

CHAPTER IV

RESULTS AND DISCUSSION

The aim of this research was to control photodegradation of LDPE by incorporating microencapsulated photosensitizer particles as an additive. The effects of coating thickness of the photosensitizer and the contents of microencapsulated particles on photodegradation behavior of the LDPE films were studied. Microencapsulation of photosensitizer was prepared by simple coacervation technique, in which the ratio of coating material (gelatin) and core material (benzophenone) and amount of hardening agent (formaldehyde) were varied. Microcapsules were characterized by scanning electron microscopy (SEM) and thermogravimetric analysis (TGA). The LDPE and LDPE films containing additives were prepared by a compression molding. The specimens were cut from these films and test for their photodegradability for 4 months. Photodegradation was studied under sunlight and accelerated condition (ultraviolet light). The evaluation of photodegradation was followed by weight loss, tensile properties, physical appearance, and carbonyl index from FTIR spectrum of the film.

4.1 Preparation of Benzophenone Microcapsules

Benzophenone was used as a core particle of microcapsule and photosensitizer for accelerating the photodegradation of LDPE. Gelatin was used as a coating material of microcapsule. Benzophenone and gelatin powder were prepared by grinding in the ball mill for 1 day and the ground powder was filtered through the sieve in order to receive the homogeneous powder. Approximately 85.7% and 70.4% of the amount of benzophenone and gelatin powder, respectively, have the average diameter of 120 - 150 μm .

The TGA thermogram of pure benzophenone and gelatin powder are shown in Figure 4.1. The thermogram shows the onset of decomposition temperature and %weight loss. The pure benzophenone powder shows one decomposition stage at 220 °C. The pure gelatin shows two decomposition stages. The first one around 100-110 °C is due to moisture; whereas the second stage presented around 276 °C belongs to the onset of decomposition temperature of gelatin powder. As seen in Figure 4.1, both pure benzophenone and gelatin powder are almost completely decomposed and the % weight residues are 0.7% and 0.9%, respectively.

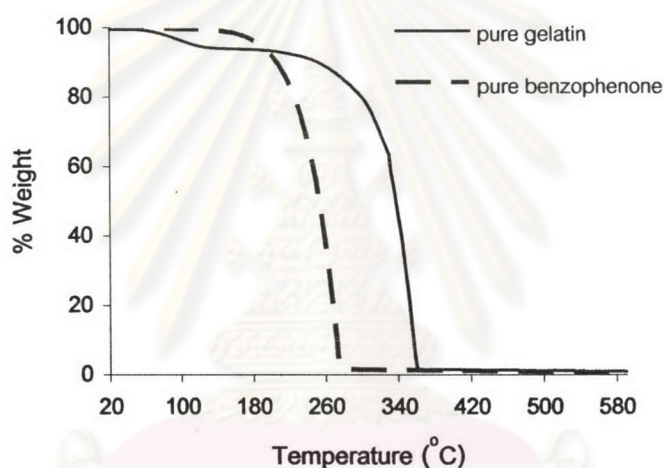


Figure 4.1 The TGA curves of pure benzophenone and pure gelatin powder

4.2 Characterization of Encapsulated Benzophenone

Encapsulated benzophenone powder was prepared by simple coacervation technique. Gelatin, water-soluble polymer, is the starting material for formation of a coating material. The formation of a coacervate was occurred by adding sodium sulphate solution (Na_2SO_4). It was found that the optimum concentration of salt solution is 20% w/v. The higher concentration made gelatin coagulated, whereas the lower concentration did not

cause any coacervation of gelatin on benzophenone. As can be seen in Figure 4.2, the TGA curve of microcapsules that were prepared by adding 15%w/v of salt solution shows only the onset of degradation temperature of benzophenone at 218 °C, while the TGA curve of microcapsules that were prepared by adding 20%w/v of sodium sulphate solution shows both benzophenone and gelatin decomposition temperature at 180 °C and 286 °C, respectively.

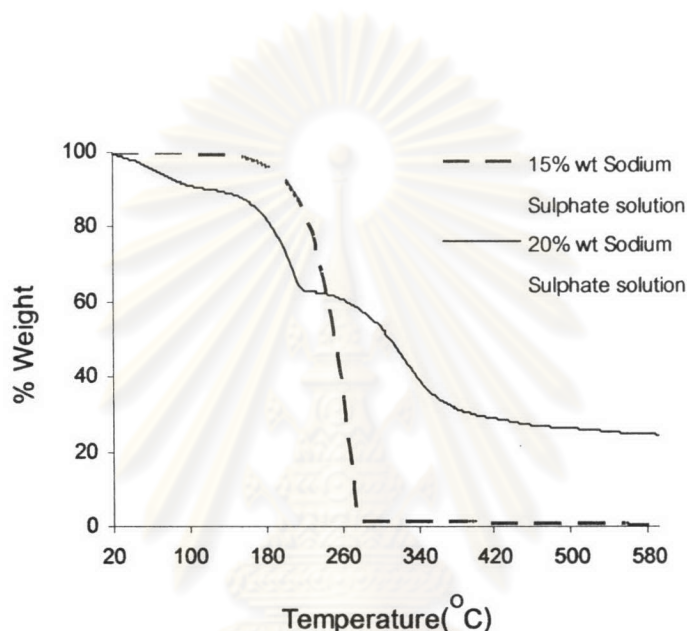


Figure 4.2 Effect of sodium sulphate solution on the TGA curves of microencapsulated benzophenone powder

Besides those 2 decomposition stages, the TGA curve of microcapsule containing 20% w/v of sodium sulphate solution also presents approximately 10% weight loss around 100 °C, which is owing to the moisture desorption of gelatin. Therefore, comparing to the TGA curve of microcapsule prepared from 15% w/v of sodium sulphate solution, these 3 decomposition stages can confirm the occurring of encapsulated benzophenone. However, the microcapsules are not completely decomposed. After the decomposition of gelatin, the %weight loss is constant at 25% from 500 °C to 600 °C. It may be explained that microcapsules had some Na_2SO_4 left that was not completely washed.

The morphology of benzophenone, gelatin, and encapsulated benzophenone particles are shown in Figure 4.3. Obviously, the surface of the microcapsule is not smooth. One possible explanation is that benzophenone particles might not be completely coated by gelatin so the uncoated reagents were washed away by ethanol leaving unsmooth surface.

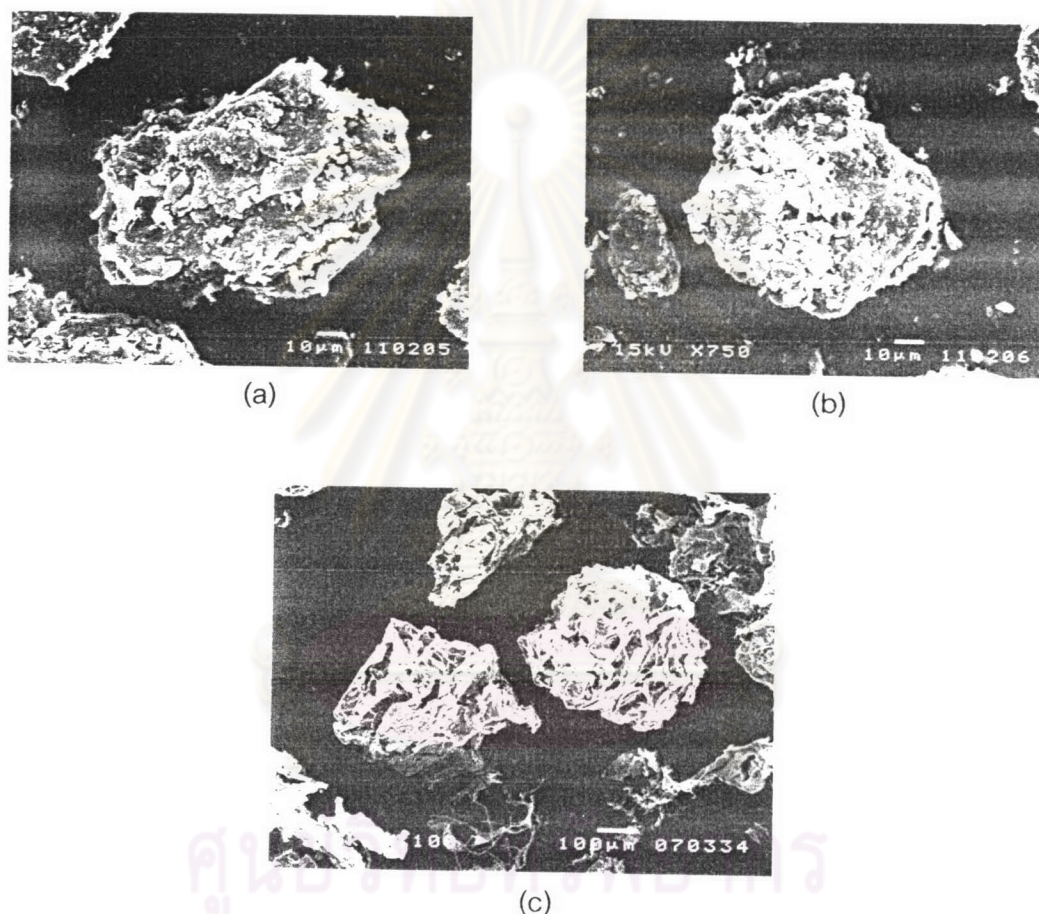
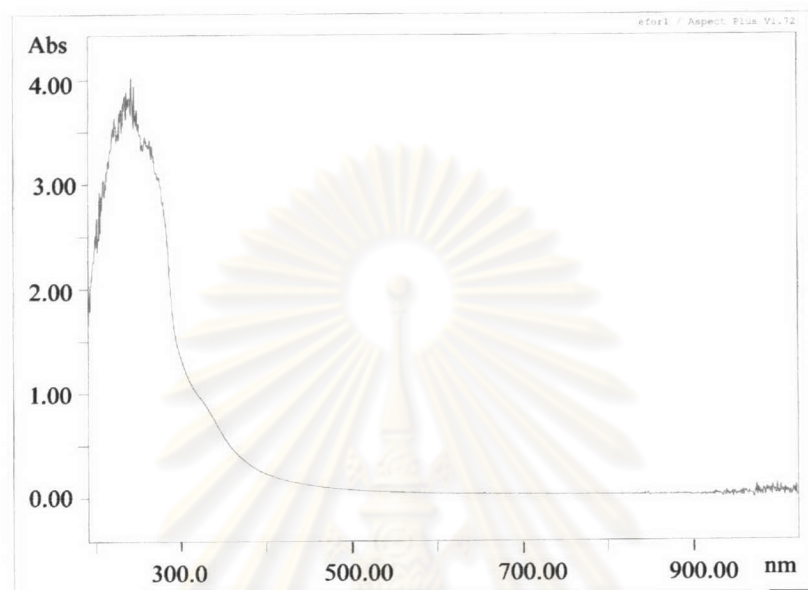


Figure 4.3 The morphology of (a) gelatin powder (b) benzophenone powder and (c) encapsulated benzophenone

The reactive gelatin was confirmed by UV-VIS spectroscopy. Figure 4.4 shows the UV-VIS spectrum of gelatin solution before and after coacervation. The spectrum of gelatin solution before coacervation shows the significant peak occurring at 200-300 μm and the intensity of the absorbance is 3.80. After coacervation, this peak becomes narrower and the

intensity of the absorbance also decreased to 0.42. These results can be confirmed that gelatin is reactive and has been used in a coacervation process.



(a)



(b)

Figure 4.4 The UV-VIS spectrum of gelatin solution (a) before and (b) after coacervation

The obtained encapsulated benzophenone was used to study the controlled photodegradation of LDPE films. Two interesting factors are the thickness of coating material and the amount of hardening agent.

4.2.1 Effect of Benzophenone to Gelatin Ratio

The effect of thickness of coating material was studied by varying the ratios of benzophenone and gelatin which are 1:0.5, 1:1, and 1:2 (EN1, EN2, and EN3). After drying microcapsules by freeze dryer, they were filtered through the sieve in order to receive the narrow size distribution powder. The average sizes of microcapsules and the amount (%) of microcapsules within these diameter ranges are presented in Table 4.1. The data show that almost 85% of EN3 microcapsule was filtered through the sieve no. 30 but does not pass no. 40 which means that the average diameter of EN3 microcapsule is less than 600 -450 μm , while both EN1 and EN2 microcapsules were filtered through the same sieve number (50). However, the amount of received microcapsule of EN1 was more than EN2 around 15%. The amount of filtered microcapsules from each formula can be implied that, among them, the EN3 is the biggest microcapsule, whereas, the EN1 is the smallest microcapsule. Based on the fact that these microcapsules were prepared from the same size of benzophenone powder, hence, the thickness of coating material, which is gelatin in this case, of EN3 microcapsules are greater than those of EN1 and EN2 microcapsules. In other words, the higher the benzophenone to gelatin ratio, the thicker the coating material.

Table 4.1 The average size and %filtered amount of EN1, EN2, and EN3 microcapsules

Formula	Sieve no.	Size (μm)	% filtered amount
EN1	50 - 60	295-150	78.79
EN2	50 - 60	295-150	63.90
EN3	30 - 40	600-450	82.34

The TGA curves of these three microcapsules are presented in Figure 4.5. The value of %weight loss is very important since they can indicate the %weight and the ratio of each material in encapsulated benzophenone. Td at 180°C and 286°C are the decomposition temperatures of benzophenone and gelatin, respectively. From Table 4.2, %weight loss of benzophenone and gelatin of EN1, EN2, and EN3 microcapsules is 70.2 and 20.1, 32.4 and 38.2, and 18.2 and 46.4, respectively. After calculating the ratios of benzophenone and gelatin of EN1, EN2, and EN3, the data show that the ratios are 1:0.29, 1:1.7, and 1:2.55, respectively. From this result, the ratios of benzophenone and gelatin after coacervation are very close to the started or initial benzophenone to gelatin ratio. Eventhough the size of EN1 and EN2 formulas are not much different, the ratios of benzophenone to gelatin in each formula are not equal. Therefore it can be implied that the releasing rate of benzophenone from the EN1 and EN2 microcapsules should not be equal due to the difference in thickness of the coating material.

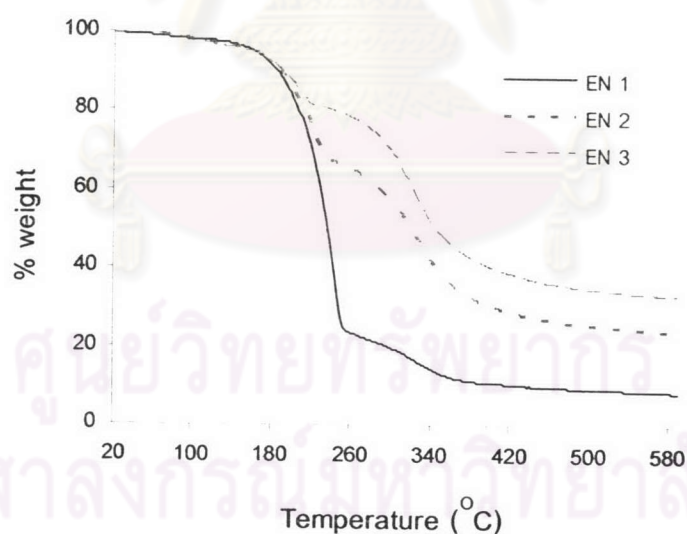


Figure 4.5 The TGA curves of EN1, EN2, and EN3 microcapsules

Table 4.2 Onset of decomposition temperature, percent weight loss, and the ratio of benzophenone and gelatin of EN1, EN2, and EN3 microcapsules

Sample	Td ($^{\circ}$ C) (onset)		% Weight Loss		The ratio of calculated Benzophenone : Gelatin
	First	second	Benzophenone	Gelatin	
EN1	180	299.1	70.2	20.1	1 : 0.29
EN2	180	286.0	32.4	38.2	1 : 1.17
EN3	180	283.3	18.2	46.4	1 : 2.55

4.2.2 Effect of Amount of Hardening Agent

The effect of amount of hardening agent was studied by varying the concentration of formaldehyde; i.e., 1, 2, and 4 ml (EN4, EN5, and EN6). After drying microcapsules by freeze dryer, they were filtered through the sieve in order to receive the narrow size distribution powder. The average size of microcapsules and the amount (%) of microcapsules within these diameter ranges are presented in Table 4.3

Table 4.3 The average size and %filtered amount of EN4, EN5, and EN6 microcapsules

Formula	Sieve no.	Size (μ m)	% filtered amount
EN4	50 - 60	295-150	67.94
EN5	50 - 60	295-150	63.72
EN6	50 - 60	295-150	65.31

From the data in Table 4.3, all formula was filtered through the same sieve no. 50 but did not pass no. 60 and the % filtered amount was similar. These results mean that the amount of hardening agent had no effect on the thickness of coating material or the deposition of gelatin coating around benzophenone core material. To confirm these results,

thermogravimetric analysis was performed and the results are presented in Figure 4.6 and Table 4.4. From Table 4.4, the ratios of benzophenone and gelatin derived from %weight loss of every formula are fall within the same range. Comparing to the starting ratio of benzophenone to gelatin which is 1:1, %weight loss of benzophenone and gelatin of EN4, EN5, and EN6 particles is 26 and 38.1, 33.2 and 40.6, and 28.9 and 43.0, respectively. The calculating ratios of benzophenone and gelatin of EN4, EN5, and EN6 particles are 1:1.46, 1:1.22, and 1:1.48, respectively. The results indicated that the increasing of the amount of formaldehyde did not increase the thickness of coating material.

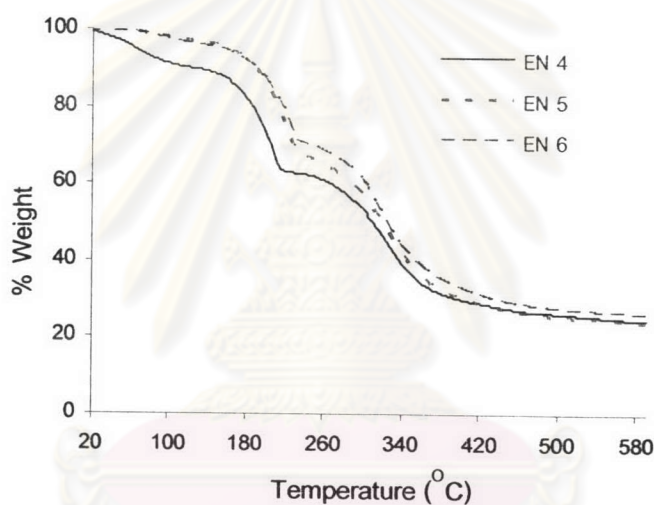


Figure 4.6 The TGA curves of EN4, EN5, and EN6 microcapsule

Table 4.4 Onset of decomposition temperature, percent weight loss, and the ratio of benzophenone and gelatin of EN4, EN5, and EN6 microcapsules

Sample	Td (°C) (onset)		% Weight Loss		The ratio of calculated Benzophenone : gelatin
	First	second	Benzophenone	Gelatin	
EN4	180	299.1	26.0	38.1	1 : 1.46
EN5	180	286.0	33.2	40.6	1 : 1.22
EN6	180	283.3	28.9	43.0	1 : 1.48

4.3 Film Preparation

LDPE films containing additives were prepared using the compression molding. Prior to do so, the constituents, LDPE and benzophenone, LDPE and gelatin, LDPE and encapsulated benzophenone, were physically premixed. In this research, benzophenone, gelatin, or encapsulated benzophenone concentrations were varied in four different levels; 0.5, 1, 3, 5 %w/w. The films were transparent and their thickness is approximately 80 μm . Figure 4.7 shows the SEM micrographs of pure LDPE and LDPE/encapsulated benzophenone films. Although the SEM micrograph shows some evidence of encapsulated particles, generally, the encapsulated benzophenone was well compatible with LDPE powder. In fact, the dispersion of microcapsules within the LDPE matrix prepared from LDPE powder was better than the dispersion of those prepared from LDPE pellet.

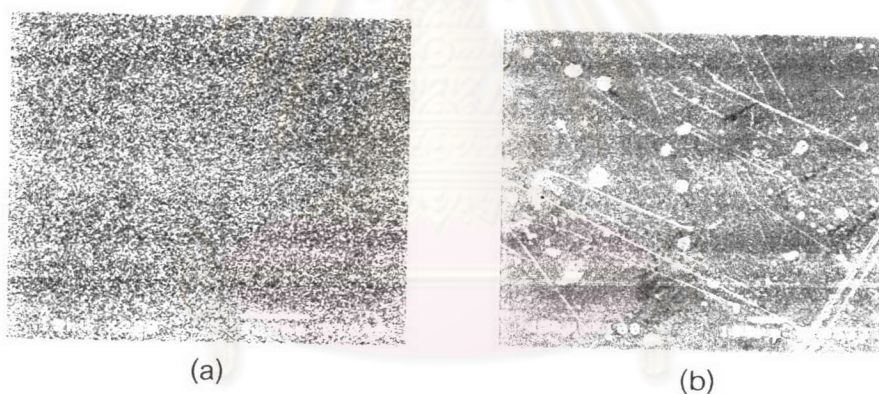


Figure 4.7 The SEM micrographs of (a) LDPE film and (b) LDPE film containing 3%EN2 microcapsule

4.3.1 Chemical Structure

FTIR technique was used to characterize the functional group of the composite films. The wavenumber of vibrations of LDPE, gelatin, and benzophenone are given in Table 4.5

Table 4.5 The wavenumber of vibrational molecule and assignments for LDPE, gelatin, and benzophenone powder

Wave number (cm ⁻¹)	Assignment and Remarks
LDPE :	
2950	-C-H stretching
1475	-C-H bending of -CH ₂
1475, 1380	-C-H bending of -CH ₃
720, 730	-CH ₂ rocking
Benzophenone :	
3050	=C-H stretching
2950	-C-H stretching
1710	-C=O stretching of ketone
1600, 1580, 1500	-C=C stretching (benzene ring)
750, 650	=C-H rocking
Gelatin :	
3000-3600	-O-H stretching with absorbed water
3300	-N-H stretching
2950	-C-H stretching
1650-1690	-C=O stretching of amide
1400	-C-N stretching

FTIR spectra of pure LDPE and LDPE/5% benzophenone films are presented in Figure 4.8. The pure LDPE film shows three main peaks of -C-H stretching, -C-H bending, and -C-H rocking at 2950 cm⁻¹, 1470 cm⁻¹, and 720 cm⁻¹, respectively. However, the spectrum of benzophenone filled LDPE film presents a different peak at 1710 cm⁻¹. This extra peak compared with pure LDPE film is assigned to the carbonyl group (-C=O) of ketone from benzophenone. The other peaks at 3050 and 1500 indicating =C-H stretching and -C=C stretching of benzene ring, respectively, do not exist because they are

overlapping with the very strong peaks of LDPE. The strong peak of carbonyl at 1710 cm^{-1} depends on benzophenone content. The spectra show that the intensity of carbonyl peak increased with an increasing of benzophenone content (Appendix D.2).

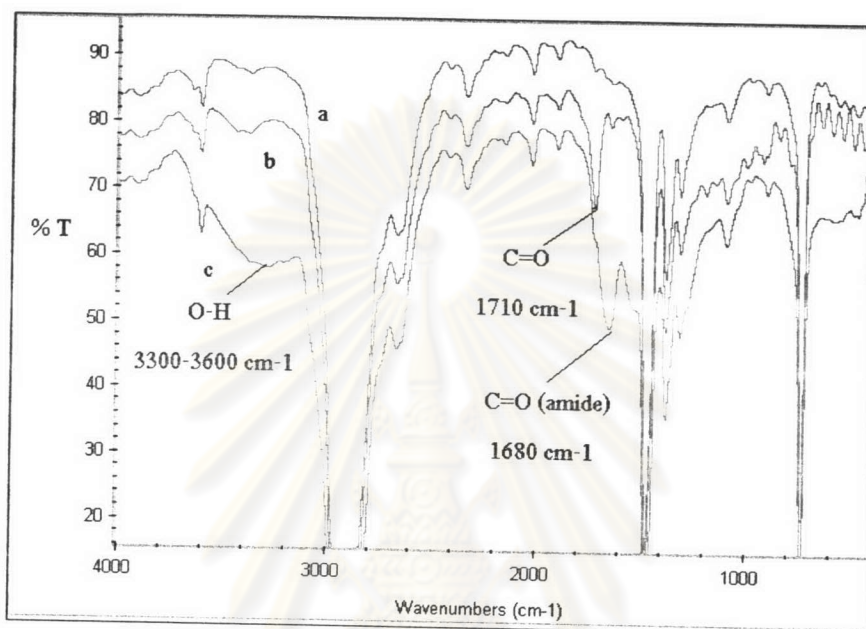


Figure 4.8 The FTIR spectrum of (a) pure LDPE film, (b) LDPE/5% benzophenone film and (c) LDPE/5% gelatin film

Spectrum of 5% gelatin filled LDPE is also shown in Figure 4.8. Comparing to the other two spectra, the different peaks of gelatin apparently appear at 3300 cm^{-1} and $1650\text{-}1690\text{ cm}^{-1}$ presenting bands of -N-H stretching and -C=O stretching of amide group, respectively. The very broad band of -O-H stretching at $3300\text{-}3600\text{ cm}^{-1}$ is the hydrogen bonding between gelatin and moisture due to moisture absorption of gelatin. However, the other peaks that can characterize gelatin overlap the strong peaks of LDPE, so they can not present in the IR spectrum. Same as the benzophenone content, the peaks at 3300 cm^{-1} and 1680 cm^{-1} increased with an increasing of gelatin content (Appendix D.1).

The IR spectrum of LDPE/5% encapsulated benzophenone is presented in Figure 4.9. It should have both characteristic peaks of gelatin and benzophenone. It can be seen that the broad peak at $3300\text{--}3600\text{ cm}^{-1}$ of --N-H stretching and --O-H stretching or the peak at 1710 cm^{-1} and 1680 cm^{-1} of carbonyl group still appear although their intensities are not so strong as those of LDPE/5%gelatin or LDPE/5%benzophenone films that presented in Figure 4.8. It must be due to the fact that encapsulated particles contain both benzophenone and gelatin so the concentration of each constituent is less than the amount of gelatin or benzophenone in the other two LDPE composite films.

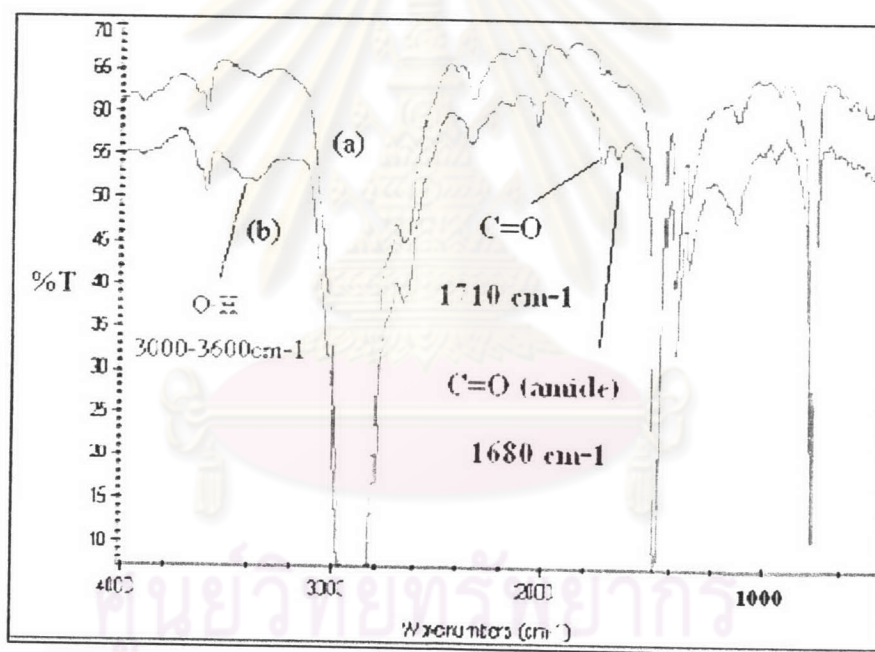


Figure 4.9 The FTIR spectrum of (a) pure LDPE and (b) LDPE/5% encapsulated benzophenone films

4.3.2 Tensile Properties

The stress-strain curves of LDPE, LDPE/5%benzophenone, LDPE/5%gelatin, and LDPE/5%encapsulated benzophenone (EN2) films are shown in Figure 4.10. Obviously, the tensile strength of LDPE film is stronger than that of LDPE/5%benzophenone, LDPE/5%gelatin, and LDPE/5%encapsulated benzophenone films, respectively. The influence of amount of gelatin, benzophenone, and microcapsule on tensile properties is shown in Figure 4.11. Upon increasing the amount of additives, the tensile properties of LDPE/gelatin and LDPE/benzophenone films show slightly decrease, whereas the LDPE/encapsulated benzophenone films present significant drop in these values. Clearly, the microcapsule filled LDPE films exhibit lowest tensile properties. From Figure 4.11, the tensile strength of LDPE/encapsulated benzophenone films decreased from 7.22 to 4.05 MPa, while the elongation at break decreased from 25.71 to 7.08%.

The compatibility between additive and matrix, including size, shape (morphology), and the dispersion of additives are the main factors for describing the lower in tensile properties of these LDPE/additives films. In particular, LDPE is a hydrophobic, while gelatin is a hydrophilic material, so they are not good in compatibility. From Figure 4.3, the shape of benzophenone and gelatin powder are quite round and their size is about 120-150 μm , while the surface of microcapsules is not smooth and their size is bigger than gelatin and benzophenone powder. This appearance has high influence on the mechanical properties. The smaller particle size of benzophenone and gelatin powder can absorb and transfer the applied force acting on the film to the LDPE matrix thoroughly and evenly because these powders can be dispersed uniformly within the LDPE matrix. As result, their tensile properties are greater than the LDPE film containing microencapsulated particles. Since their particles are bigger and not compatible with the LDPE matrix due to its hydrophilicity and unsmooth surface of coated gelatin, these particles tend to form an aggregate rather than individual particles as evidenced by SEM micrographs which will be presented later in the next section (Figure 4.22 and 4.23). Hence, when the force is applied

to the LDPE/additives film, these aggregates or microcapsules will response to the force as a defect or stress concentration of the film, rather than helping distributing the applied forces. As a result, their tensile properties are lowest.

Comparing between the effect of benzophenone and gelatin as presented in Figure 4.11, the lower in tensile strength and higher in elongation at break of LDPE/gelatin film might be due to its moisture absorption. Since gelatin is a hydrophilic material, it is very sensitive to moisture and can absorb a lot of moisture upon increasing its amount in the LDPE film. Moisture will play an important role in the film as a plasticizer resulting in lower tensile strength and higher elongation at break.

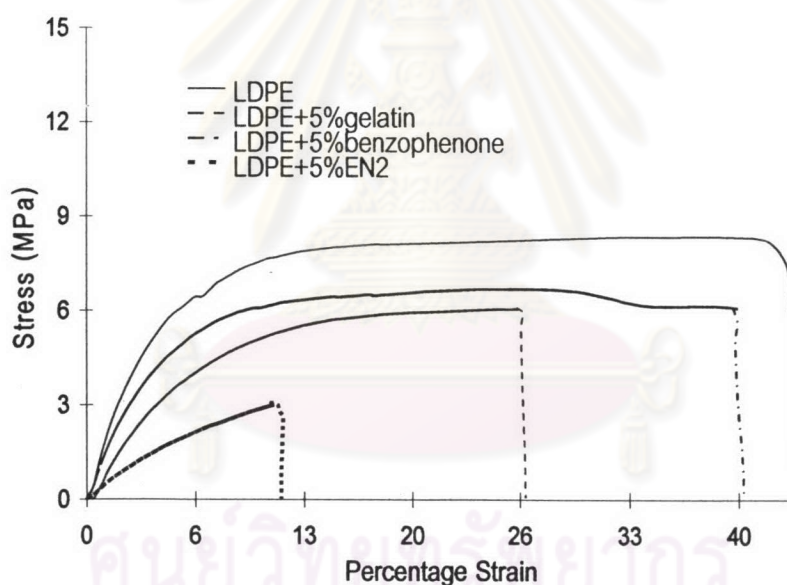


Figure 4.10 Stress-Strain curves of LDPE, LDPE/5%benzophenone, LDPE/5%gelatin, and LDPE/5%encapsulated benzophenone films

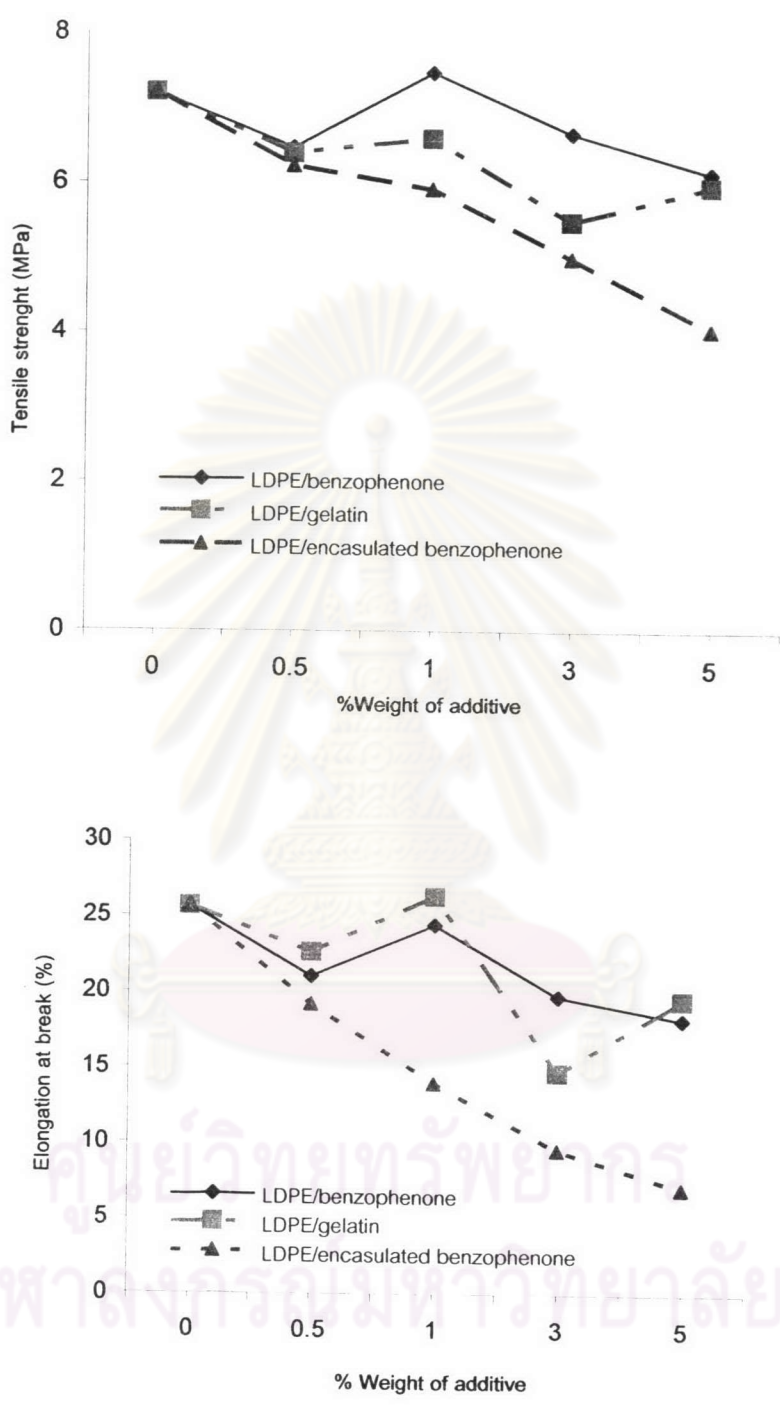


Figure 4.11 Tensile strength and elongation at break of LDPE films with different amount of benzophenone, gelatin, and encapsulated benzophenone

4.4 Evaluation of Photodegradation

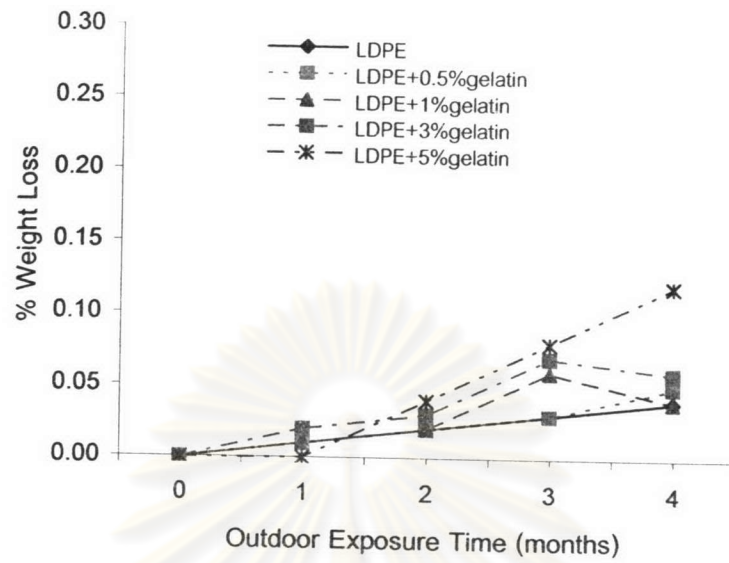
Photodegradation was studied under sunlight and accelerated condition (UVB-light) exposure. The change in chemical structure and physical appearance was followed by FTIR and scanning electron microscopy (SEM), respectively. In addition, photodegradation rate was also evaluated by changing in tensile properties and weight loss of the films.

4.4.1 Weight Loss

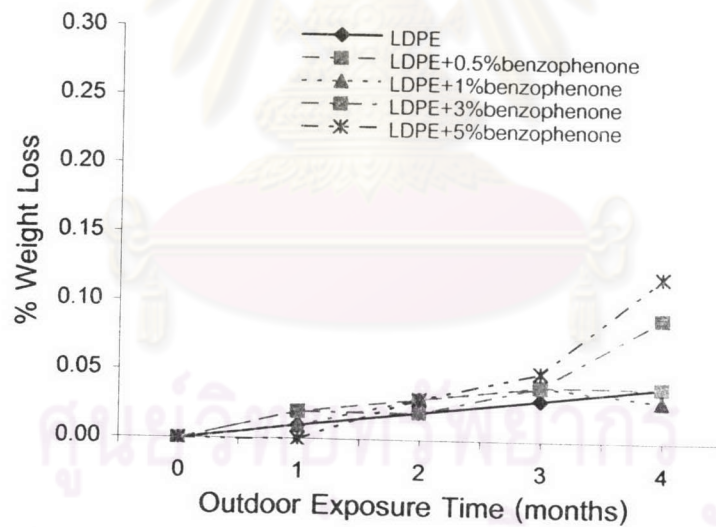
4.4.1.1 Outdoor Exposure

4.4.1.1.1. Effect of Gelatin and Benzophenone

The results of weight loss of LDPE and LDPE/gelatin films are shown in Figure 4.12 (a). The data of LDPE films exposed to sunlight for 4 months did not show any significant weight loss. The weight loss changed only 0.05% at the 4th month. Similar to the LDPE films, LDPE/0.5% and 1%gelatin films showed a little increase in weight loss after 4 months of exposure. However, the 5%gelatin filled LDPE films showed greatest increase in weight loss. From the results, it can be seen that at low concentration (0-3%wt) of gelatin in LDPE films, the amount of gelatin did not have any influence on %weight loss of the LDPE films. Figure 4.12 (b) displays %weight loss of the benzophenone filled LDPE films. The data showed that %weight loss of the films increased with increasing the duration time of exposure. Eventhough, at 0.5% and 1%benzophenone %weight loss increased slowly upon increasing exposure time, these changes in %weight loss was continuously observed. The photodegradation rate rapidly increased for the LDPE blended with 3% and 5%benzophenone after the 3rd month of exposure. Similar to the exposure time, %weight loss of the LDPE/benzophenone films increased when the amount of benzophenone increased. It can be concluded that the exposure time and amount of benzophenone have an effect on photodegradation, especially at longer exposure time (more than 4 months) and higher benzophenone content (3-5%).



(a)



(b)

Figure 4.12 Weight loss of pure LDPE film and LDPE films containing (a) gelatin and (b) benzophenone at different concentration under outdoor exposure

4.4.1.1.2 The Effect of Encapsulated Benzophenone

(a) Effect of Benzophenone to Gelatin Ratio

As can be seen in Figure 4.13, %weight loss of every formula was rapidly increased at the 4th month. The greatest value of %weight loss was observed in LDPE/5%EN3 films, especially at the 4th month of exposure. It may be due to the higher amount of gelatin of EN3 microcapsule, compared with the other two microcapsules, which is sensitive to the environmental factors such as moisture and so on. However, longer period of exposure time is needed in order to be able to differentiate the effectiveness of each microcapsule and confirm the result.

(b) Effect of Amount of Hardening Agent

From Figure 4.14, %weight loss of the LDPE composite films increased with increasing of the exposure time. %Weight loss of all formula clearly increased at the 4th month. However the results showed no significant difference in %weight loss of the three LDPE/encapsulated benzophenone films. This result implies that the hardening agent (formaldehyde) had no effect on the photodegradation behavior of the films.

In order to clarify the effect of each additive on the %weight loss of LDPE films under an outdoor exposure test, Figure 4.15 presents %weight loss of pure LDPE films and LDPE films containing 5%gelatin, 5%benzophenone, and 5%EN1 microcapsule under outdoor exposure. Eventhough no conclusive result can be drawn from this figure which additives is the most influence on the photodegradation, from the figure it can be seen that at longer exposure time (4th month) LDPE/5%EN1 film showed the greatest in weight loss. Other evaluation methods and/or longer exposure time, i.e., more than 4 months should be employed in order to identify the most important additive for promoting the photodegradation.

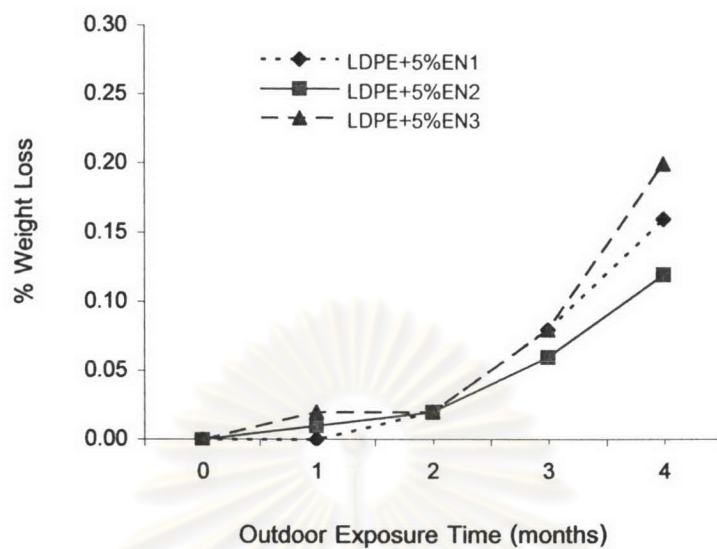


Figure 4.13 Weight loss of LDPE films containing 5% EN1, EN2, and EN3 microcapsules under outdoor exposure

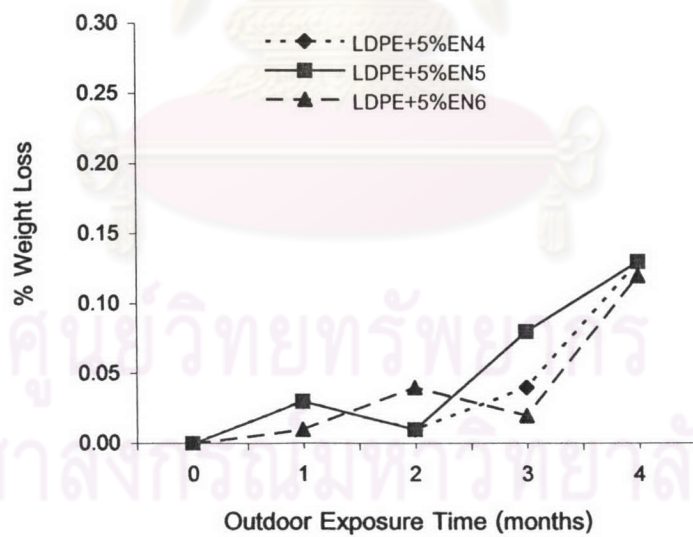


Figure 4.14 Weight loss of LDPE films containing 5% EN4, EN5, and EN6 microcapsules under outdoor exposure

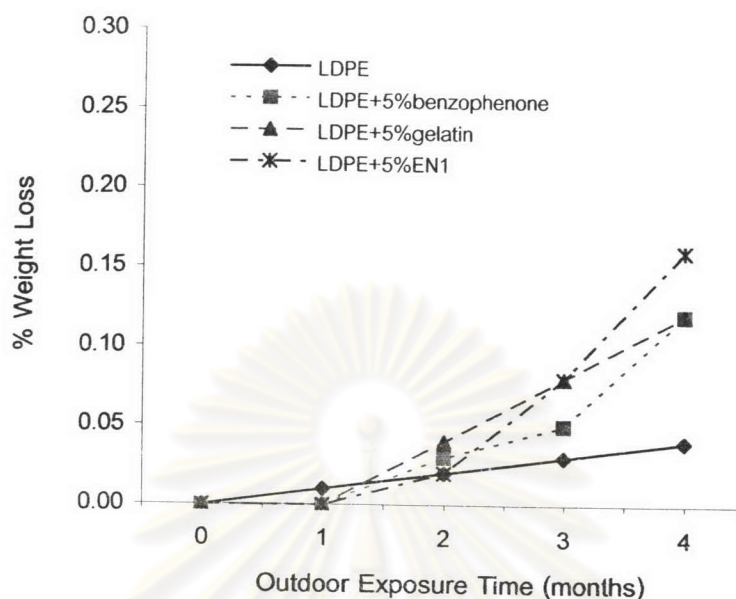


Figure 4.15 Weight loss of pure LDPE film and LDPE films containing benzophenone, gelatin, and encapsulated benzophenone under outdoor exposure

4.4.1.2 Accelerated Exposure

4.4.1.2.1 Effect of Gelatin and Benzophenone

Weight loss of LDPE, LDPE/5%gelatin, and LDPE/5%benzophenone films during accelerated exposure is shown in Figure 4.16. Similar trend was observed in LDPE and LDPE containing 5%benzophenone. The %weight loss of both films slightly increased during the first period of exposure time; i.e., 20.5 hours for LDPE/5%benzophenone and 41 hours for pure LDPE films, and then %weight loss seemed to decrease and then remained constant. These data are different from outdoor exposure test that %weight loss of pure LDPE and LDPE/5%benzophenone films increased with an increase of the exposure time.

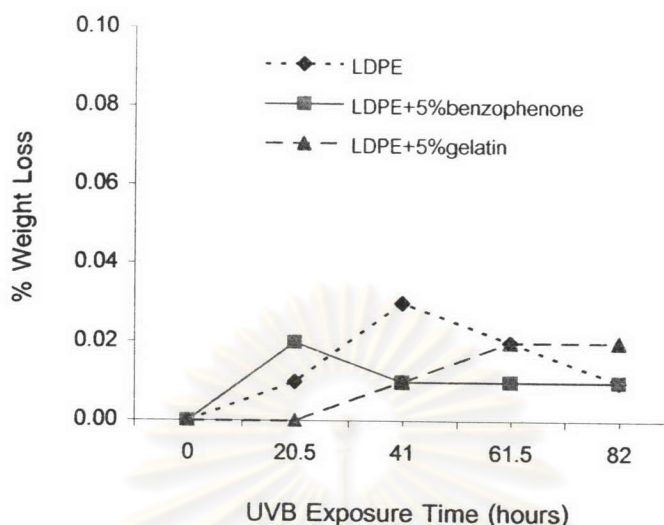


Figure 4.16 Weight loss of pure LDPE film and LDPE films containing 5%gelatin and 5%benzophenone under UVB exposure

Unlike the other two films, the change in %weight loss of LDPE/5%gelatin film had a similar trend to the outdoor exposure test that %weight loss increased with an increase in exposure time. However, it should be noted that the magnitude of weight loss was approximately 5 times less than the results from outdoor exposure test. For example, at 82 hours or 4 months of exposure %weight loss of LDPE/5%gelatin under accelerated and outdoor exposure test was 0.02% and 0.1%, respectively. The higher in %weight loss of the outdoor exposure test suggests that the pure LDPE and LDPE films containing additives can be degraded by other mechanisms besides photodegradation; i.e., thermal degradation, oxidation, and so on. In other words, under outdoor exposure the environmental conditions (except UV intensity) such as %RH, temperature, O₂ concentration, etc., must be more severe than those under UVB exposure. Therefore, these parameters can assist or promote the degradation process of the films via several mechanisms besides photodegradation. In particular, for LDPE/gelatin film, under accelerated exposure the film was not in direct contact with water or rain. It can only absorb moisture or condensed water during the condensation period.

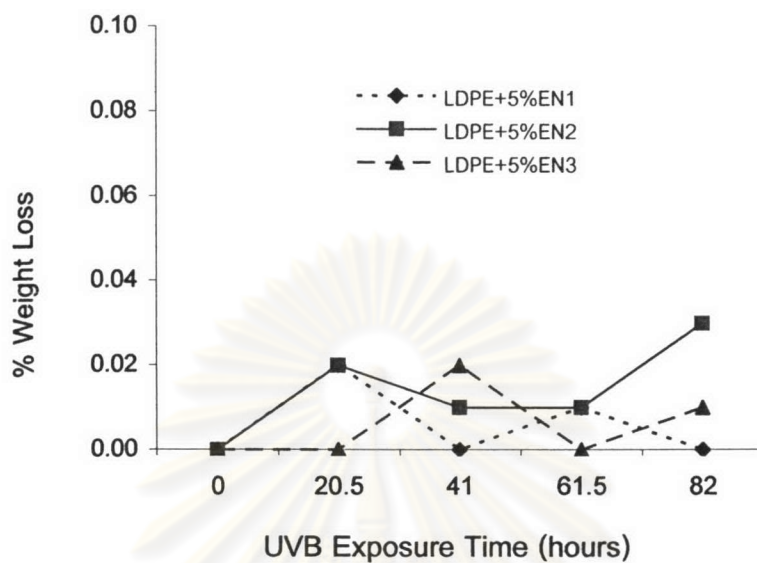
4.4.1.2.2. Effect of Encapsulated Benzophenone

%Weight loss of EN1, EN2, and EN3 filled LDPE films during UVB exposure is displayed in Figure 4.17 (a). Their %weight loss did not show any obvious difference, comparing to Figure 4.13. Unlike the outdoor exposure test, it seems that the benzophenone and gelatin ratio did not influence on %weight loss. In addition, only approximately 0.02 %weight loss was observed in every formula upon increasing exposure time.

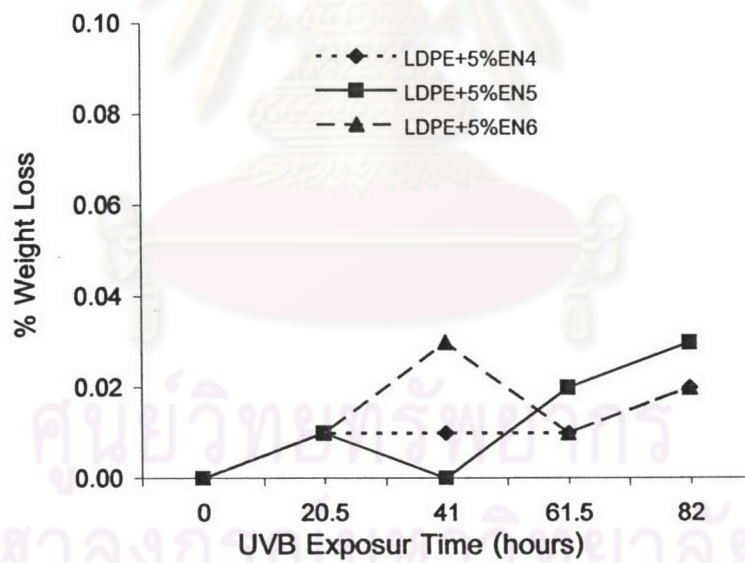
Similarly, %weight loss of LDPE/EN4, EN5, and EN6 films increased only 0.02-0.03% with an increase of exposure time and there was no significant difference among these three formula. %Weight loss of EN4, EN5, and EN6 microcapsules filled LDPE films during UVB exposure is displayed in Figure 4.17 (b). These results were similar to an outdoor exposure test and can be confirmed the outdoor exposure test that the formaldehyde did not affect the amount of %weight loss or photodegradation rate of LDPE composite films.

4.4.2 Physical Appearance

Figure 4.18 presents SEM morphology of pure LDPE films before and after photodegradation test by an outdoor and QUV exposure test. There were tiny holes on the surface of LDPE films after exposed to the sunlight and QUV lamp. It can be seen that the surface of outdoor exposed film appears more holes than the accelerated exposed film indicating that the photodegradation of outdoor exposure test was greater than QUV test. It may be due to the other possible degradation mechanism or other factors, as mentioned earlier, occurring concurrently besides photodegradation when the LDPE film was exposed to the sunlight. However, the photodegradation of LDPE film became more severe with increasing the exposure time in QUV test. As seen in Figure 4.19 (b), a greater numbers of tiny holes can be observed when the QUV exposure time was increased to 145 hours



(a)



(b)

Figure 4.17 Weight loss of LDPE films containing (a) 5%EN1, 5%EN2, and 5%EN3 microcapsules (b) 5%EN4, 5%EN5, and 5%EN6 microcapsules under UVB exposure

(7 months). The result proves that LDPE films can be degraded by themselves via photodegradation process but it would take longer period of time than the films with some additives such as photosensitizer, as will be discussed shortly.

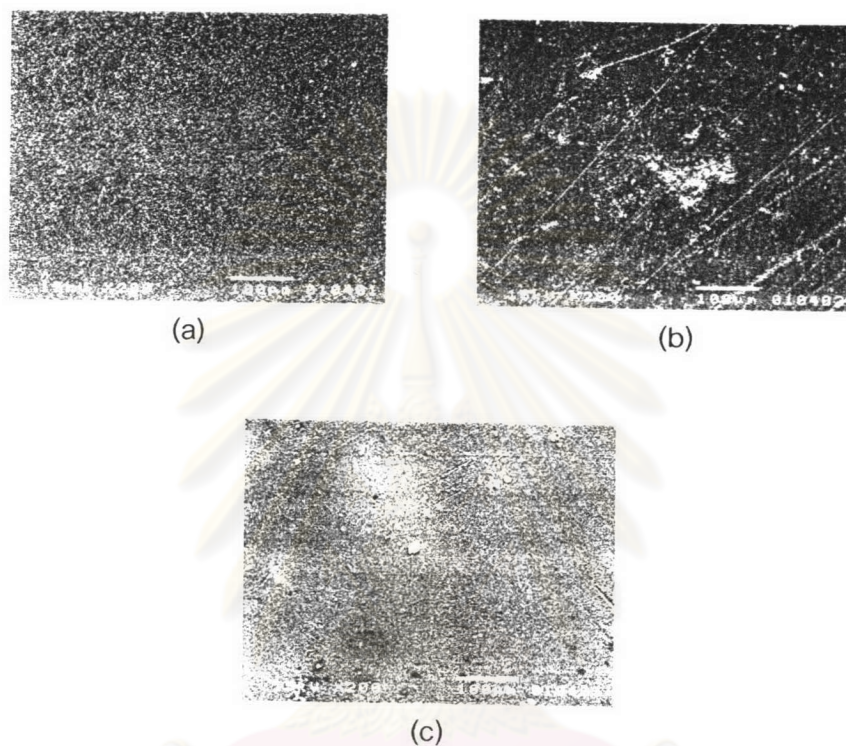


Figure 4.18 SEM micrographs of pure LDPE films (a) before photodegradation test, (b) after 4 months of outdoor exposure, and (c) after 82 hours of QUV exposure

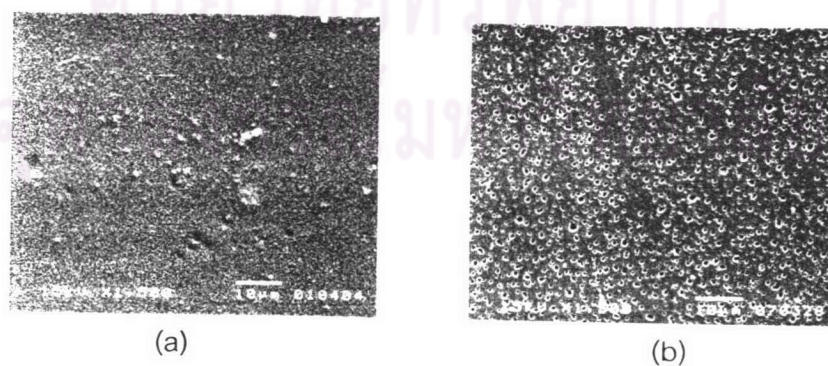


Figure 4.19 SEM micrographs of pure LDPE films (a) after 82 hours and (b) after 145 hours of QUV exposure

4.4.2.1 Effect of gelatin

The SEM micrographs for LDPE/5%gelatin films before and after exposed to the sunlight and QUV lamp are presented in Figure 4.20. The results showed that after 4 months of outdoor exposure, there are little holes appeared on the surface of composite film, in particular at the gelatin particles (white powder on the film). Similar to the outdoor exposure test, the physical appearance of LDPE/5%gelatin films presented tiny holes after QUV test for 82 hours, as shown in Figure 4.20 (c).

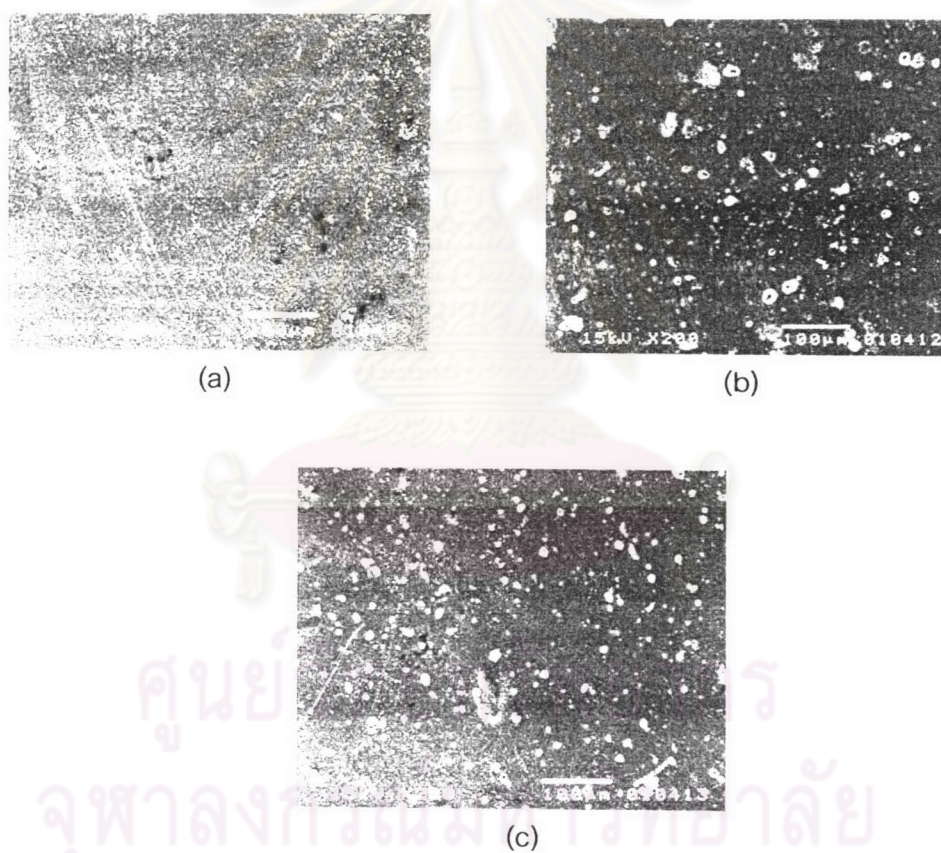


Figure 4.20 SEM micrographs of LDPE/5%gelatin films (a) before photodegradation test
(b) after 4 months of outdoor exposure and (c) after 82 hours of QUV exposure

4.4.2.2 Effect of Benzophenone

Benzophenone had very high influence on photodegradation of LDPE film. As shown in Figure 4.21(b), many tiny holes appear on the surface of LDPE film containing 5% benzophenone. The SEM micrographs indicated that benzophenone increased the photodegradation rate of LDPE film. However, SEM micrograph of LDPE/5% benzophenone after QUV exposure did not show the evidence of photodegradation as much as outdoor test. It can be seen in Figure 4.21 (c) that after QUV exposure less holes can be noticed.

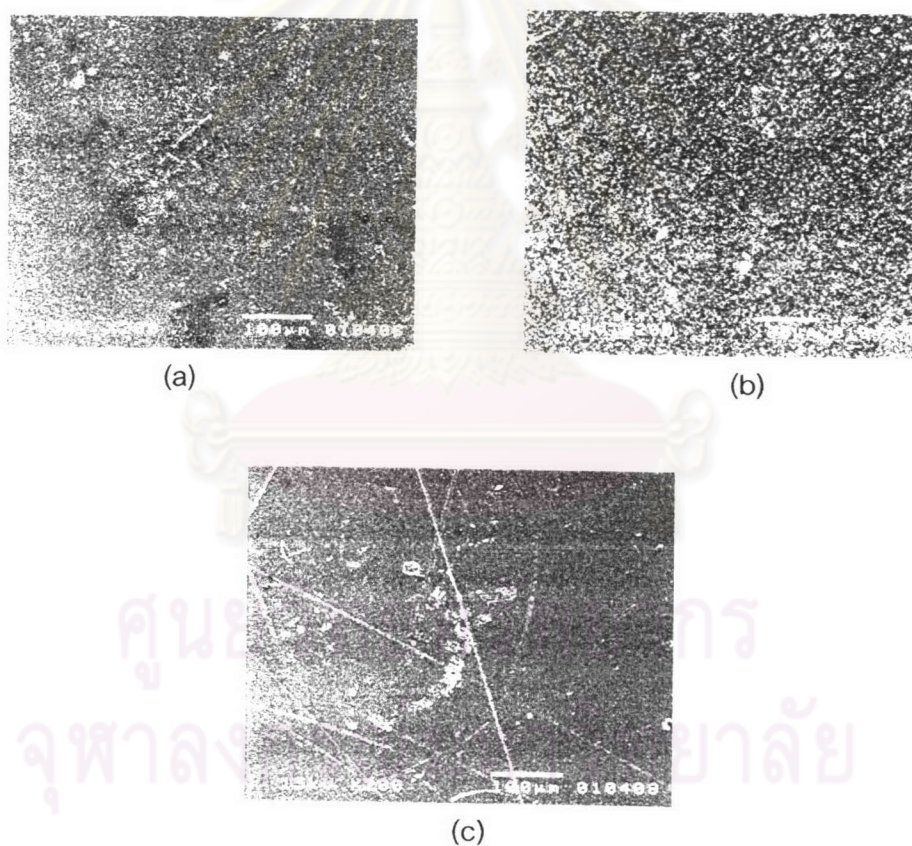


Figure 4.21 SEM micrographs of LDPE/5% benzophenone films (a) before photodegradation test, (b) after 4 months of outdoor exposure, and (c) after 82 hours of QUV exposure

4.4.2.3 Effect of Encapsulated Benzophenone

(a) Effect of Benzophenone to Gelatin Ratio

Figure 4.22 (a) shows the SEM micrograph of LDPE film containing 5%EN1 microcapsules after 4 months of outdoor exposure. Obviously, the results are different from the LDPE films containing gelatin and benzophenone. It can be seen that not only the size of holes are bigger, but the dispersion of these holes are not uniform as well. These results may suggest that one microcapsule contains several benzophenone particles so called multinuclear spherical, so after all benzophenone particles releasing from the microcapsules, the big holes were left behind. In fact, the size of hole should be approximately the same as the size of microcapsule. SEM micrograph of LDPE/5%EN1 microcapsules after QUV test showed similar results to the outdoor exposure test. The holes from degradation were bigger than those of LDPE/gelatin and LDPE/benzophenone films.



Figure 4.22 SEM micrographs of LDPE/5%EN1 microcapsule films (a) after 4 months of outdoor exposure and (b) after 82 hours of QUV exposure

(b) Effect of Amount of Hardening Agent

Figure 4.23 shows the SEM micrographs of LDPE/5%EN4 film after 4 months of outdoor exposure and 82 hours of QUV test. The micrographs of both films

are more distinct than those of pure LDPE and LDPE containing gelatin and benzophenone films. Similar to the effect of gelatin to benzophenone ratio, the big holes, appeared in the area of microcapsule, indicated that the degradation must be initially occurred at the microcapsules.

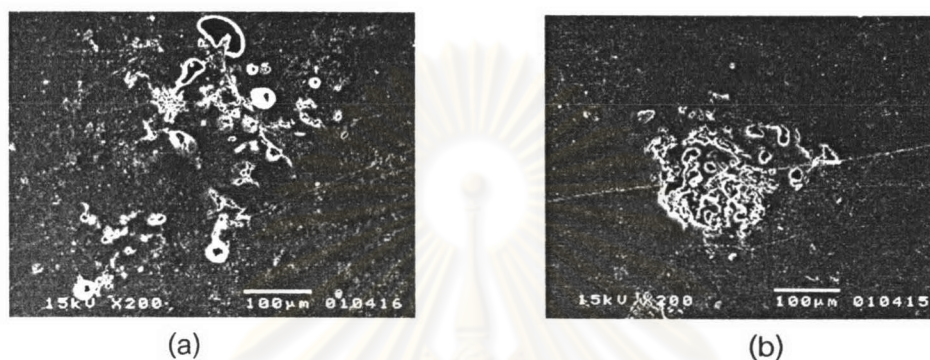


Figure 4.23 SEM micrographs of LDPE/5%EN4 microcapsule films (a) after 4 months of outdoor exposure and (b) after 82 hours of QUV exposure

The spectrophotometer was used to confirm the changes of physical appearance of the films after UVB exposure. The changes in the color of the films before and after photodegradation test were evaluated in terms of their yellowness and whiteness. White paper was used as a standard material. The results are shown in Table 4.6

From Table 4.6, it can be said that after UVB exposure all the films have changed their colors. Obviously, their whiteness decreased significantly, especially the LDPE/gelatin film, whereas their yellowness increased. These results confirmed that pure LDPE, LDPE/benzophenone, and LDPE/gelatin films can be degraded via photodegradation process. From the table, it was also found that the addition of benzophenone and gelatin as additives into the LDPE films caused a decrease in whiteness about 14.50 and 18.29%, respectively, after UVB exposure for 102.5 hours or 6 months. However, it should be noted that the addition of gelatin into LDPE cause a slight increase in the yellowness and a

decrease in the whiteness even before UVB exposure. These results emphasize the role of these two additives in promoting and enhancing the photodegradation process of LDPE film.

Table 4.6 Yellowness and Whiteness of pure LDPE and LDPE films containing benzophenone and gelatin after UVB exposure

Sample	Before exposure		102.5 hours	
	Yellowness	Whiteness	Yellowness	Whiteness
White paper	-23.438	131.435	-	-
White paper + pure LDPE film	-21.822	126.350	-21.006	123.928
White paper + LDPE/benzophenone film	-21.638	126.471	-17.275	110.346
White paper + LDPE/gelatin film	-20.427	123.075	-16.868	106.812

4.4.3 Carbonyl Index

The photoreaction is a result of making the polymer chain shorter and changing in chemical structure. The degree of chemical degradation was calculated from absorption changes of the functional group by IR.

4.4.3.1 Outdoor Exposure

The IR spectrum of sunlight exposed LDPE films for 0 – 4 months are shown in Figure 4.24. It can be seen that the intensity at 1715 cm^{-1} of carbonyl peak increased with an increase of exposure time. This can be confirmed that the

photodegradation occurred after the LDPE films were exposed to the sunlight. UV light can accelerate the degradation of polymer molecule, as explained earlier in Chapter II.

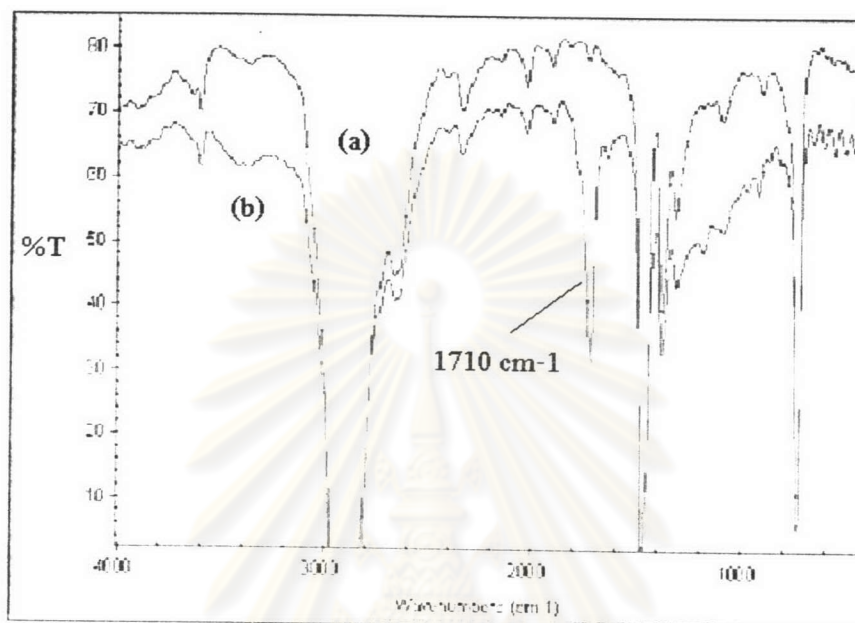


Figure 4.24 IR spectra of pure LDPE films (a) before and (b) after 4 months of outdoor exposure

4.4.3.1.1 Effect of Gelatin

From Figure 4.25, the comparison of IR spectra of LDPE/5%gelatin films before and after 4 months of exposure time shows the difference in the intensity of carbonyl peak at 1710 cm^{-1} . The intensity increased after exposed the films for 4 months.

The effect of gelatin content on the carbonyl index as a function of exposure time is presented in Figure 4.26. The carbonyl index of LDPE/gelatin films linearly increased with an increase of exposure time and the same trend can be observed in the case of pure LDPE film. Obviously, the addition of gelatin into the LDPE film

caused an increase in the carbonyl index of the LDPE film. The carbonyl index of pure LDPE film was less than those of LDPE/gelatin films. Although, the effect of gelatin concentration on the carbonyl index or photodegradation behavior was not so explicit, these results are in good agreement with the weight loss measurement in that inclusion of gelatin help promoting the photodegradation of the LDPE film as evidenced by an increase in both weight loss and carbonyl index of LDPE/gelatin films. As can be seen, the carbonyl index of LDPE films containing different amount of gelatin showed no significant difference among each other except at the 4th month of exposure time that LDPE/5%gelatin showed the greatest carbonyl index value. Although the mechanism of photodegradation of gelatin is unknown, as mentioned, from the results the existence of gelatin in LDPE film resulted in an increase in carbonyl index. Therefore, eventhough gelatin can not directly induce the photodegradation of LDPE film, since it is not a photosensitizer, similar to other polymers including LDPE itself, gelatin may be degraded by other mechanisms such as oxidation reaction or biodegradation.

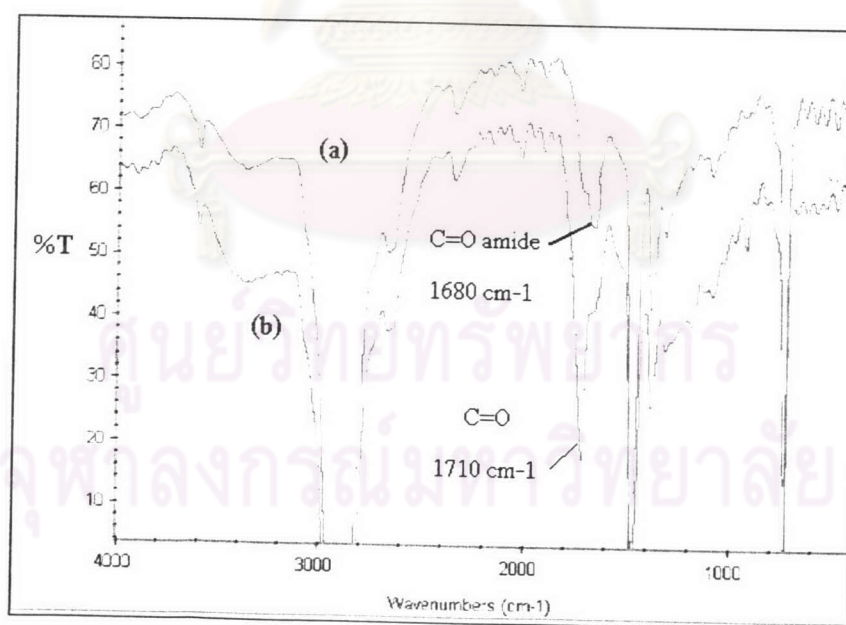


Figure 4.25 IR spectra of LDPE/5%gelatin films (a) before and (b) after 4 months of outdoor exposure

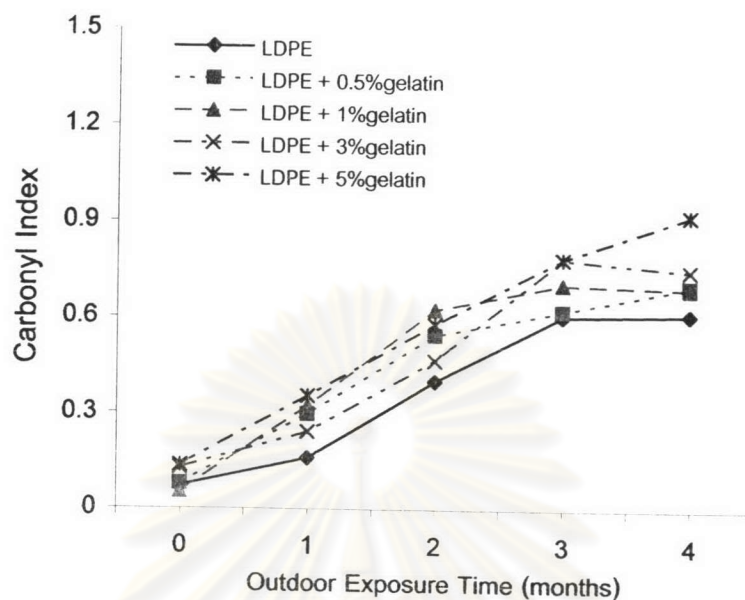


Figure 4.26 Carbonyl index of pure LDPE and LDPE films containing different amount of gelatin

4.4.3.1.2 Effect of Benzophenone

From Figure 4.27, the carbonyl peak intensity of LDPE/benzophenone film rapidly increased after exposed to the sunlight for 4 months. It is very clear that benzophenone have an effect on the photodegradation rate of LDPE film. This is because of the fact that the radicals in the unsaturated molecules of benzophenone lead to the formation of hydroperoxide in the LDPE film. After that, hydroperoxide molecules break down and give the carbonyl compound, as seen in Figure 4.28.

Figure 4.29 presents the carbonyl index of LDPE films containing different amount of benzophenone as a function of exposure time. Carbonyl index of LDPE films containing 0.5% and 1% benzophenone slowly increased upon increasing exposure time, while that of LDPE/3% and 5% benzophenone films rapidly

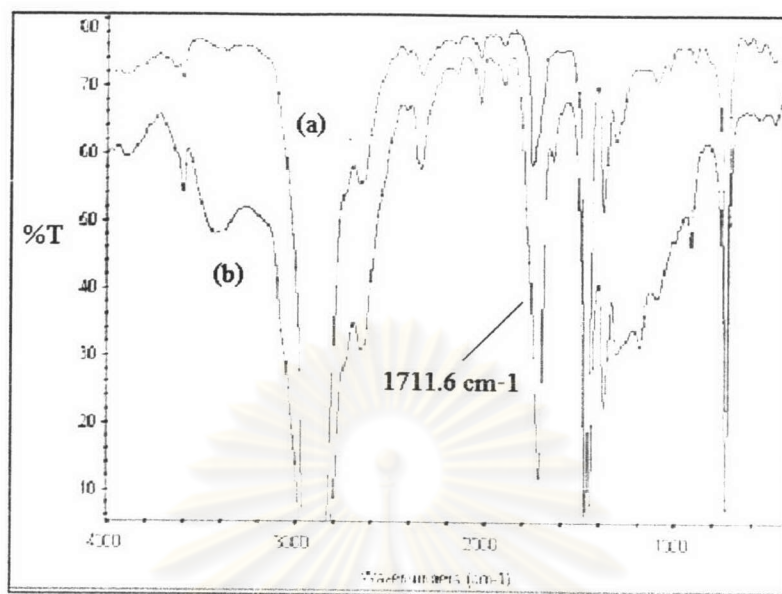


Figure 4.27 IR spectra of LDPE/5%benzophenone films (a) before and (b) after 4 months of outdoor exposure

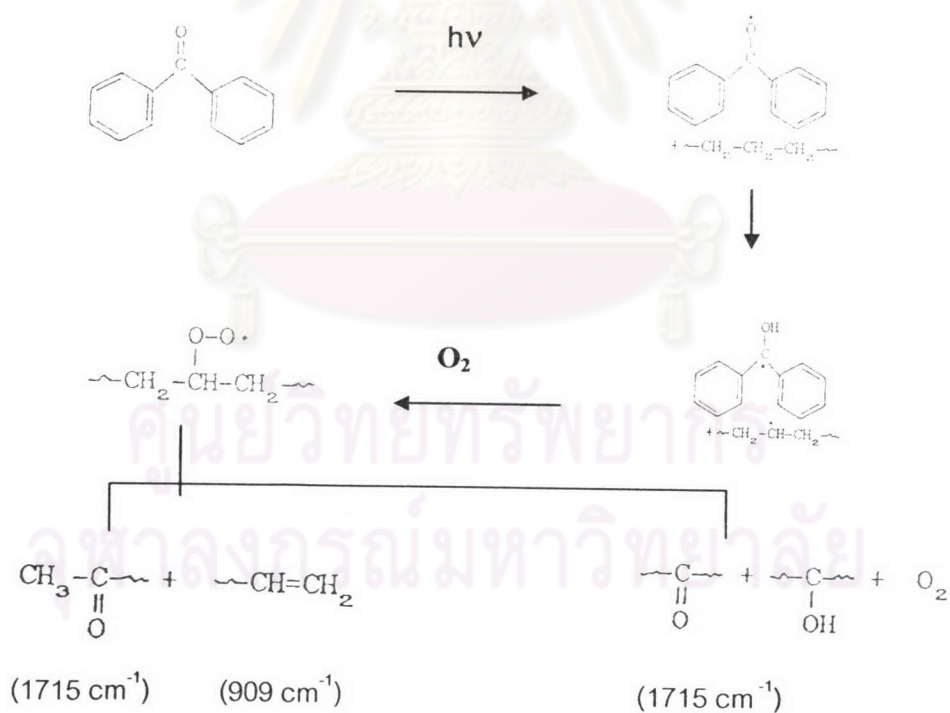


Figure 4.28 Schematic of photodegradation reaction of LDPE containing benzophenone as a photosensitizer

increased after 2 months of exposure. The results showed that benzophenone has great effect on photodegradation. In particular, comparing to Figure 4.26, the carbonyl index of LDPE containing 5% benzophenone film was greater than that of LDPE with 5% gelatin. It can be concluded that the carbonyl index increased with increasing exposure time and amount of benzophenone.

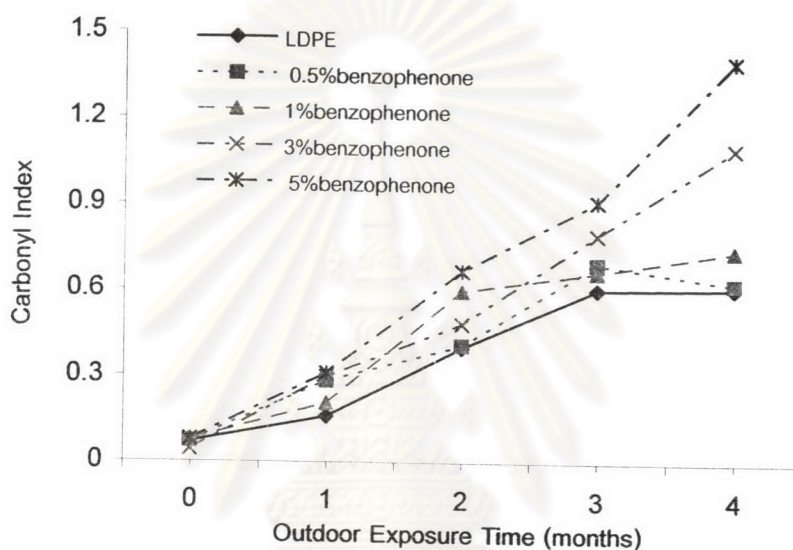


Figure 4.29 Carbonyl index of pure LDPE and LDPE films containing different amount of benzophenone

4.4.3.1.3 Effect of Encapsulated Benzophenone

(a) Effect of Benzophenone to Gelatin Ratio

The influence of benzophenone to gelatin ratio of microcapsule on the photodegradation of LDPE is displayed from Figure 4.30 through 4.32. Figure 4.30 presents the carbonyl index of pure LDPE and LDPE films containing different amount of EN3 microcapsules as a function of exposure time. From this figure, it was shown that the carbonyl index of pure LDPE and LDPE/EN3 films increased as increasing the

exposure time and it seemed that increasing amount of EN3 did not make the difference in carbonyl index in particular at longer exposure time. This appearance indicates that the gelatin layer of coated benzophenone was not decomposed during the initial 4 months. It may be the result from the very thick of gelatin layer, so the releasing rate of benzophenone requires time more than 4 months. Hence, the increasing of carbonyl index values of the LDPE/EN3 films as a function of exposure time should be mainly from the photodegradation of LDPE matrix.

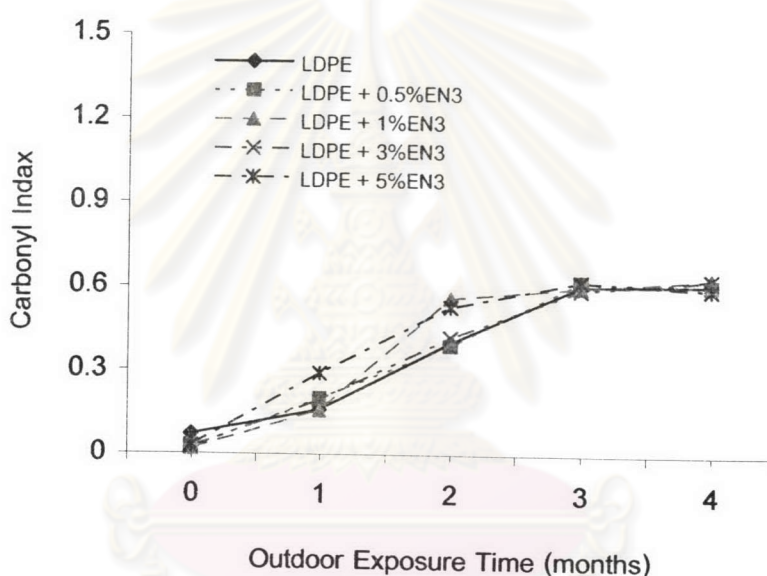


Figure 4.30 Carbonyl index of pure LDPE and LDPE/EN3 films containing different amount of microcapsule

Similar trend was also observed in the LDPE/EN2 films, as shown in Figure 4.31. For LDPE/0.5% and 1%EN2 films, the results presented the same trend as LDPE films. While the LDPE/3% and 5%EN2 films exhibited difference in carbonyl index at the last month of exposure time. Their carbonyl index in the last month are greater than 0.6. This result probably implies that the benzophenone started releasing from the microcapsule after exposure to sunlight for 3-4 months.

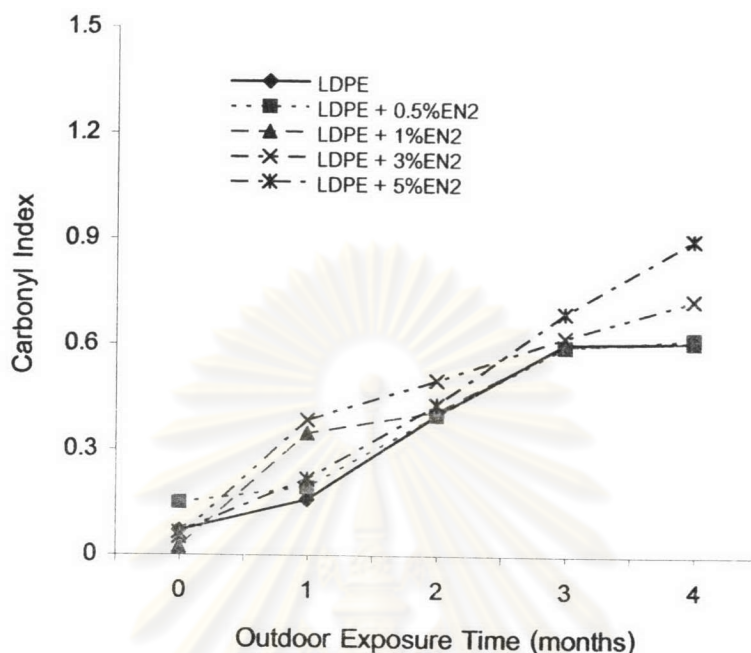


Figure 4.31 Carbonyl index of pure LDPE and LDPE/EN2 films containing different amount of microcapsule

The result of LDPE/EN1 films was not similar to the others. From Figure 4.32, the carbonyl index increased after 1 month exposure time and it also increased with an increase of amount of microcapsules. The highest carbonyl index value belonged to the LDPE/5%EN1 film. This result can be explained that the gelatin layer of EN 1 formula was decomposed more rapid than the others. Owing to the thinnest of gelatin coating on EN1 formula, the benzophenone can be released quickly from the microcapsule to initiate and/or promote the photodegradation of LDPE matrix. Therefore, the increasing of carbonyl index values of the LDPE/EN1 films upon increasing exposure time to sunlight should be contributed not only from the LDPE itself but also from the benzophenone released from microencapsulated particles.

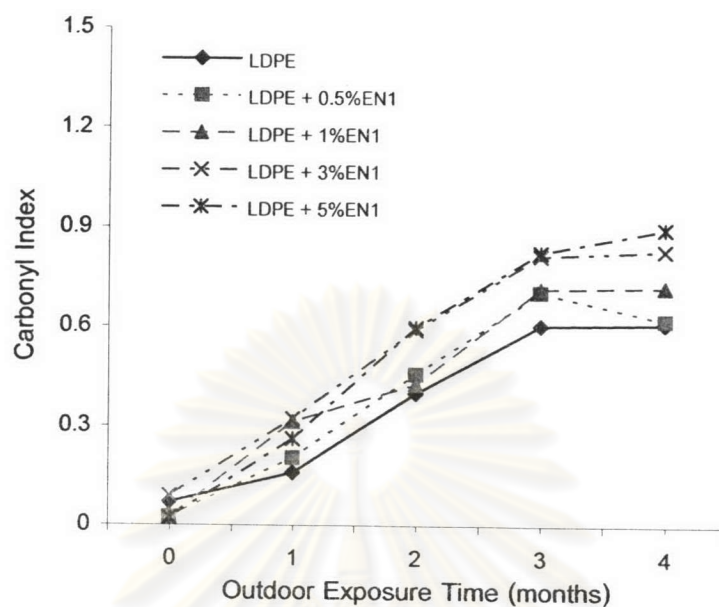


Figure 4.32 Carbonyl index of pure LDPE and LDPE/EN1 films containing different amount of microcapsule

The comparative results of carbonyl index values of LDPE/5% EN1, EN2, and EN3 films are shown in Figure 4.33. Obviously, it can be seen that the degradation rate of LDPE/5%EN1 film was greater than the LDPE films containing EN2 and EN3 microcapsules, respectively. As described in section 4.2.1, benzophenone to gelatin ratio of EN3 is greater than EN2 and EN1, respectively, so the releasing rate of the benzophenone from microcapsule of EN3 must be slower than EN2 and EN1. In other words, the thickness of coating is directly related to the releasing rate of benzophenone and photodegradation rate of LDPE film. It can then be concluded that the effect of benzophenone to gelatin ratio affected the rate of photodegradation.

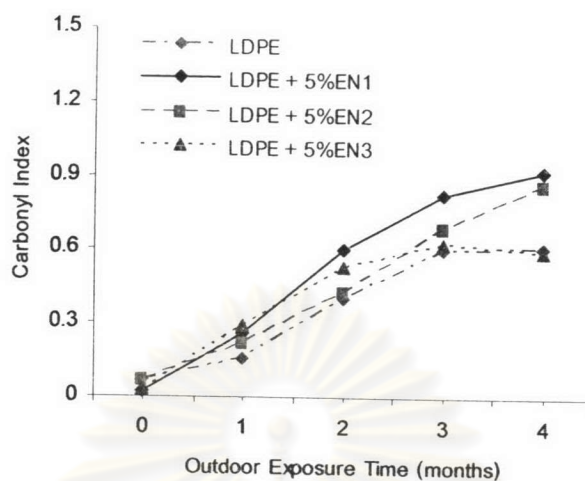


Figure 4.33 The comparison of carbonyl index of outdoor exposed LDPE/5%EN1, 5%EN2 and 5%EN3 films

(b) Effect of Amount of Hardening Agent

Figure 4.34 through 4.36 present the carbonyl index of LDPE films containing different amount of EN4, EN5, and EN6, respectively. Similar to LDPE film, the carbonyl index of LDPE/EN4, EN5, and EN6 films linearly increased as a function of exposure time and the change in carbonyl index of all formula shows similar trend. In addition, although not so obvious, it seemed that the increasing amount of microcapsules increased the carbonyl index values, especially, the carbonyl index of LDPE/5%microcapsules obviously increased at the last month. It can be indicated that benzophenone was released after exposure to the sunlight for 4 months. However, to clarify the influence of hardening agent concentration, the comparative carbonyl index values of LDPE/5% EN4, EN5 and EN6 films is shown in Figure 4.37. As shown, no significant difference in carbonyl index values among three LDPE/microcapsule films can be observed. Comparing to the pure LDPE film, the higher in carbonyl index values of the LDPE/5%EN4, 5%EN5, and 5%EN6 films, especially after one month of exposure, resulted solely from the existence of microcapsules since the gelatin to benzophenone ratios and the amount of

microcapsules are the same, as a result, it is reasonable to conclude that, unlike the benzophenone to gelatin ratio, the amount of hardening agent or formaldehyde has no influence on the photodegradation rate of the LDPE films.

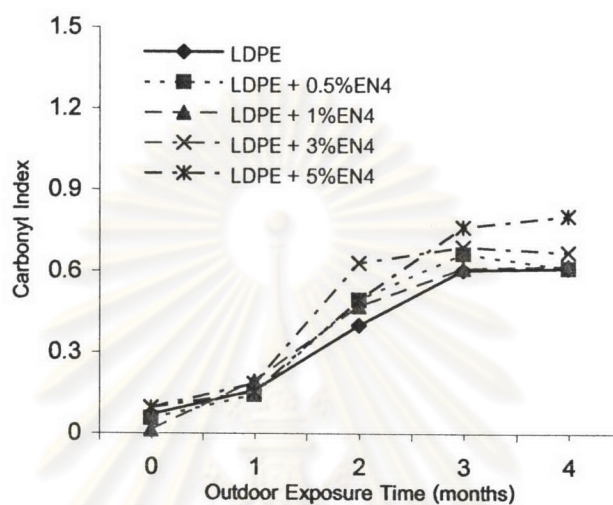


Figure 4.34 Carbonyl index of pure LDPE and LDPE/EN4 films containing different amount of microcapsules

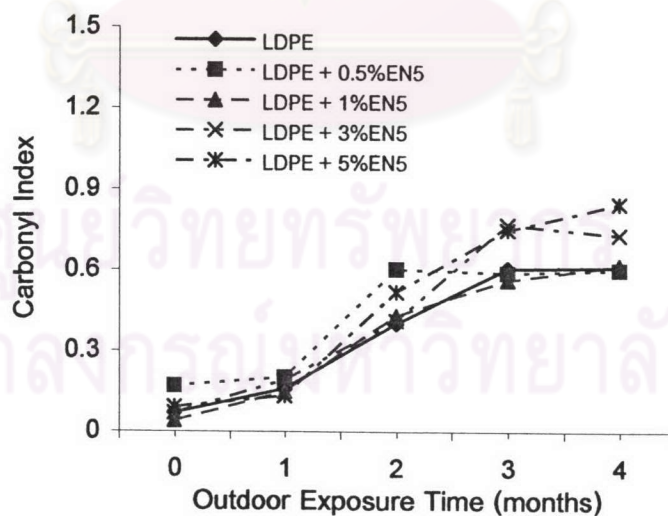


Figure 4.35 Carbonyl index of pure LDPE and LDPE/EN5 films containing different amount of microcapsules

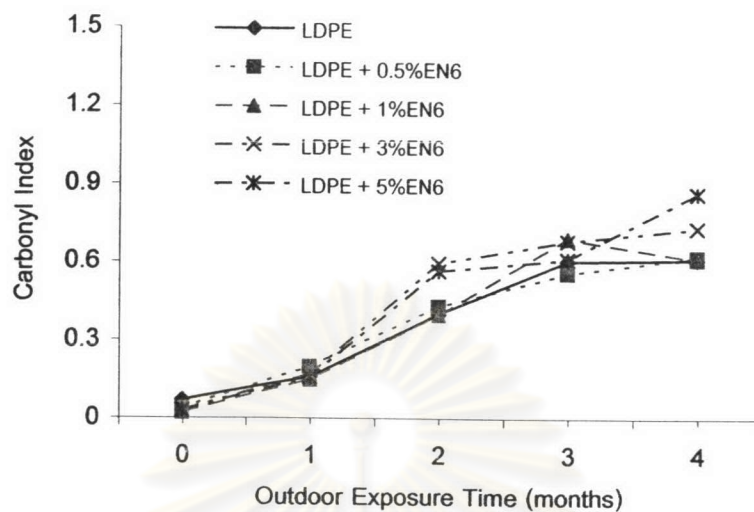


Figure 4.36 Carbonyl index of pure LDPE and LDPE/EN6 films containing different amount of microcapsules

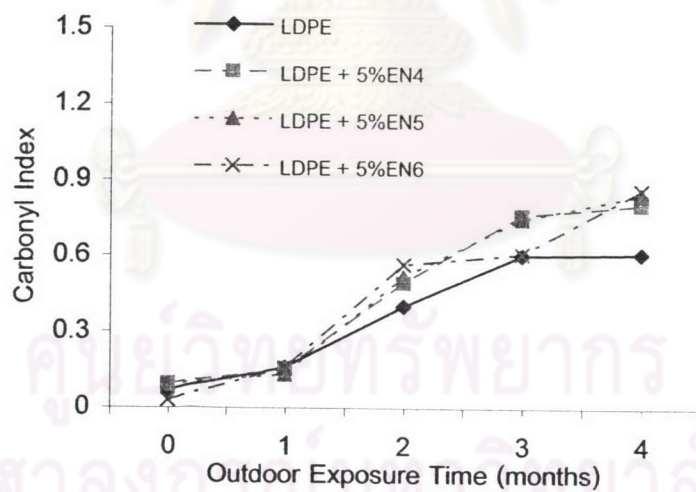


Figure 4.37 The comparison of carbonyl index of outdoor exposed LDPE/5%EN4, 5%EN5 and 5%EN6 films

Figure 4.38 presents the comparison of carbonyl index of LDPE film and LDPE films containing 5%gelatin, 5%benzophenone, and 5%EN1 under the outdoor exposure test. It can be seen that LDPE/5%benzophenone film showed the greatest photodegradation rate. The photodegradation of LDPE/5%EN1 was slower than LDPE/5%benzophenone film which means that the gelatin (or coating material) can retard the photodegradation of LDPE films before benzophenone can be released from microcapsules to accelerate the photodegradation of the films.

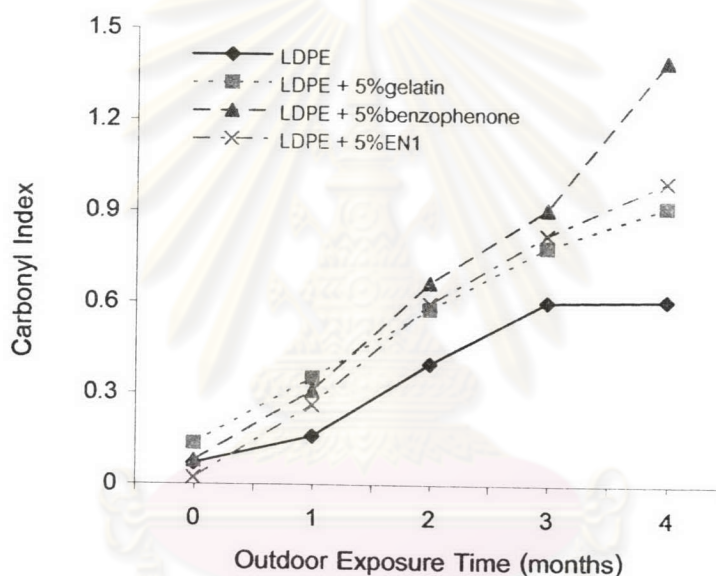


Figure 4.38 The comparison of carbonyl index of outdoor exposed LDPE film and LDPE films containing 5%gelatin, 5%benzophenone, and 5%EN1

4.4.3.2 Accelerated Exposure

The film sample was cut into 8 X 20 cm and placed into the Accelerated Weathering Tester (QUV) chamber. The machine releases UVB at 280-315 nm that is the shortest wavelength found in sunlight and this region is responsible for considerable polymer damage.

Figure 4.39 shows that both films exposed to outdoor and accelerated conditions exhibited the same behavior that is their carbonyl index values increased upon increasing exposure time. Although it is clearly seen that the increasing rate of pure LDPE film exposed under accelerated is less than that of the film under outdoor exposure test. This result implies that not only the intensity of UV light that is the key factors for photodegradation process, the other parameters coexisting in the outdoor exposure, i.e., temperature, %RH, and amount of rainfall, are also important variables playing significant roles in promoting photodegradation process of the LDPE film. Under accelerated test, the above parameters including oxygen gas are limited and different from the real environment so the ability of the film to be degraded under this condition is less than under outdoor exposure test.

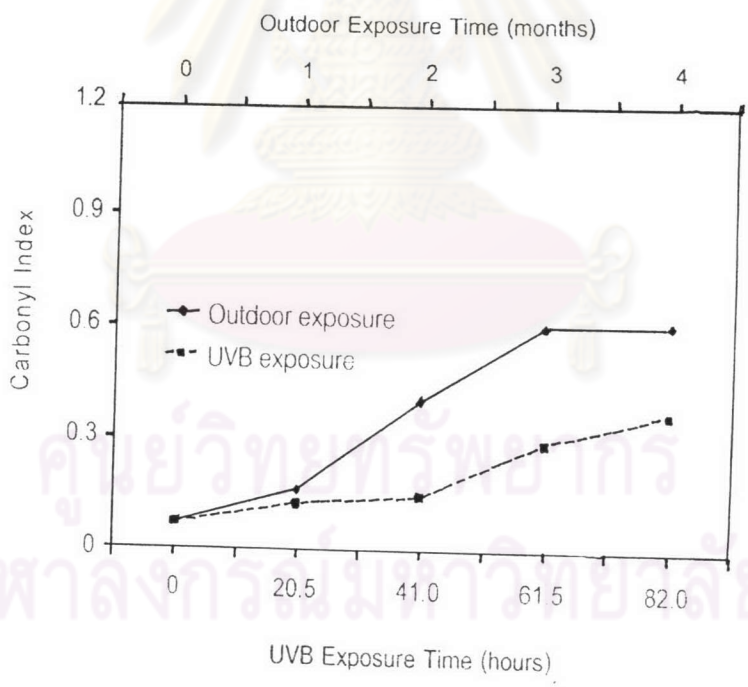


Figure 4.39 Carbonyl index of outdoor and accelerated exposure of LDPE film

4.4.3.2.1 Effect of Gelatin and Benzophenone

The influence of gelatin and benzophenone on carbonyl index of QUV tested films is similar to the outdoor exposure test. The tendency of carbonyl index values of LDPE/gelatin films is quite similar to LDPE films. As seen in figure 4.40, the LDPE/gelatin films show slowly increasing of carbonyl index with increasing of QUV exposure time, except at the last hour of exposure time when the carbonyl index start rising its value significantly. Same as the outdoor exposure, the addition of gelatin particularly at higher concentration (5%) resulted in an increase in carbonyl index values compared with the pure LDPE film. Similarly, the amount of benzophenone also had an influence on photodegradation. From Figure 4.41, after 20.5 hours of exposure the carbonyl index values of LDPE/benzophenone films increased to greater extent compared with the pure LDPE film, and their values keep increasing continuously, especially for the LDPE/5%benzophenone film. Conclusively, an increase in the amount of benzophenone resulted in increasing in carbonyl index values. Therefore, the results ensure the role of benzophenone in promoting the photodegradation.

Figure 4.42 shows the carbonyl index as a function of exposure time of pure LDPE, LDPE/5%gelatin and LDPE/5%benzophenone films from 0-143.5 hours in QUV chamber (0-7 months of outdoor exposure). It can be seen that pure LDPE film exhibited linearly change in carbonyl index. For LDPE/5%gelatin film, the carbonyl index increased with an increasing of exposure time and its values are also greater than those of pure LDPE film, especially after 82 hours of exposure. As discussed earlier, although gelatin is not a photosensitizer, it can promote the photodegradation via other mechanisms depending on the environmental conditions such as oxygen or relative humidity. Based on these results, it can be said that the lower gelatin concentration (0.5-3 %) is not sufficient to help increasing the photodegradation of pure LDPE film. For LDPE/5%benzophenone film, as expected, benzophenone directly affected the

photodegradation of LDPE films. Figure 4.42 clearly shows high rate of photodegradation with an increase in exposure time, in particular after 40 hours of exposure.

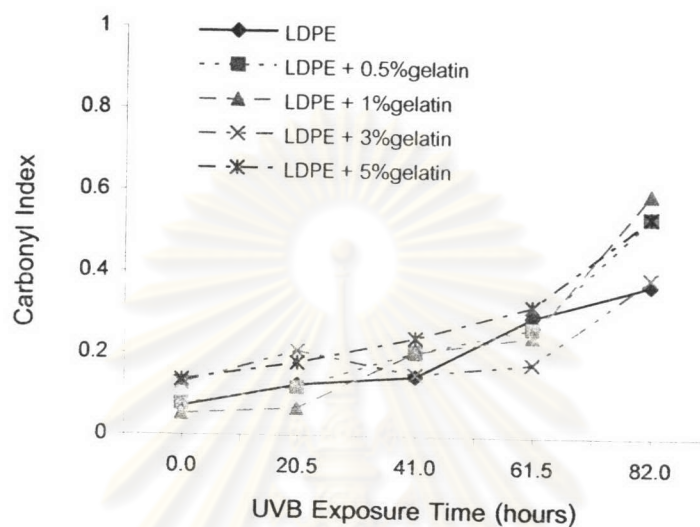


Figure 4.40 Carbonyl index of pure LDPE and LDPE films containing different amount of gelatin under accelerated exposure

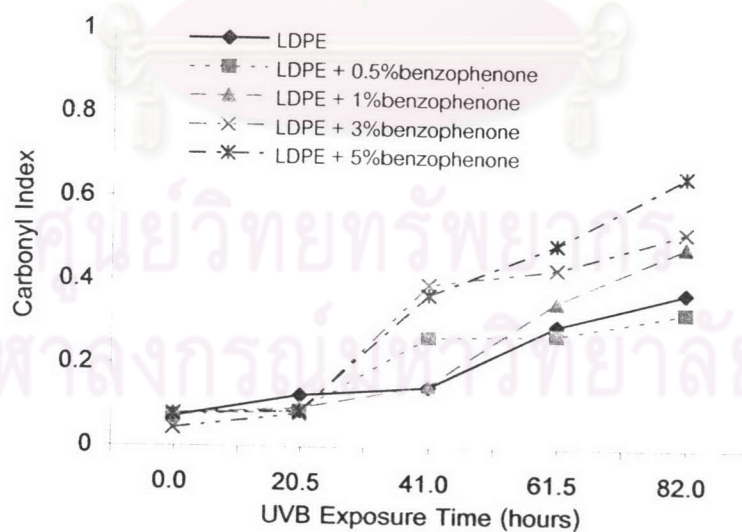


Figure 4.41 Carbonyl index of pure LDPE and LDPE films containing different amount of benzophenone under accelerated exposure

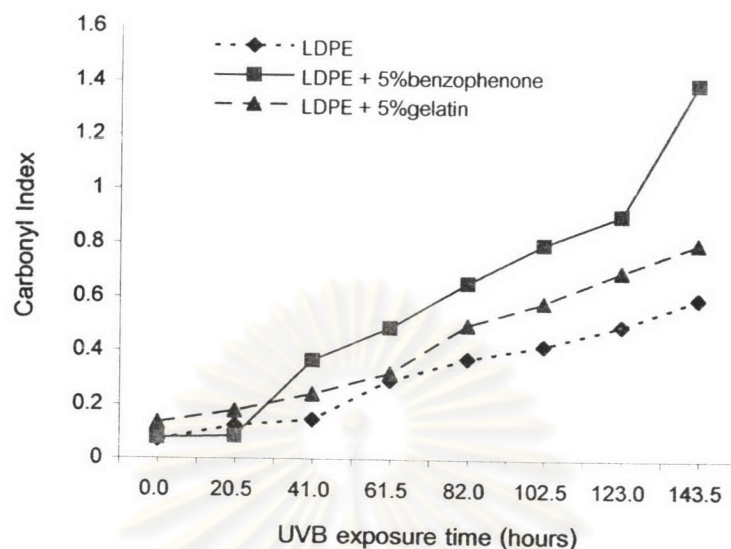


Figure 4.42 Carbonyl index of pure LDPE, LDPE/5%gelatin, and LDPE/5%benzophenone films under accelerated exposure

4.4.3.2.2 Effect of Encapsulated Benzophenone

(a) Effect of Benzophenone to Gelatin Ratio

Similar to the outdoor exposure test, no significant difference between the carbonyl index values of pure and LDPE/EN2 or LDPE/EN3 films upon increasing amount of EN2 or EN3 microcapsules into the LDPE film can be observed. In contrast, as shown in Figure 4.43, the carbonyl index increased with increasing EN1 concentration, especially after 41 hours of exposure. As described earlier, the lower gelatin to benzophenone ratio of EN1 microcapsules resulted in thinner coating material compared with EN2 and EN3 microcapsules, as a result, benzophenone can be released from the EN1 microcapsules faster than other two types of microcapsule. To clarify the effectiveness of these 3 microcapsules, Figure 4.44 shows the carbonyl index of LDPE/5%EN1, EN2, EN3 until 143.5 hours of exposure. Obviously, LDPE/5%EN1 film had the highest carbonyl index values among three films, in particular after 61.5 hours or 3 months of exposure. It can then

be confirmed the outdoor test that benzophenone to gelatin ratio has an effect on photodegradation rate.

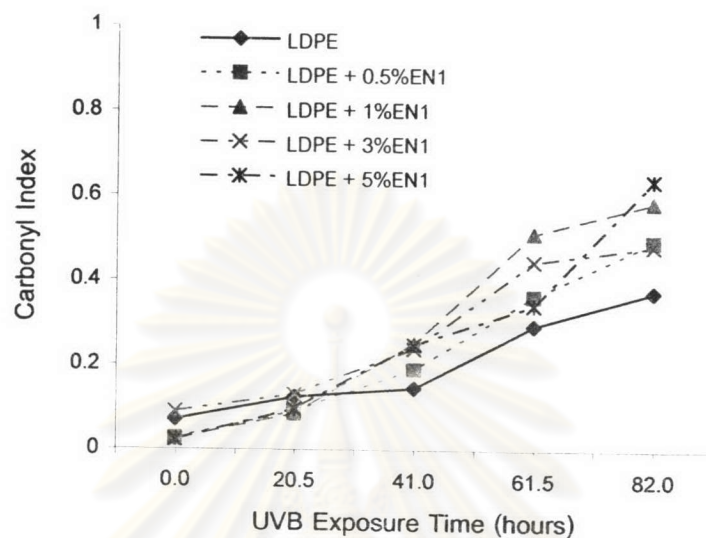


Figure 4.43 Carbonyl index of LDPE/EN1 films containing different amount of microcapsule under accelerated exposure

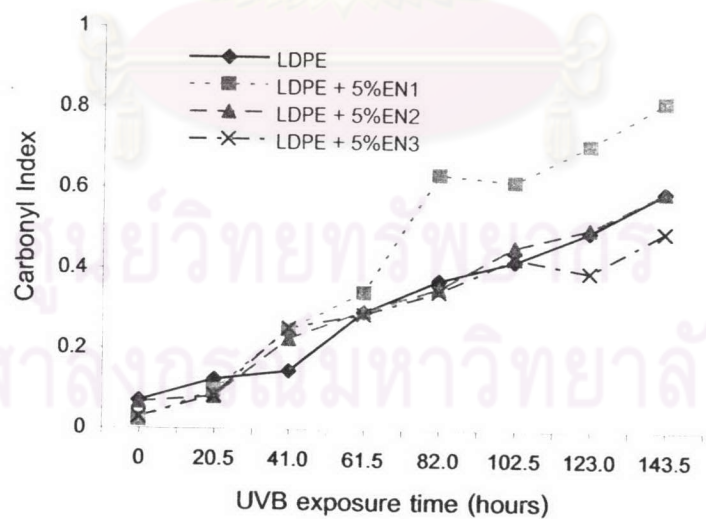


Figure 4.44 Carbonyl index of pure LDPE, LDPE/5%EN1, LDPE/5%EN2, and LDPE/5%EN3 films under accelerated exposure

(b) Effect of Amount of Hardening Agent

Similar to Figure 4.37 of outdoor test, the results show no significant difference of carbonyl index in each formula. The carbonyl index of LDPE/EN4, EN5 and EN6 films was linearly increased as a function of exposure time like LDPE films. From Figure 4.45, it can be concluded that the amount of hardening agent had no effect on photodegradation of LDPE film.

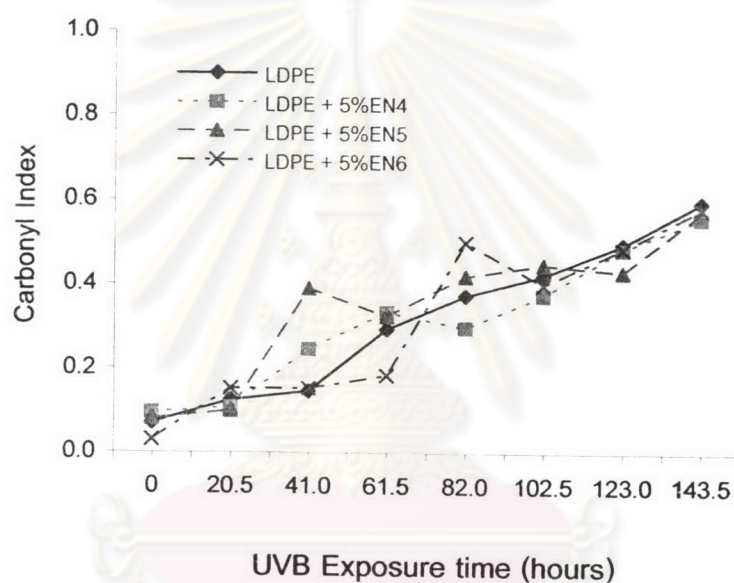


Figure 4.45 Carbonyl index of pure LDPE, LDPE/5%EN4, LDPE/5%EN5, and LDPE/5%EN6 films under accelerated exposure

Similar to the outdoor exposure test, Figure 4.46 shows that carbonyl index of LDPE/EN1 films were higher than pure LDPE and LDPE/gelatin films but lower than LDPE/benzophenone films. These results indicate that the encapsulated benzophenone can be used to control the photodegradation of LDPE films.

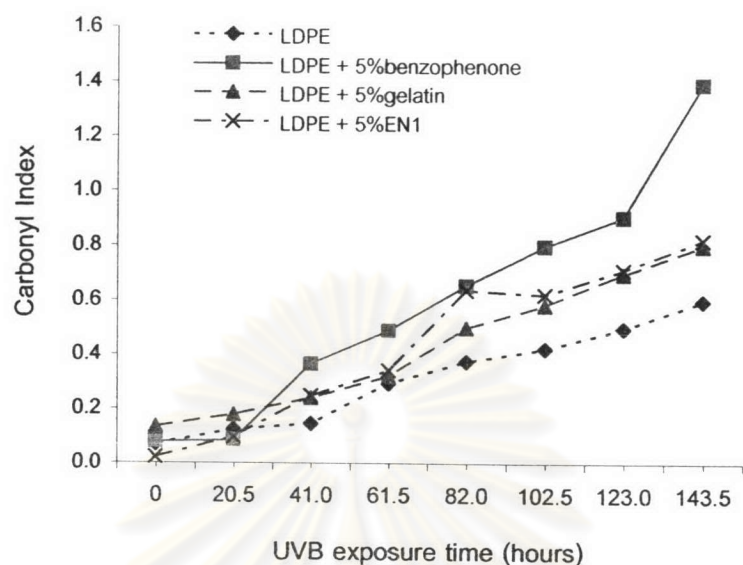


Figure 4.46 The comparison of carbonyl index of pure LDPE film and LDPE film containing 5%gelatin, 5%benzophenone, and 5%EN1 under accelerated exposure

4.4.4 Tensile properties

The film samples were removed for mechanical test every month after being exposed to the sunlight. Figure 4.47 shows stress-strain curve of LDPE films during 4 months of outdoor exposure. The results indicate that tensile properties decreased when the exposure time increased. In fact, the tensile strength and elongation at break of LDPE films were found to be lower than LDPE film prepared from other process; i.e., the LDPE film prepared from chill roll cast film technique has 19 MPa and 249% in tensile strength and elongation at break, respectively [9]. This might be because of the thickness of the compressed LDPE film which is very thin (80 μm) in order to facilitate the photodegradation process.

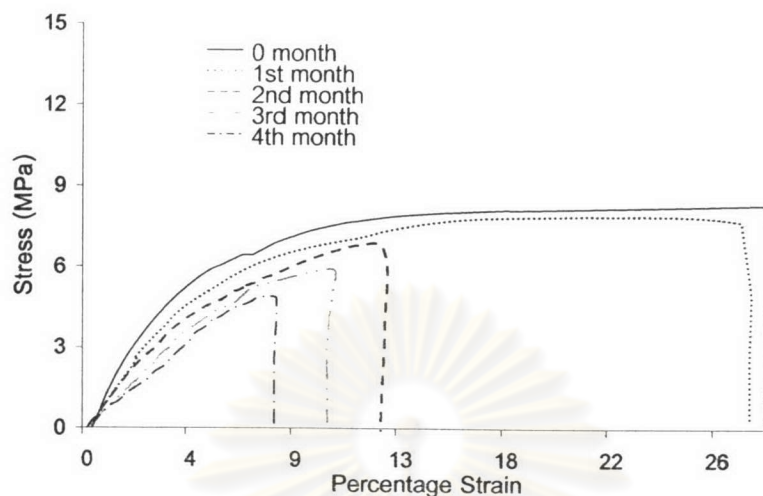


Figure 4.47 Stress-strain curves of pure LDPE films during sunlight exposure

4.4.4.1 Outdoor Exposure

4.4.4.1.1 Effect of Gelatin

Figure 4.48 shows the tensile strength and elongation at break of pure LDPE film and LDPE films containing gelatin as a function of exposure time. Both LDPE and LDPE/gelatin films present the slight decreasing of tensile strength after outdoor exposure for 4 months. It seems that at lower gelatin concentration (0.5-1%) the tensile strength of LDPE/gelatin film was not different from that of pure LDPE film. However, at higher gelatin concentration, the tensile strength decreased with increasing gelatin content. For LDPE/5%gelatin film, the tensile strength decreased from 5.2 to 4.8 MPa after 4 months of exposure, which is approximately 7.69%. The same trend was also found in elongation at break. After 4 months of outdoor exposure, the elongation at break of LDPE/5%gelatin film significantly decreased from 20% to 6%, or 14% decrease from its original value.

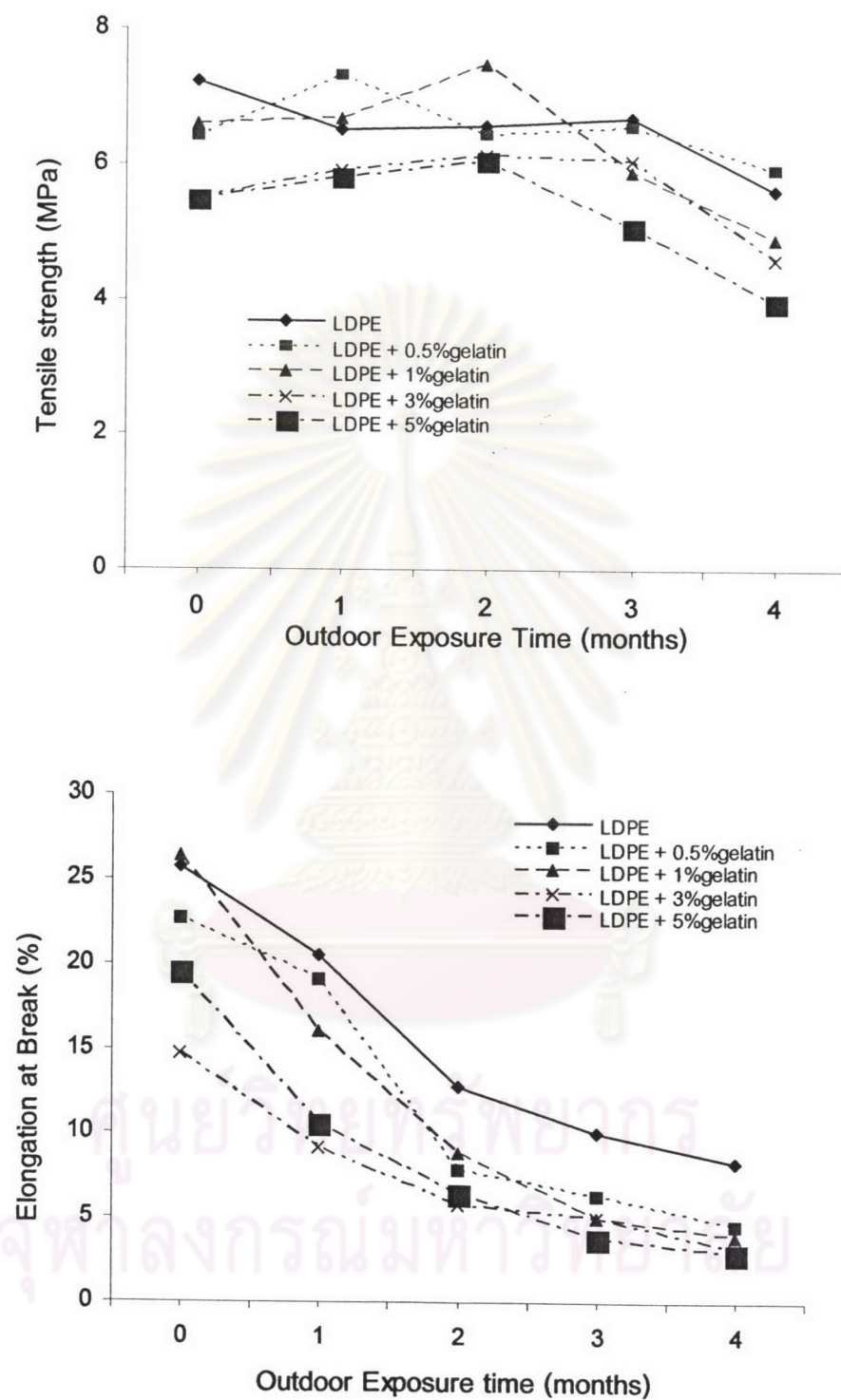


Figure 4.48 Tensile properties of pure LDPE film and LDPE/gelatin films.

4.4.4.1.2 Effect of Benzophenone

Similar to the effect of gelatin, the tensile strength and elongation at break of pure LDPE and LDPE/benzophenone films decreased with increasing of exposure time, as seen in Figure 4.49. The results showed that the amount of benzophenone has an influence on tensile properties. LDPE film containing 5% benzophenone showed the highest decreasing after 4 months of exposure time. Its tensile strength decreased from 6.13 to 3.12 MPa, which is approximately 49.10%. For elongation at break, a decrease was observed with increasing of exposure time and amount of benzophenone. Elongation at break of LDPE/5% benzophenone film decreased from 18.26 to 1.56%. The reduction of tensile properties with increasing exposure time and benzophenone content is due to chain scission reaction occurring during exposure. These results mean that after certain period of exposure time, the LDPE films containing some amount of photosensitizer started losing their strength and became brittle.

4.4.4.1.3 Effect of Encapsulated Benzophenone

(a) Effect of Benzophenone to Gelatin Ratio

Figure 4.50 presents the tensile strength and elongation at break of pure LDPE and LDPE films containing 5%EN1, 5%EN2, and 5%EN3 plotted against exposure time. It is clearly seen that the addition of microcapsules affected on the tensile strength of pure LDPE film. From this figure, tensile properties of LDPE/5%EN1, 5%EN2, and 5%EN3 films were lower than pure LDPE film. It should be due to the incompatible between microcapsules and LDPE matrix. The morphology of microcapsule showed rough surface so the uncompatibilized composite had some gaps between encapsulated benzophenone and LDPE matrix. When forces were applied on the films, these gaps will act as a weak point or defect of the LDPE/encapsulated particles films resulting in lower tensile properties.

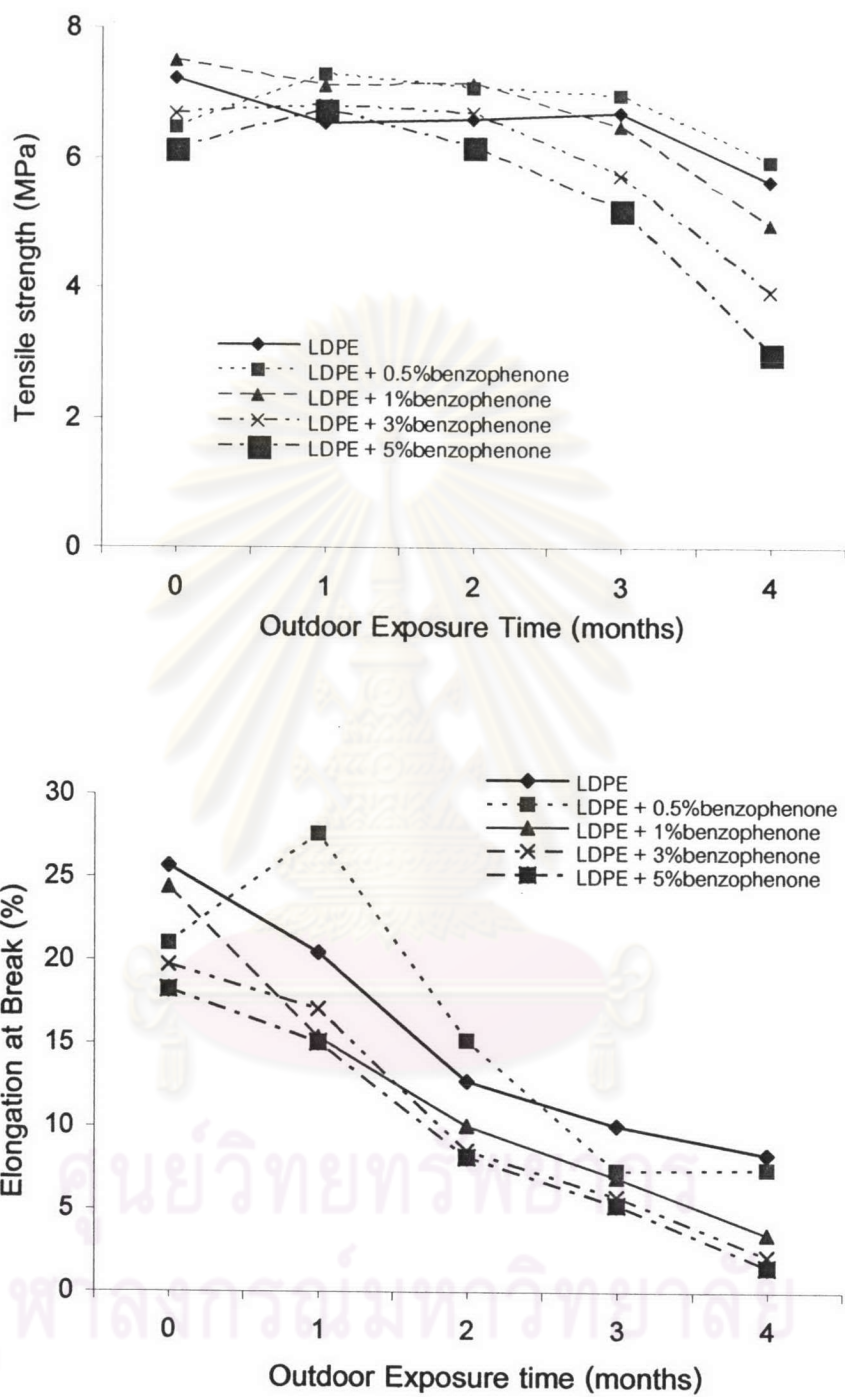


Figure 4.49 Tensile properties of pure LDPE and LDPE/benzophenone films

Considering the effect of benzophenone to gelatin ratio or the thickness of the coating material, it was shown that the tensile strength of LDPE/5%EN1 film clearly presented a continuous decrease after 2 months, whereas the LDPE/5%EN2 and 5%EN3 films started losing their tensile strength after 3-4 months of exposure. Obviously, after 2 months the tensile strength of LDPE/5%EN1 film was lowest among the three LDPE/microcapsules films. This result is in good agreement with the carbonyl index results and can be indicated that the degradation of LDPE/5%EN1 films must be faster than LDPE/5%EN2 and LDPE/5%EN3 films owing to its thinner coating material or lower benzophenone to gelatin ratio of EN1 particles.

(b) Effect of Amount of Hardening Agent

Figure 4.51 presents the plot of tensile properties of pure LDPE and LDPE films containing 5%EN4, 5%EN5, and 5%EN6 microcapsules as a function of exposure time. As seen, tensile properties of LDPE/encapsulated particle films were lower than pure LDPE film. In addition, tensile properties of all formula decreased in the same trend upon increasing exposure time. However, similar to other properties discussed earlier; i.e., carbonyl index and weight loss, the amount of hardening agent did not have an effect on thickness of coating material, so the photodegradation rate of all formula showed no significant difference.

ศูนย์วิทยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย

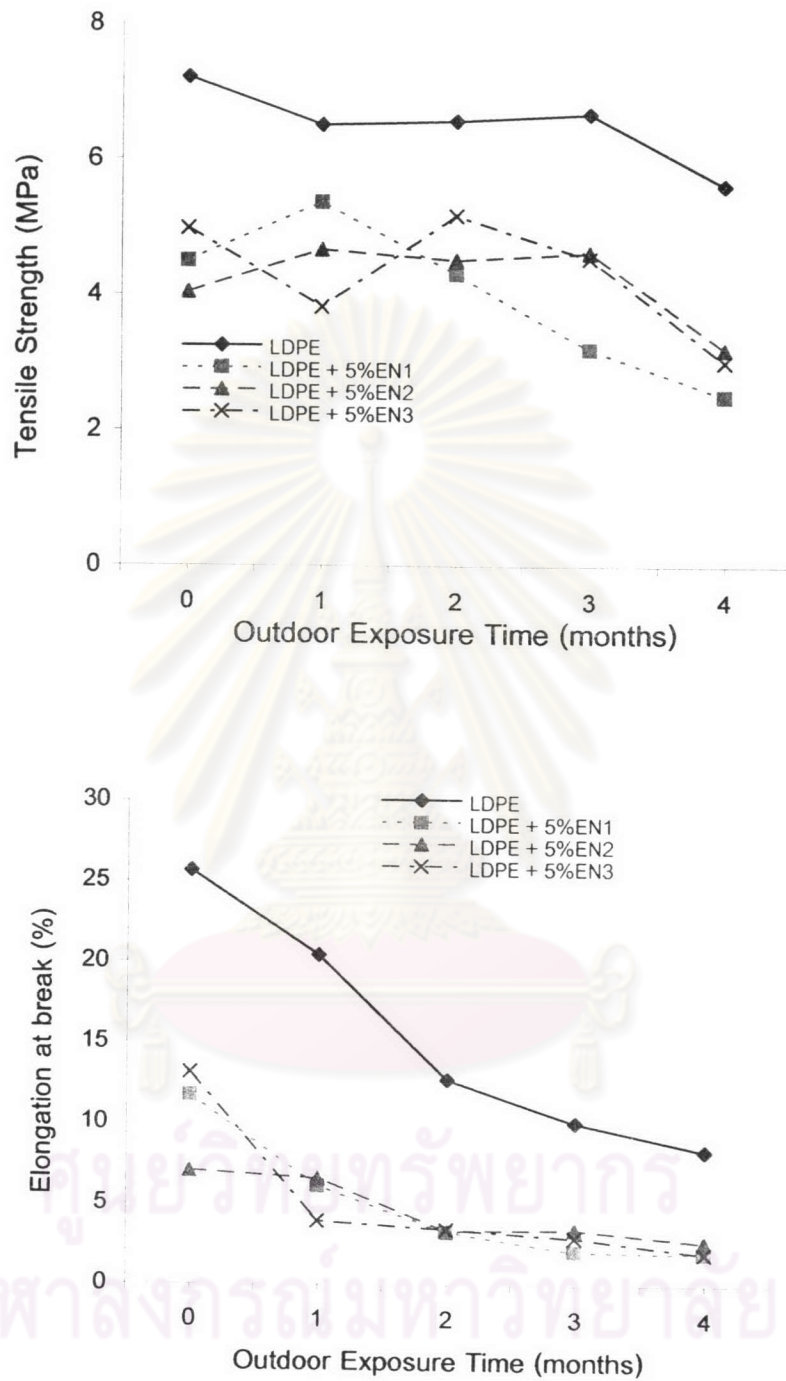


Figure 4.50 Tensile properties of pure LDPE and LDPE films containing 5%EN1, 5%EN2, and 5%EN3 microcapsules

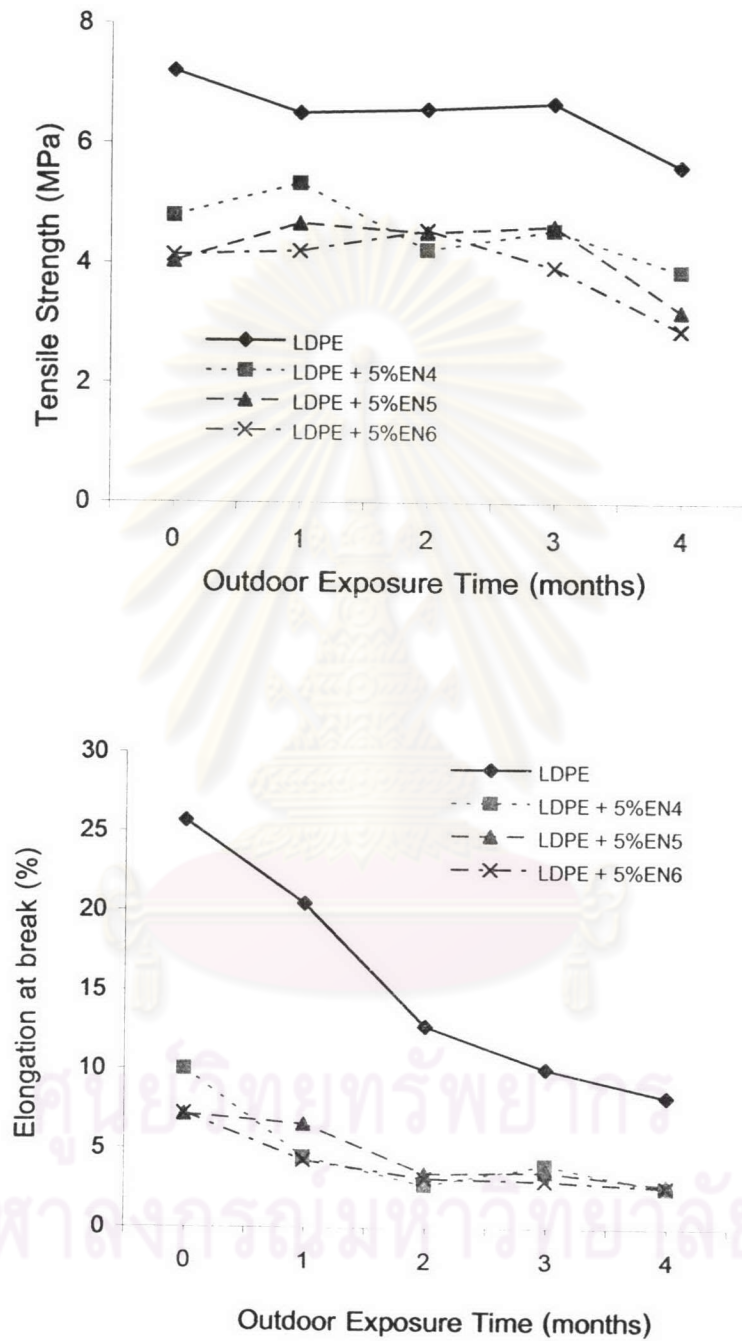


Figure 4.51 Tensile properties of pure LDPE and LDPE films containing 5%EN4, 5%EN5, and 5%EN6 microcapsules

Similar to the other properties, the comparative effects of additives on the photodegradation behavior, in term of tensile properties, are displayed as a function of exposure time in Figure 4.52. Obviously, LDPE film had highest tensile properties, whereas the LDPE/additives films showed lower tensile properties than LDPE film. It is because the LDPE/additives film had no interfacial adhesion between additives and LDPE matrix. As discussed earlier, the incompatibility between LDPE matrix and these three additives is responsible for lowering in the tensile strength and elongation at break of the composite films. Specifically, the LDPE filled with microencapsulated particles had lowest tensile properties which can be described based on their particle size and dispersion. Since the average diameter of benzophenone and gelatin powder are 120-150 μm which is smaller than the particle size of microcapsules (section 4.2.1 and 4.2.2); therefore these two powders can be dispersed uniformly within the LDPE matrix more than the microcapsules. In other words, the bigger particle size and non-uniform dispersion of the microencapsulated particles, as evidenced from SEM micrographs (Figure 4.22 and 4.23), are probably the reasons for the lowest tensile properties of LDPE/encapsulated particles film. When the forces are applied to the film, these microcapsules presenting as aggregates will act as a stress concentration or defect of the film. For LDPE/benzophenone film, small particles of benzophenone powder can absorb and transfer the applied forces uniformly and evenly so their tensile properties are greater.

Considering the photodegradation rate, it was found that LDPE/5%benzophenone showed a rapid decrease of tensile strength after 1 month of outdoor exposure. For LDPE/5%gelatin, the tensile strength clearly decreased after 2 months of outdoor exposure, whereas LDPE/microcapsule showed the constant tensile strength until the 3rd month and then decreased afterwards. The results indicated that gelatin which was coated on the benzophenone particles can retard the photodegradation. Actually, these results are in good agreement with the carbonyl index values presented in Figure 4.38. Both results confirm each other that benzophenone can accelerate the photodegradation process of the LDPE film even after 1 month of the outdoor exposure,

while the microencapsulated particles can be used to control or retard the photodegradation rate.

4.4.4.2 Accelerated Exposure

4.4.4.2.1 Effect of Gelatin and Benzophenone

Tensile properties as a function of QUV exposure time of pure and 5%gelatin filled LDPE films are shown in Figure 4.53. Unlike an outdoor exposure test, tensile properties of pure LDPE films slightly decreased during 82 hours of exposure time. Although the decrease in tensile strength of LDPE/5%gelatin film after 82 hours of exposure was not so obvious, i.e., the tensile strength dropped from 5.46 to 4.59 MPa; the tremendous decrease in elongation at break can be observed. From this figure, elongation at break decreased from 19.56 to 5.94%.

Benzophenone clearly showed an influence on elongation at break as a function of exposure time. As seen in Figure 4.53, tensile strength of LDPE film containing 5%benzophenone seemed to remain constant during 82 hours of UVB exposure. However, elongation at break decreased profoundly with an increase of exposure time. The elongation at break of LDPE/5%benzophenone dropped from 18.26% to 10.53% after being exposed for 82 hours.

ศูนย์วิทยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย

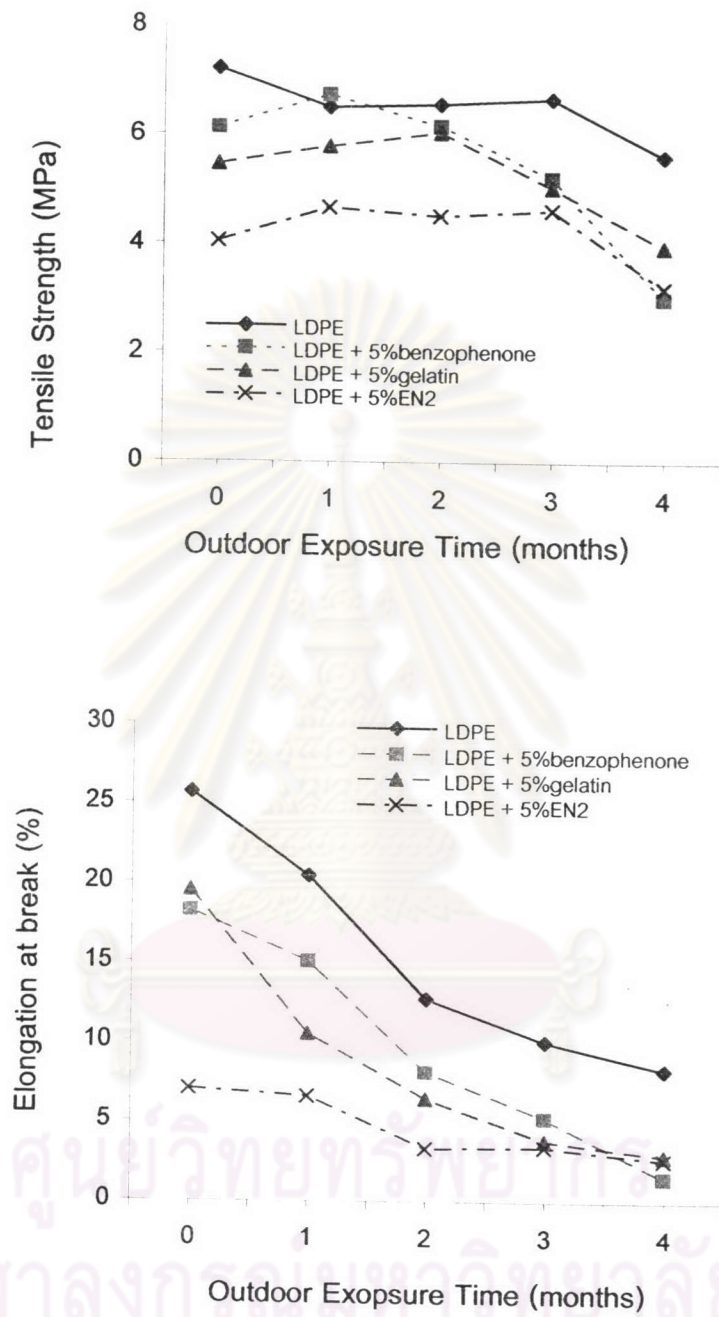


Figure 4.52 Tensile properties of pure LDPE and LDPE films containing 5%benzophenone, 5%gelatin and 5%EN2 microcapsule after QUV test

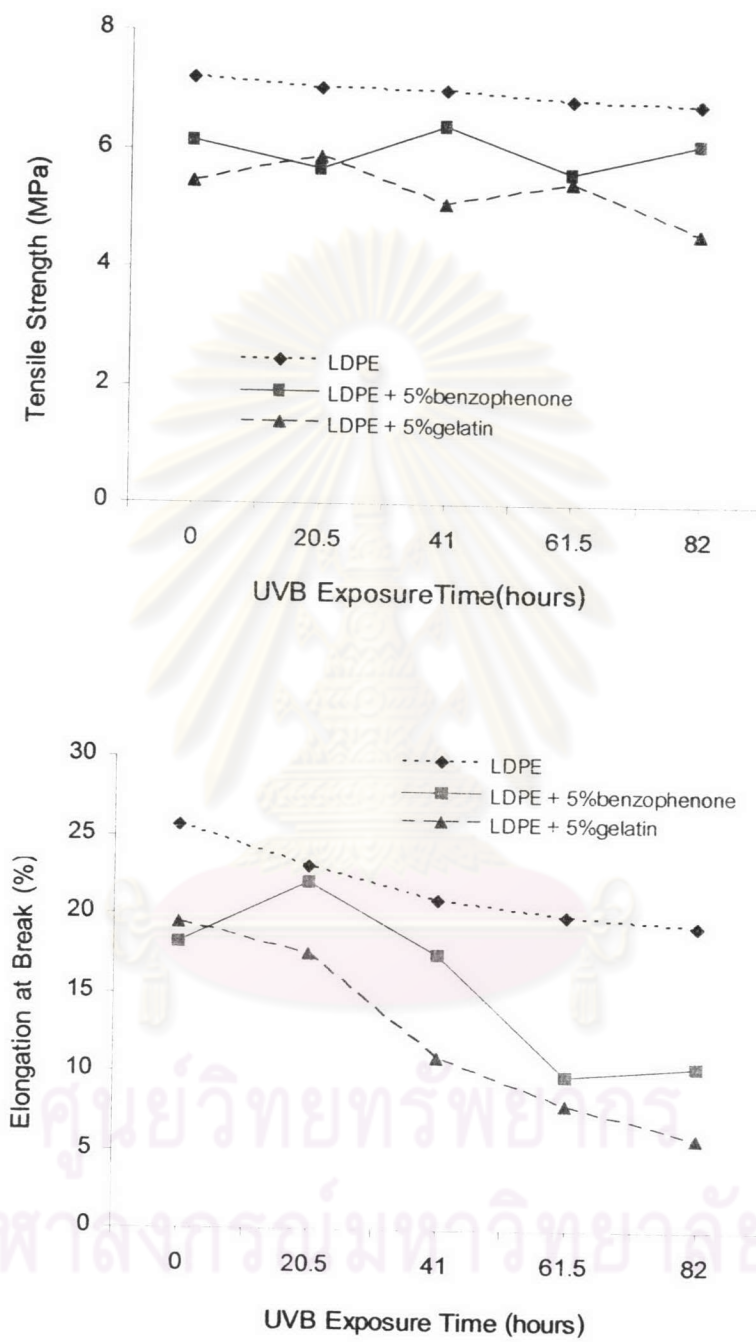


Figure 4.53 Tensile properties of pure LDPE and LDPE films containing 5%gelatin and 5%benzophenone after QUV test

4.4.4.2.2 Effect of Encapsulated Benzophenone

(a) Effect of Benzophenone to Gelatin Ratio

Figure 4.54 displays tensile properties of pure LDPE and LDPE films containing 5%EN1, 5%EN2, and 5%EN3 microcapsules. Similar to the outdoor exposure test, the addition of encapsulated benzophenone affected on the tensile properties of the LDPE/microcapsules films. Tensile properties of all formula were lower than LDPE films. However, unlike the outdoor exposure test, the tensile properties of LDPE/encapsulated particle films slightly decreased with increasing the exposure time and no significant difference among them can be noticed. For example, tensile strength of LDPE/5%EN1 decreased from 4.50 to 4.44 MPa, which is approximately 1.33%, whereas elongation at break decreased from 11.74 to 2.43% or 9.31% decreased from its original value.

(b) Effect of Amount of Hardening Agent

The decreasing of tensile properties of 5%EN4, 5%EN5, and 5%EN6 filled LDPE films compared with pure LDPE film is shown in Figure 4.55. Similar to the effect of benzophenone to gelatin, tensile properties of LDPE/microcapsules films were lower than LDPE film. In addition, with increasing the amount of microcapsules, the results showed no significant changes of tensile properties. All formula showed the same trend of decreasing. These results indicated that the amount of hardening agent had no effect on the photodegradation. For example, both tensile strength of LDPE/5%EN4 and LDPE/5%EN6 decreased from 4.50 to 4.44 MPa which is approximately 33.16%, whereas the elongation at break of these two films decreased approximately 5.89% and 4.90% from its original value, respectively.

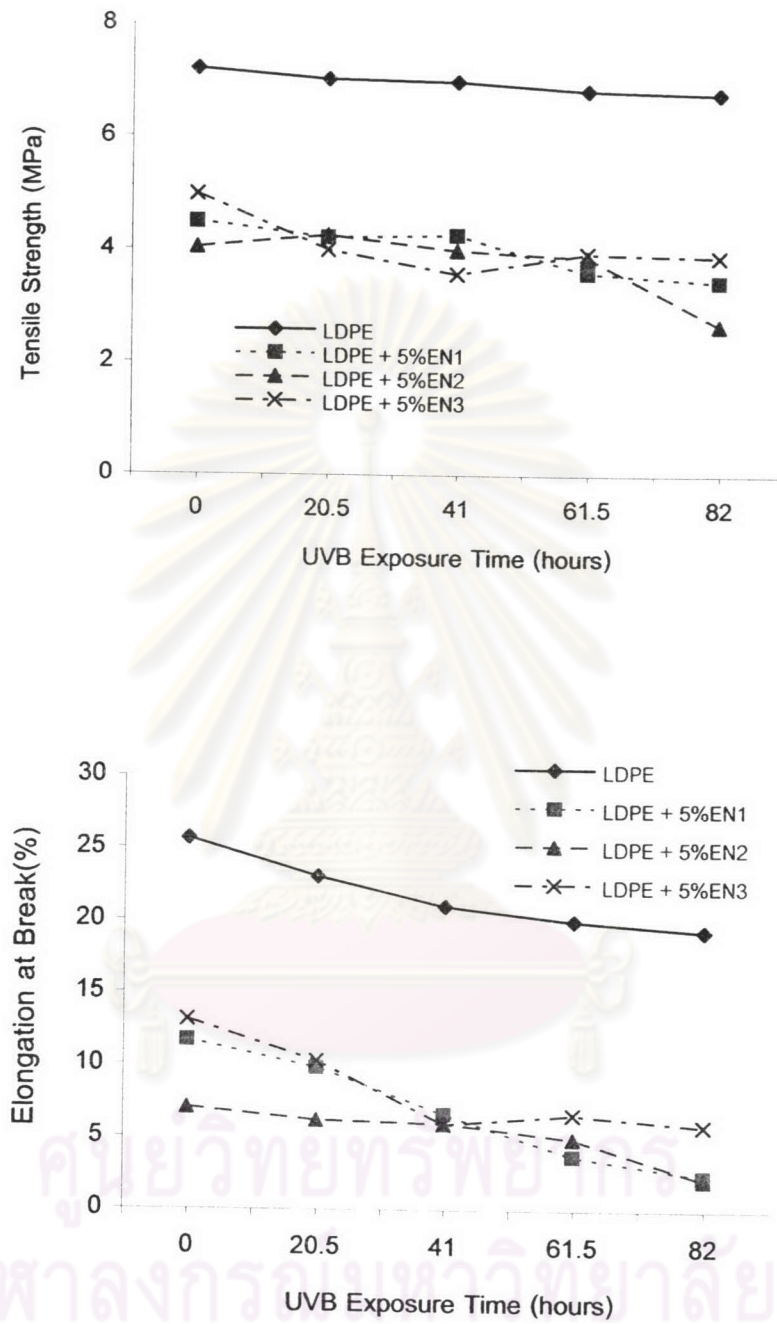


Figure 4.54 Tensile properties of pure LDPE and LDPE films containing 5%EN1, 5%EN2, and 5%EN3 films after QUV test

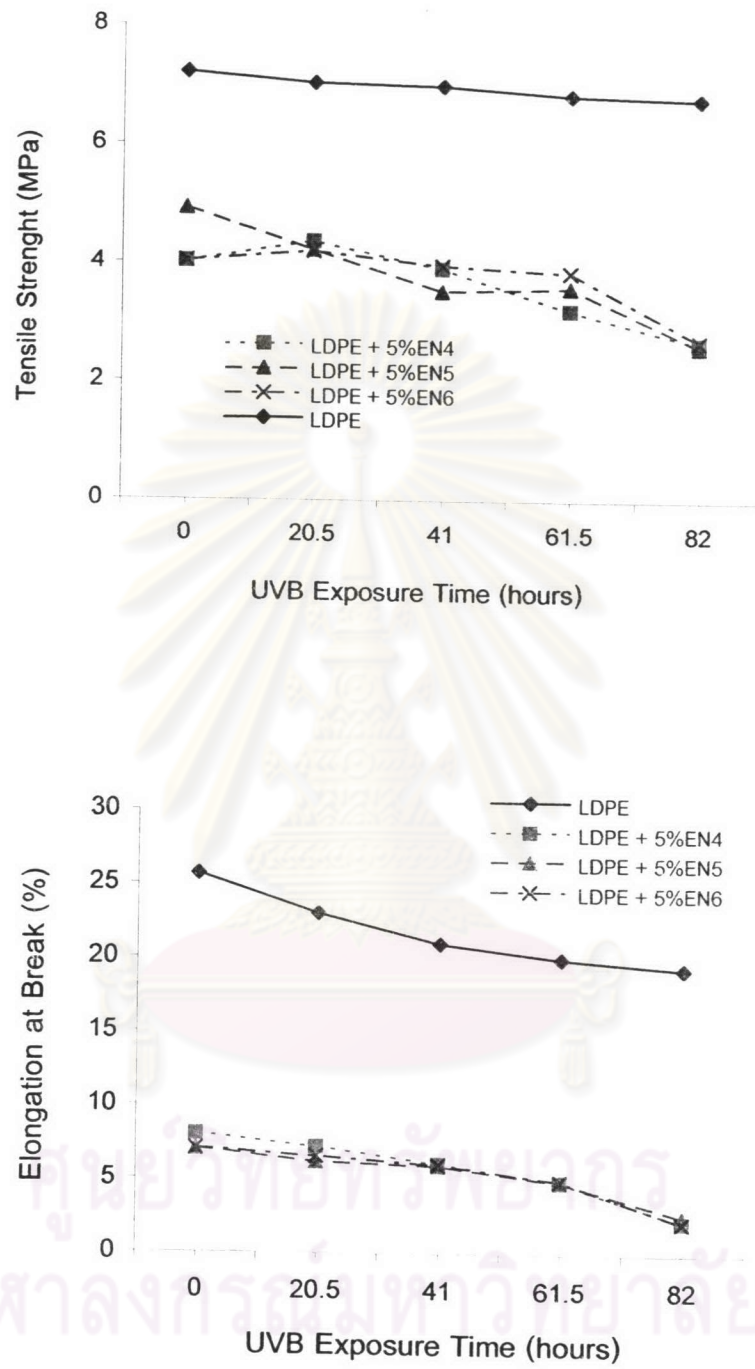


Figure 4.55 Tensile properties of pure LDPE and LDPE films containing 5%EN4, 5%EN5, and 5%EN6 films after QUV test