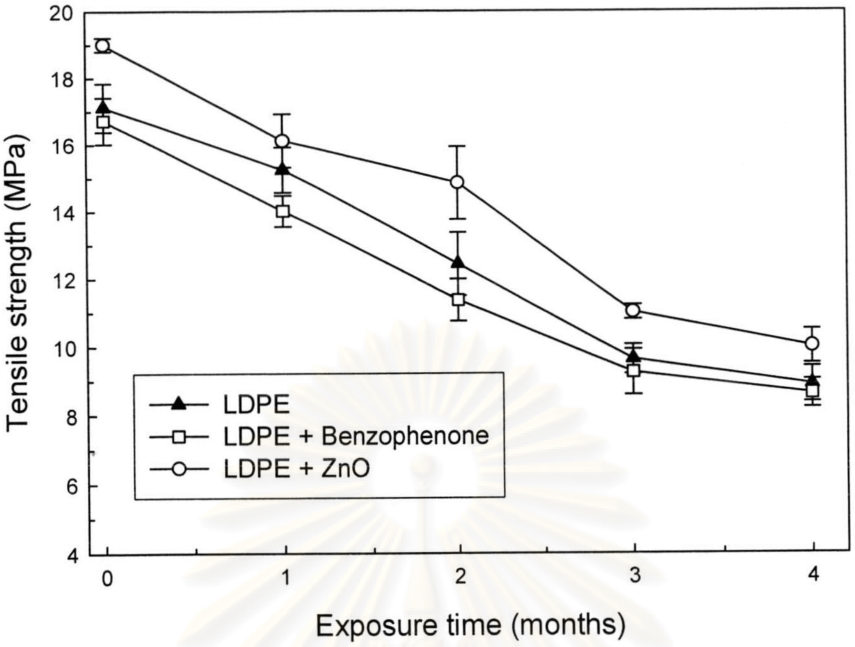


Figure 4.2 Carbonyl index of pure LDPE, LDPE/1%benzophenone and LDPE/1%ZnO blend film as a function of exposure time

4.1.2 Tensile Properties

Figure 4.3 displays the tensile properties of pure LDPE, LDPE with 1%benzophenone, and LDPE with 1%ZnO. The tensile strength and elongation at break of all films decreased as a function of exposure time. It can be seen that the tensile strength and elongation at break of the blend film containing 1%benzophenone were lower than those of pure LDPE and LDPE/1%ZnO. LDPE/1%ZnO blend film showed greatest in tensile strength and elongation at break. This might be because ZnO acts as a filler, promoting hardness and strength of LDPE film.

Although the film containing 1%benzophenone had lower in tensile properties than the one with 1%ZnO, benzophenone was found to be an effective photosensitizer since it accelerated the photodegradation reaction of the LDPE film better than ZnO. Therefore, benzophenone was chosen as a photosensitizer in the LDPE/banana starch system.



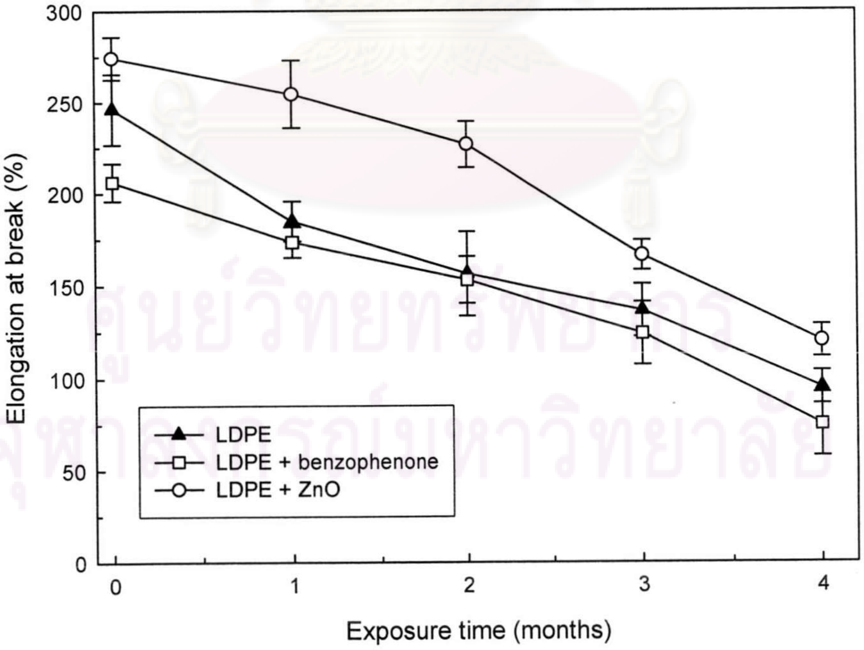


Figure 4.3 Tensile strength and elongation at break of pure LDPE, LDPE/1% benzophenone, and LDPE /1%ZnO during outdoor exposure

4.2 Characterization of LDPE/Banana Starch Film

4.2.1 Chemical Structure

Functional groups of the blend films were characterized using FTIR technique. The IR vibrations of LDPE and starch are given in Table 4.1. Spectra of LDPE, LDPE/starch, and LDPE/starch blend films containing PE-g-MA with or without benzophenone are shown in Figure 4.4 through 4.6.

Table 4.1 Infrared Vibrations and Assignments for Starch/LDPE Blends [15]

Major IR Bands of Components	
Wavenumber (cm^{-1})	Assignment and Remarks
LDPE	
2850, 2920 (s)	C-H stretching
1460, 1471 (m-s)	CH_2 scissor
1377, 1369, 1352 (w)	C-H bending 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)	(O-H) bending (absorbed water)
1462 (m, sh)	CH_2 bending
1445-1325 (m-s)	C-H bending and wagging
1243, 1205 (m-s)	O-H bending
960-1190 (s, br)	C-O strecting (C-O-C and C-O-H)
400-930 (w-m, br)	O-H deformation (broadened by water), ring vibrations

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

The comparison of FTIR spectra of pure LDPE and LDPE/20% starch blend is presented Figure 4.4. The IR spectra of starch filled LDPE film displayed a different band from the pure LDPE spectra. Obviously, due to the presence of starch in the LDPE film, three significant IR bands occurring at 3000 – 3650 cm^{-1}, 1640 cm^{-1}, and 960 - 1190 cm^{-1} are designated as O-H stretching, O-H bending, and C-O stretching, respectively.

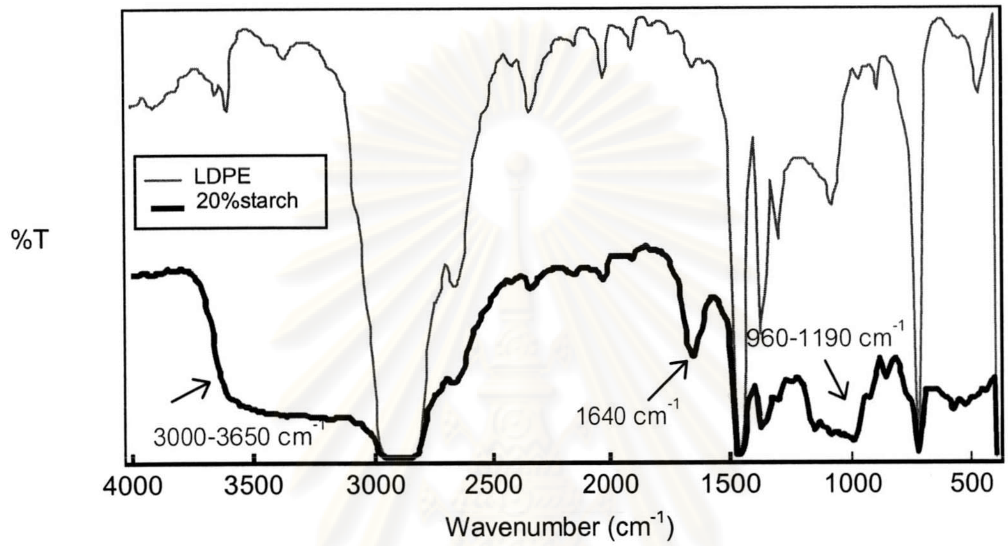


Figure 4.4 Infrared spectra of pure LDPE and LDPE/20% starch blend films

Spectra of the uncompatibilized blend and compatibilized blend with 10%PE-g-MA are demonstrated in Figure 4.5. It can be seen that even after using the PE-g-MA as a compatibilizer, there was no significant different between the two spectra. It was anticipated that PE-g-MA, which contains anhydride group, could develop hydrogen bonds with the hydroxyl groups of starch and form ester groups at 1735 cm^{-1}. However, it must be realized that the concentration of anhydride groups in the blend is very low. For example, for a blend containing 20 wt% starch and 10 wt% PE-g-MA (based on starch), the total concentration of PE-g-MA in the blend film is 2 wt%. Taking into account that PE-g-MA contains 0.5-1 wt% anhydride groups, the total concentration of the later in this blend will not exceed 0.01-0.02 wt%. With such a low concentration, the degree of hydrogen bonding is very limited. Nevertheless, it can still affect compatibilization of the blend films as will be discussed later.

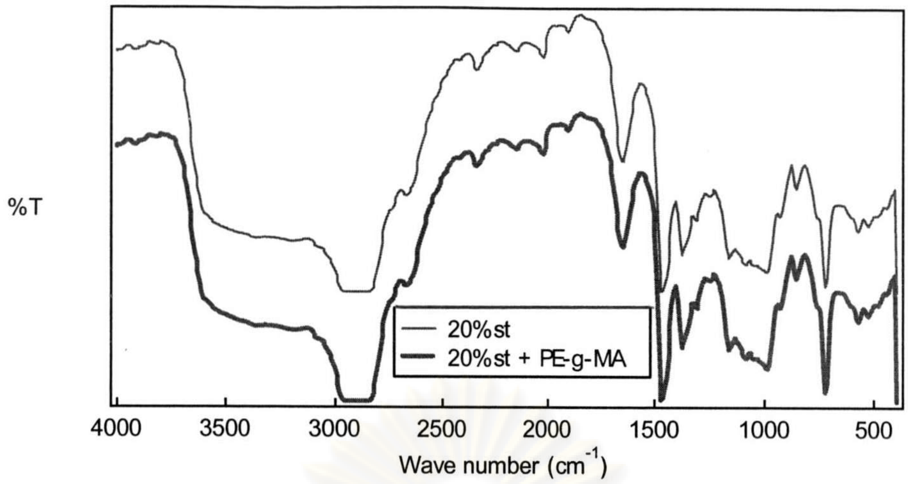


Figure 4.5 Infrared spectra of LDPE/20% starch with and without 10% PE-g-MA

For LDPE /starch blends with and without photosensitizer (1.0% benzophenone), their IR spectra are shown in Figure 4.6. The spectrum of LDPE/starch blend with 1%benzophenone was almost the same as that of the uncompatibilized blend except a tiny peak occurred at 1710 cm^{-1}. A little difference in the blend with photosensitizer is assigned to the carbonyl group (C=O) from benzophenone. Whereas the expected broad band at 3000 cm^{-1} owing to the aromatic groups (=C-H stretching) of benzophenone was coincidently occurred with the broad and intense O-H stretching band of starch molecule.

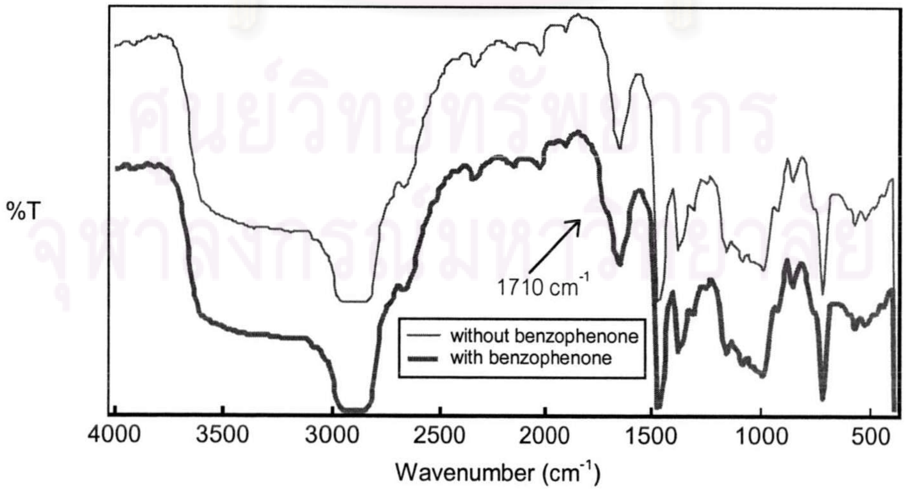
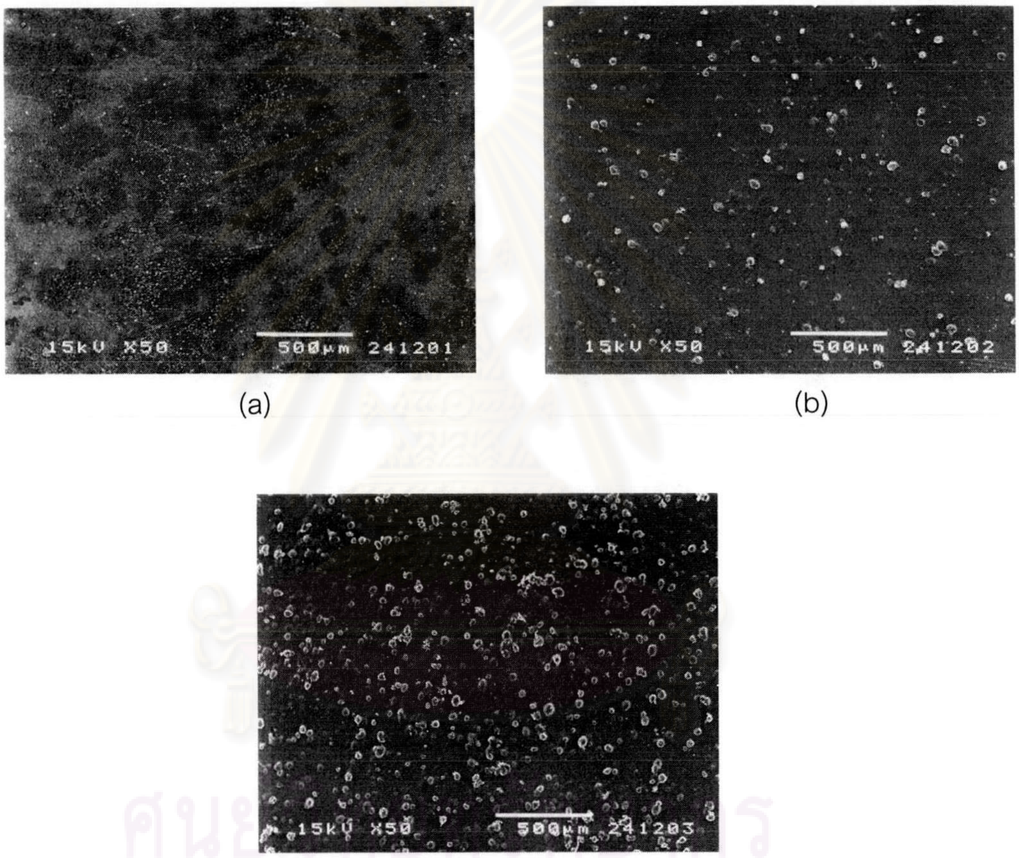


Figure 4.6 Infrared spectra of 20%starch/10%PE-g-MA/LDPE films with and without 1%benzophenone

4.2.2 Morphological Studies

The SEM micrographs of pure LDPE and LDPE/starch blend films are presented in Figure 4.7. Morphology of LDPE surface revealed a uniform continuous matrix, while the presence of starch granules made the blend films surface rougher. Obviously, it can be seen that starch on the surface of film increased with an increasing amount of starch in the blend films.

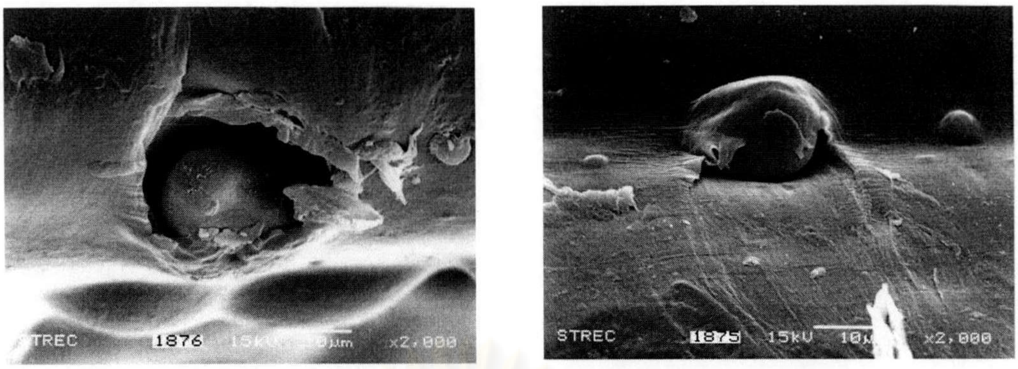


(a) (b)

(c)

Figure 4.7 SEM micrographs of (a) pure LDPE and LDPE blended with (b) 5%starch and (c) 20%starch

LDPE and starch are incompatible and their interfacial adhesion is very poor. Lack of interfacial adhesion leads to a separation between the LDPE matrix and banana starch. Therefore, PE-g-MA was used as a compatibilizer to reduce the interfacial tension and increase the adhesion between two components. This can be verified by the SEM micrographs shown in Figure 4.8.



(a) (b)

Figure 4.8 SEM micrographs of LDPE/starch of (a) uncompatibilized blend and (b) compatibilized blend with 10% PE-g-MA

The morphology of the fractured surface of uncompatibilized blend is different from the blend containing PE-g-MA. The difference between the uncompatibilized blend and compatibilized blend is that the uncompatibilized blend exhibited a gap between starch granule and LDPE matrix, whereas the blend containing compatibilizer showed the bond between starch granule and LDPE matrix. The above results indicate that the addition of PE-g-MA improved interfacial bond strength of LDPE/starch blends. A good compatibility and enhanced adhesion between the two phases was evidenced by the increase in tensile properties of the blend film compared to the uncompatibilized blends, as will be discussed in section 4.3. Conclusively, SEM micrographs ensure the role of a compatibilizer in reducing the interfacial energy and thus promoting the interfacial adhesion between the banana starch phase and LDPE phase.

4.2.3 Thermal Properties

4.2.3.1 Thermogravimetric Analysis (TGA)

The decomposition temperature (Td) of films was studied by TGA. The values of the onset of the decomposition temperature are very important, since they could indicate the processing and manufacturing temperature without continuing or initiating a process of decomposition.

The blend of LDPE with banana starch showed two decomposition stages, as presented in Figure 4.9. The first one around 290-300°C is due to banana starch decomposition as it is similar to that of pure banana starch [22]. The second stage appearing at higher temperature around 450°C is due to LDPE decomposition. Table 4.2 summarizes the onset of degradation temperature (Td (onset)) for both stages, weight loss, and residue at specific temperature for all the blends. As expected, the first Td (onset) showed no significant different when the amount of starch increased. This is because starch content does not affect the Td (onset). However, as listed in Table 4.2, weight loss of films at 350°C increased as a function of banana starch content. Therefore, at this first stage, the amount of weight loss of the blend films was effected by the banana starch content. Nevertheless, there was no effect from banana starch content at the second stage of thermal decomposition. The LDPE blend films absolutely decompose approximately at the same temperature, 500°C.

The effect of benzophenone content on the thermal degradation behavior of the blend films is presented in Figure 4.10. As shown, pure benzophenone exhibited Td around 227°C. However, the blend films showed only two stages of thermal decomposition as previously described. The first Td (onset) was the banana starch decomposition (around 290-300°C) and the second stage was of the LDPE decomposition (around 450°C). No evidence of benzophenone decomposition was found in the blend films. This is probably due to the fact that the amount of benzophenone is quite small compared to other composition. The highest content was only 1 wt%. Therefore, as the amount of starch and PE-g-MA were kept constant, all the thermograms for all the blends were completely superimposed. Similar to Figure 4.9, all the blends further degrade up to about 500°C, where the blends almost completely decomposed. Table 4.3 shows the onset of degradation temperature and percent weight loss for LDPE blend films at various amount of benzophenone.

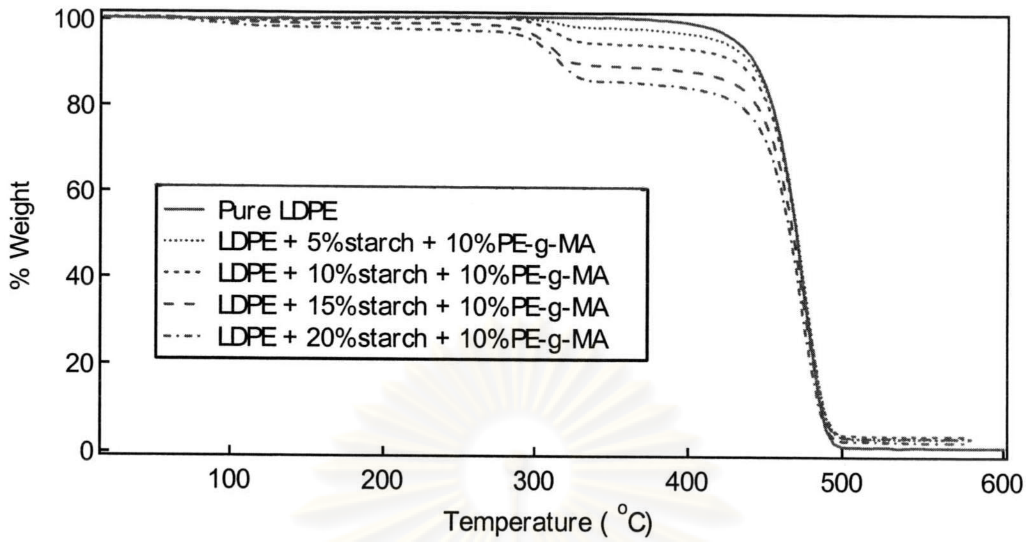


Figure 4.9 TGA curves of LDPE blend films containing 10% PE-g-MA and varying starch content

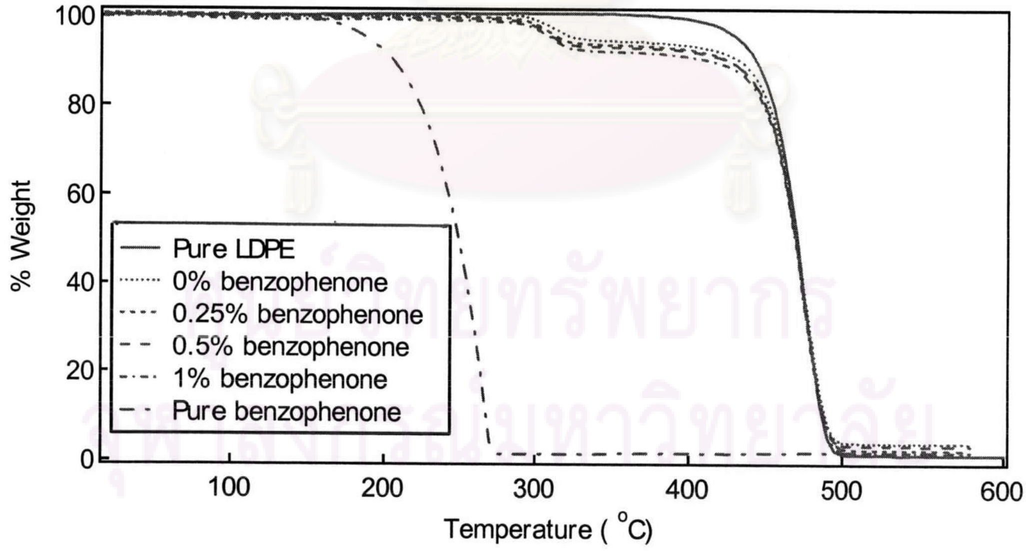


Figure 4.10 TGA curves of LDPE blend film with 10%starch, 10%PE-g-MA and different amount of benzophenone

Table 4.2 Onset of Decomposition Temperature and Percent Weight Loss for LDPE Blend Films at Various Amount of Banana Starch

Sample	Td (^{o}C) (onset)		Percent Weight Loss		Residue at 550 ^{o}C (%)
	First	Second	At 350^{o}C	At 450^{o}C	
LDPE	-	450.3	-	15.06	1.38
5%starch + PE-g-MA	295.0	451.1	1.65	15.87	3.31
10%starch + PE-g-MA	295.2	451.6	5.30	18.35	3.96
15%starch + PE-g-MA	294.5	450.3	10.61	23.75	3.50
20%starch + PE-g-MA	293.6	452.9	14.14	27.87	2.57

Table 4.3 Onset of Decomposition Temperature and Percent Weight Loss for 10% starch/10% PE-g-MA/LDPE blend Films at Different Amount of Benzophenone

Sample	Td (^{o}C) (onset)		Percent Weight Loss		Residue at 550 ^{o}C (%)
	First	Second	At 350^{o}C	At 450^{o}C	
LDPE	-	450.3	-	15.06	1.48
0%benzophenone	295.2	451.6	5.30	18.35	3.96
0.25%benzophenone	293.9	450.0	6.30	20.33	2.49
0.5%benzophenone	292.4	448.8	6.80	20.53	3.40
1%benzophenone	292.0	448.2	7.81	21.48	1.85

4.2.3.2 Different Scanning Calorimetry (DSC)

Thermal transition temperature was characterized by a differential scanning calorimetry (DSC). The melting temperature (Tm) of the blend film was taken as the maximum of the endothermic peak from the second heating while the crystallization temperature (Tc) was taken as the maximum of the exothermic peak from the cooling cycle.

The second heating and cooling cycle of DSC thermograms for pure LDPE and the blend films are displayed in Figure 4.11 and Figure 4.12, respectively. It is well known that the area enclosed under the melting endothermic peak, so called heat of fusion (ΔH_f^*), can be used to calculate the degree of crystallinity. Therefore, by knowing the heat of fusion of fully crystalline PE (ΔH_f^0) (276 J/g) [25], the degree of crystallinity can be determined. The degree of crystallinity was calculated by dividing the measured heat of fusion (ΔH_f^*) by the referenced value for the complete PE crystal (ΔH_f^0). The melting temperature (Tm), crystallization temperature (Tc), heat of fusion (ΔH_f^*), and degree of crystallinity of LDPE phase in the blend determined from the DSC thermograms are given in Table 4.4.

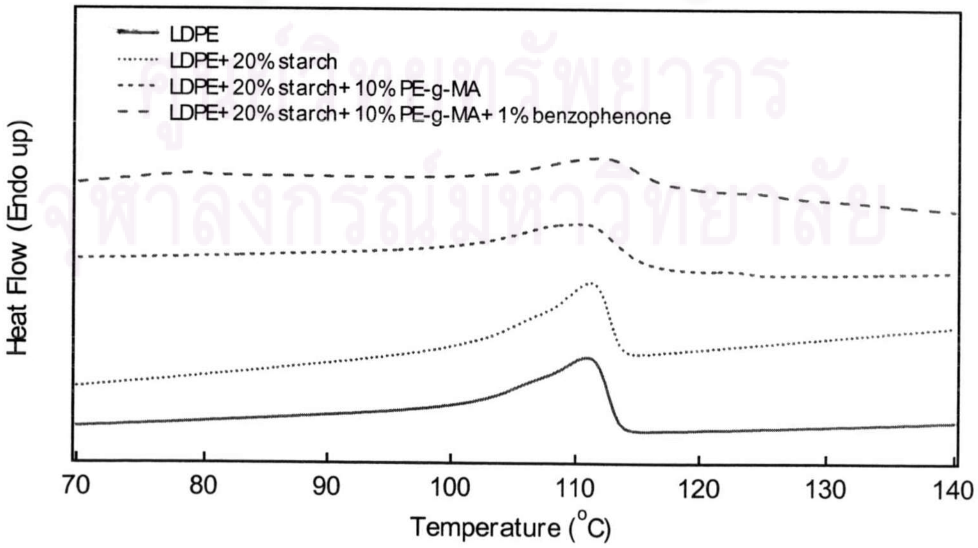


Figure 4.11 The melting temperature of pure LDPE and LDPE blend films

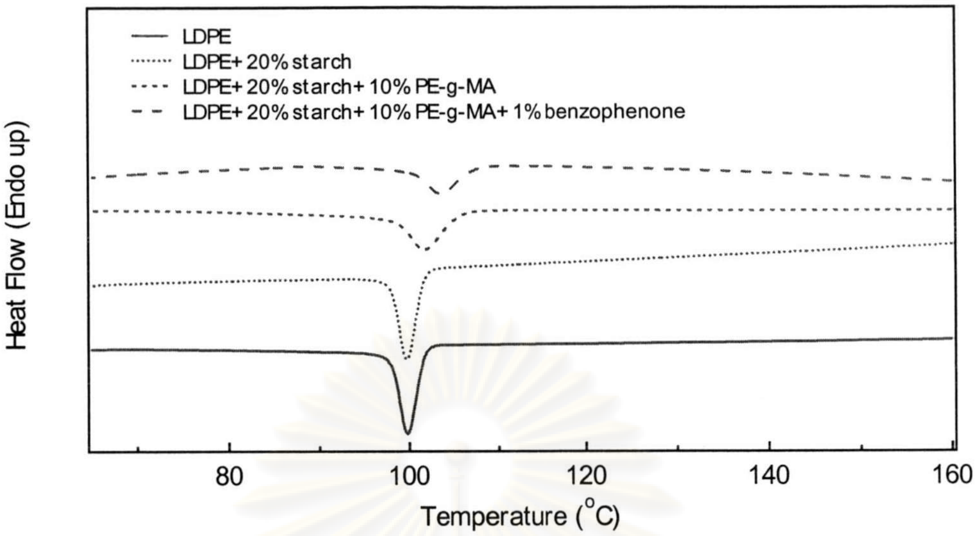


Figure 4.12 The crystallization temperature of pure LDPE and LDPE blend films

It is found that Tm and Tc of LDPE/20%starch and LDPE/20%starch/10%PE-g-MA presented no significant different compared with the pure component at about 110°C and 100°C, respectively. Although there is no other endothermic peaks occurred for the LDPE/20%starch and LDPE/20%starch/10%PE-g-MA blend films, this does not mean that the blends are compatible. The endothermic transition occurred is solely attributed from the LDPE phase since the banana starch, like any other starch, has no melting temperature, but gelatinization and degradation tempeature.

Table 4.4 shows the degree of crystallinity for LDPE and LDPE/starch blend films. Comparing the difference of pure LDPE and 20%starch blends, there is apparent decrease in the heat of fusion for the film with 20%starch. However, when the heat of fusion is corrected by taking into account only the LDPE content in the blend, there is no change in the crystallinity of LDPE phase. It can be concluded that LDPE is hardly miscible with starch.

Table 4.4 Thermal properties and Degree of Crystallinity for LDPE and LDPE/starch blend films

Sample	Tm (°C)	Tc (°C)	(ΔH_f^*)		% Crystallinity	
			Total (J/g)	LDPE (J/g)	Total	LDPE
LDPE	111.13	100.20	48.68	48.68	17.64	17.64
LDPE+20%starch	111.23	100.08	42.60	47.33	15.43	17.15
LDPE+20%starch +10%PE-g-MA	110.76	101.78	33.55	41.02	12.16	14.86
LDPE+20%starch +10%PE-g-MA +1%benzophenone	112.23	103.86	19.19	23.62	6.95	8.56

For the compatibilized blend with PE-g-MA, the presence of PE-g-MA significantly decreased the degree of crystallinity of the LDPE phase in the blend. This decrease is due to the interaction between LDPE and starch, which hinders the close packing of LDPE chains.

For the LDPE/20%starch/10%PE-g-MA/1%benzophenone, addition of benzophenone caused an increasing in Tc. It might be implied that benzophenone functions as a nucleating agent allowing LDPE to form its crystals on the nucleating site very fast and at higher temperature compared to pure LDPE and the blend without benzophenone. These nucleating agents provide nuclei for heterogeneous crystallization, raising the crystallization rate and crystallization temperature. In addition, the degree of crystallinity of the LDPE phase was dramatically decreased. This is because more and smaller spherulites are consequently produced resulting in the lowering of degree of crystallinity.

4.3 Tensile Properties

A chill roll cast film was used to prepare starch-based LDPE films. Sample specimens were cut from these films and the tensile properties were tested.

4.3.1 Effect of starch content

Figure 4.13 illustrates the effect of starch content on the tensile properties of pure LDPE and LDPE/starch blend films. Obviously, the tensile properties are highly dependent on starch content. The tensile strength and elongation at break decrease with increasing amount of starch. This decrease can be associated with lacking of compatibility between the blend components due to the difference in the hydrophilic - hydrophobic character of starch and LDPE, respectively, resulting in the separation between two phases.

Because the adhesion between starch particle and LDPE matrix was poor, poor stress transfer at starch particle-polymer interface happened. Stress concentration was occurred around the starch particles, causing the reduction in tensile strength of the blends.

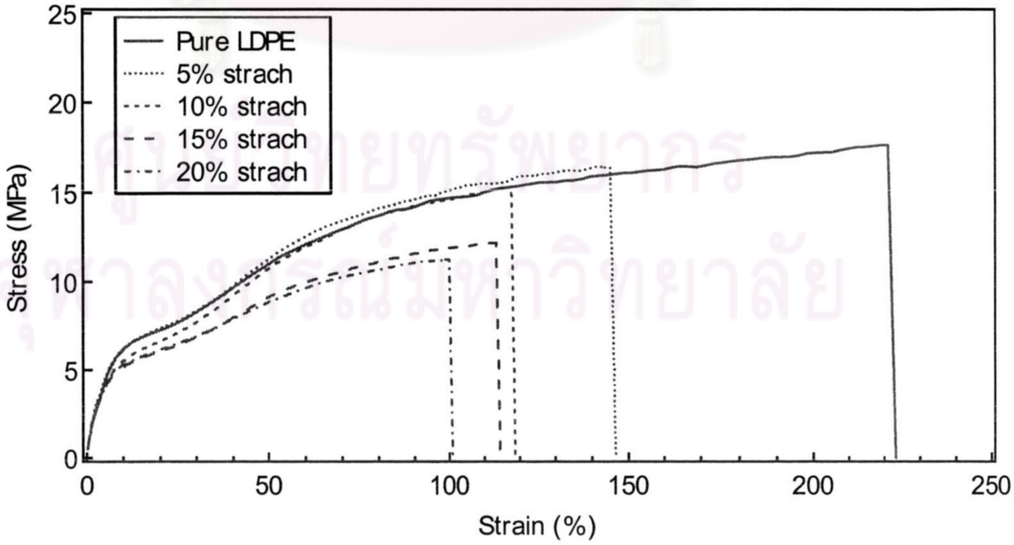


Figure 4.13 Stress–strain curve of pure LDPE and LDPE/starch blends films with different content of starch

4.3.2 Effect of compatibilizer

Blending the starch with LDPE causes a decrease in both tensile strength and elongation at break and the resulting materials have poor film forming properties. This deterioration arises from the different polar characteristic of starch from LDPE, which leads to poor interfacial adhesion. In order to increase the adhesion, and therefore to improve the tensile properties, a compatibilizer must be used.

Tensile strength of the blend films with and without compatibilizer are shown in Figure 4.14. In both cases, a decrease in tensile strength was observed as the amount of starch increased. The decrease in the compatibilized blend, however, was smaller compared with the corresponding decrease in the uncompatibilized blend. The compatibilized blends also exhibited a slightly greater in the elongation at break compared to the uncompatibilized ones, as seen in Figure 4.15. Although not much difference between the compatibilized and uncompatibilized blends was observed, the trend was similar to that of the tensile strength. It is very clear that the addition of the PE-g-MA as a compatibilizer into the blend increases the tensile strength and elongation at break compared with the uncompatibilized blend.

As previously described, the tensile strength properties in polymer blends are partly affected by the interfacial adhesion between the polymers. LDPE and banana starch are immiscible blend because of their different polar character. In contrast to the 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 blend decreased. The addition of PE-g-MA is proved to be a very effective compatibilizer.

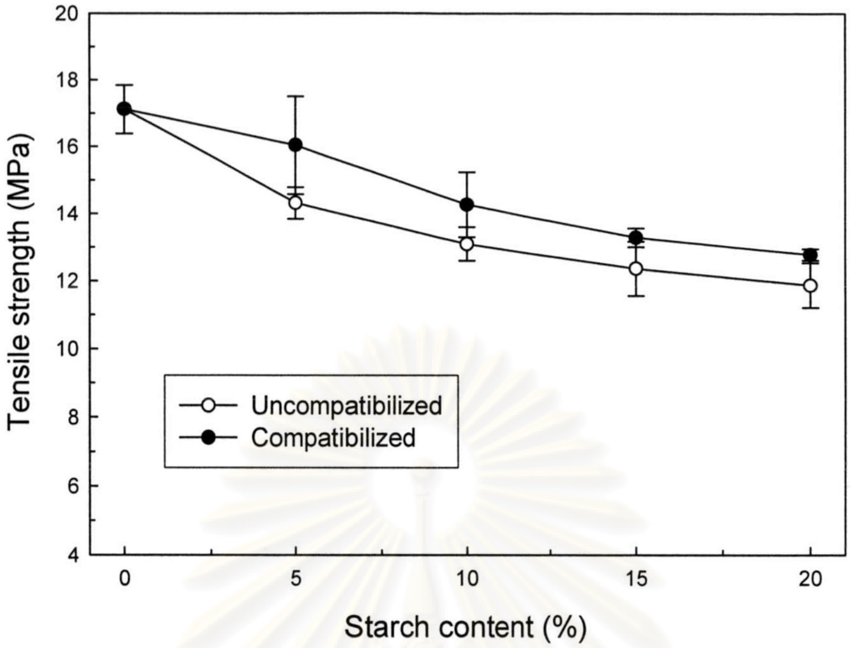


Figure 4.14 Tensile strength of LDPE/starch blends of uncompatibilized and compatibilized with 10 wt% PE-g-MA

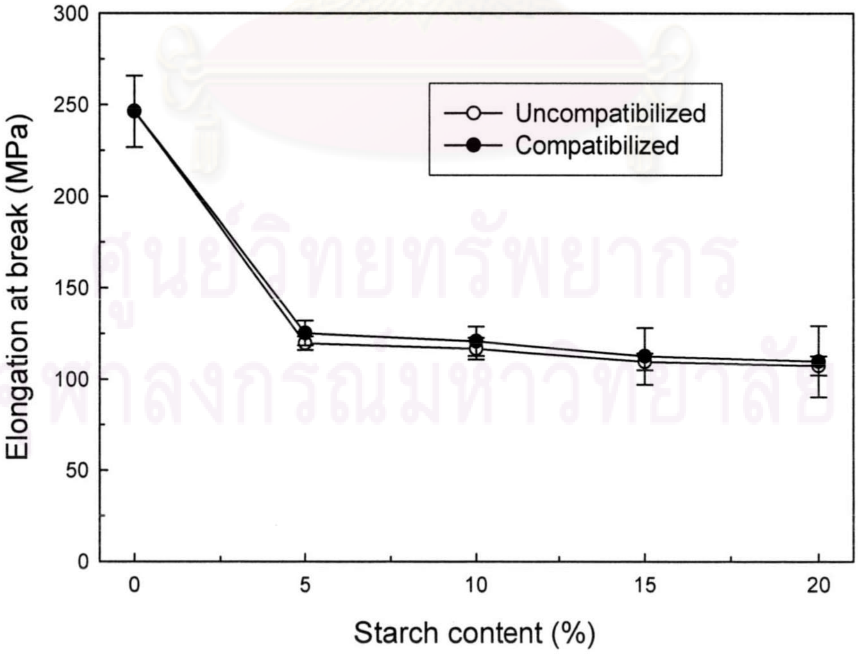
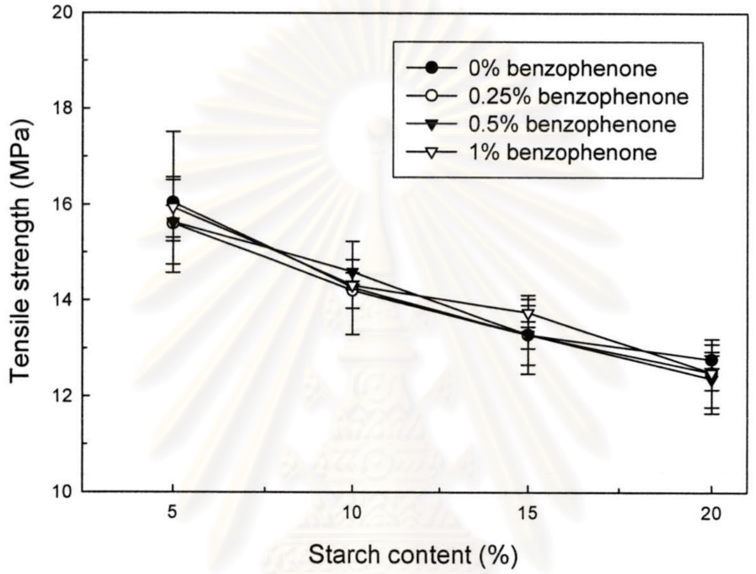


Figure 4.15 Elongation at break of LDPE/starch blends of uncompatibilized and compatibilized with 10 wt% PE-g-MA

4.3.3 Effect of photosensitizer content

The tensile strength and elongation at break of the LDPE/starch/PE-g-MA blend films containing various amount of benzophenone are presented in Figure 4.16. As shown, there is no effect of benzophenone on the tensile strength and elongation at break of the blend films.



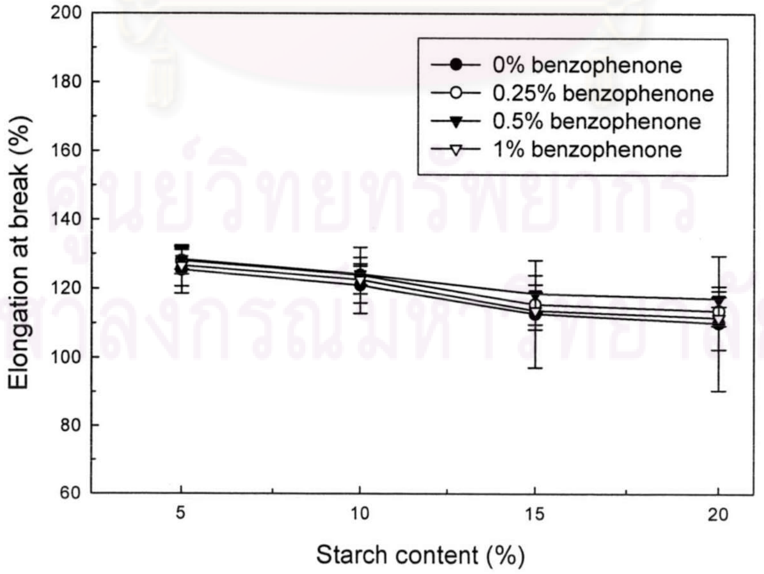


Figure 4.16 Tensile strength and elongation at break of LDPE/10%starch/10%PE-g-MA blends containing different amount of benzophenone

4.4 Evaluation of Photodegradation

Photodegradation of LDPE blend films was performed by outdoor exposure test and accelerated UV exposure by using a xenon arc lamp. FT-IR was used to observe the change in chemical structure of the films. In addition, photodegradation rate was also evaluated by changing in tensile properties of the films.

4.4.1 Carbonyl index

The chemical properties of blend films were affected by photoreaction as a result of chemical structure change in the polymer molecules. Due to the photooxidation, the polymer chains were broken, which can be confirmed by the increasing of carbonyl index.

4.4.1.1 Outdoor exposure

After being exposed to the outdoor sunlight, LDPE film samples were removed for testing at every month. Figure 4.17 shows the IR spectrum during outdoor exposure for 0, 1, 2, 3, and 4 months.

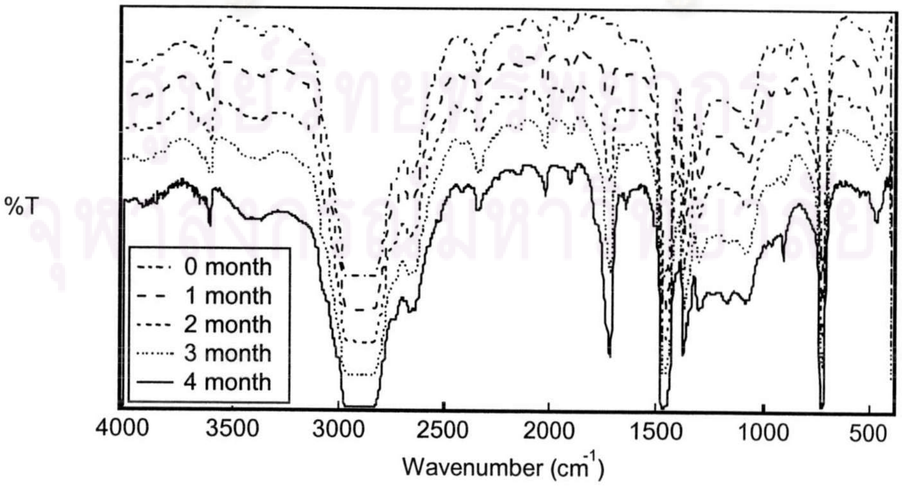
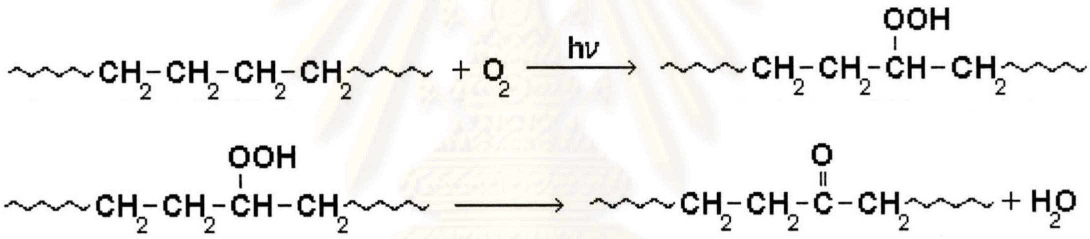


Figure 4.17 IR spectrum of pure LDPE during outdoor exposure for 0, 1, 2, 3 and 4 months.

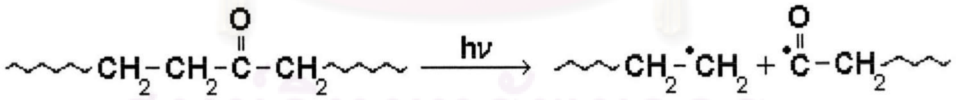
It can be seen that the intensity of carbonyl peak (1715 cm^{-1}) increasing with increasing in exposure time. This can be explained that the decomposition of LDPE under condition of outdoor exposure was occurred by the photodegradation. UV light causes the formation of various free radicals which some of them combine with oxygen dissolved in the polymer to initiate chain reaction and form unstable products. The oxidation process will involve peroxide radicals derived directly from the radiation reaction and also these initial peroxide radicals attack on the polymer, give hydroperoxide. Hydroperoxide is believed to slowly breakdown and produce carbonyl compound. The carbonyl compound predominates those expected from the Norrish type I and II process. An increase in carbonyl peak height as exposure time increased is due to the formation of carbonyl compounds which are degradation products of LDPE, as seen in the following mechanism:



$$\sim\sim CH_2-CH_2-CH_2-CH_2\sim\sim + O_2 \xrightarrow{h\nu} \sim\sim CH_2-CH_2-\overset{\overset{\displaystyle OOH}{|}}{C}H-CH_2\sim\sim$$

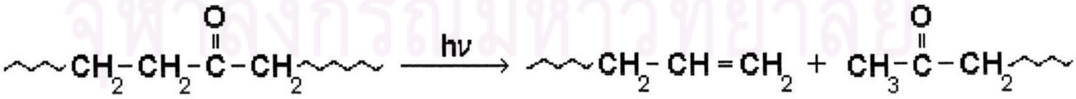
$$\sim\sim CH_2-CH_2-\overset{\overset{\displaystyle OOH}{|}}{C}H-CH_2\sim\sim \longrightarrow \sim\sim CH_2-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-CH_2\sim\sim + H_2O$$

Norrish type I



$$\sim\sim CH_2-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-CH_2\sim\sim \xrightarrow{h\nu} \sim\sim CH_2-\dot{C}H_2 + \dot{\overset{\overset{\displaystyle O}{\|}}{C}}-CH_2\sim\sim$$

Norrish type II



$$\sim\sim CH_2-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-CH_2\sim\sim \xrightarrow{h\nu} \sim\sim CH_2-CH=CH_2 + CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_2\sim\sim$$

4.4.1.1.1 Effect of starch content

Figure 4.18 illustrates the effect of starch content on carbonyl index as a function of exposure time. The data shows that as the exposure time and starch content increased, the carbonyl index increased. This can be due to the microstructure of starch granules that are embedded within the LDPE matrix. Because, there is a gap between starch granule and LDPE matrix. The higher starch content led to an increase in porosity of the LDPE matrix which can then easily allowed the permeation of light and oxygen throughout the inner part of the LDPE, resulting in the higher carbonyl index. The IR spectra of blend films with different amount of starch are shown in Figure 4.19.

4.4.1.1.2 Effect of Compatibilizer

Figure 4.20 shows the influence of compatibilizer on the change of carbonyl index as a function of exposure time. For the blends containing 10%banana starch, the carbonyl index increased as a function of exposure time for both compatibilized and uncompatibilized blends. Although it might be expected that PE-g-MA may retard the photodegradation by decreasing the porosity between LDPE matrix and starch, leading to the decrease of permeation of light and oxygen through the inner part of LDPE matrix. As a result, the carbonyl index of the compatibilized blends should be lower than the uncompatibilized ones. However, it was found that the blend containing PE-g-MA did not show any significant difference in carbonyl index as compared to the uncompatibilized blend. This result is probably owing to the small amount of PE-g-MA which was only 10% (base on starch content). Therefore, based on the amount of PE-g-MA used in this work, it can be concluded that there is no effect from the compatibilizer on the carbonyl index of the blend films. The IR spectra of LDPE/10%starch blend films with and without 10%PE-g-MA are shown in Figure 4.21.

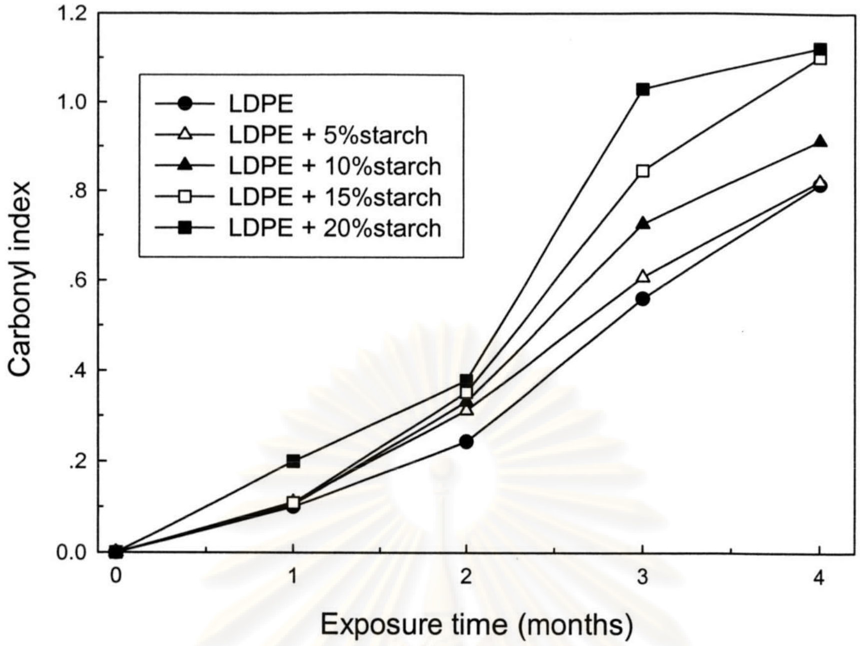


Figure 4.18 Carbonyl index of blend films with different amount of starch

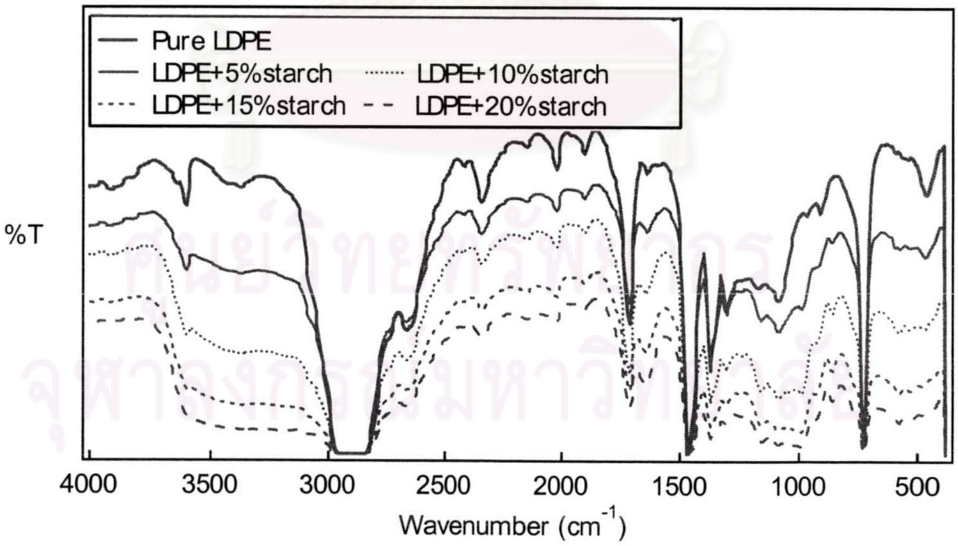


Figure 4.19 Infrared spectra of pure LDPE and LDPE blend films with different amount of starch after 3 months outdoor exposure

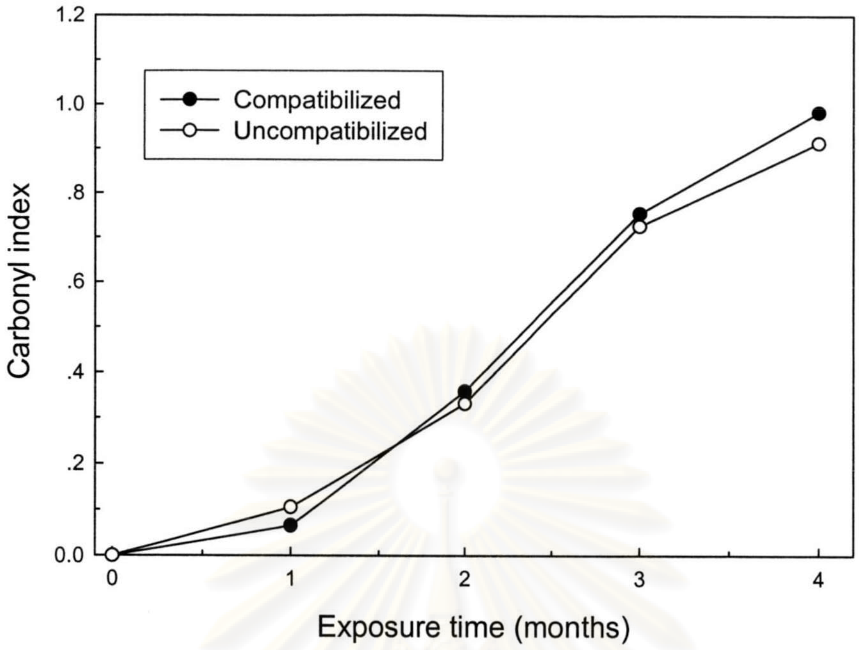


Figure 4.20 Carbonyl index of LDPE/10%starch uncompatibilized and compatibilized blend with 10% PE-g-MA

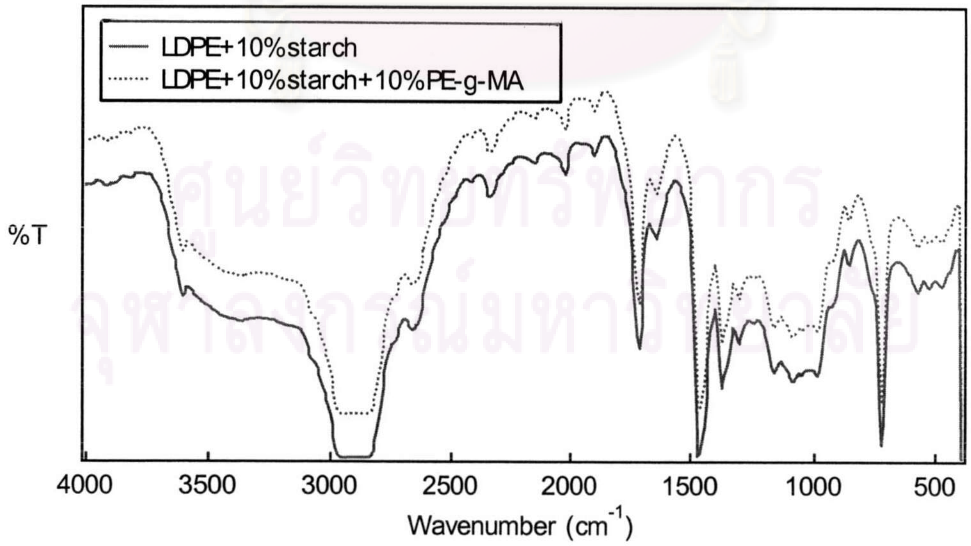


Figure 4.21 Infrared spectra of LDPE/10%starch blend films with and without 10%PE-g-MA after 3 months outdoor exposure

4.4.1.1.3 Effect of photosensitizer content

The effect of photosensitizer content on the carbonyl index as a function of exposure time is presented in Figure 4.22. Clearly, for the blends containing the same amount of starch but different amount of benzophenone, the carbonyl index increased with increasing of benzophenone content and exposure time. This is because of the fact that the radicals in the unsaturated molecules of benzophenone led to the formation of hydroperoxide. The hydroperoxide molecules breakdown and give the carbonyl compounds. The higher content of benzophenone in the blends, the greater value of carbonyl index obtained. This is due to the increased number of double bonds which are more easily oxidized and generated free radicals. The more radicals in the system lead to an increase in the probability for carbonyl formation. It can be concluded that benzophenone promoted photodegradation of the blend films. However, it should be noted that carbonyl compound may come from either benzophenone degradation or LDPE degradation. The IR spectra of LDPE/10%starch/10%PE-g-MA blend films with different amount of benzophenone are shown in Figure 4.23.

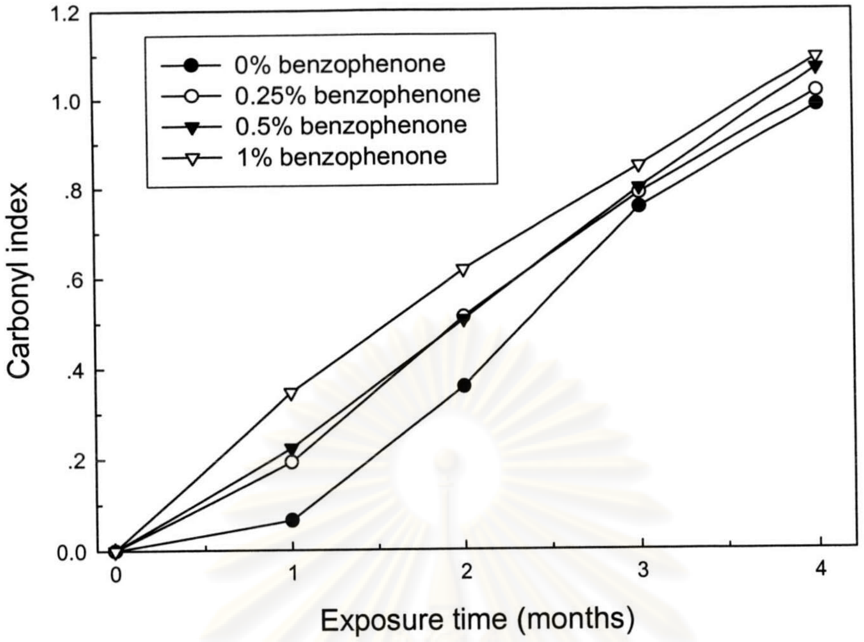


Figure 4.22 Carbonyl index of LDPE/10%starch/10%PE-g-MA blend films with different amount of benzophenone

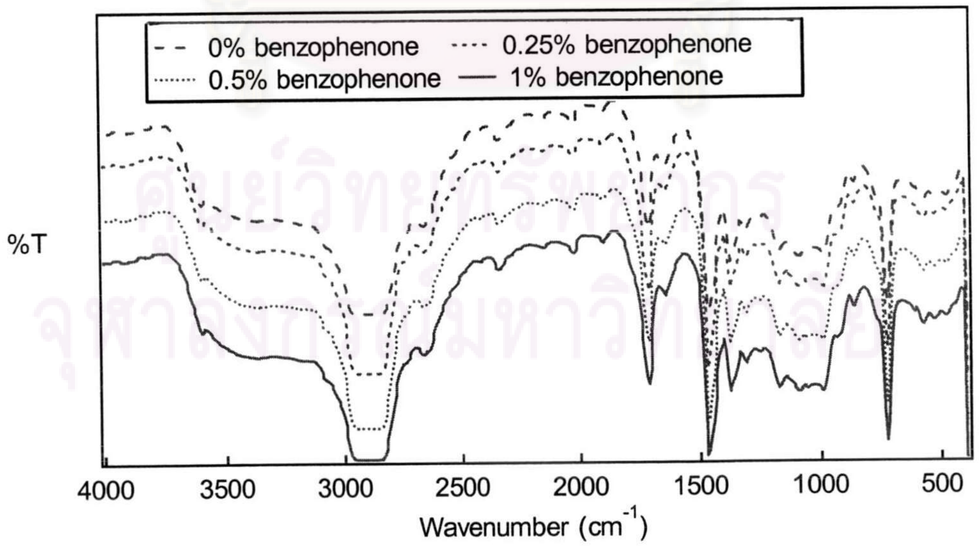


Figure 4.23 Infrared spectra of LDPE/10%starch/10%PE-g-MA blend films with different amount of benzophenone after 3 months outdoor exposure

4.4.1.2 Accelerated exposure

Film samples were cut into 1.5 cm × 20 cm and placed into the Xenotest Beta Lamp chamber. Samples were removed for testing at every 5 hours for 20 hours.

4.4.1.2.1 Effect of compatibilizer and starch content

Surprisingly, there was no detection of carbonyl index in LDPE/starch and LDPE/starch/PE-g-MA systems. In contrast, pure LDPE film exhibited gradual change in carbonyl index as a function of time as presented in Figure 4.24. These results are different from the outdoor exposure test, and may be explained by two following reasons. First, according to Figure 4.29, as will be discussed later, the exposure time in Xenotest Beta Lamp is equal to a few days in outdoor test. For example, the film samples exposed to the simulated condition in Xenotest for 20 hours is equal to 8 days in outdoor test. This means that within the scope of this experiment, the exposure time in Xenotest was less than the exposure time in outdoor test. Hence, the effect from UV light in Xenotest should be less severe than in the outdoor test. Secondly, the value of carbonyl index was calculated from the peak height at 1715 cm^{-1}. But since the starch in blend films shows O-H bending peak at 1640 cm^{-1}, the overlap of this peak with carbonyl group at 1715 cm^{-1} may be occurred, as displayed in Figure 4.25. For pure LDPE, there is no influence of the O-H bending peak. Therefore, pure LDPE showed a little increase in carbonyl index compared to LDPE/starch and LDPE/starch/PE-g-MA blends. These IR spectra were different from the IR spectra of the films under outdoor exposure, as presented in Figure 4.26. Obviously, the peaks at 1715 cm^{-1} and 1640 cm^{-1} of all films were clearly separated, no interference of the O-H bending peak on the calculation of carbonyl index values.

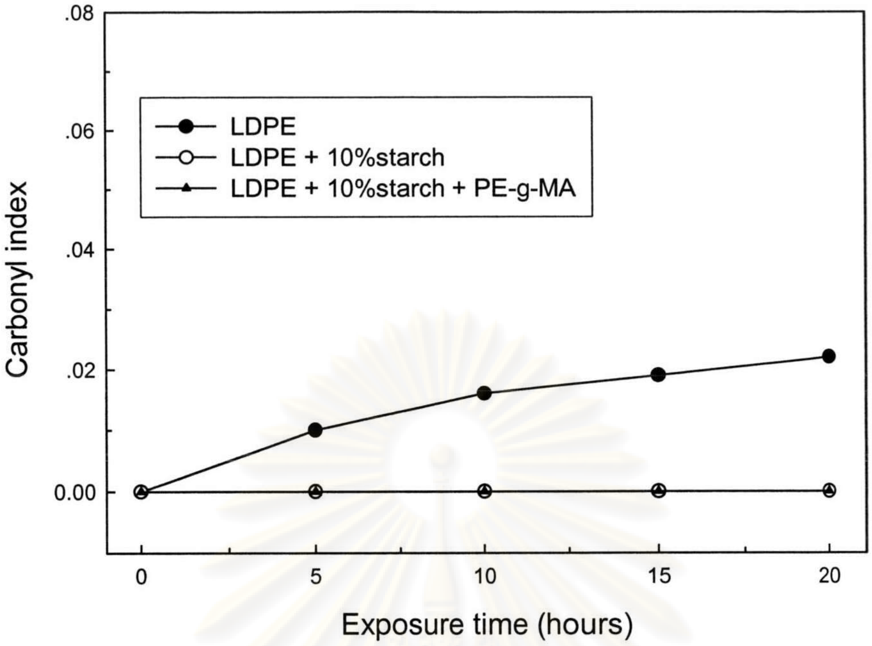


Figure 4.24 Carbonyl index of LDPE, LDPE/10%starch, and LDPE/10%starch/10%PE-g-MA blend films

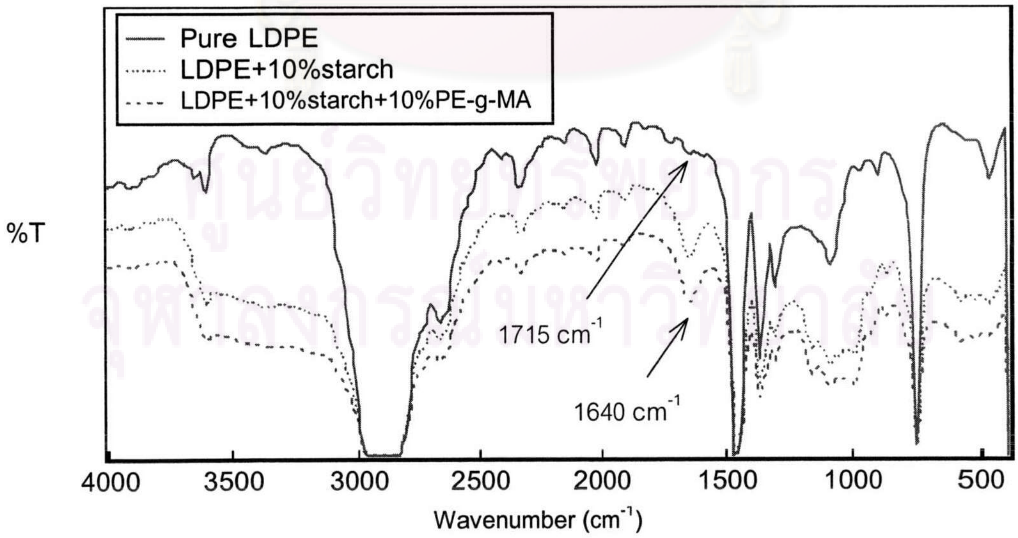


Figure 4.25 Infrared spectra of pure LDPE, LDPE/10%starch and LDPE/10%starch/10%PE-g-MA after 15 hours exposure in Xenotest Beta Lamp

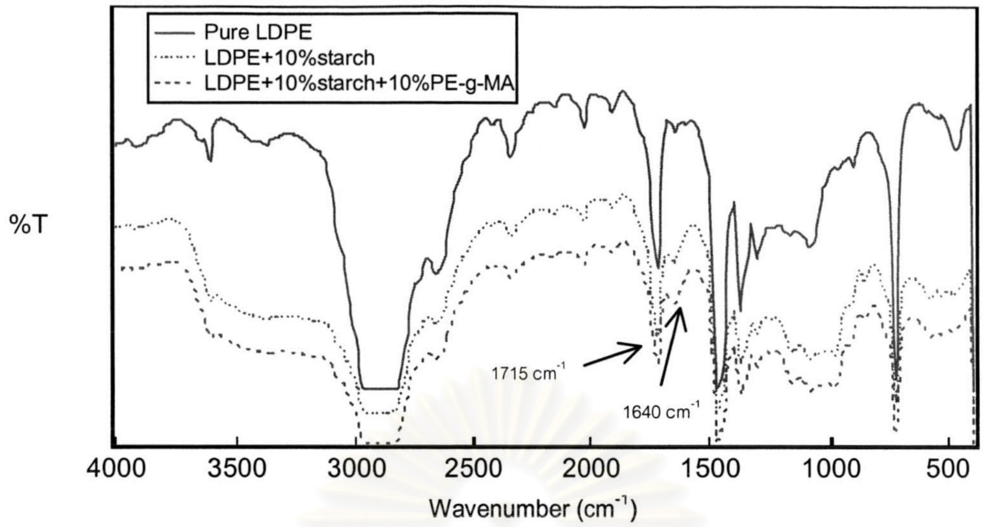


Figure 4.26 Infrared spectra of pure LDPE, LDPE/10%starch and LDPE/10%starch/10%PE-g-MA after 3 months outdoor exposure

4.4.1.2.2 Effect of photosensitizer content

The influence of photosensitizer content on the carbonyl index as a function of exposure time is displayed in Figure 4.27. Similar to the outdoor exposure test, the carbonyl index increased with an increase of benzophenone content and exposure time, except for the blends containing 0%benzophenone. There was no evidence of carbonyl index up to the 20 hours of exposure time. This result is different from the outdoor exposure test that the carbonyl index of the blend film without benzophenone increased as a function of exposure time. The discrepancy of the result from these two tests is unknown and need to be further clarified. However, these results ensure the role of benzophenone in promoting the photodegradation, especially for the accelerated test which the exposure time was shorter than that of the outdoor exposure test, as previously discussed. The IR spectra of LDPE/10%starch/10%PE-g-MA blend films with different amount of benzophenone are shown in Figure 4.28.

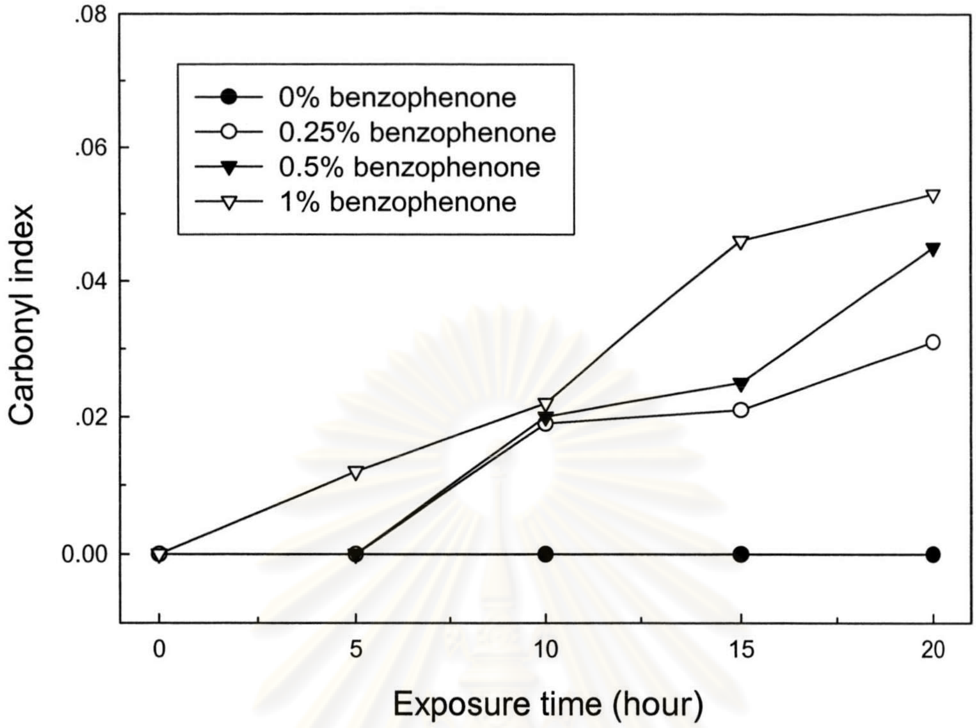


Figure 4.27 Carbonyl index of LDPE/10%starch/10%PE-g-MA blend films with different amount of benzophenone

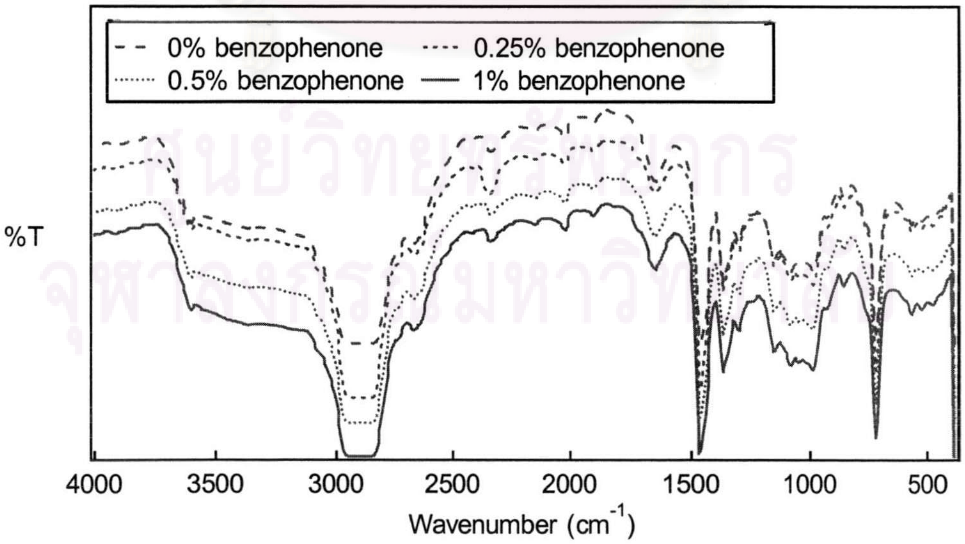


Figure 4.28 Infrared spectra of LDPE/10%starch/10%PE-g-MA blend films with different amount of benzophenone after 15 hours exposure in Xenotest Beta Lamp

4.4.1.3 The comparative result of carbonyl index

The comparison between outdoor exposure time and accelerated exposure time was calculated as follow:

Thailand UV radiation in 1 year = 328 MJ/m^{2} * (1 MJ = 10^{6} Watts sec)
= 328×10^{6} Watts sec/m^{2}
Radiation in Xenotest Beta Lamp = 100 Watts/m^{2}
1 year of outdoor exposure equivalent to = (328×10^{6} Watts sec/m^{2}) / (100 Watts/m^{2})
= 3.28×10^{6} sec in Xenotest Beta Lamp
= 911.11 hrs. in Xenotest Beta Lamp
≈ 38 days in Xenotest Beta Lamp

* Average data of UV radiation in 1 year recorded during 1986-1995 by the Meteorological Department.

Therefore, the exposure time in Xenotest Beta Lamp chamber, 5, 10, 15, and 20 hours is equivalent to 2, 4, 6, and 8 days in outdoor exposure time, respectively.

The comparison between carbonyl index from outdoor exposure and accelerated exposure of LDPE/10%starch/10%PE-g-MA/0.5%benzophenone at the same time is shown in Figure 4.29. The plot suggests that the carbonyl index of outdoor exposure blend films was higher than that of accelerated UV exposure blend films. This may be resulted from the higher disordered structure in LDPE. The attack of oxygen causing degradation is easily done. Therefore, photooxidation degradation is not only responsible by UV light but also oxygen. Although, the intensity of UV light can be regularly controlled in Xenotest, but oxygen permeability also has an important role on the rate of oxidation.

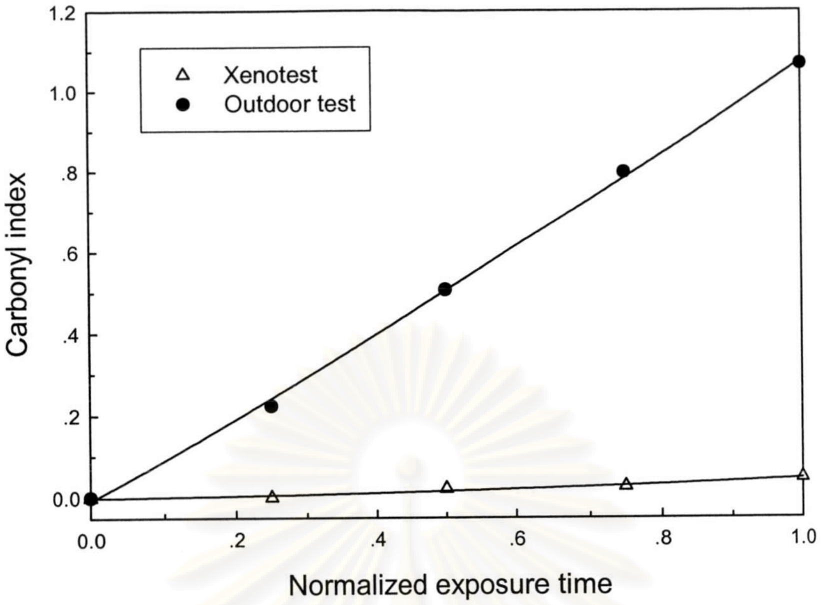


Figure 4.29 Normalized plots of carbonyl index between outdoor exposure and accelerated exposure at the same time of LDPE/10%starch/10%PE-g-MA/0.5% benzophenone film

4.4.2 Tensile Properties

Tensile properties are the common methods for evaluation the degradation of plastic materials. The change of tensile properties in both outdoor exposure and accelerated UV exposure were determined by tensile strength and elongation at break.

4.4.2.1 Outdoor exposure

Figure 4.30 demonstrates the stress-strain curve of the blend film during outdoor exposure for 4 months. The trend is clearly show that the tensile properties decreased when the exposure time increased.

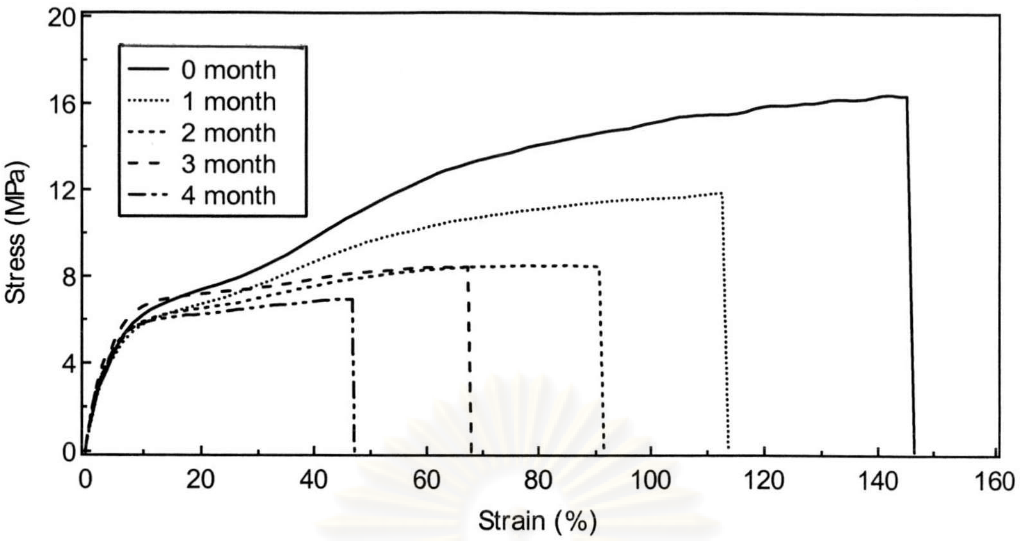


Figure 4.30 Stress-Strain curve of LDPE/5%starch/10%PE-g-MA/0.25%benzophenone blend film during outdoor exposure

4.4.2.1.1 Effect of starch content

The tensile properties of pure LDPE and LDPE/starch films decreased with the exposure time, as seen in Figure 4.31. 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. Obviously, there was a continuous reduction in tensile strength and elongation at break as the time of exposure increased. For example, for the LDPE film with 20 wt% starch, its tensile strength and elongation at break decreased 46.51% and 91.94%, respectively after 4 month of outdoor exposure. In fact, the decrease in tensile strength and elongation at break of pure LDPE film was greater and than that of the blend films. Due to its higher amount of LDPE in the film, LDPE film showed 48.07% and 151.22% reduction in tensile strength and elongation at break, respectively.

4.4.2.1.2 Effect of compatibilizer

Figure 4.32 shows the plot of tensile strength and elongation at break of the uncompatibilized and compatibilized blends with 10% PE-g-MA as a function of exposure time. In consistent with the film before being subjected to sunlight, the compatibilized blend also exhibited an increase in the tensile strength compared to the uncompatibilized one. But as the exposure time increased, the tensile strength decreased. The trend was identical to that of the elongation at break. Decreasing in elongation at break was drastically occurred at the last stage.

Because starch granules of the uncompatibilized blend had no interfacial adhesion with LDPE matrix with respect to the compatibilized blends, the uncompatibilized blend had more gap between starch granules and LDPE matrix. This facilitated oxygen and light to penetrate into the inner part of the LDPE matrix. Therefore, the uncompatibilized blend had lower tensile strength and elongation at break than the compatibilized blend as the time of exposure increased.

4.4.2.1.3 Effect of photosensitizer content

Tensile properties of blend films containing different content of benzophenone as a function of time are displayed in Figure 4.33. The tensile strength and elongation at break of the blend films decreased with increasing of exposure time. In addition, the increase in benzophenone concentration decreased the tensile properties as a fuction of time as well. The reduction in both tensile strength and elongation at break with increasing exposure time and benzophenone content is due to chain scission reaction occurring during exposure. As described in previous section, benzophenone can generate free radical and breakdown the long polymer chain into the shorter ones. As a result, the lowest tensile strength and elongation at break were obtained from the blend with 1%benzophenone. Clearly, as seen in Figure 4.33, its elongation at break was almost zero for the blend films containing 0.5-1% benzophenone at 4 months of exposure. Similarly, the tensile strength of the blend film containing 1%benzophenone was drastically dropped about 62.54% after being exposed for 4 months. These results mean that after the certain period of exposure time, the blend film containing some amount of photosensitizer started losing its strength and become brittle.

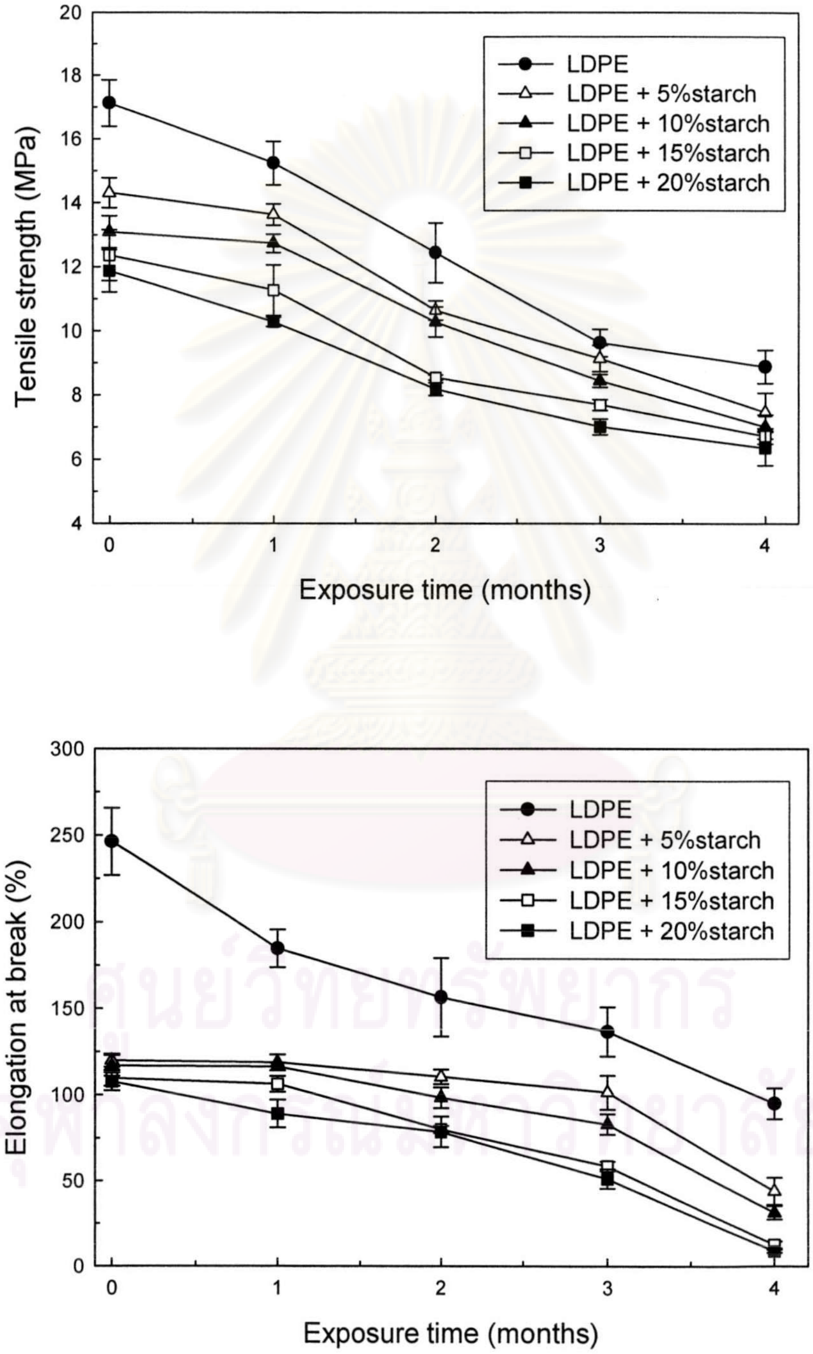
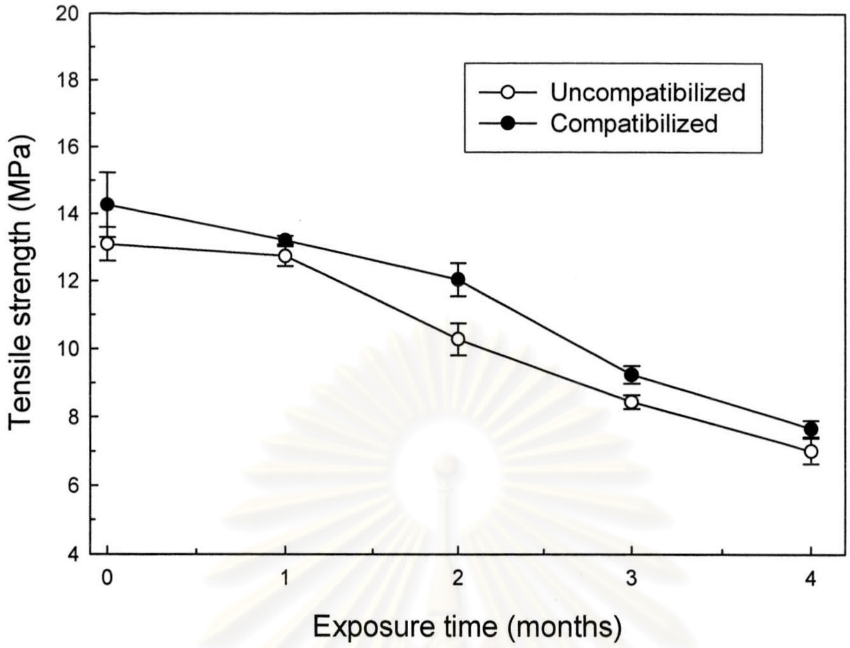


Figure 4.31 Tensile strength and elongation at break of LDPE/starch blends during outdoor exposure test



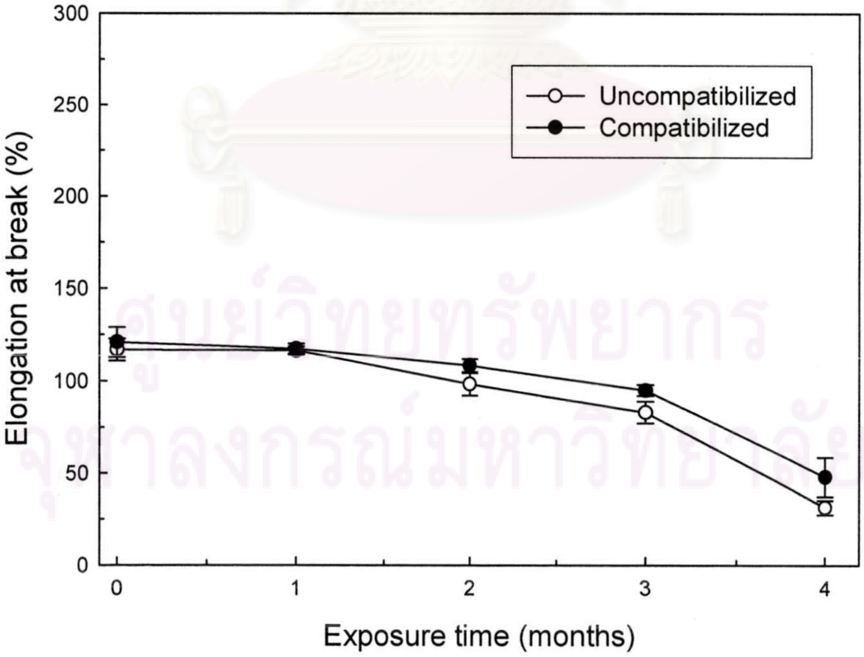
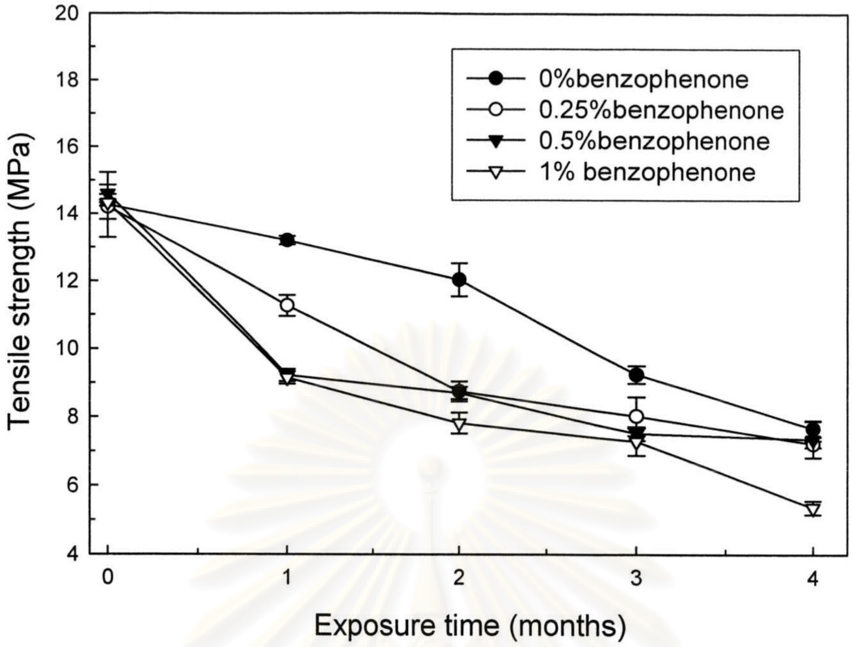


Figure 4.32 Tensile strength and elongation at break of LDPE/10%starch and LDPE/10%starch blend films containing 10% PE-g-MA during outdoor exposure test



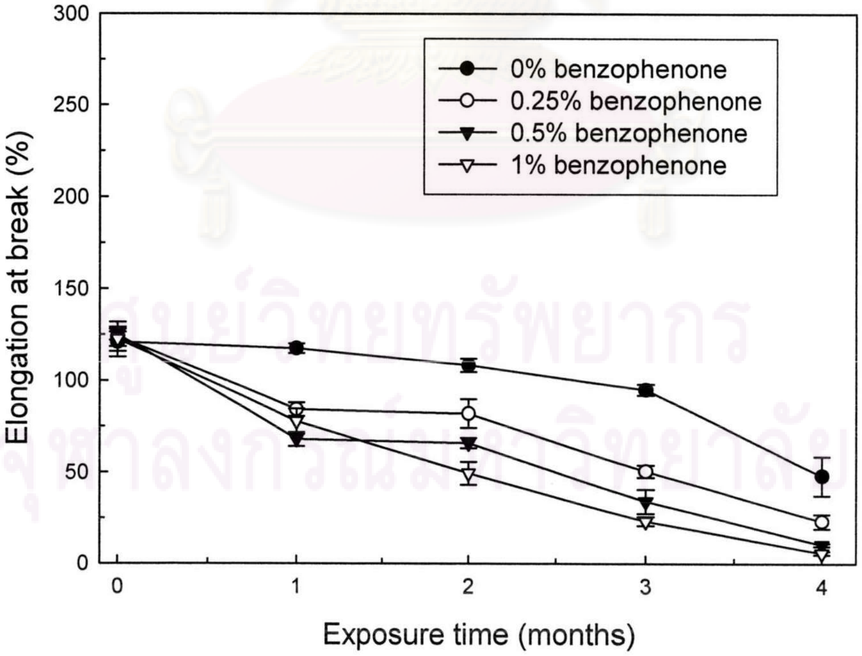


Figure 4.33 Tensile strength and elongation at break of LDPE/10%starch/10%PE-g-MA blend film with various content of benzophenone during outdoor exposure test

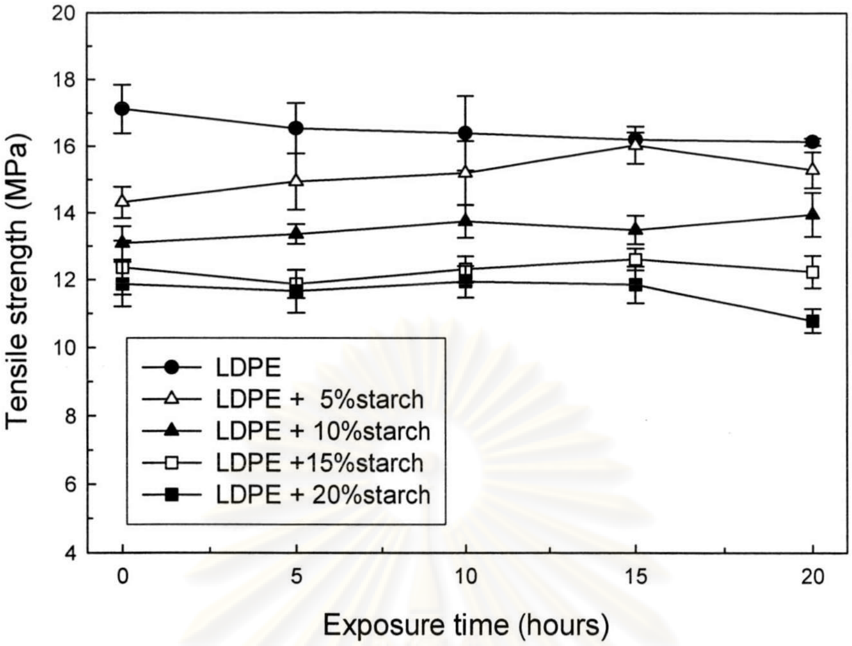
4.4.2.2 Accelerated exposure

After being subjected to UV radiation in Xenotest Beta Lamp chamber, samples were removed for tensile test at every 5 hours for 20 hours.

4.4.2.2.1 Effect of starch content

The influence of starch content on the tensile strength and elongation at break of pure LDPE and LDPE/starch blend films is presented in Figure 4.34. As expected, the tensile strength of the blend films decreased as increasing of starch content. Regarding to the exposure time, the tensile strength of the LDPE/starch films in accelerated exposure increased slightly in the beginning stage of the exposure time. This may be due to crosslinking between the polymer chains that occurred within the polymer blends.

For the elongation at break, obviously, pure LDPE exhibited the outstanding elongation at break compared to LDPE/starch blend films. For the blends with various content of starch, the elongation at break gradually decreased when the amount of starch increased. The change of elongation at break as a function of exposure time showed no significant different among the blend films.



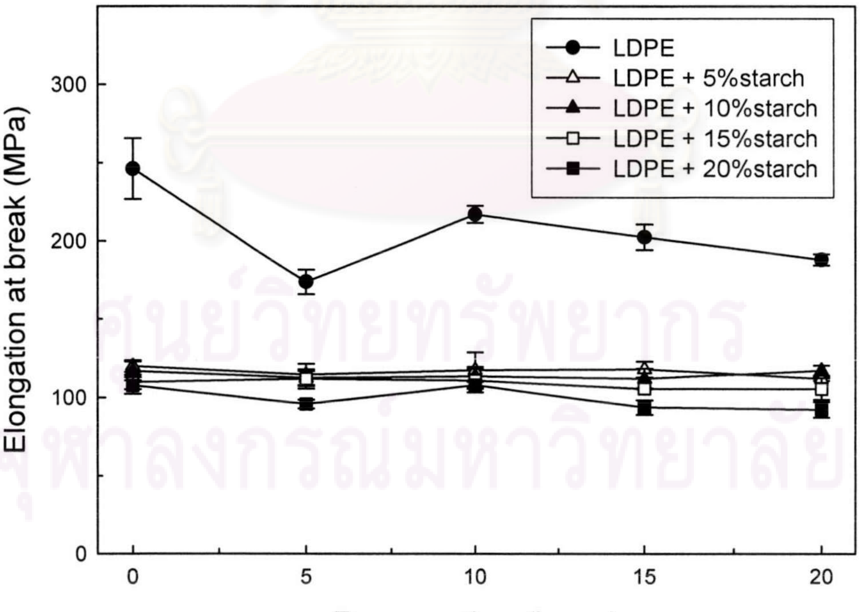


Figure 4.34 Tensile strength and elongation at break of LDPE/starch blends during accelerated test

4.4.2.2.2 Effect of compatibilizer

Figure 4.35 illustrates the comparison of tensile properties between uncompatibilized and compatibilized blend with 10% PE-g-MA. For compatibilized blend , there was a significant improvement in both tensile strength and elongation at break. The tensile strength of both compatibilized and uncompatibilized blend increased slightly as a function of time. This may be because of crosslinking in polymer chain during photooxidation process [29].

Reaction in Figure 4.36 shows the proposed mechanism to explain this behavior. In photooxidation mechanism, many radicals were produced. It is possible that two radicals may join together.

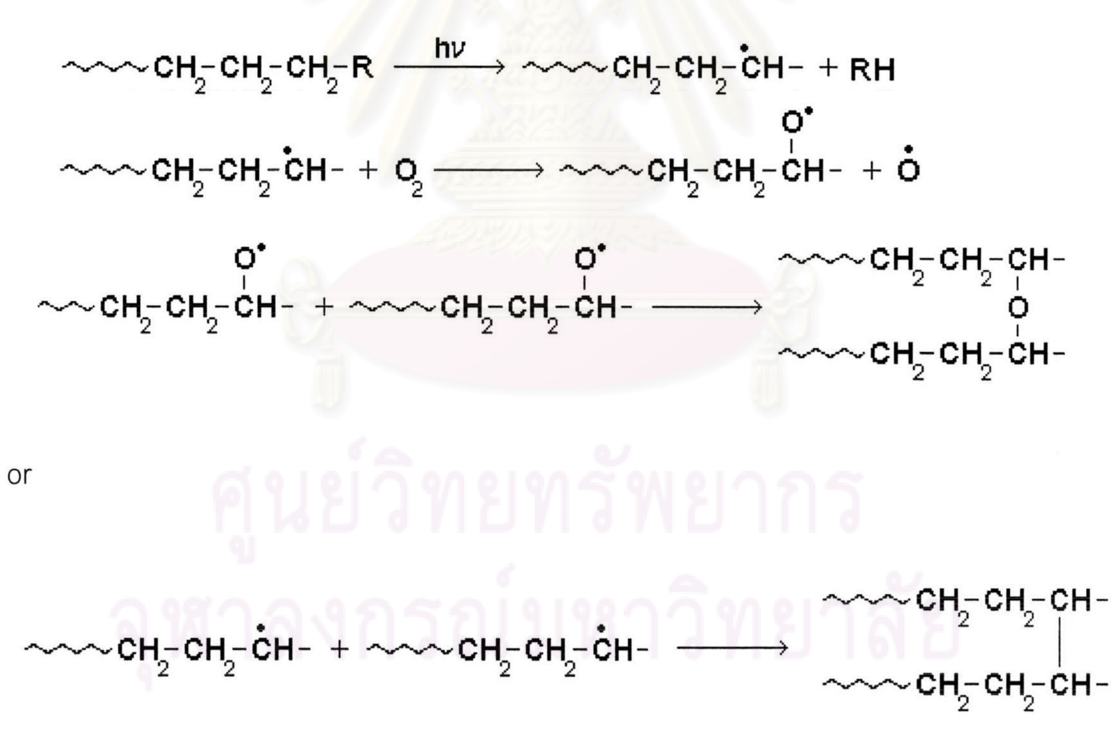


Figure 4.36 Mechanism of chain branching or crosslinking of PE during accelerated exposure

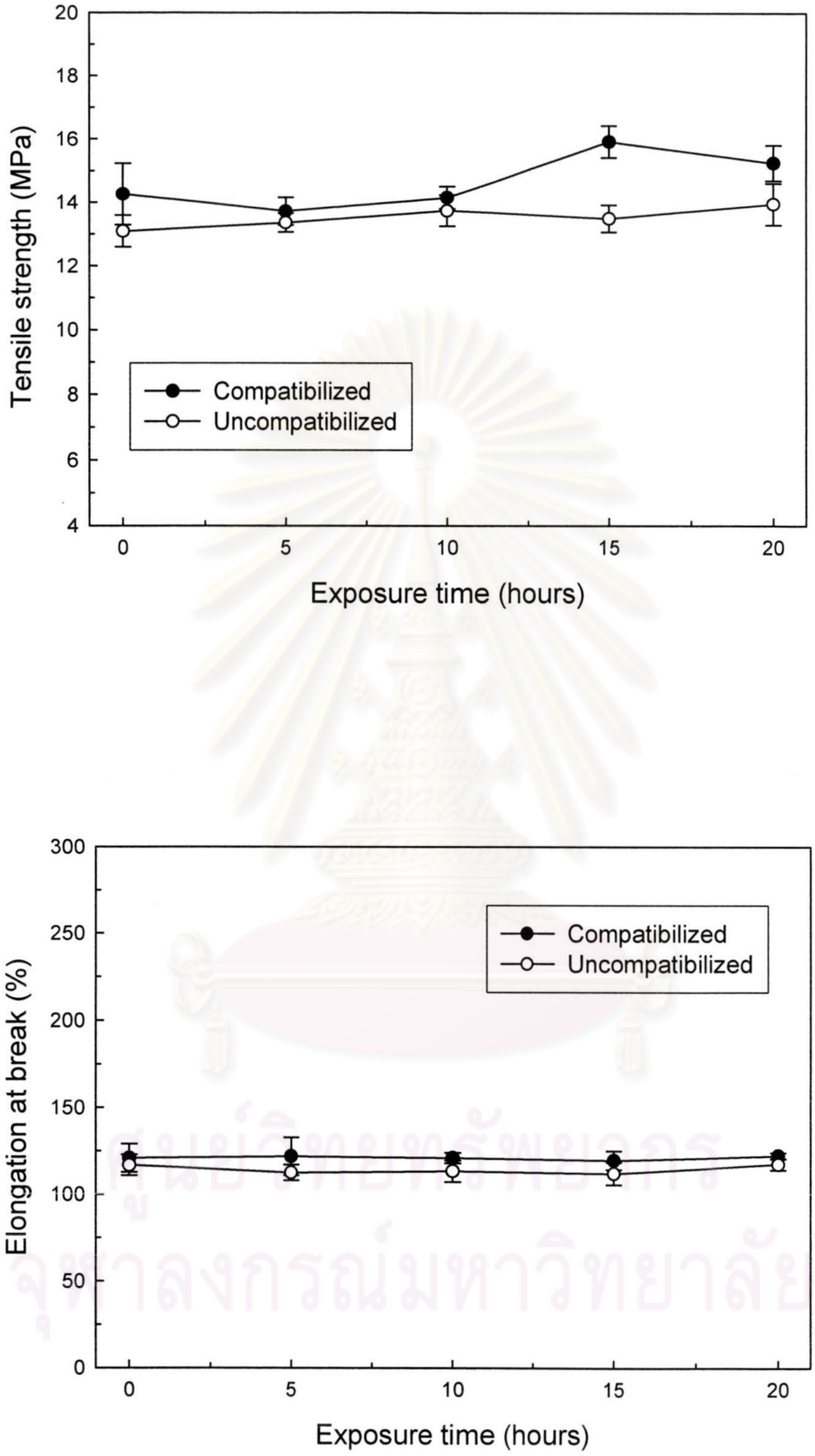
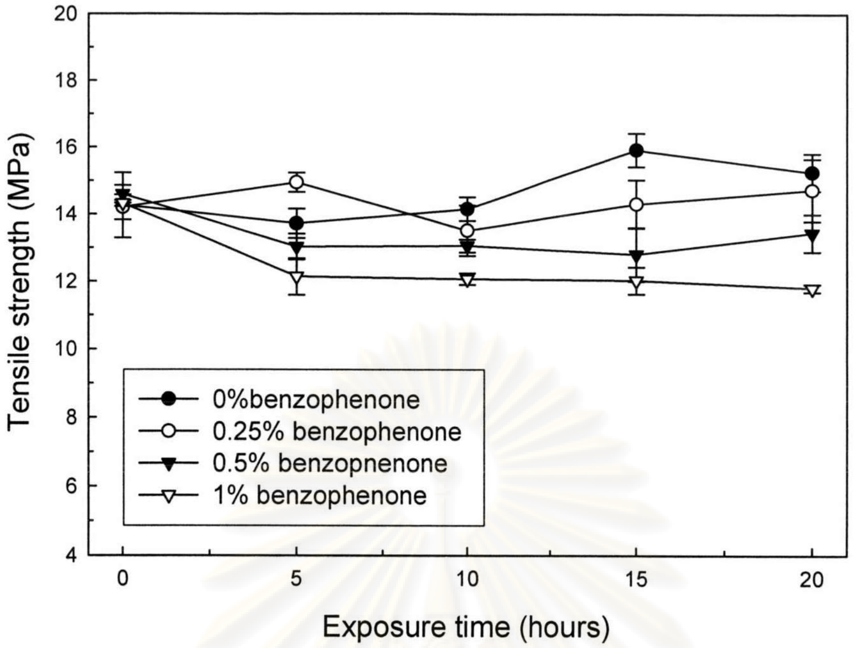


Figure 4.35 Tensile strength and elongation at break of LDPE/10%starch and LDPE/10%starch compatibilized with 10%PE-g-MA during accelerated test

4.4.2.2.3 Effect of Photosensitizer content

Figure 4.37 shows the plot of tensile strength and elongation at break as a function of time and photosensitizer content. Similar to the films being subjected to the outdoor exposure, the blends containing higher amount of benzophenone also exhibited a lower in tensile strength and elongation at break than the others. But as the exposure time increased, the blend films with 0% or 0.25% benzophenone showed no significant changes in both tensile strength and elongation at break. However, at the greater amount of benzophenone, there was a drop of both tensile strength and elongation at break of the blend films after 5 hours of exposure, and these values started levelling off afterwards. From these two plots, the tensile strength and elongation at break of the blend films with 1%benzophenone decreased about 17.54% and 47.27%, respectively, after 20 hours of exposure under the accelerated test.



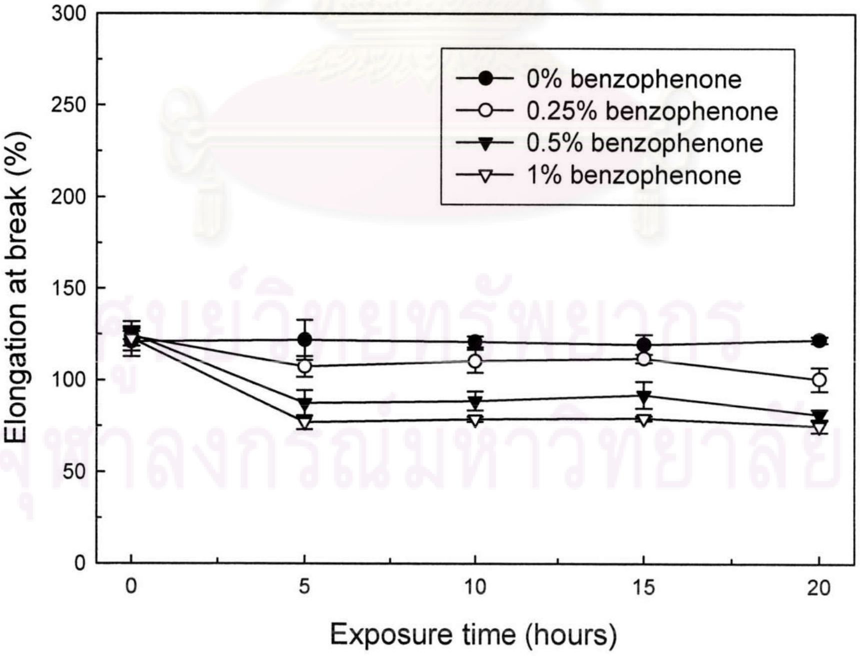


Figure 4.37 Tensile strength and elongation at break of the LDPE/10%starch/10%PE-g-MA blend films with different amount of benzophenone during accelerated test

4.4.2.3 The comparative result of tensile properties

Figure 4.38 exhibits the comparison between tensile properties from outdoor exposure and accelerated exposure of LDPE/10%starch/10%PE-g-MA/1%benzophenone. The plot shows that both of tensile strength and elongation at break of outdoor exposure blend films was higher than that of accelerated exposure in Xenotest Beta Lamp. This is due to the fact that in outdoor condition, the erosion by rain and dew also plays an important role on responsible for these lost of tensile properties.

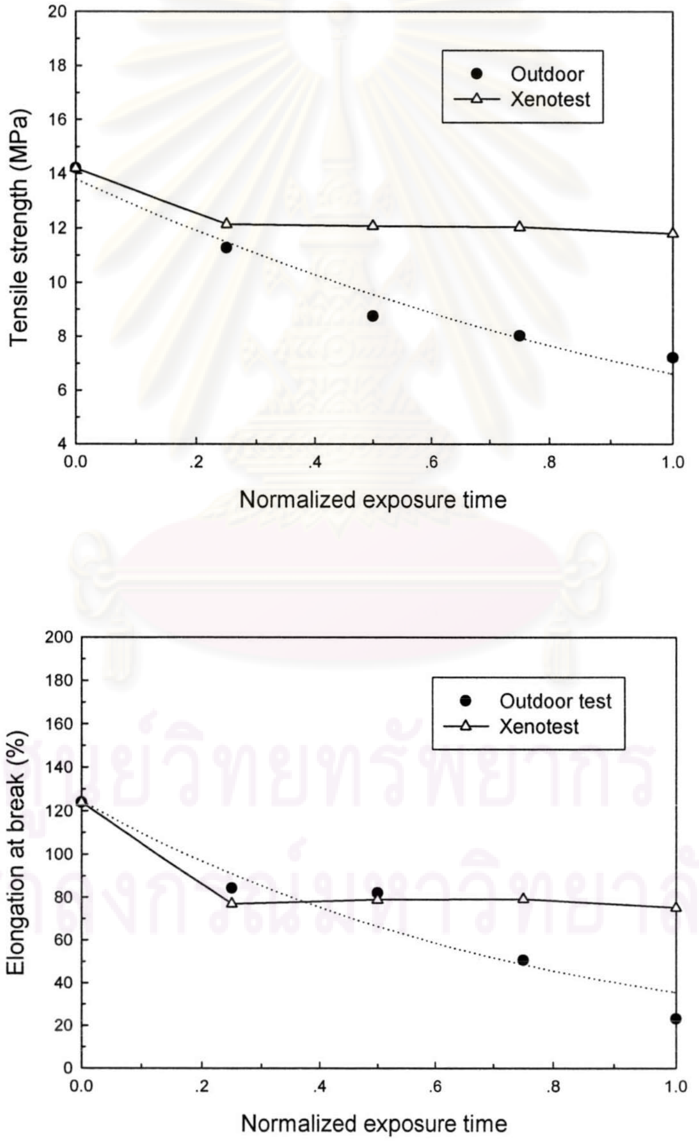


Figure 4.38 Normalized plots of tensile properties between outdoor and accelerated exposure of the LDPE/10%starch/10%PE-g-MA/1%benzophenone blend film

4.5 Evaluation of Biodegradation

Biodegradation of LDPE/starch blends were performed by soil burial method and resistance of LDPE/starch films to fungi according the ASTM G21-96.

4.5.1 Soil Burial Test

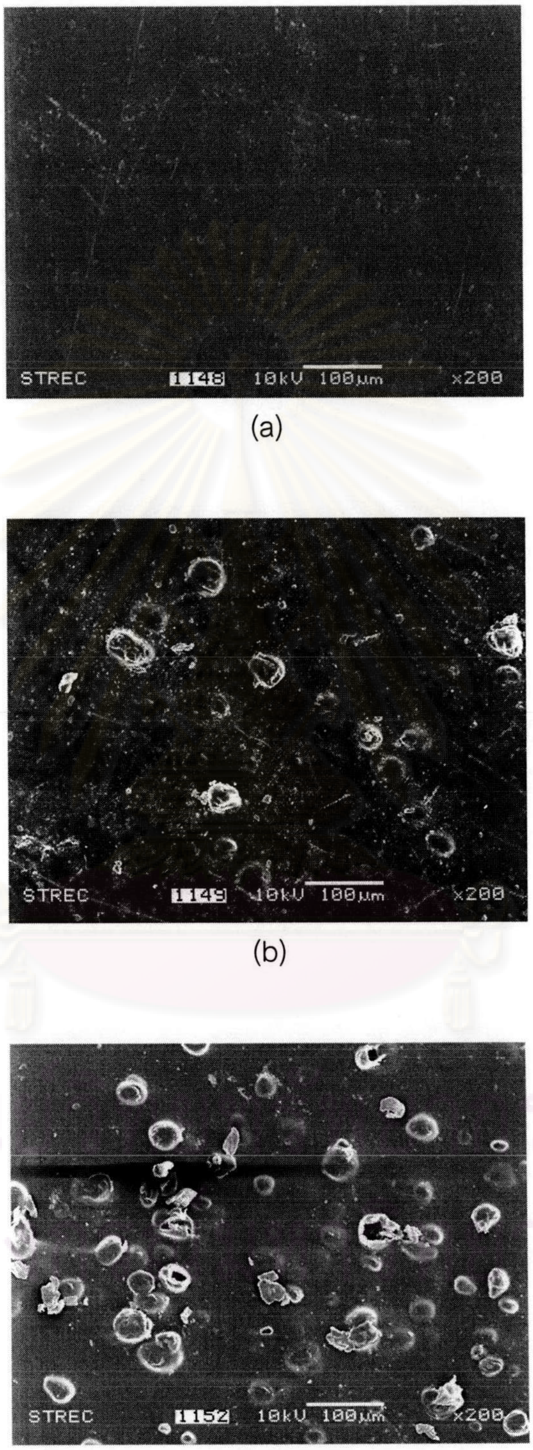
After being subjected to the soil, samples were removed for testing every month. Physical appearance of the film surface was observed by SEM. In addition, biodegradation rate was also evaluated by measuring weight loss and tensile properties of the films.

4.5.1.1 Morphological Studies

The change in surface morphology and physical appearance of the blends after being exposed to soil for 3 months was studied in terms of the amount of banana starch, the effect of compatibilizer, the effect of photosensitizer and the duration time of testing.

4.5.1.1.1 Effect of starch content

The SEM micrographs for LDPE/starch blend containing different amount of starch are shown in Figure 4.39. After 3 months exposure, there was no indication of biodegradation for pure LDPE film. However, the films with 5% and 20% starch were obviously degraded as evidenced by the existence of small holes on the surface of the film. The numerous tiny holes appeared on the surface of the films confirmed starch removal. This is because there are more sites on the film surface that can be attacked by microorganisms. These SEM micrographs prove that starch is the main carbon source for microorganism while the LDPE matrix remains unaffected. Therefore, the oxygen can attack the newly generated surface with the formation of peroxides and hydroperoxides. These radicals promote the scission of the LDPE main chain into small fragments that are more susceptible to attack by microorganisms. As expected, more minute holes increased when starch content increased.



(a)

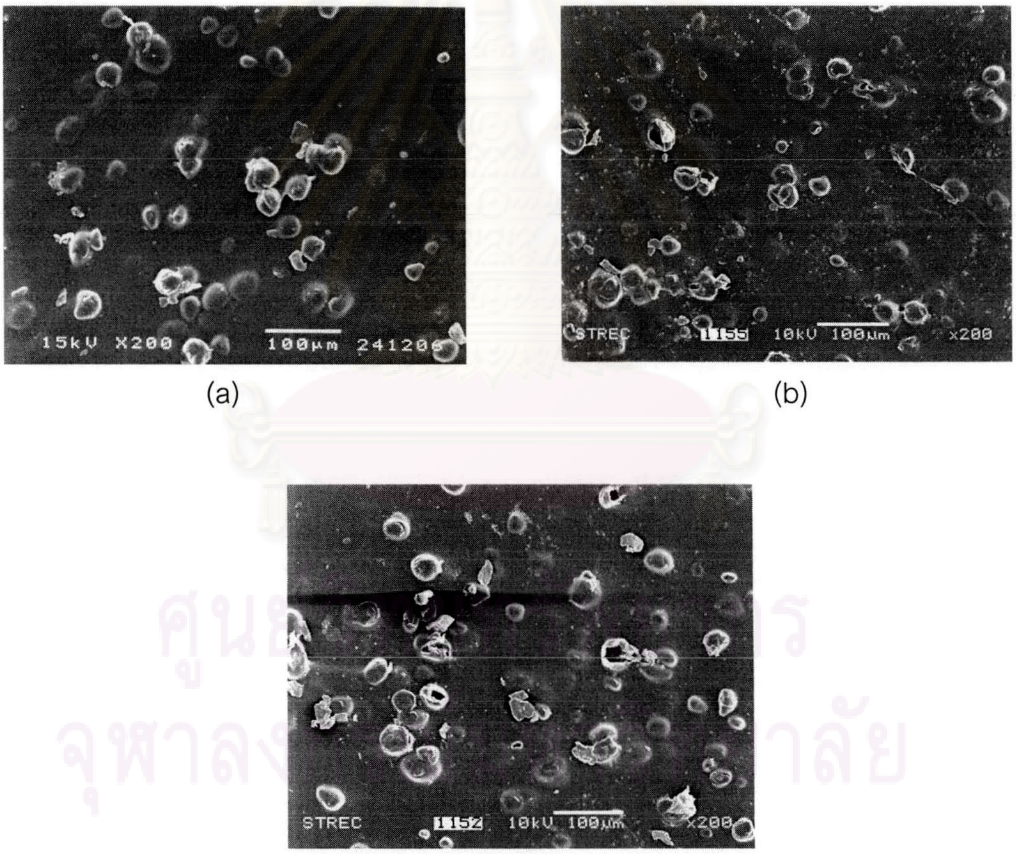
(b)

(c)

Figure 4.39 SEM micrographs of (a) pure LDPE and LDPE blends with (b) 5% starch and (c) 20% starch after 3 months of exposure in soil

4.5.1.1.2 Effect of Exposure Time

Figure 4.40 exhibits the micrographs of the LDPE/20% starch blend film for different exposure time. Starch grains can be seen on the sample before burial in soil. After 1 month of burial, these grains started to disappear because they were consumed by microorganisms. This left a film with a surface full of cavities, which became more abundant as the burial time increased. The consumption of the starch was continued up to 3rd month when relatively many holes arised, suggesting starch consumption.



(a)

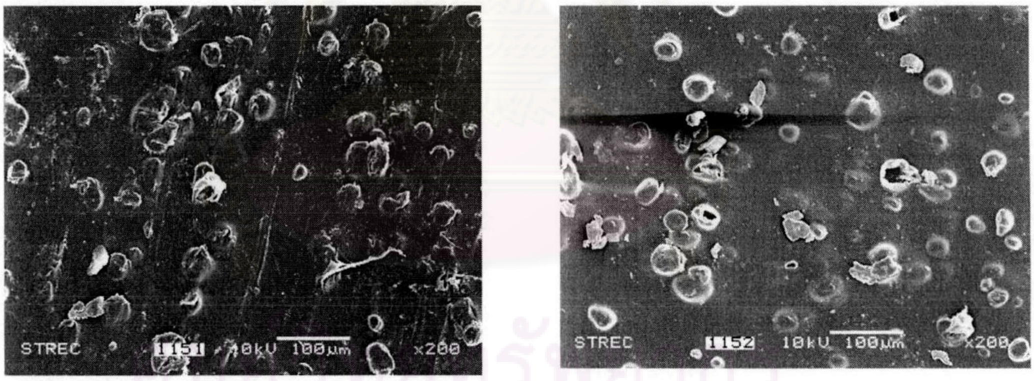
(b)

(c)

Figure 4.40 SEM micrographs of LDPE/starch blend with 20% starch during exposed in soil for (a) 0 month, (b) 1 month and (c) 3 months

4.5.1.1.3 Effect of Compatibilizer

The comparison of the compatibilized and uncompatibilized blend films are displayed in Figure 4.41 (a) and (b), respectively. As seen in Figure 4.41 (a) less significant retardation in starch consumption can be detected. In contrast, the uncompatibilized blend showed many number of tiny holes. The difference between the uncompatibilized and compatibilized blends can be clarified by the following reasons. For uncompatibilized blends, LDPE matrix only encapsulates the starch granules without any bonding. Thus, there is a gap between LDPE matrix and starch granules. This gap increases porosity of the LDPE matrix, which can then easily permit the microorganism attacking throughout the LDPE matrix. For LDPE/starch blend with compatibilizer, the interfacial adhesion between the two components makes the removing of starch granules from the films more difficult. These results are in good agreement with the tensile properties, as will be described in the next section.

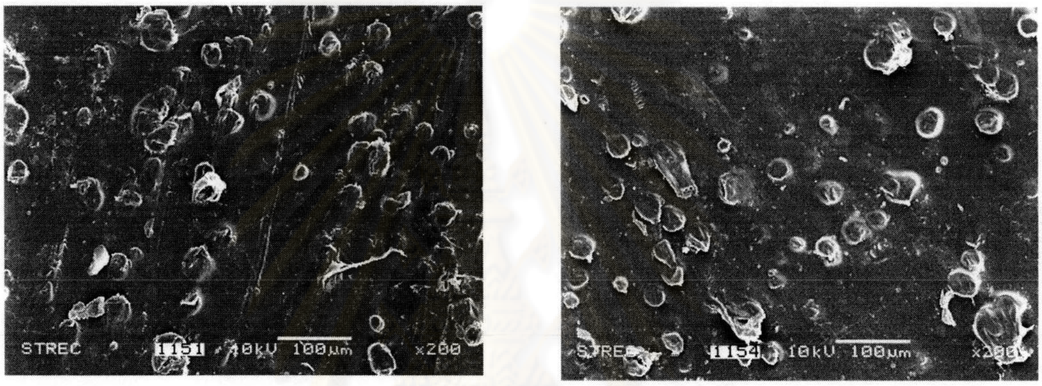


(a) (b)

Figure 4.41 SEM micrographs of LDPE/20% starch blend after burial in soil for 3 months: (a) compatibilized blend with 10% PE-g-MA and (b) uncompatibilized blend

4.5.1.1.4 Effect of Photosensitizer

As shown in Figure 4.42, it is very difficult to distinguish the difference between LDPE/starch blend added 1%benzophenone and the blend film without benzophenone. After 3 months of exposure in soil, the result showed that there were few small cavities in both of the blends. This is because of the presence of the compatibilizer and photosensitizer. Benzophenone is an aromatic carbonyl conpound photosensitizer that might be sufficiently toxic to inhibit microbial growth in culture.



(a) (b)

Figure 4.42 SEM micrographs of LDPE/20%starch/10% PE-g-MA blend (a) with 1%benzophenone and (b) without benzophenone after 3 months exposure in soil

4.5.1.2 Weight loss

Weight loss measurement is the most simple technique to determine the biodegradability of the biodegradable films.

4.5.1.2.1 Effect of starch content

Starch consumption by microorganism resulted in weight loss of the blends. These results are shown more clearly in Figure 4.43, which illustrates the weight loss of the LDPE/starch blends as a function of the exposure time in soil.

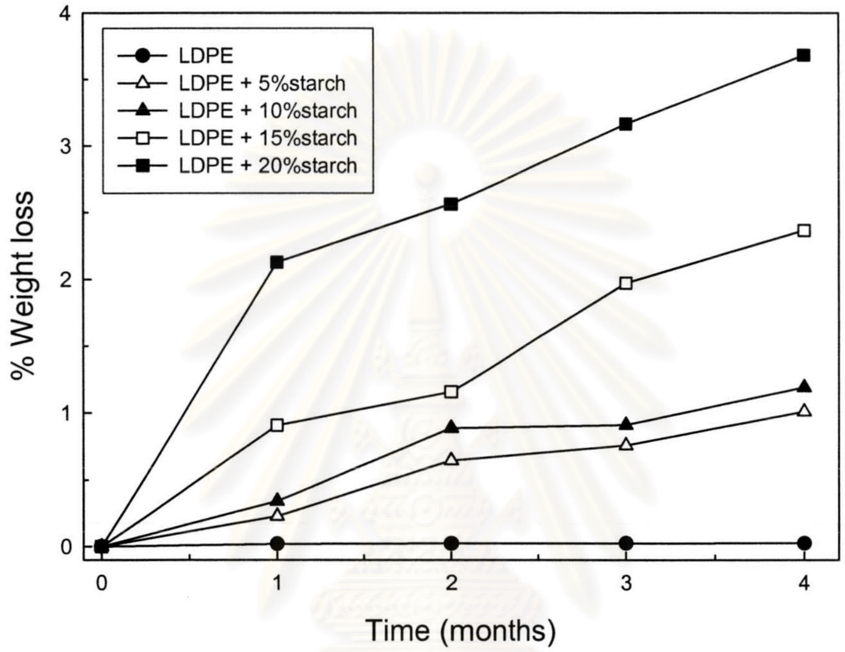


Figure 4.43 Weight loss of LDPE/starch blends during soil burial

As can be observed, LDPE exposed in soil for 4 months did not show any significant weight loss (around 0.02%), while blends with starch exhibited greater weight loss. For the blends containing 5% and 10% starch, the amount of starch consumption was insignificant since the weight loss was very small (up to 1%), even after 4 month of exposure. The biodegradation rate rapidly increased for the blend with 20% starch even after the first month of exposure.

Conclusively, the percentage of weight loss increased with the duration time of exposure in soil and the starch content. For the blends with high starch content, starch was more exposed, as result, a greater portion of it was consumed by microorganisms. In contrast, for the blends containing low amount of starch, the starch almost completely covered by LDPE and was not accessible by microorganisms. The starch diameter was about one fourth of the film thickness, and the microorganisms would consume only the starch that was located on the surface of the film.

4.5.1.2.2 Effect of Compatibilizer

Figure 4.44 displays weight loss of the compatibilized blends. Comparing to Figure 4.43, the same behavior was also observed in the compatibilized blends. The blend with 20% starch showed a significant weight loss compared to the others.

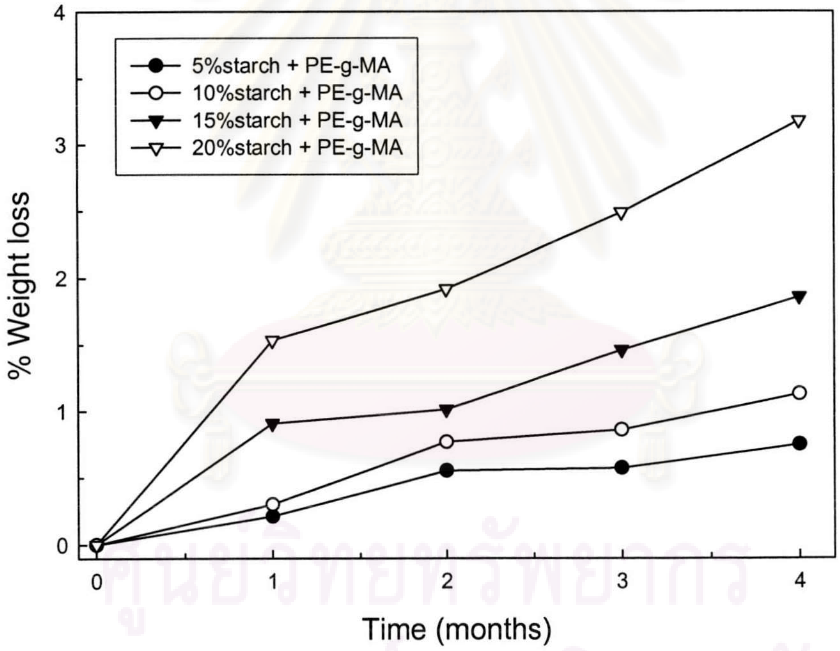


Figure 4.44 Weight loss of LDPE with different amount of starch and 10% of PE-g-MA

The comparison between compatibilized and uncompatibilized blends is shown in Figure 4.45. From this plot, it can be suggested that the degradation rate of the compatibilized blends slightly lower than that of the corresponding uncompatibilized ones. This might be implied that the compatibilizer has an inhibiting effect to the biodegradation of the blend film. This effect of PE-g-MA may be due to the bonding between anhydride groups of the PE-g-MA and the hydroxyl groups of starch, which presents or obstructs the consumption of starch from microorganisms in the soil.

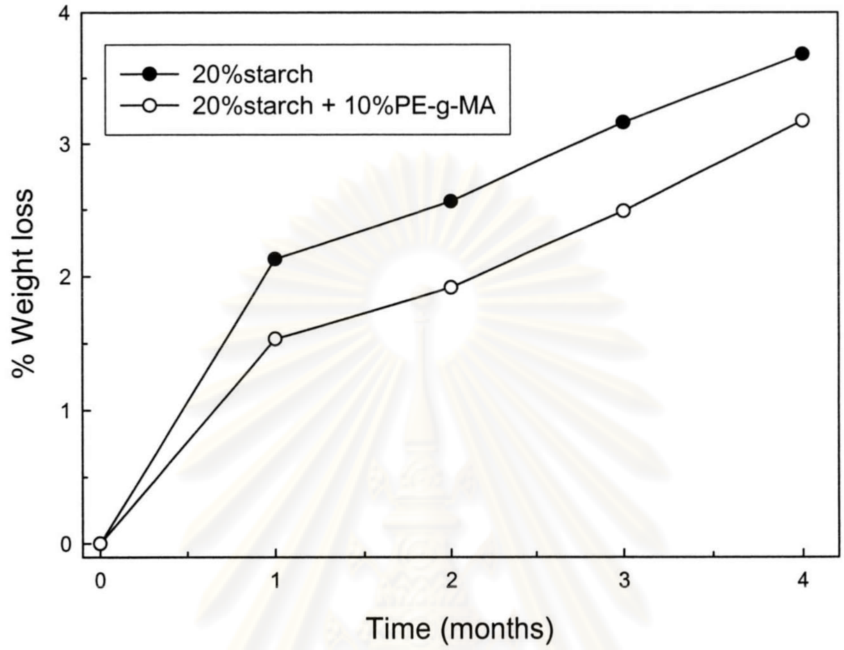


Figure 4.45 The comparison between LDPE/ 20% starch blends with and without 10% PE-g-MA as compatibilizer

4.5.1.2.3 Effect of Photosensitizer

The effect of photosensitizer on weight loss of the LDPE/starch blends containing 20% of starch and 10% of a compatibilizer as a function of exposure time can be seen in Figure 4.46. The data showed that as the amount of benzophenone increased, weight loss of the films decreased. The result is similar to the case of the compatibilizer, PE-g-MA, that both PE-g-MA and benzophenone act as an inhibitor reducing the effectiveness of the biodegradability of the blend films. As clearly depicted in Figure 4.47, without these two components, weight loss the LDPE/starch blend film can be as high as 3.68% after 4 months of exposure. However, the addition of 10% PE-g-MA had reduced weight loss of the blend film to 3.17%. Likewise, weight loss of the blend film had further decreased to 1.71% after adding 1% of benzophenone.

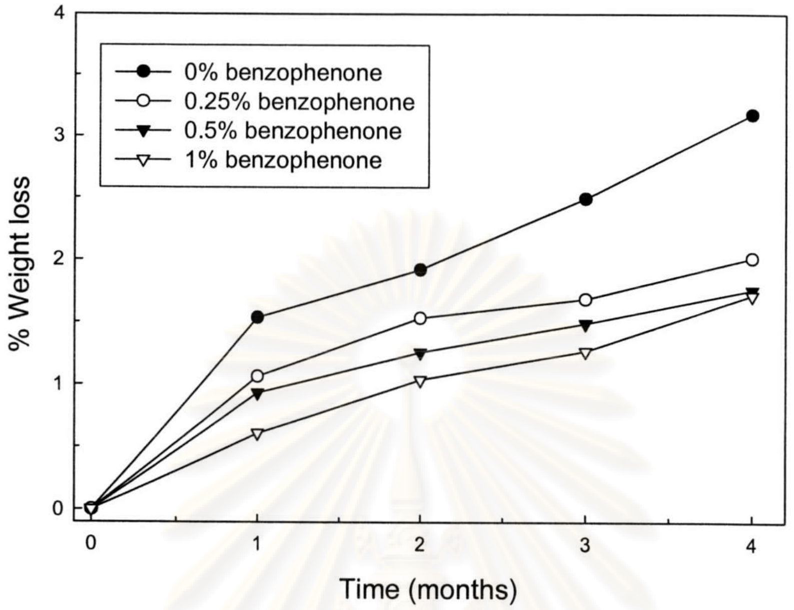


Figure 4.46 Weight loss of the LDPE/20%starch/10%PE-g-MA blends with different amount of photosensitizer

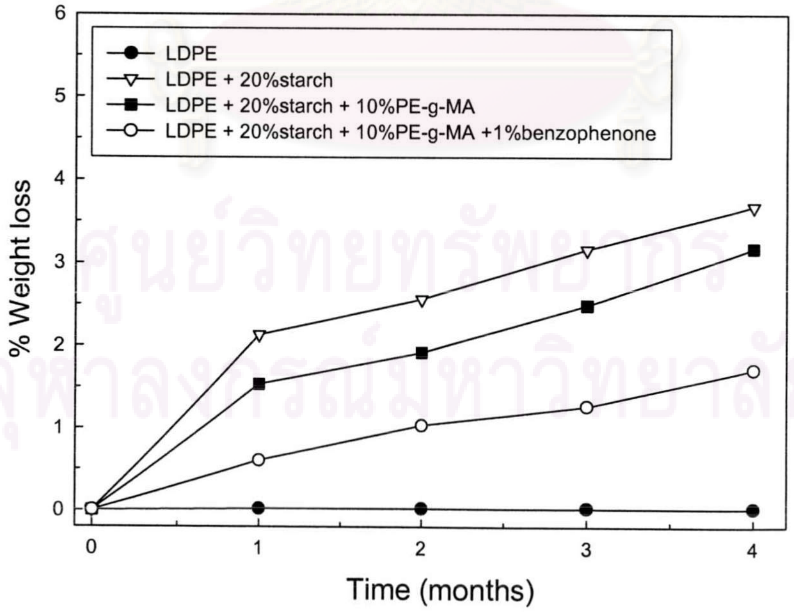


Figure 4.47 Weight loss of pure LDPE, LDPE/20%starch, LDPE/20%starch/10%PE-MA, and LDPE/20%starch/10%PE-g-MA/1%benzophenone blends films

4.5.1.3 Tensile properties

4.5.1.3.1 Effect of starch content

As presented in Figure 4.48, tensile properties of the LDPE/starch blend films decreased slowly with an increase in the soil burial time. In fact, such a decrease can be observed in both the tensile strength as well as elongation at break. As shown, there was a slight reduction in tensile strength and elongation at break as the time of exposure increased. In addition, increasing of the starch content reduced the tensile properties as a function of time as well. The reason for this is the starch consumption by microorganism. Starch consumption results in the destruction of the adhesion between the two phases and creates a large number of cavities in the LDPE matrix. These changes are reflected to the tensile properties of the blend films. In comparison with the photodegradation test by outdoor exposure demonstrated in Figure 4.31, the decrease in tensile properties as a function of exposure time and starch content was more distinct than the soil burial test. Obviously, after 4 months of outdoor exposure, the tensile strength of the LDPE and LDPE/starch films decreased up to about 48.07-53.49%, where as those of the films buried in the soil decreased only 7.53-8.00%.

4.5.1.3.2 Effect of compatibilizer

Figure 4.49 shows the tensile strength and elongation at break of the compatibilized and uncompatibilized blends. As the exposure time increased, the tensile strength and elongation at break of the compatibilized and uncompatibilized blends decreased slowly. However, the compatibilized blend with 10%PE-g-MA exhibited an increase in the tensile properties compared to the uncompatibilized ones. After 4 months, tensile strength of the LDPE/10%starch blend film without PE-g-MA decreased about 16.58%, while that of the compatibilized blend film decreased 11.50%. At the same amount of starch and degradation time, the elongation at break of the uncompatibilized blend and the blend containing 10%PE-g-MA was decreased about 51.63 % and 28.17%, respectively. This is because starch granules of the uncompatibilized blend have no interfacial adhesion with the LDPE matrix with respect to the compatibilized blend. The uncompatibilized blend has more surface areas of starch to be attacked by microorganisms than the compatibilized blend, as seen in Figure 4.7. Therefore, the uncompatibilized blend has more microscopic holes randomly scattering in the film than the compatibilized blend. Consequently, the tensile strength and elongation at break of the uncompatibilized blend were lower than the compatibilized blend.

4.5.1.3.3 Effect of Photosensitizer content

Figure 4.50 displays the plot of tensile strength and elongation at break as a function of time and photosensitizer content. The tensile properties of all blends slightly decreased as a function of burial time. Similar trend can be observed in both tensile strength and elongation at break that the blend film without benzophenone had the greatest decrease in tensile properties compared to the others. These results were different from the photodegradation test that the increase in benzophenone content helped promoting the decrease in tensile properties of the blend films being subjected to the outdoor and accelerated exposure tests. However, those results were similar to the weight loss measurement in which the increasing of benzophenone concentration decreased the biodegradabillity of the films.

In addition, these results are in good agreement with the SEM micrographs shown in Figure 4.42. The LDPE/starch blend films containing 1%benzophenone showed small amount of holes on the film surface. This is because benzophenone in the blend films inhibits the growth of microorganisms, resulting in the reduction of the starch consumption by microorganisms. Therefore, the blends containing higher content of benzophenone had small decrease in tensile strength and elongation at break as a function of time. After 4 months, the tensile strength and elongation at break of the blend film with 1%benzophenone decreased about 1.89% and 17.59%, respectively. Whereas the tensile strength and elongation at break of the blend film without benzophenone decreased approximatly 11.50%, and 28.17%, respectively. It can then be concluded that benzophenone has a small inhibiting effect on the biodegradation rate of these systems.

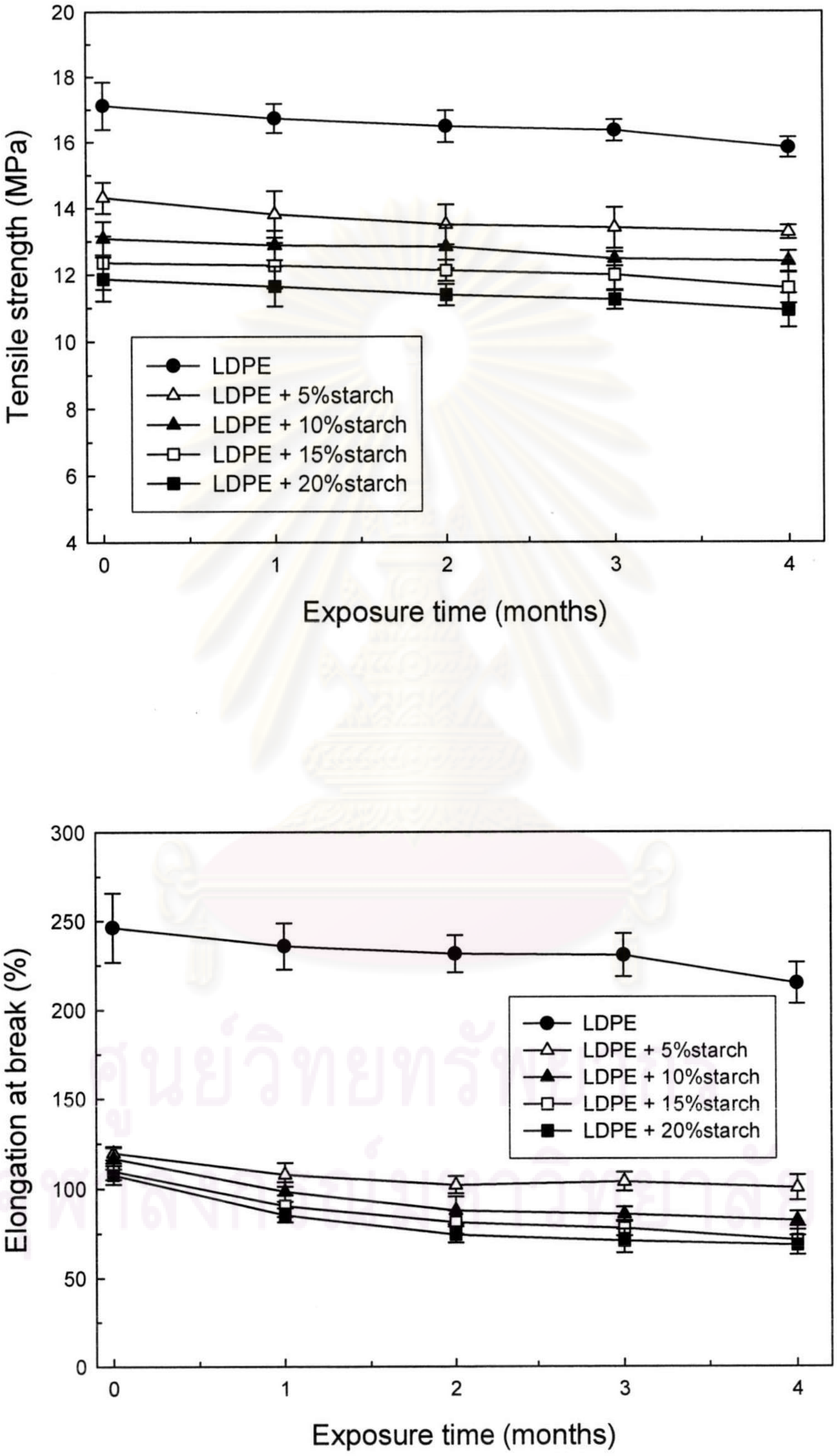
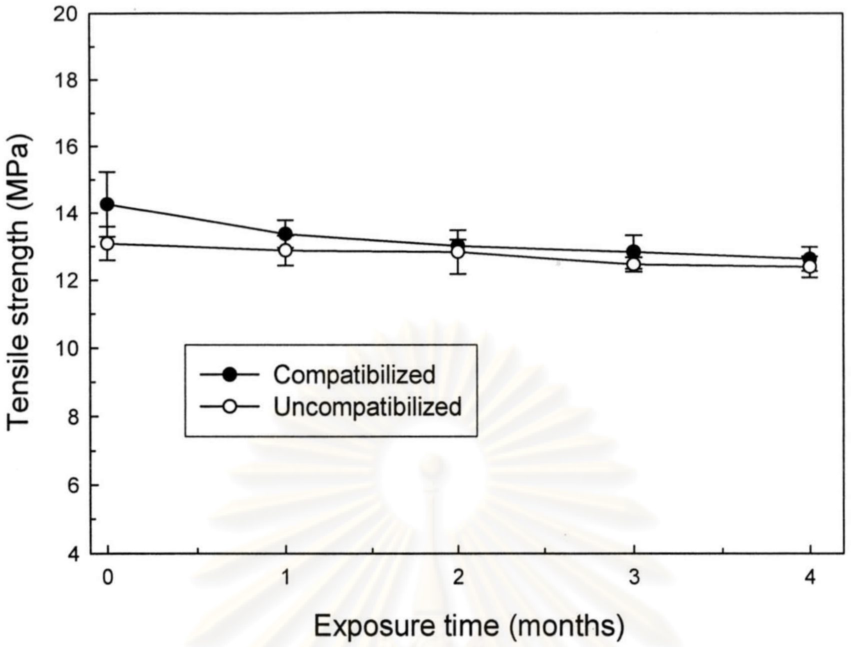


Figure 4.48 Tensile strength and elongation at break of LDPE/starch blend during soil burial test for 4 months



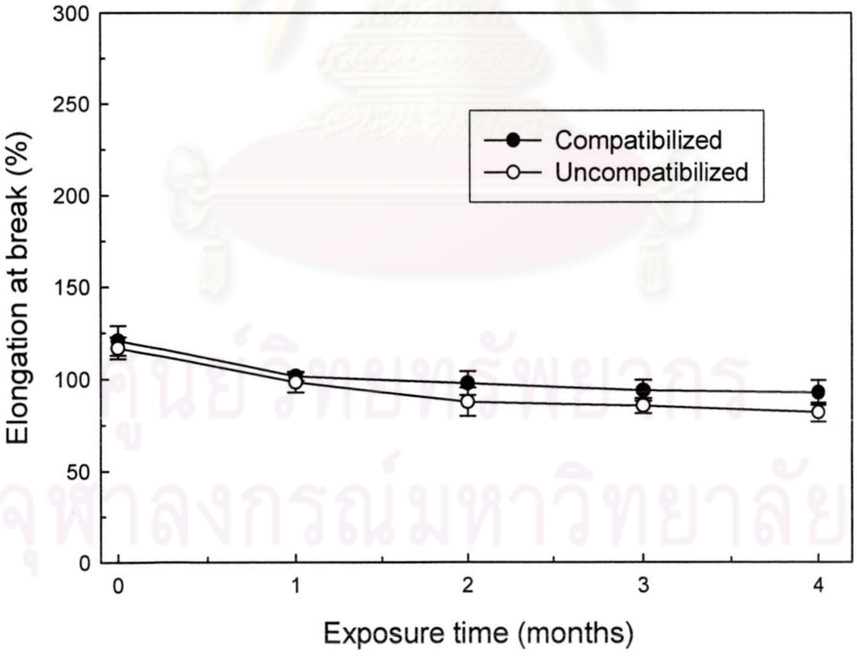
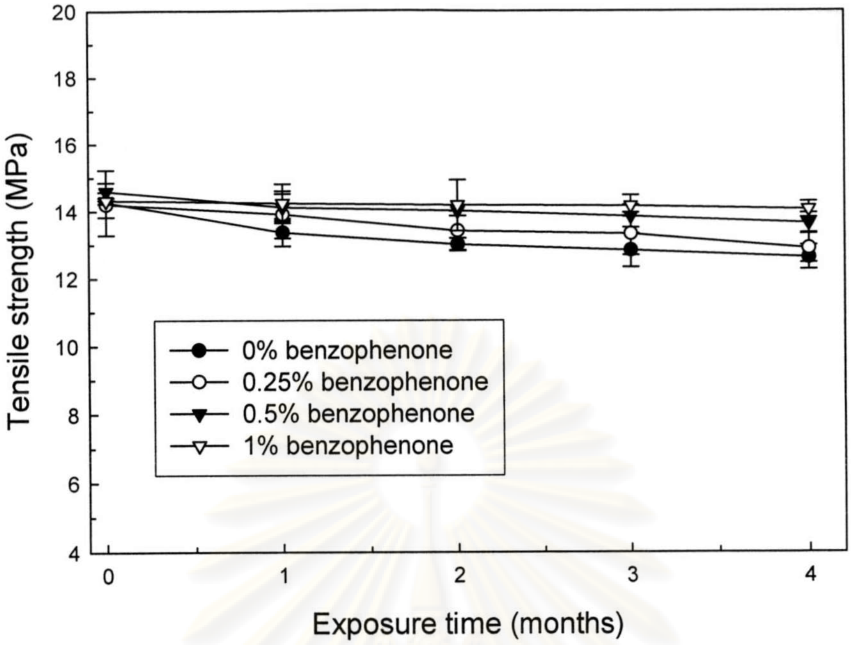


Figure 4.49 Tensile strength and elongation at break of 10% starch films uncompatibilized and compatibilized with 10% PE-g-MA during soil burial test



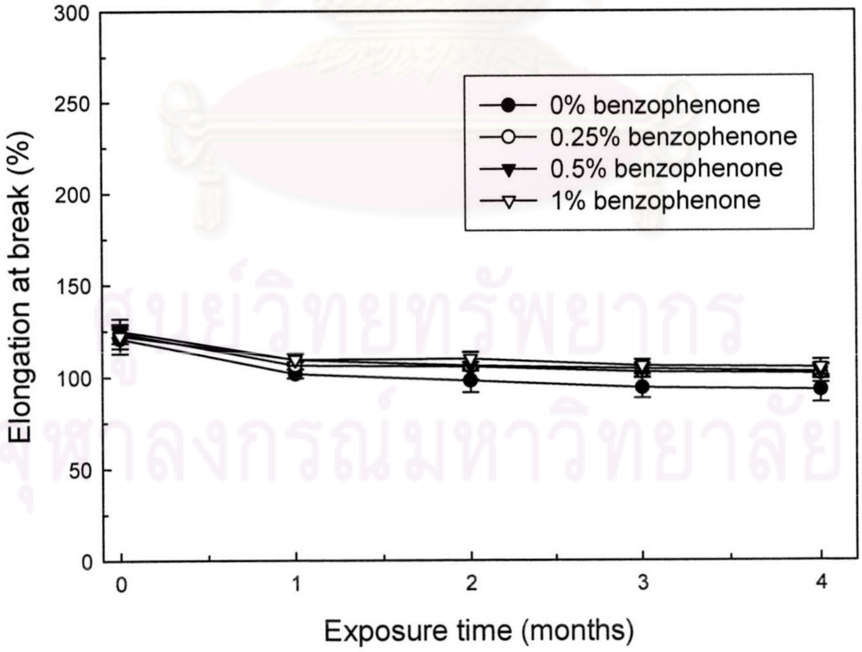


Figure 4.50 Tensile strength and elongation at break of LDPE/10%starch /10% PE-g-MA blend containing different amount of benzophenone during soil burial test

4.5.2 Determination of Film Resistance to Fungi

4.5.2.1 Growth Rate

Table 4.4 summarizes the biodegradation results obtained from the film resistance to fungi test.

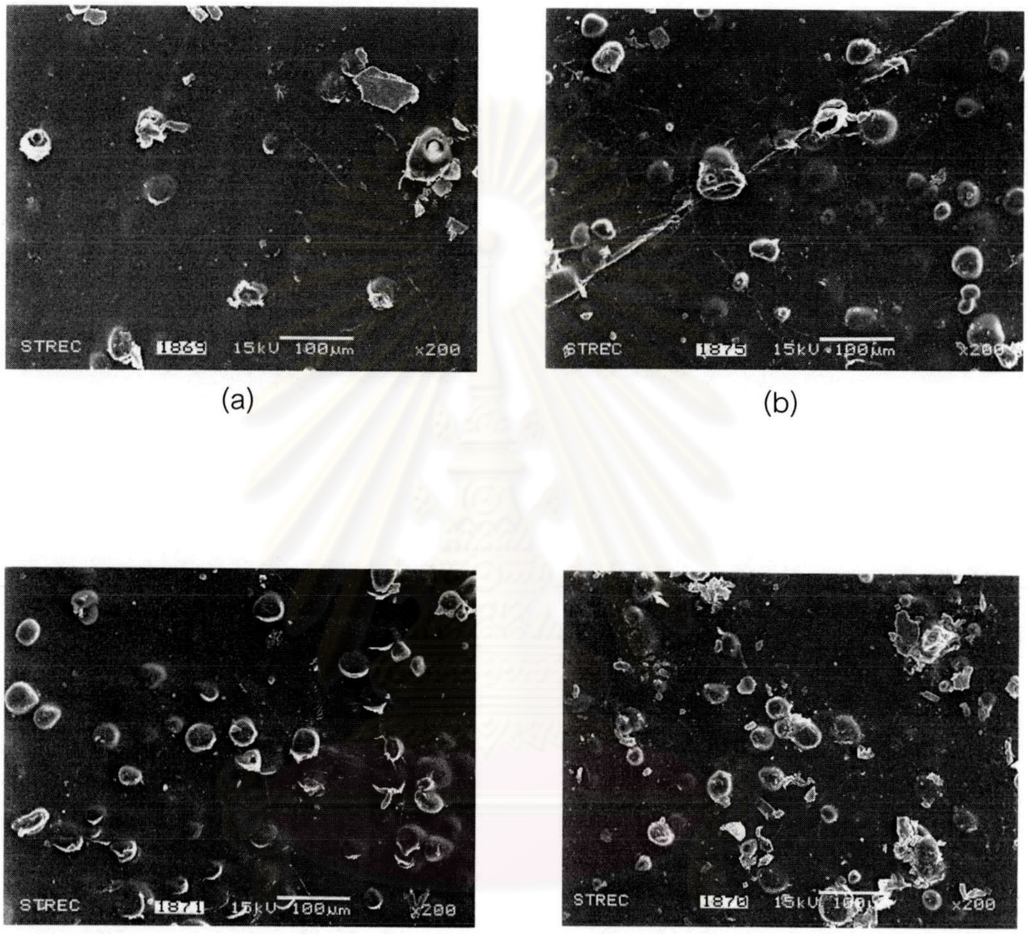
Table 4.6 Growth rate of the films after 58 days test

Sample	Growth rate
LDPE film	0 (no growth)
LDPE + 5%starch	1 (less than 10%covered)
LDPE + 20%starch	1 (less than 10%covered)
LDPE + 20%starch + 10%PE-g-MA	0 (no growth)
LDPE + 20%starch + 10%PE-g-MA + 1%benzophenone	0 (no growth)
Banana starch film	4 (60-100%covered)

4.5.2.2 Morphological Studies

In order to investigate in more detailed, the micrographs for the LDPE/5%starch, LDPE/20%starch, LDPE/20%starch/10%PE-g-MA, and LDPE/20%starch/10%PE-g-MA/1%benzophenone blend films after 58 days test are presented in Figure 4.51. The empty craters resulted from the consumption of starch granules by Aspergillus niger fungus were seen in the LDPE/5%starch and LDPE/20%starch blends. This fungus can produce enzyme phosphorylase capable of hydrolyizing amylose and amylopectin which are constituents in starch [13]. The LDPE/20%starch blend exhibited the larger holes than the LDPE/5%starch blend, suggesting an extensive starch consumption.

In contrast, the blend films containing PE-g-MA and benzophenone were found to become more resistant towards microbial attack. Both films showed no sign of cavity on the film surface. This result is similar to the result from soil burial test. Thus, it might be confirmed that PE-g-MA and benzophenone act as an inhibitor reducing the efficiency of the biodegradation of the blend films.



(a) (b) (c) (d)

Figure 4.51 SEM micrograph of (a) LDPE/5%starch, (b) LDPE/20%starch, (c) LDPE/20%starch/10%PE-g-MA, and (d) LDPE/20%starch/10%PE-g-MA/1%benzophenone blend films after 58 days test