



CHAPTER IV RESULTS AND DISCUSSION

4.1 Part I : Thermal Oxidative Degradation

4.1.1 Melt Flow Index

Changes in the molecular weight of the PE blends were determined indirectly by measuring melt flow index. Melt flow index is inversely proportional to the molecular weight.

4.1.1.1 *Effect of Prooxidant.*

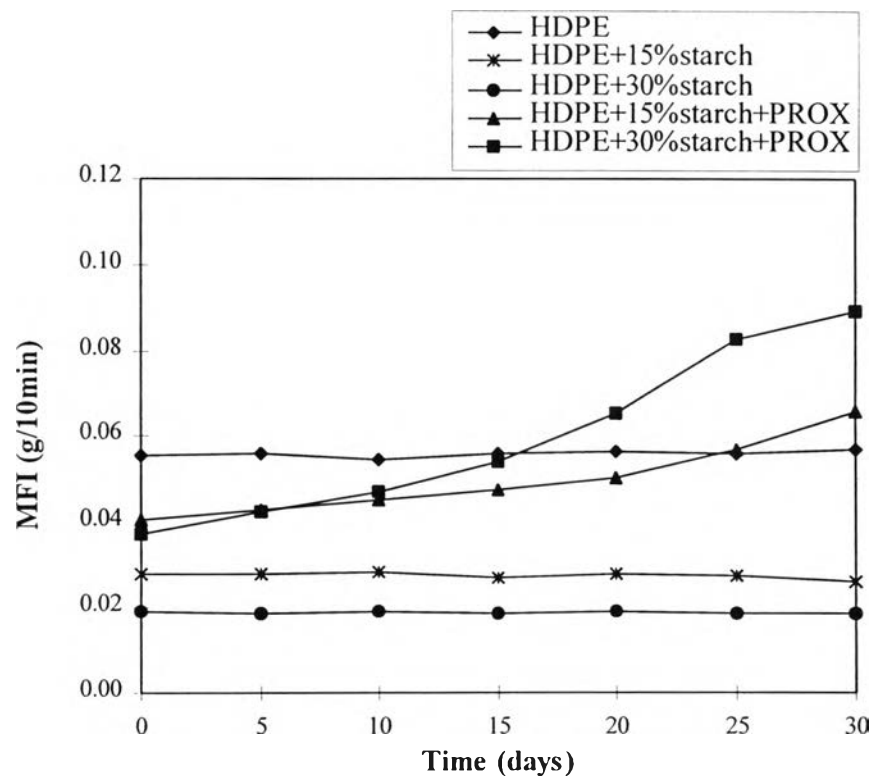
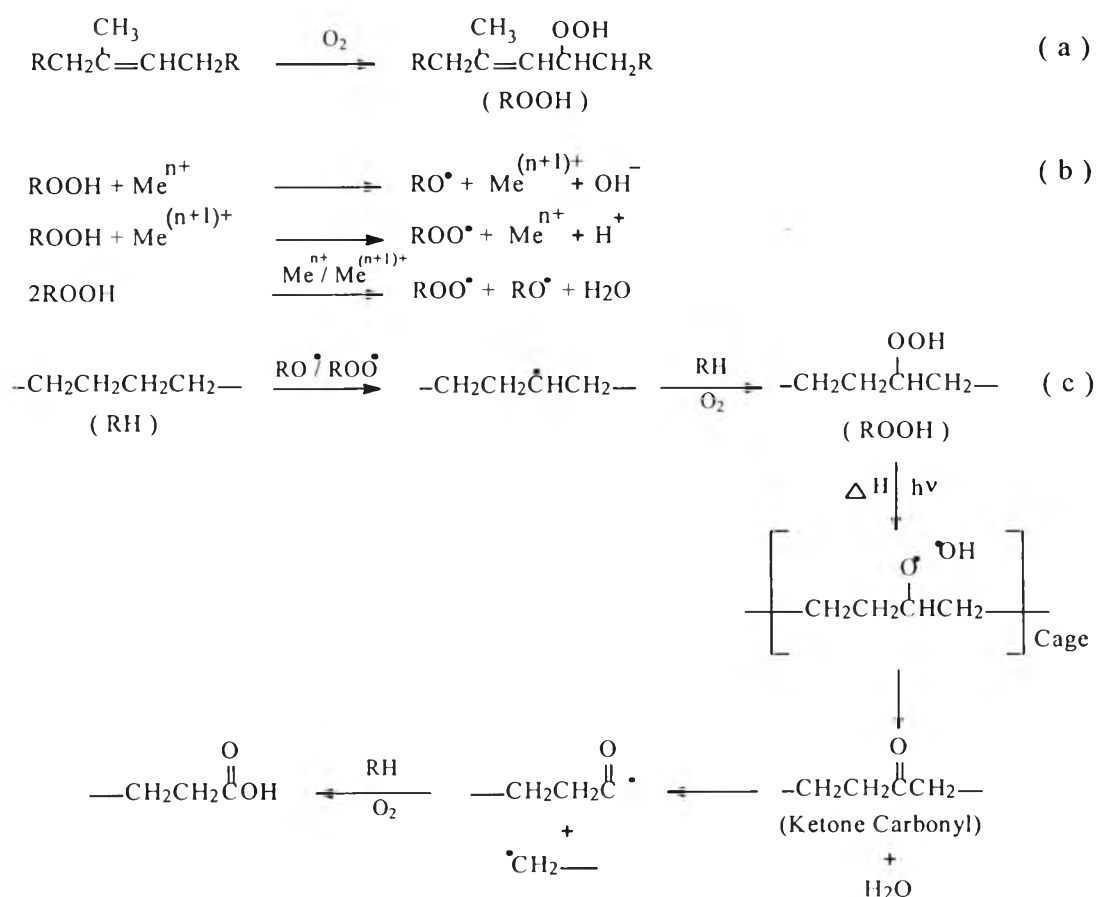


Figure 4.1 Melt flow index after heat treatment at 80°C.

The changes in melt flow index for the thermally aged samples are presented in Figure 4.1. It shows negligible changes in the MFI of HDPE and HDPE containing only starch compared with the starch-based HDPE blends containing prooxidant. Due to the large content of unsaturation (oxidizable sites) in natural rubber, the oxidation starts in this phase, yielding hydroperoxides (Scheme 4.1, reaction a). Hydroperoxides are unstable to heat and it is well known that their decomposition is catalysed by transition metal ions, for example zinc ions (Scheme 4.1, reaction b). The decomposition of hydroperoxides generate free radicals that initiate autoxidation of the PE matrix, lead to a reduction in its molecular weight, according to the mechanisms shown in Scheme 4.1, reaction c.



Scheme 4.1 Mechanism of oxidative degradation of polyethylene enhanced by prooxidant.

4.1.1.2 Effect of Starch Content.

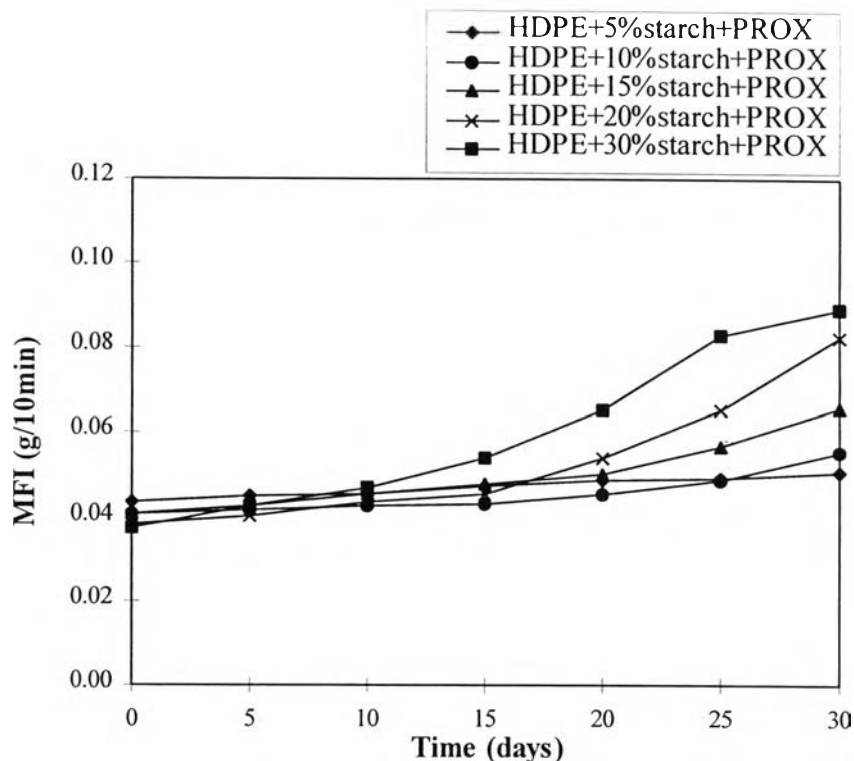


Figure 4.2 Effect of starch content on MFI of samples containing prooxidant after heat treatment at 80°C.

Figure 4.2 shows the effect of different percentages of starch in samples on MFI during heat treatment at 80°C. It shows that melt flow index increased with increasing starch content. This can be explained by reference to the model shown in Figure 4.3.

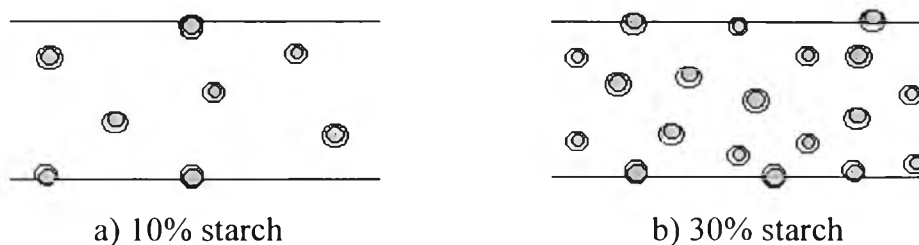


Figure 4.3 Effect of starch content on the structure of PE matrix :

a) 10% starch and b) 30% starch.

Starch granules are merely encapsulated within the polyethylene matrix without any bonding (Figures 4.3 and 4.4). Therefore, there is a gap between a starch particle and the PE matrix. A higher starch content results in an increase in porosity of the PE matrix which can then easily allow the permeation of heat, oxygen and light throughout the inner parts of the PE. These triggering factors initiate autoxidation of the unstable prooxidant, thus resulting in generation of free radicals which can attack the molecular structure of the PE. This leads to a more rapid decrease in molecular weight of the starch/PE blend compared with a blend of lower starch content.

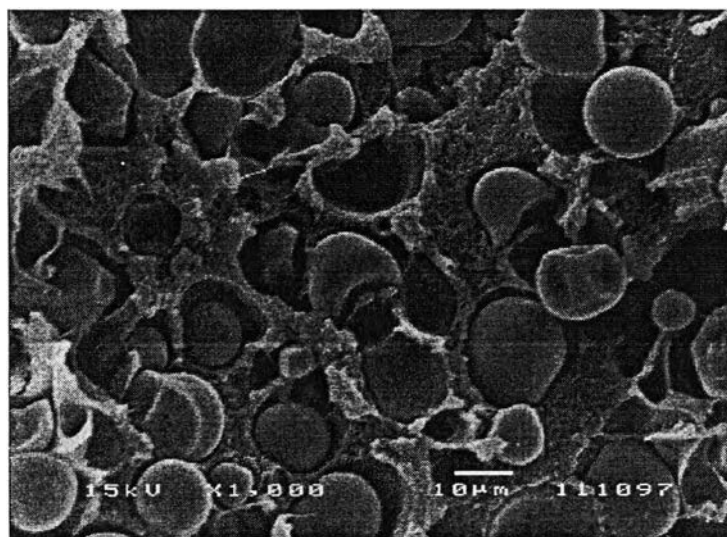


Figure 4.4 SEM micrograph of starch granules in PE matrix.

From Figure 4.2, the MFI remained almost constant or slightly increased during the first 10 days of exposure due to the effect of the antioxidant that was added in the commercial PE compound. This period is called the “induction time”. Thus, material will have a shelf life during their use which no degradation takes place during the initial lifetime of materials. After the depletion of the antioxidant, oxidation will commence, resulting in a decrease in molecular weight or an increase in melt flow index.

4.1.1.3 Effect of Temperature.

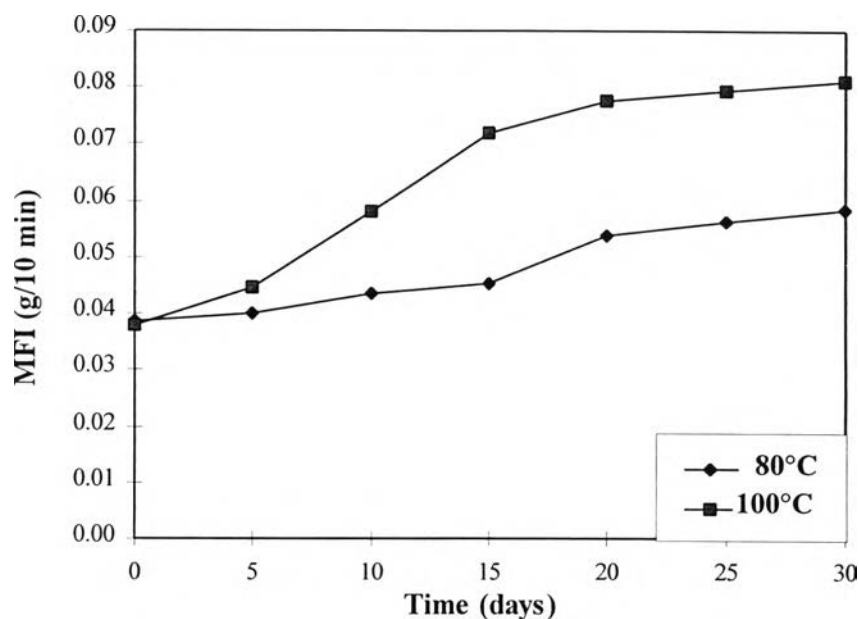


Figure 4.5 Effect of temperature on MFI of 20% starch/HDPE blends containing prooxidant after heat treatment.

Figure 4.5 shows that, at 100°C, the MFI increased more rapidly than at 80°C. The higher temperature thus increased the rate of oxidation. The results also show that there was no induction period for the heat-treated blends at 100°C because the large amount of free radicals generated overwhelmed the effect of the antioxidant.

4.1.2 Carbonyl Index

The formation of carbonyl compounds (Scheme 4.1) as products of polyethylene oxidation was easily detected by IR spectroscopy (Figure 4.6a). Figure 4.6b shows an IR spectra of 0-60 days heat-treated of 20% starch/HDPE blends containing prooxidant in the carbonyl region. The spectrum shows that the height of the carbonyl peaks (1715 cm^{-1}) increased with increasing the duration time of heat treatment up to 30 days, after which it remained constant.

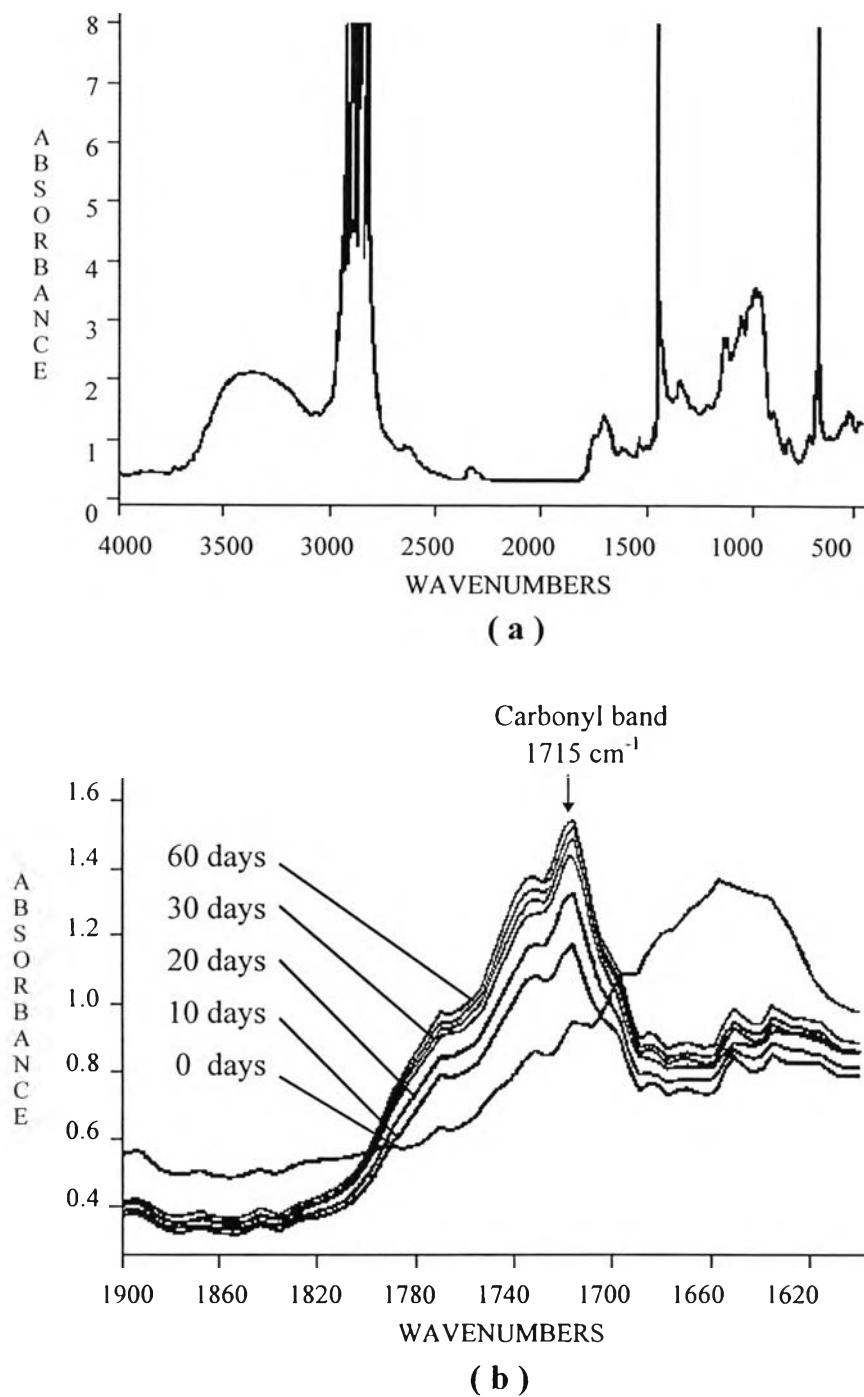


Figure 4.6 Infrared spectra of a heat-treated 20% starch/HDPE blends containing prooxidant, at 80°C. (a) Entire IR spectra of the 60 days heat-treated samples. (b) IR spectra of 0-60 days heat-treated samples in the carbonyl region.

Carbonyl index (CI), defined as the ratio of carbonyl (1715 cm^{-1}) absorbance to methylene (1465 cm^{-1}) absorbance, was used to express the measured levels of carbonyl compounds.

4.1.2.1 Effect of Prooxidant.

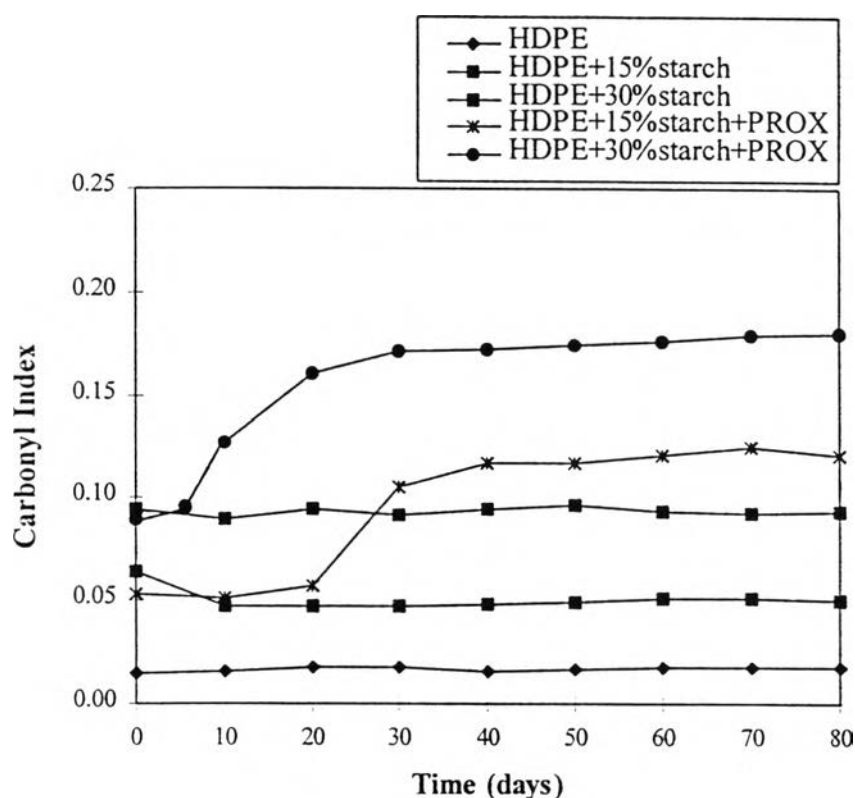


Figure 4.7 Carbonyl index (A_{1715}/A_{1465}) after heat treatment at 80°C .

For samples which did not contain prooxidant, the carbonyl index remained very low, essentially unchanged, during the heat treatment process. On the other hand, for samples containing prooxidant, the carbonyl index remained almost constant for the first few days because of the effect of the antioxidant containing in the samples. When the antioxidant was depleted the CI rapidly increased. After that, the CI increased gradually, presumably due to the depletion of oxidizable sites on the rubber.

4.1.2.2 Effect of Starch Content.

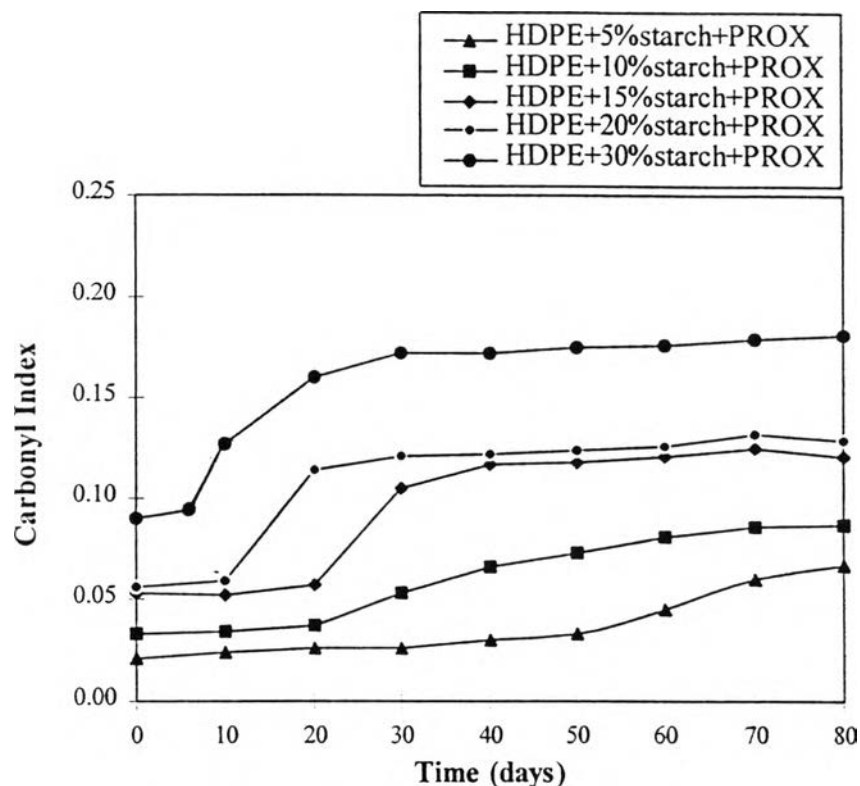


Figure 4.8 Effect of starch content on CI of the blends containing prooxidant after heat treatment at 80°C.

The effect of starch content on CI of the blends containing prooxidant additive during heat treatment at 80°C is shown in Figure 4.8. The CI of prooxidant containing samples increased with increasing starch content. After 20 days of heat treatment, the CI of 5 wt% and 30 wt% starch/HDPE blends containing prooxidant increased by 12.09% and 75.40% of their initial CI values, respectively. These results can be explained using the same model as that used to explain the change of melt flow index (Figure 4.3). A higher starch content offers more porosity in PE matrix which increases the permeation of heat, oxygen and light throughout the inner part of

PE. Therefore the oxidation reaction of PE can occur more rapidly than at lower starch content. The increase in CI confirms the decrease in MW of PE as the oxidation reaction proceeds.

4.1.2.3 Effect of Temperature.

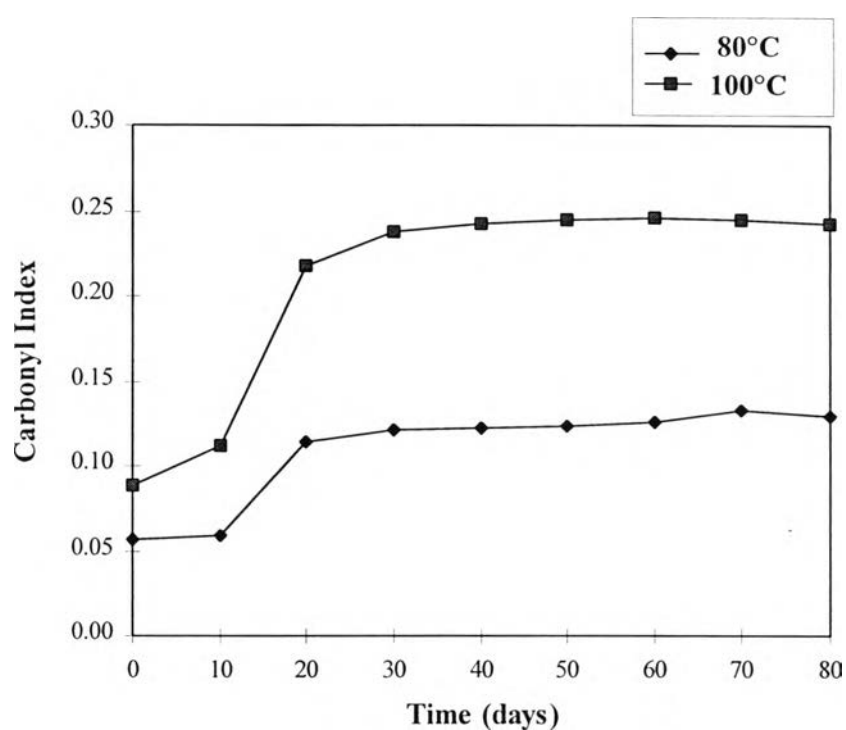


Figure 4.9 Effect of temperature on CI of 20% starch/HDPE blends containing prooxidant after heat treatment.

Figure 4.9 shows that the CI of HDPE the blends containing 20% starch and a prooxidant additive at 100°C increased about 2 times when compared to corresponding samples at 80°C. Higher temperatures will speed up the oxidation reaction of the PE matrix.

4.1.3 Mechanical Properties

One of the most common methods for assessing the degradation of plastic materials is by measuring changes in their mechanical properties.

4.1.3.1 Effect of Prooxidant.

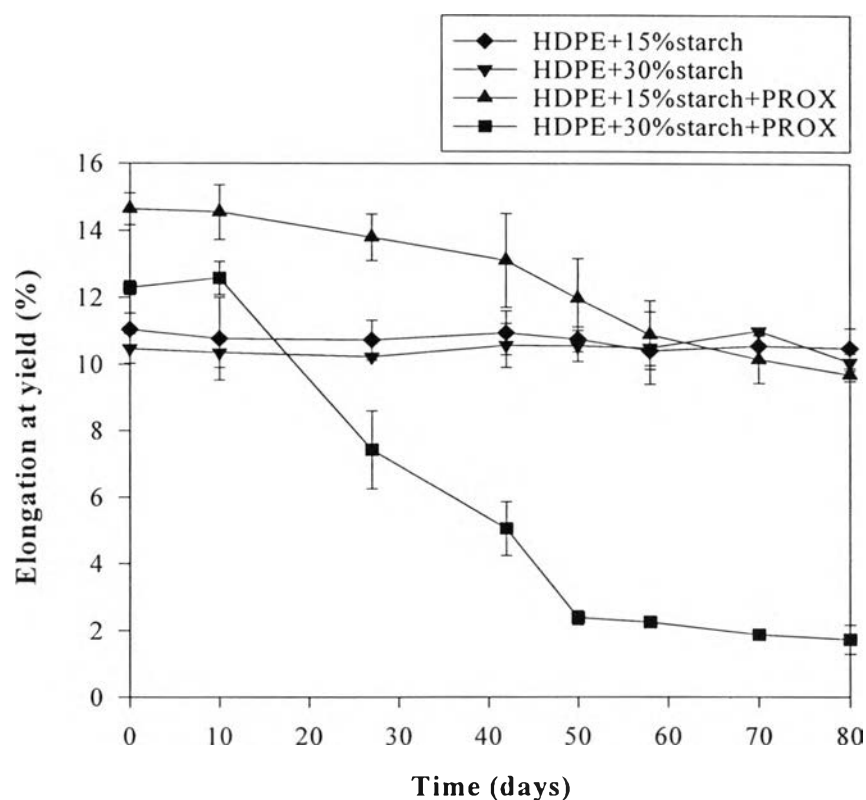


Figure 4.10 Elongation at yield after heat treatment at 80°C.

Figure 4.10 shows negligible changes in the elongation at yield with heat aging of the blends containing only starch compared with the blends containing a prooxidant additive. This indicated that the prooxidant promoted oxidative degradation of the PE matrix. The blends containing prooxidant showed a decrease in elongation at yield that parallel changes in the molecular weight and carbonyl index of the corresponding samples.

4.1.3.2 Effect of Starch Content.

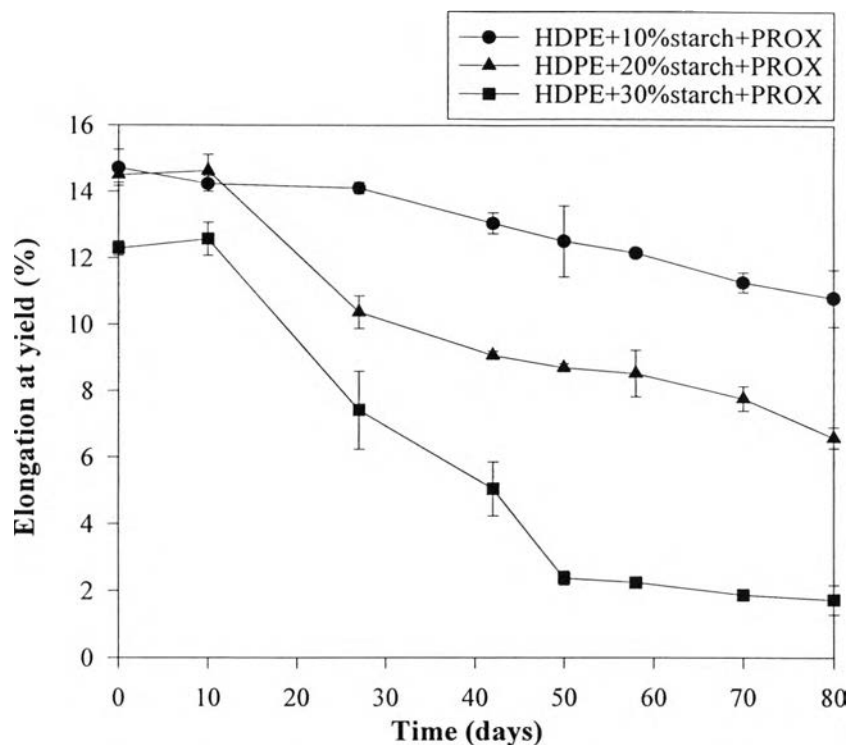


Figure 4.11 Effect of starch content on the elongation at yield of starch/HDPE blends containing prooxidant after heat treatment at 80°C.

Figure 4.11 shows that for prooxidant-containing blends subjected to heat treatment at 80°C, the elongation at yield decreased with increasing starch content. For the 30 wt% starch-based HDPE blend containing prooxidant, the elongation at yield dropped rapidly to 2% during 50 days of heat treatment.

4.1.3.3 Effect of Temperature.

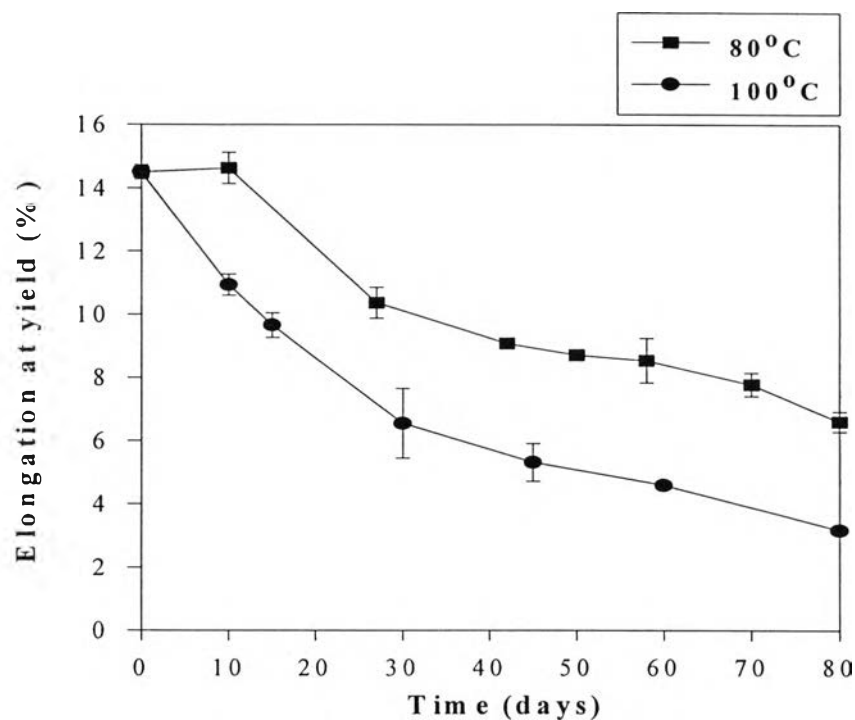


Figure 4.12 Effect of temperature on the elongation at yield of 20% starch/HDPE blends with prooxidant after heat treatments at 80° and 100°C.

The results from Figure 4.12 show that for a 20 wt% starch-based HDPE blend containing prooxidant the elongation at yield decreased more rapidly at 100°C than at 80°C. The results also show that there was no induction period for the heat-treated blends at 100°C since the large amount of free radicals generated overwhelms the effect of the antioxidant.



4.2 Part II : Biodegradation of Starch

The starch-based HDPE films showed weight losses after treatment with α -amylase at 80°C for 12 hours. The weight loss was due to hydrolysis and leaching of the starch from HDPE matrix. A control experiment, in which the film samples were shaken in a buffer solution without α -amylase, was found that the leaching of starch occurred. Figure 4.13 shows the percentage of weight loss with and without the enzyme α -amylase in samples containing different starch contents.

The percentage of weight loss due to starch hydrolysis and the percentage of starch hydrolysis of starch/HDPE films containing different starch contents together with prooxidant are shown in Figure 4.14. The rate of starch hydrolysis increased with increasing starch content. This is because a higher starch content offers more sites for the hydrolysis reaction.

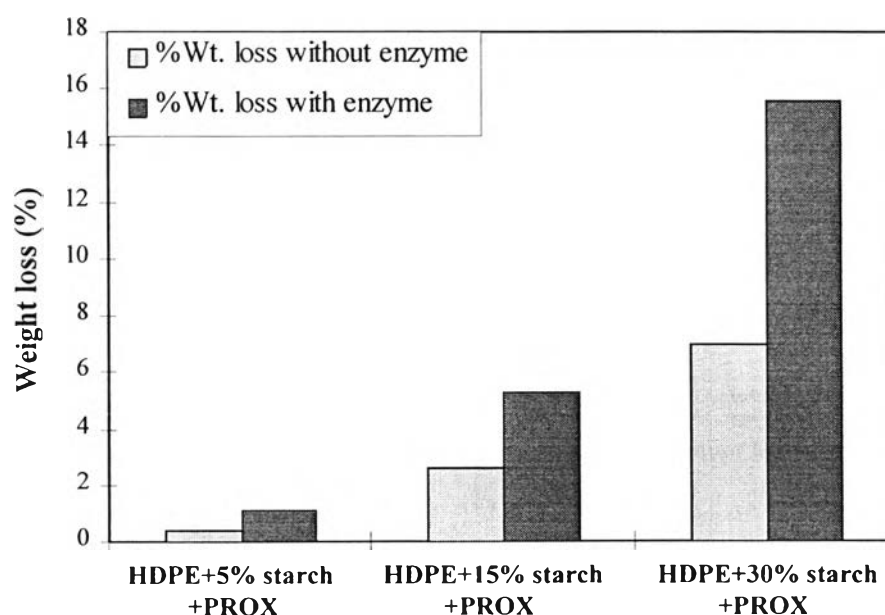


Figure 4.13 Effect of enzyme treatment on weight loss of starch/HDPE films containing prooxidant after shaking for 12 hours at 80°C.

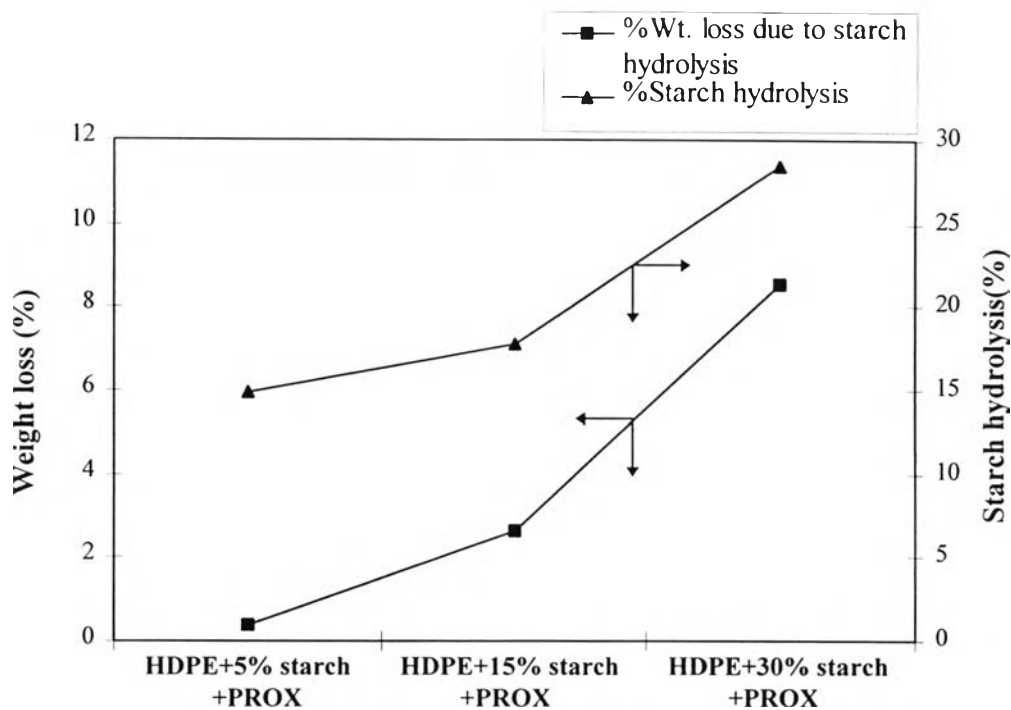
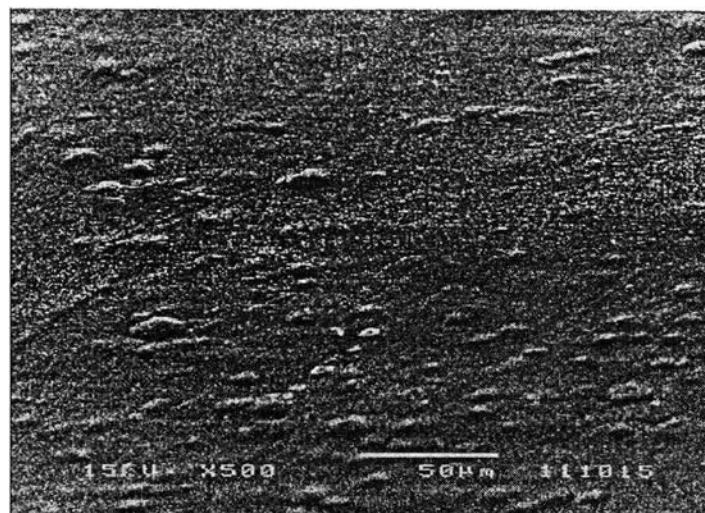


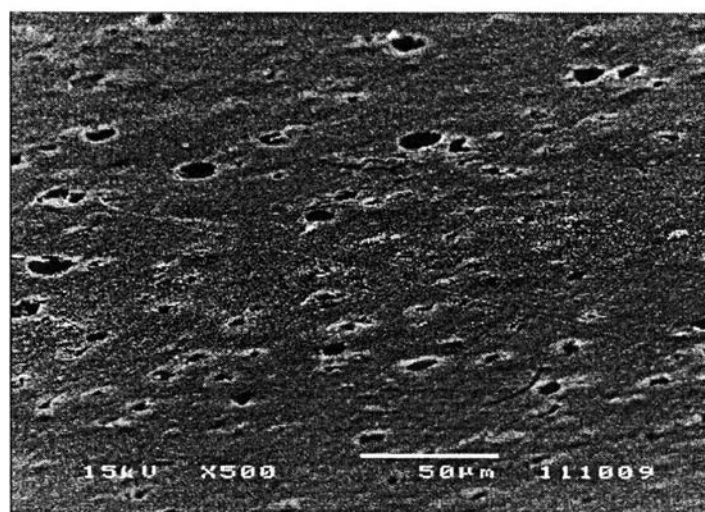
Figure 4.14 Percentage of weight loss and starch hydrolysis after treatment with enzyme α -amylase by shaking for 12 hours at 80°C.

The starch removal was probably due to the loss of partially exposed starch granules near the surface of the films that were not completely coated with polyethylene. In addition, swollen starch granules that eventually ruptured the thin PE coating would also be susceptible to enzyme attack. The starch granules which were either embedded in or completely covered with PE matrix were securely encapsulated within the polyethylene matrix and were therefore not removed.

SEM was used to examine the effect of enzymatic hydrolysis of starch component on the surface of the starch-based HDPE films (Figures 4.15 and 4.16).



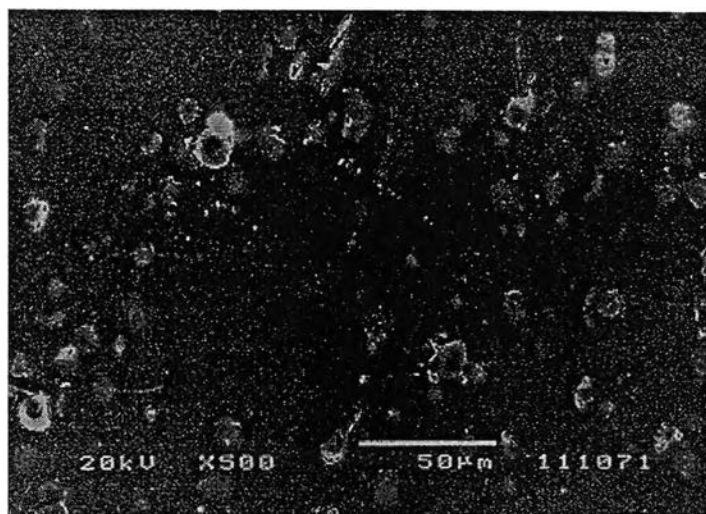
a)



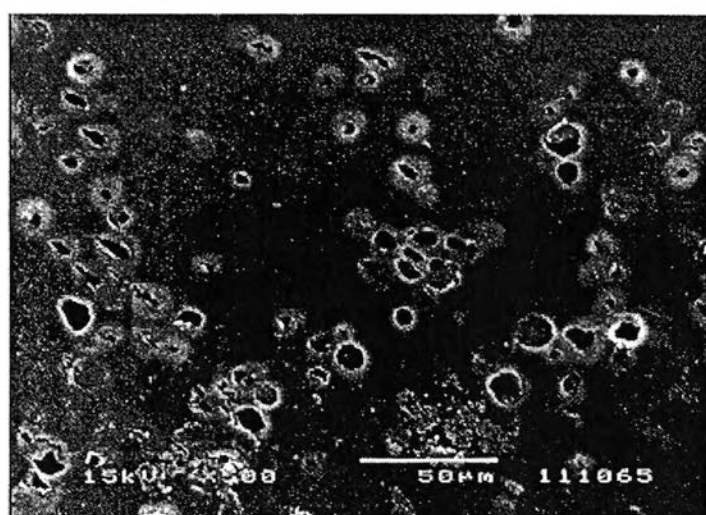
b)

Figure 4.15 SEM micrographs (angle of inclination) of the surface of 30% starch/HDPE films containing prooxidant (a) before and (b) after enzyme treatment. (Magnification $\times 500$)

Partly exposed and well-covered starch granules before enzyme treatment are shown in Figures 4.15a and 4.16a. The empty craters (Figure 4.15b and 4.16b) resulted from the hydrolysis of starch granules that were accessible to α -amylase activity. Covered starch granules on the film surfaces remained intact. The destruction of the surface depends on the content of the starch.



a)



b)

Figure 4.16 SEM micrographs of the surface of 30% starch/HDPE films containing prooxidant (a) before and (b) after enzyme treatment. (Magnification $\times 500$)

Starch hydrolysis by the action of enzyme α -amylase as a function of hydrolysing time is shown in Figure 4.17. It shows that the percentage of starch hydrolysis increased as hydrolysing time increased. Infrared spectrum shown in Figure 4.19 confirmed the increase in starch hydrolysis with time.

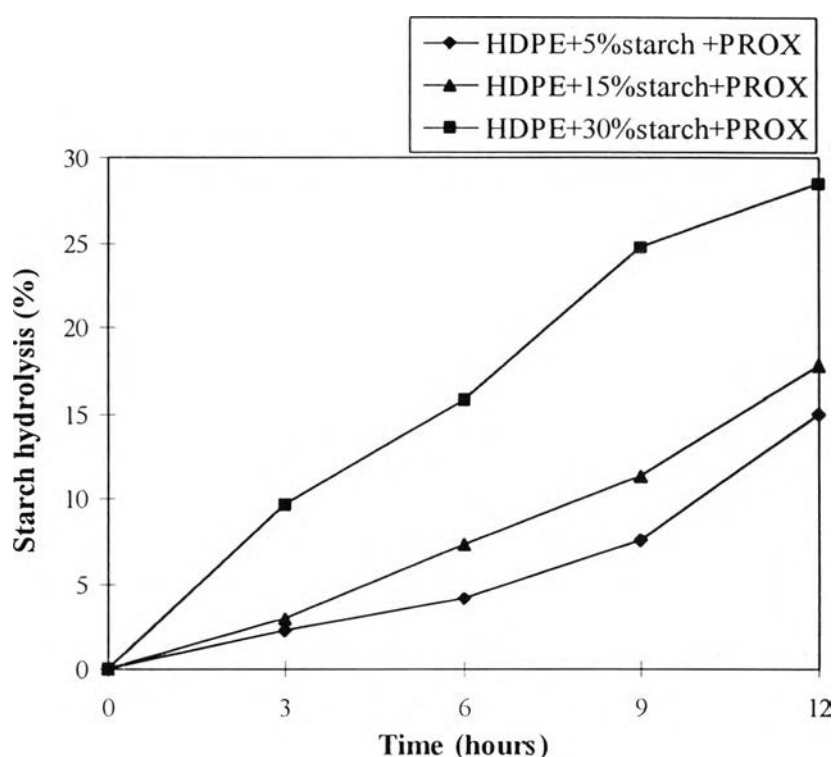


Figure 4.17 Starch hydrolysis by the action of enzyme α -amylase as a function of time.

Table 4.1 shows IR vibrations of high density polyethylene and starch. Spectra of HDPE and a 20% by weight starch/HDPE blend are shown in Figures 4.18(a) and (b). The additional bands to those recorded for pure HDPE are C-O and O-H stretching bands that came from the starch components.

Table 4.1 Infrared Vibrations and Assignments for HDPE and Starch

Major IR Bands of Components	
Frequency (cm ⁻¹)	Assignment and Remarks
HDPE	
2850, 2920 (s)	C-H stretching
1460, 1471 (m-s)	CH ₂ scissor and asym bending
1377, 1369, 1352 (w)	C-H bend due to CH ₂ and CH ₃
720, 730 (m-w)	CH ₂ rocking
Starch	
3000-3650 (s, br)	O-H stretching with absorbed water
2850, 2920 (s)	C-H stretching
1640 (w-m)	δ(O-H) 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 stretching (C-O-C and C-O-H)
400-930 (w-m, br)	O-H deformation, C-O-C band

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

Infrared spectra of 30% starch/HDPE blends containing prooxidant during enzyme treatment are shown in Figure 4.19. Absorbance of both C-O and O-H stretching bands decreased with the length of enzyme treatment since the starch granules were hydrolysed by enzyme α -amylase.

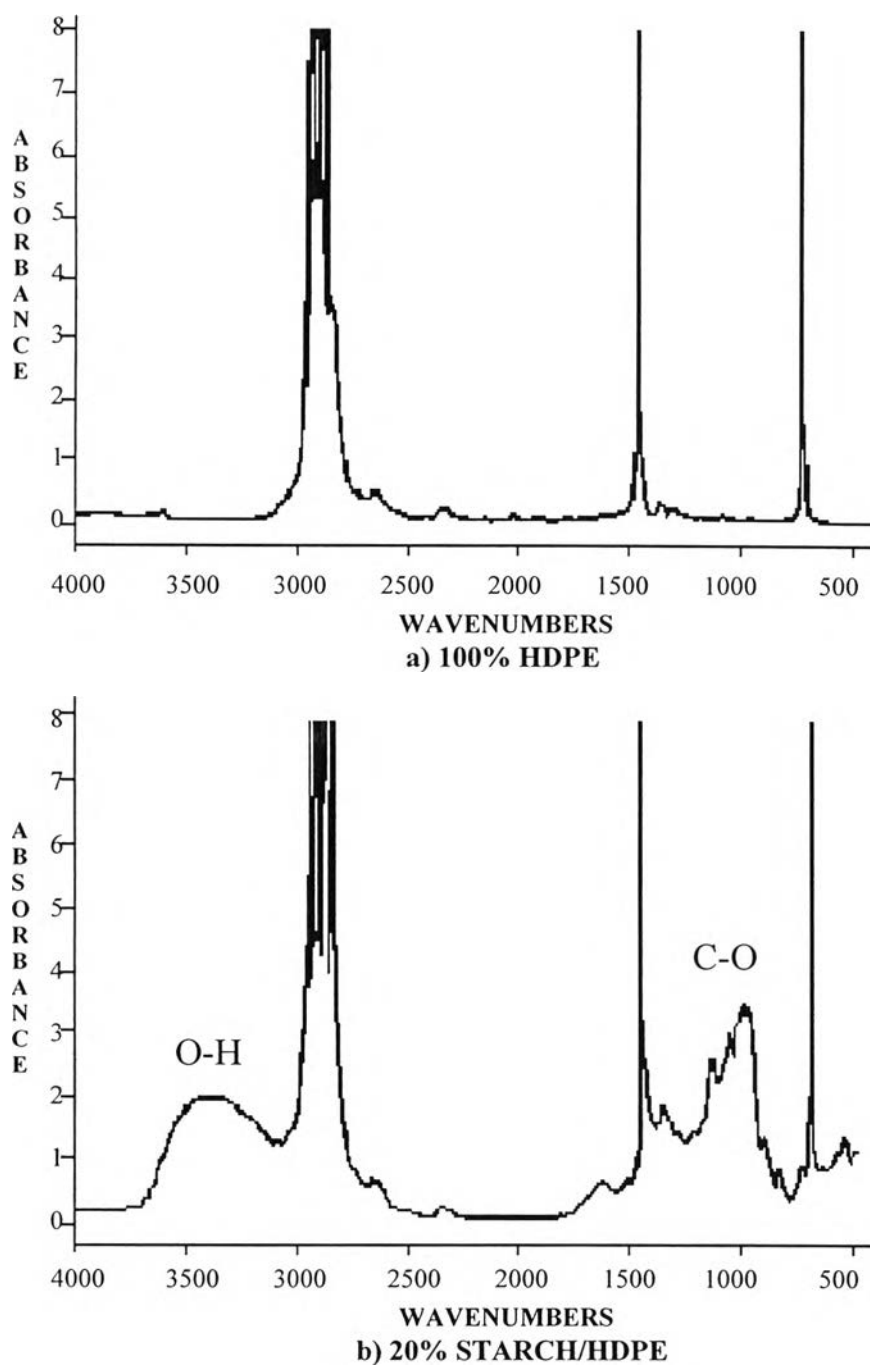


Figure 4.18 Infrared spectra of (a) 100% HDPE and (b) 20% starch/HDPE blends.

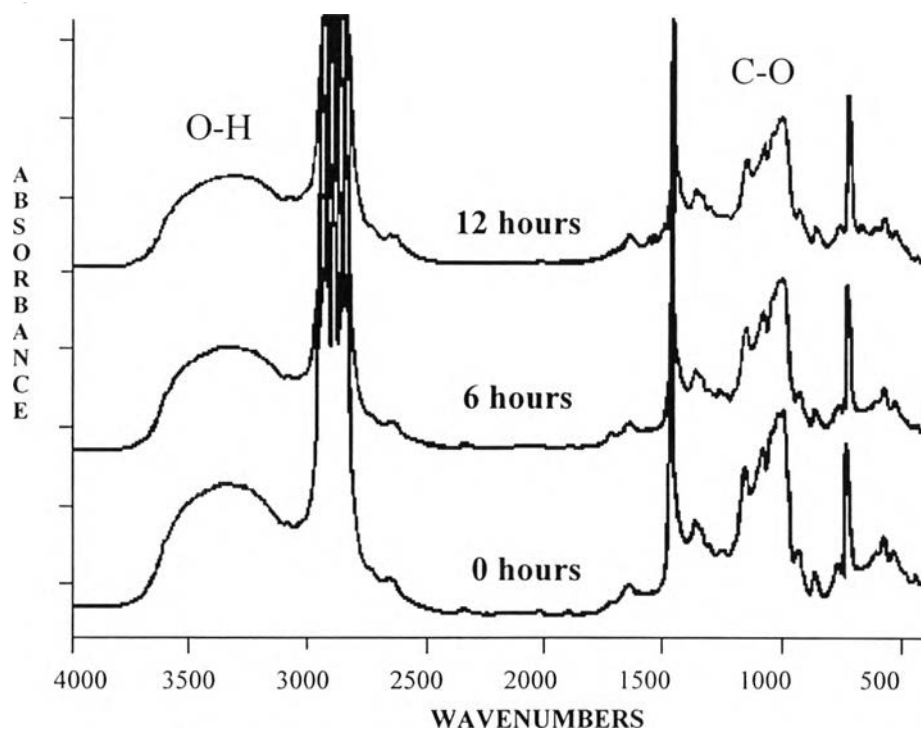


Figure 4.19 Infrared spectra of 30% starch/HDPE film containing prooxidant after hydrolysis by enzyme α -amylase for 0, 6 and 12 hours..

4.3 Part III : Combined Thermal Oxidative Degradation and Biodegradation

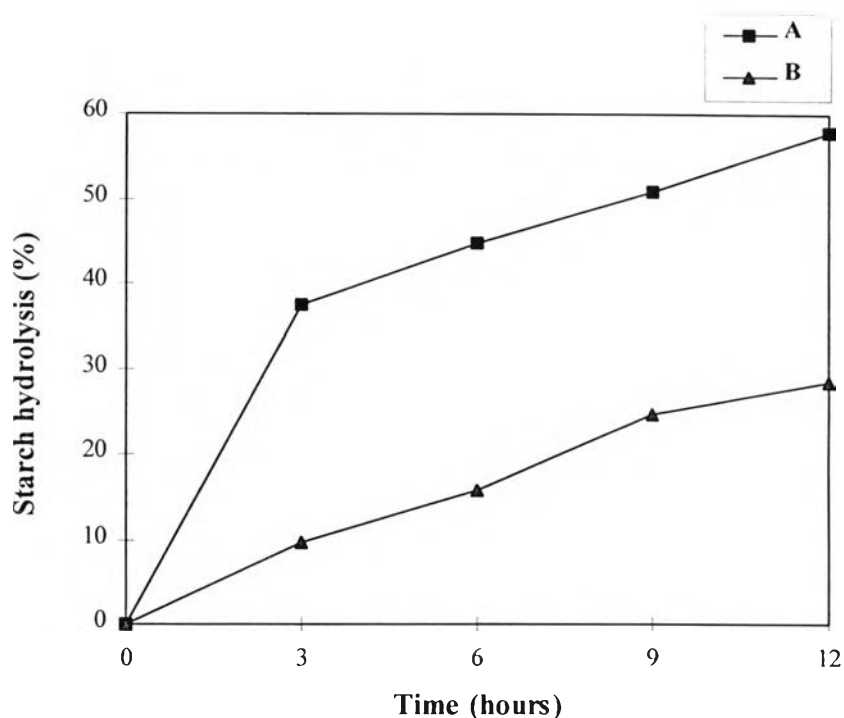


Figure 4.20 Percentage of starch hydrolysis by enzyme α -amylase as a function of time for 30% starch/HDPE films containing prooxidant. (A) Incubated after heating at 80°C for 20 days (B) incubated without prior heating.

Figure 4.20 shows a significant increase in the extent of starch hydrolysis after 20 days of heat treatment. The enzymatic hydrolysis of starch for the 0 and 20 days preheat-treated films was 28 and 58 wt% after 12 hours of incubation, respectively. The higher starch hydrolysis after heat treatment is because the prooxidant will promote oxidative degradation of the polyethylene. Deteriorated PE films apparently allowed water and enzyme to access embedded starch granules, resulting in increased starch removal. This

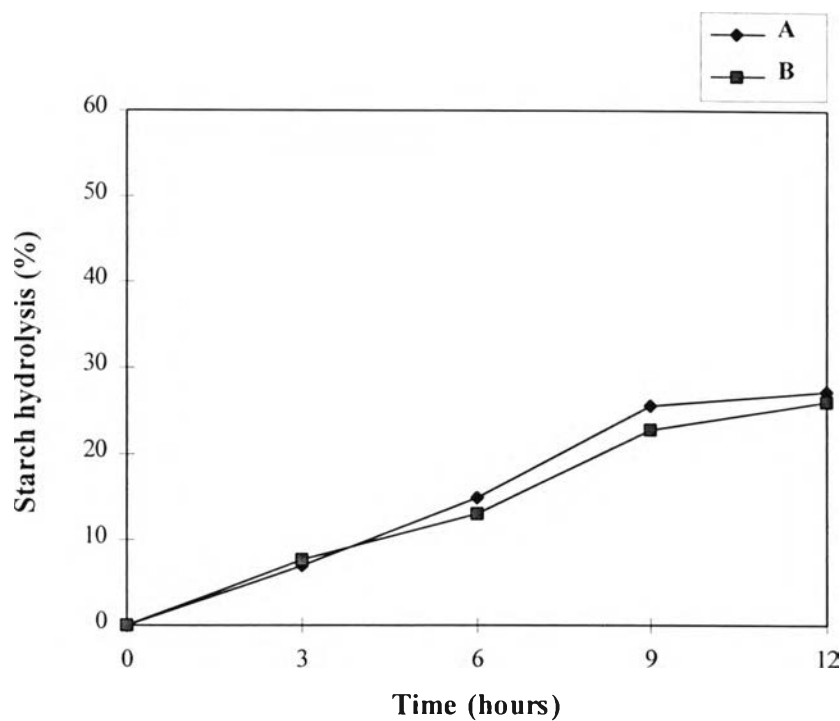


Figure 4.21 Percentage of starch hydrolysis by enzyme α -amylase as a function of time for 30% starch/HDPE films. (A) Incubated after heating at 80°C for 20 days (B) incubated without prior heating.

Figure 4.21 shows no significant difference in the percentage of starch hydrolysis between 0 and 20 days of preheated-treated films in enzyme α -amylase. This indicated that heat treatment had no significant effect on starch hydrolysis for the samples containing starch without a prooxidant additive compared with samples containing a prooxidant additive .