

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Part I : Themooxidative Degradation

4.1.1 Effect of Prooxidant and Starch

FTIR spectra of PE containing zinc stearate as a prooxidant during incubation at 75°C for 0, 2, 5, 8, 12, 16 and 20 days are showed in Figure 4.1. The significant changes in the FTIR spectra appeared in the carbonyl region at 1675-1750 cm^{-1} , as shown in Figure 4.2.

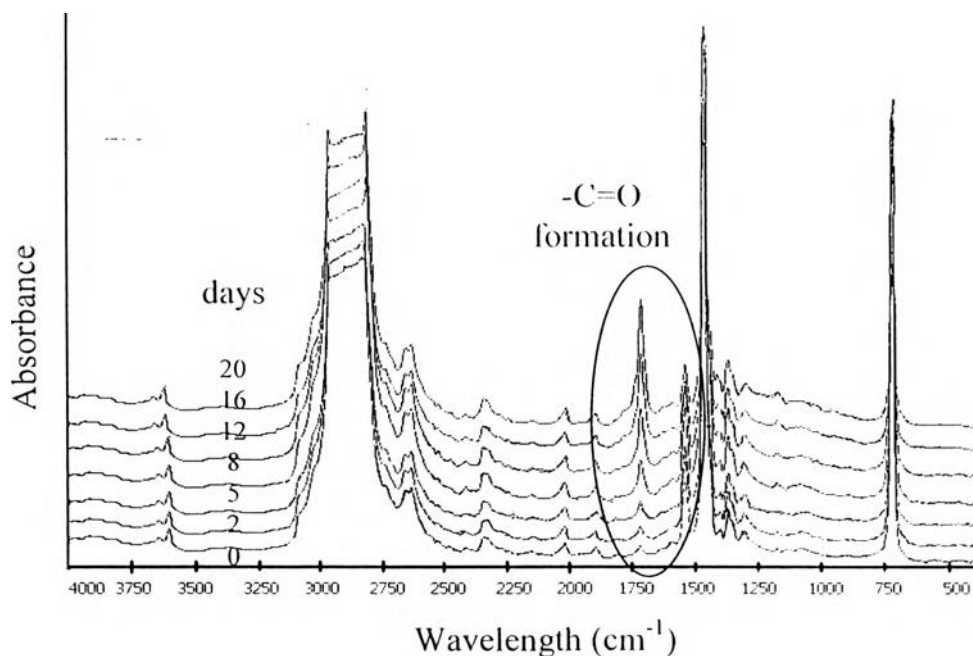


Figure 4.1 FTIR spectra of PE containing zinc stearate as a prooxidant during incubation at 75°C.

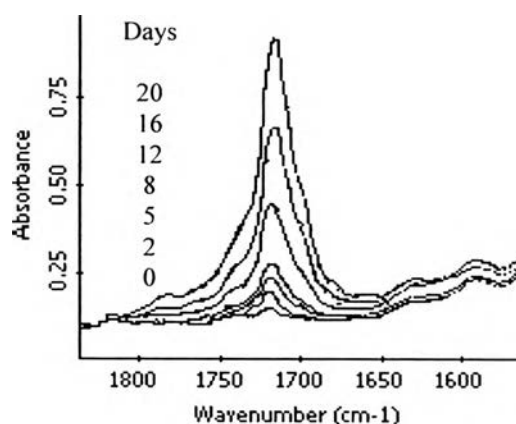


Figure 4.2 Carbonyl region of FTIR spectra of PE containing zinc stearate as a prooxidant during incubation at 75°C.

An increase in the carbonyl peak height as incubation time increased is due to the formation of carbonyl compounds which are degradation products of PE. The thermooxidation mechanism is proposed in scheme 4.1 involving in radical mechanism of peroxide and hydroperoxide decomposition (Costa, 1997).

The main products produced during the thermooxidation are carbonyl compounds which are products from chain scission process (Grassie, 1988). Karlsson *et al.* (1999) reported that the major degradation products of PE were a homologous series of carboxylic acids, ketones, hydrocarbons and lactone.

For the blends containing prooxidant with various amounts of starch, the effect of prooxidant and starch on carbonyl index as a function of induction time is showed in Figure 4.3. In case of pure PE, there are no changes in carbonyl index even after incubation for many days. On the contrary, the carbonyl index of the blends containing zinc stearate without starch increased after incubation for 5 days.

It can be seen that the addition of zinc stearate could reduce the induction period because zinc ion catalyzed hydroperoxide decomposition in

thermooxidation reaction of PE. The catalytic effect of transition metal ions is shown in Scheme 4.2 (Grassie, 1988).

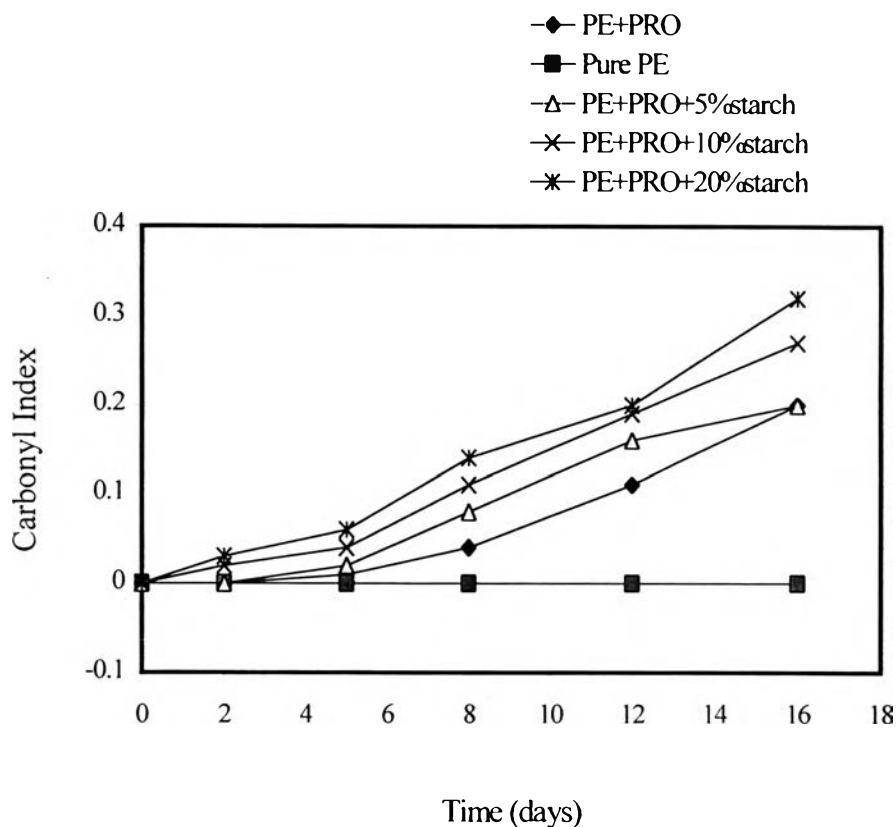
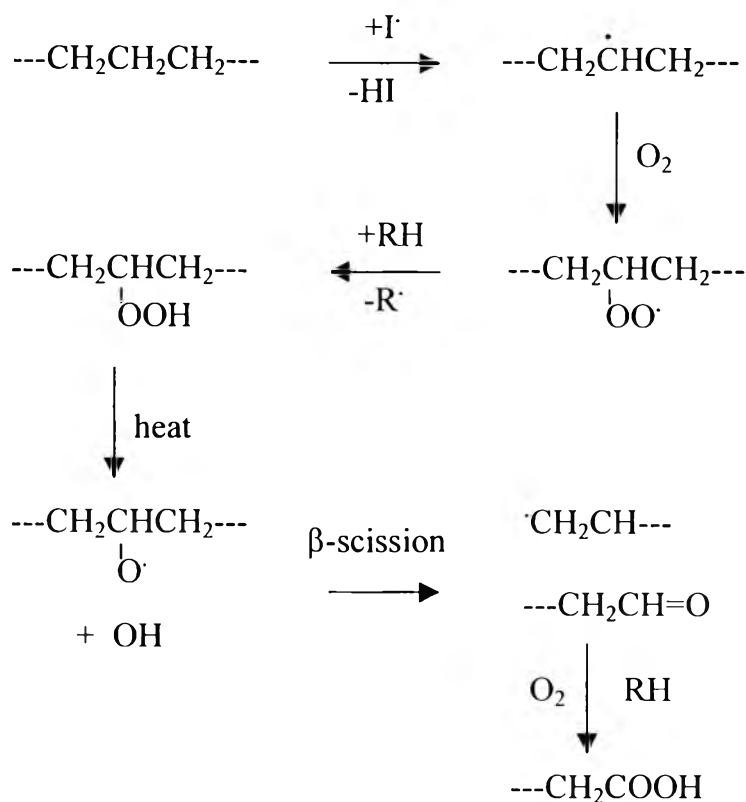


Figure 4.3 Carbonyl index of PE containing zinc stearate and starch during incubation at 75°C.

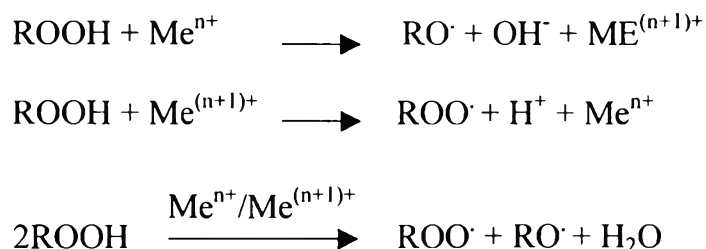
Figure 4.3 shows that the blends containing starch have higher carbonyl index than the blends without starch and as the starch content increased, the carbonyl index increased. It seems that the presence of starch in the blends could enhance the thermooxidative degradation of PE.

This can be explained by the microstructure of starch granules in PE matrix. Figure 4 shows that starch granules are embedded within the PE matrix. Therefore, there is a gap between starch granule and PE matrix. The

scheme of PE/starch blends with different starch contents is shown in Figure 4.5.



Scheme 4.1 Thermooxidation mechanism of PE.



Scheme 4.2 Catalytic effect of transition metal.

The higher starch content led to an increase in porosity of the PE matrix which can then easily allow the permeation of heat and oxygen throughout the inner part of the PE resulting in higher carbonyl index.

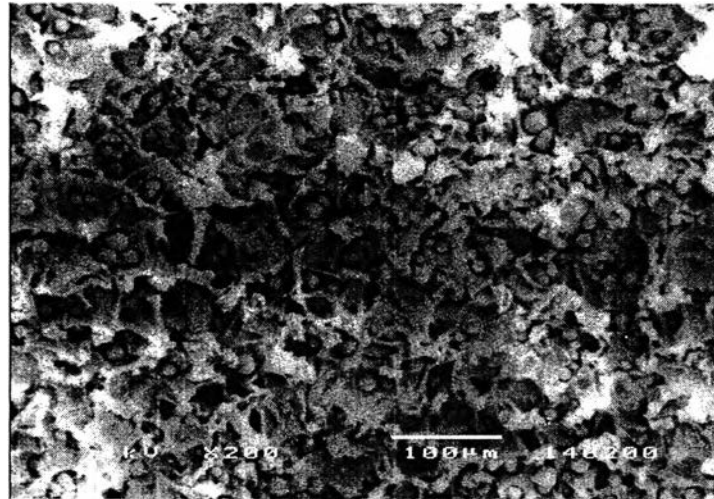


Figure 4.4 Microstructure of granular starch-filled PE matrix.

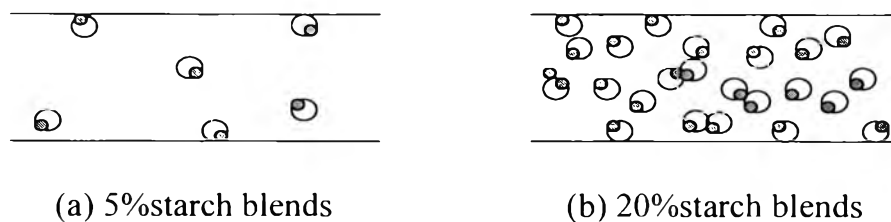


Figure 4.5 Models of granular starch filled-PE matrix showing cross section of the films.

It can be seen that starch promoted thermooxidation by increasing in the surface area of the PE matrix. The degradation results of PE/granular starch blends are in contrast with the degradation results of PE/plasticized starch (PLST) blends. PLST refers to starch in which all the crystal structure has been destroyed by applying heat and shearing forces in the presence of plasticizer (Bikiaris, 1997). Bikiaris *et al.* (1997) studied the degradation of PE/PLST, and blends reported that PLST inhibited thermooxidative degradation of PE matrix due to the presence of various leftovers which remain in starch. They proposed that phosphoric esters in

starch are complexed with transition metal ions leading to deactivation of prooxidant.

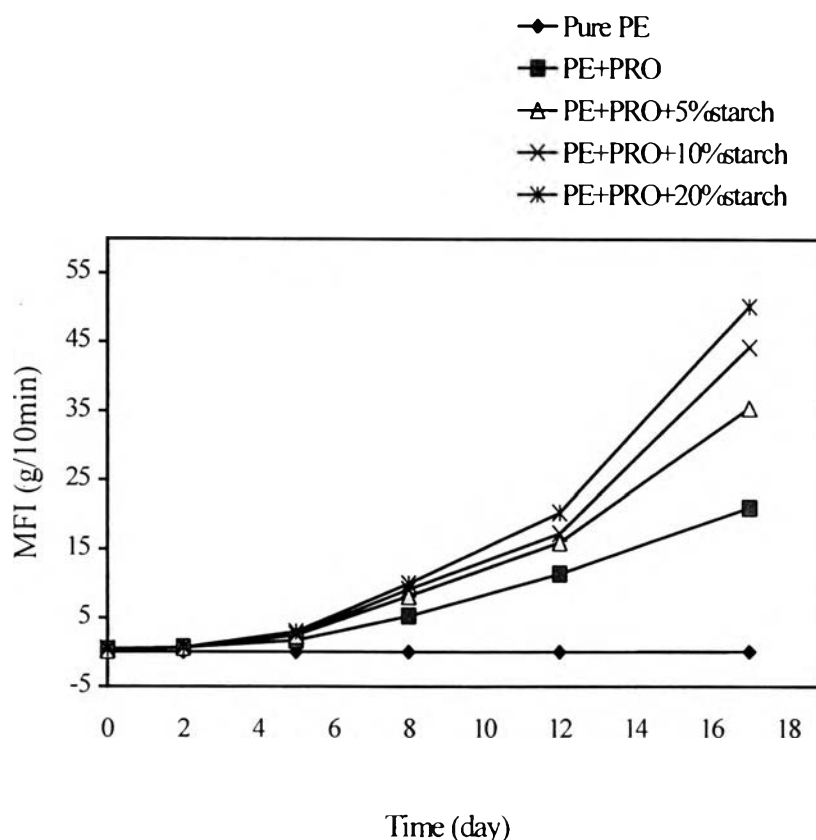


Figure 4.6 Melt flow index of PE containing zinc stearate and starch during incubation at 75°C.

Starch in plasticized form produces more homogeneous blends with PE. It is possible that leftovers in starch may effect on the thermooxidation reaction. But in granular starch, it is in PE matrix by having gap between its particle and matrix, as shown in Figure 4.4. Thus, the effect of leftovers is negligible.

The results obtained from carbonyl index measurements are in accordance with the results obtained from melt flow index (MFI) measurements. Figure 4.6 shows the changes in MFI during incubation at 75°C. The MFI of the blends containing zinc stearate increased gradually after

incubation for 5 days. This indicated that the degradation occurring during incubation led to chain scission which resulted in an increase in both carbonyl index and MFI.

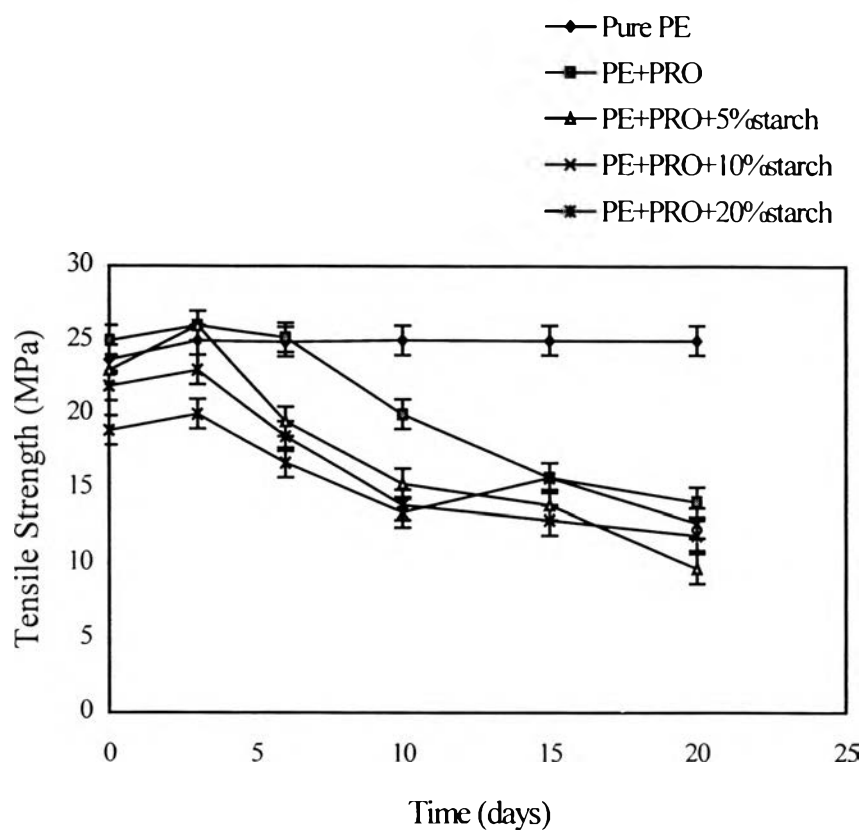


Figure 4.7 Tensile strength of PE containing zinc stearate and starch during incubation at 75°C.

For blends containing both prooxidant and starch, the MFI increased with increasing incubation time. An increase in starch content led to an increase in holes in PE matrix, as shown in Figure 4.5. This is an increase the surface area accessible to heat and oxygen to penetrate into the inner parts, resulting in a decrease in molecular weight and an increase in MFI.

It is known that mechanical properties depend on the molecular weight and molecular weight distribution of polymer. Figure 4.7 shows the tensile strength of the blends as a function of time. Pure PE shows negligible changes in tensile strength during incubation at 75°C for 20 days. But for the blends containing prooxidant, the tensile strength decreased after 3 day of incubation and decreased with increasing starch content.

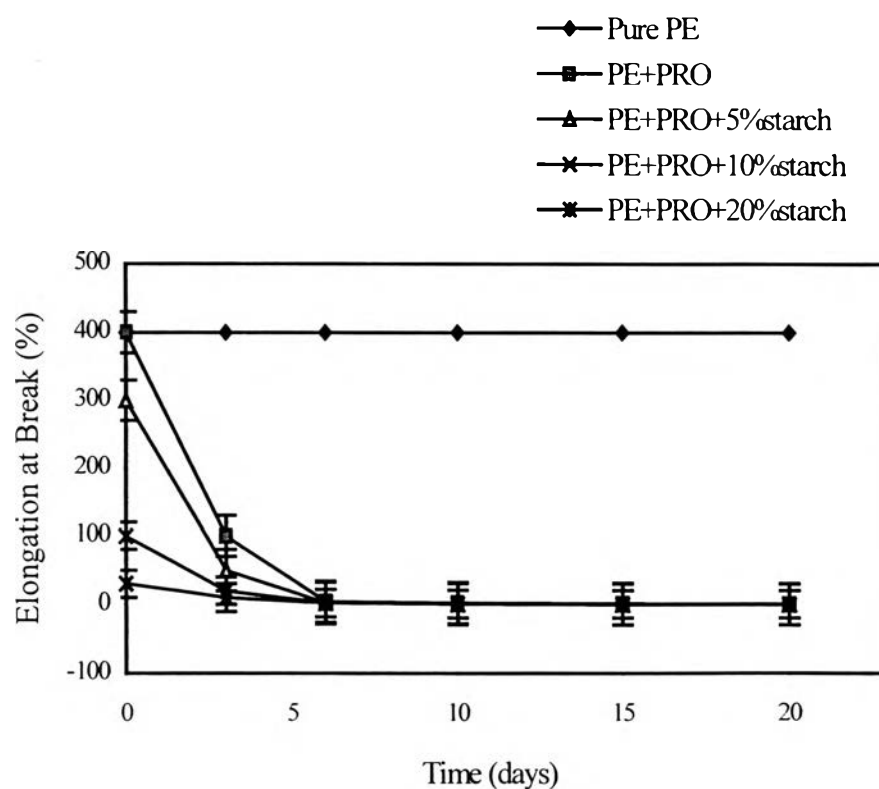


Figure 4.8 Elongation at break of PE containing zinc stearate and starch during incubation at 75°C.

The elongation at break of the blends as a function of time is shown in Figure 4.8. There are no changes in elongation at break of pure PE during incubation whereas the elongation at break of the blends containing prooxidant rapidly dropped to 10% after 6 days of incubation and dropped with increasing starch content.

The reduction in both the tensile strength and elongation at break with increasing incubation time and starch content is due to chain scission reactions occurring during incubation. After incubation, the characteristics of the blends changed from tough materials to be brittle materials. It is concluded that zinc stearate used as a prooxidant and starch used as biodegradable filler can promote thermooxidation of PE matrix.

4.1.2 Effect of Autooxidant and the Combination of Prooxidant and Autooxidant

An autooxidant is defined to an unstable substance which is easily oxidized and generates free radicals during heat treatment. The oxidation of less reactive polymers may be facilitated by the propagation of free radicals to its backbone.

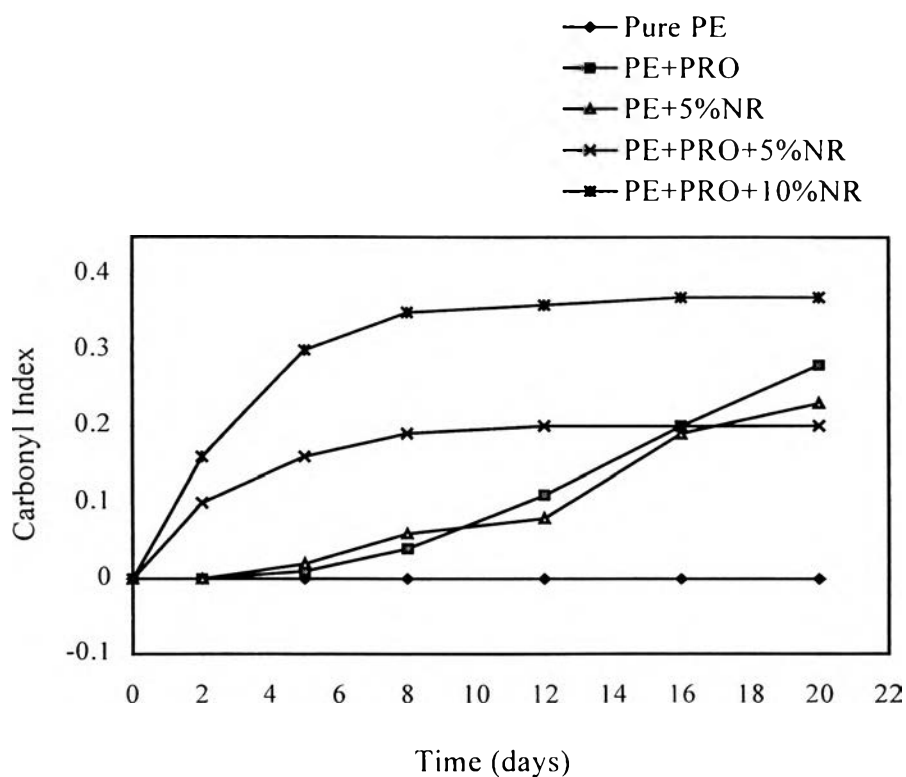
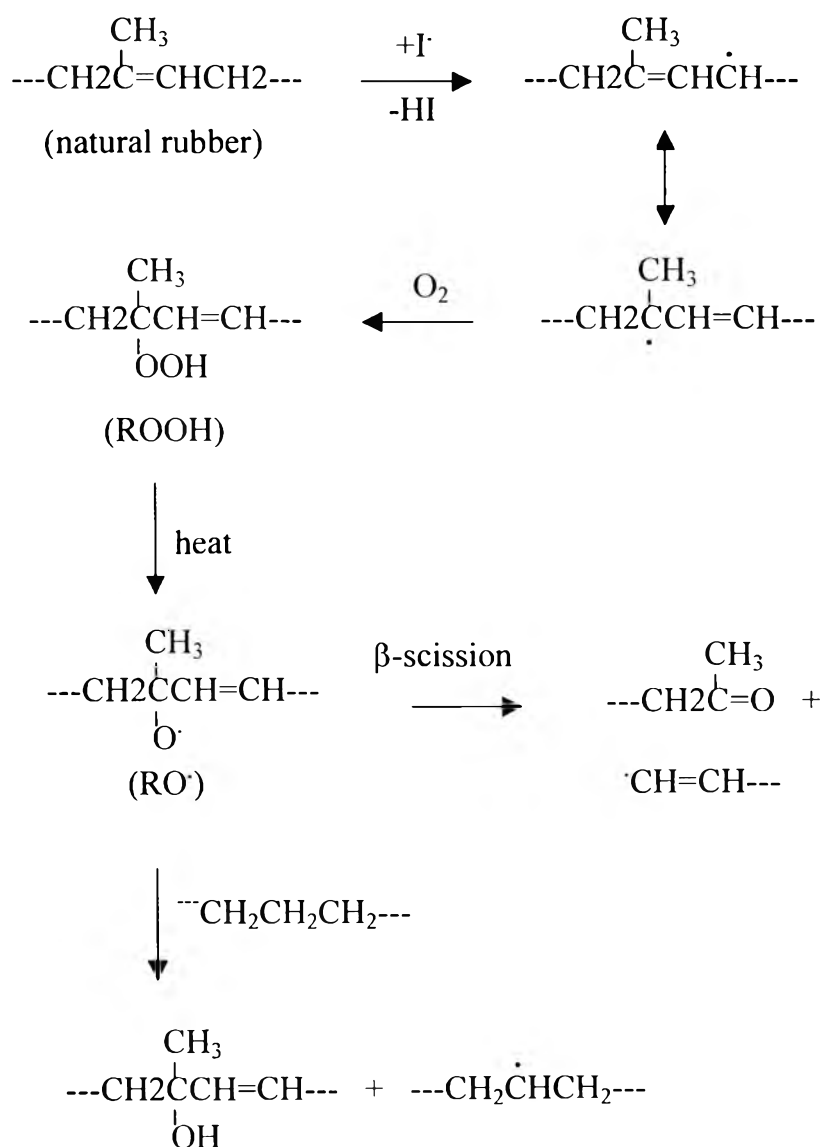


Figure 4.9 Carbonyl index of the blends containing natural rubber during incubation at 75°C.

The effect of natural rubber on the carbonyl index of the blends is presented in Figure 4.9. The carbonyl index of PE containing natural rubber increased with increasing incubation time. It is attributed to the presence of double bonds in natural rubber which are unstable during heat treatment (Bikiaris, 1997).



Scheme 4.3 Thermooxidation mechanism of PE enhanced by autooxidant.

Scheme 4.3 shows thermooxidation mechanism of PE enhanced by natural rubber. Radical formation occurs at unsaturated bonds easier than saturated bonds. The radicals formed in natural rubber react with oxygen to produce hydroperoxides. As a consequence, hydroperoxides decompose to alkoxy radicals that either form carbonyl compounds or initiate the thermooxidation of PE. It should be noted that carbonyl compounds may come from either natural rubber degradation or PE degradation.

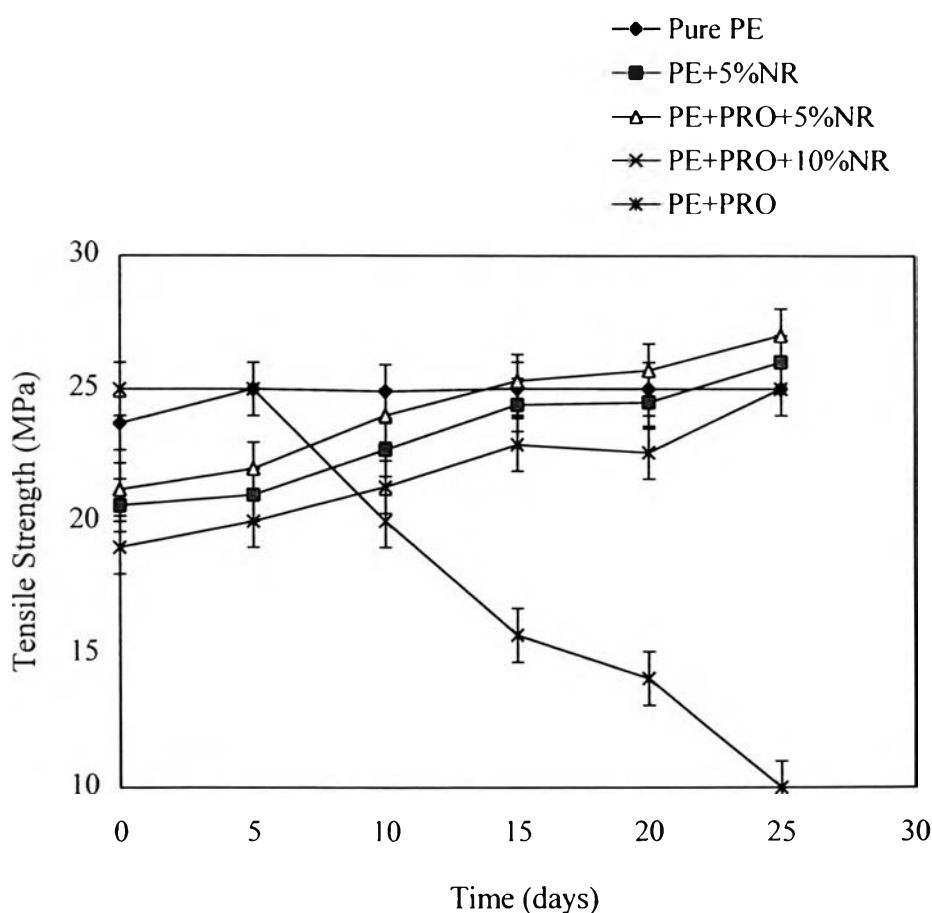


Figure 4.10 Tensile strength of PE containing zinc stearate and natural rubber during incubation at 75°C.

In Figure 4.9, the effect of a combination of prooxidant and autooxidant on carbonyl index of the blends during incubation at 75°C for 20 days is shown. The carbonyl index of the blends containing zinc stearate and natural rubber increased rapidly after incubation. The color of the blends changed from light yellow to yellow from the first few days and became darker as the incubation time increased.

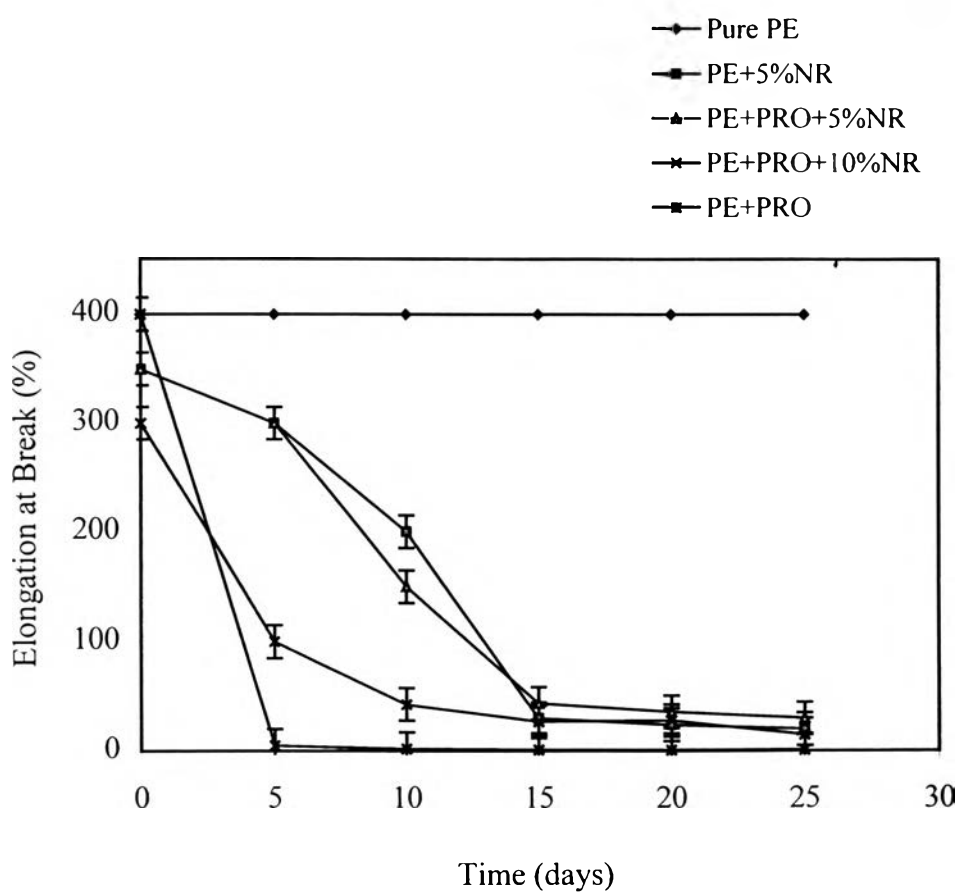
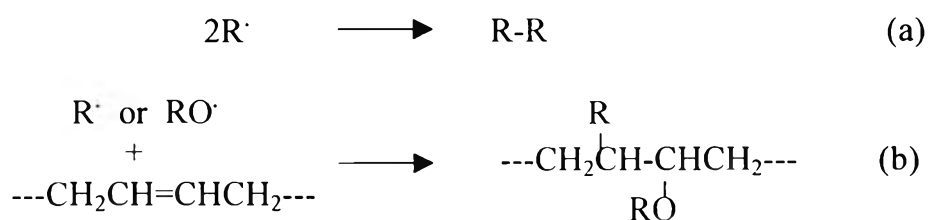


Figure 4.11 Elongation at break of PE containing zinc stearate and natural rubber during incubation at 75°C.

This is due to the fact that radicals formed in the unsaturated molecules led to the formation of hydroperoxide. The hydroperoxide was catalyzed by the transition metal to decompose to alkoxy radicals and peroxy radicals at the further stage of degradation. The higher the content of natural rubber content in the blends, the higher carbonyl index obtained. This is due to the increased number of double bonds which are more easily oxidized and generate free radicals. The more radicals in the system leads to an increase in the probability for carbonyl formation.

For the mechanical properties, the changes in tensile strength and elongation at break of the blends containing natural rubber as a function of incubation time are presented in Figure 4.10 and 4.11. The tensile strength of the blends containing natural rubber increased slightly, whereas the elongation at break decreased during incubation at 75°C for 25 days. This may be due to crosslinking between the polymer chains that occurred within the polymer blends.

Reaction a in Scheme 4.4 shows the proposed mechanism to explain this behavior. In thermooxidation mechanism, many radicals were produced. It is possible that two radicals may join together or radicals may react with double bond resulting in chain branching (Locost, 1991). Another possible way is that radicals reacted with double bonds of natural rubber. The addition is favored by the formation of a π -bond in stead of a σ -bond (Hinsken,1991).



Scheme 4.4 Mechanism of chain branching or crosslinking of PE during incubation.

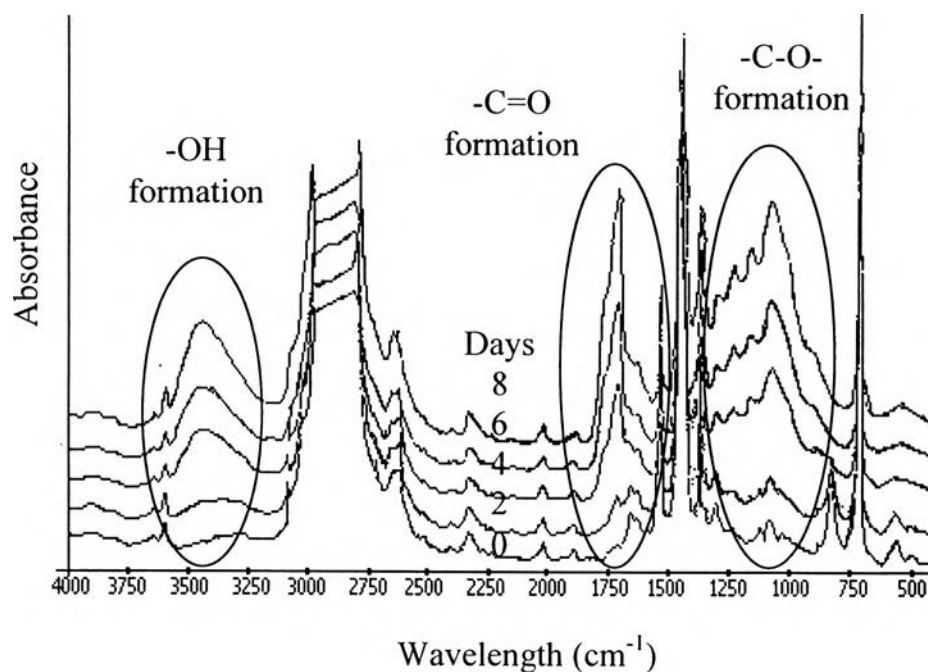


Figure 4.12 FTIR spectra of PE containing zinc stearate and 10 wt% of natural rubber during incubation at 75°C.

Reactions leading to a chain branching or crosslinking. IR spectra of the blends containing natural rubber are shown in Figure 4.12. Not only did the carbonyl peak increased but also the hydroxyl peak and the peak around 1000 to 1200 cm^{-1} which is a C-O stretching peak increased as the incubation time increased. This means that compounds containing carbonyl and hydroxyl were formed during incubation due to the natural rubber degradation and/or PE degradation.

4.1.3 Effect of Compatibilizers

The effect of compatibilizers on the carbonyl index is shown in Figure 4.13. The highest carbonyl index was found in the blends containing EAA as a compatibilizer. This can be explained that EAA can accelerate the thermooxidation reaction because of the ease of abstraction of carboxylic hydrogen radical (-COOH) of acrylic group to form hydroperoxide (Bikiaris,

1997). Bikiaris *et al.* (1997) found that the abstraction rate of carboxylic hydrogen with peroxy radicals (ROO^\cdot) was 5 times higher than the abstraction rate of hydrogen in polyethylene backbone ($\text{--CH}_2\text{--}$). As a result, EAA is a potent oxidation accelerator.

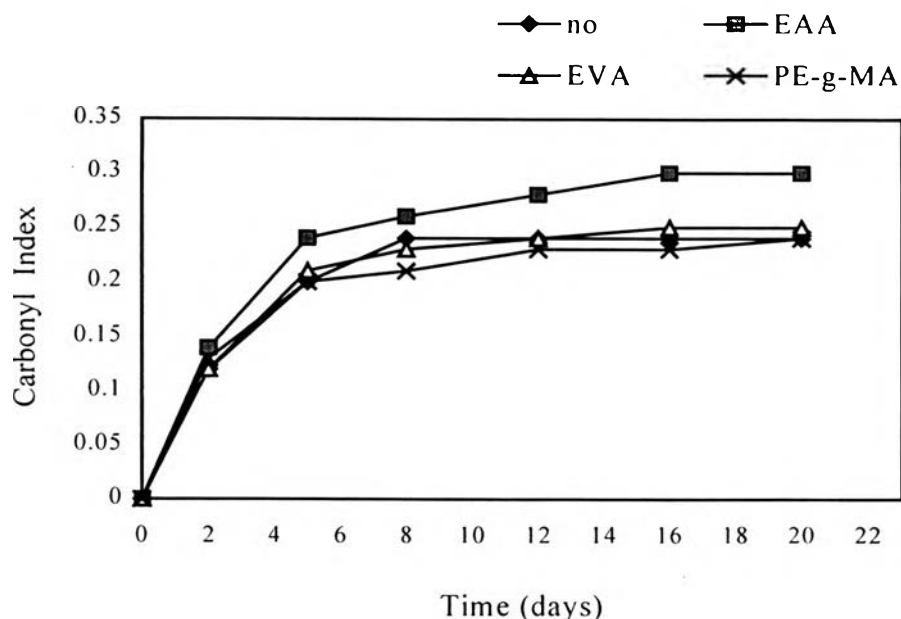


Figure 4.13 Carbonyl index of the PE containing 1wt% of zinc stearate, 5 wt% of natural rubber and 20wt% of starch with various types of compatibilizers during incubation at 75°C.

For the blends containing EVA and PE-g-MA, they did not show a significant increase in the carbonyl index as compared to the uncompatibilized blends. The changes in mechanical properties of the blends, tensile strength and elongation at break, as a function of incubation time are present in Figure 4.14 and 4.15, respectively. The blends containing EAA and PE-g-MA have higher tensile strength than the uncompatibilized blends. This is due to the improved the compatibility between the two phases. The PE-g-MA compatibilized blends had outstanding property in term of elongation at break. It is possible that PE-g-MA may act as a plasticizer in the blends.

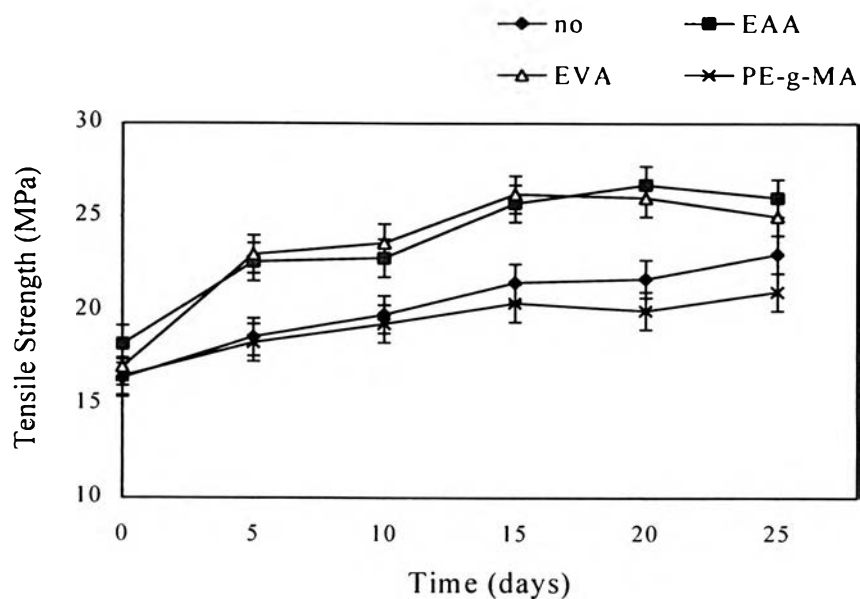


Figure 4.14 Tensile strength of the PE containing 1 wt% of zinc stearate, 5 wt% of natural rubber and 20 wt% of starch with various types of compatibilizers during incubation at 75°C.

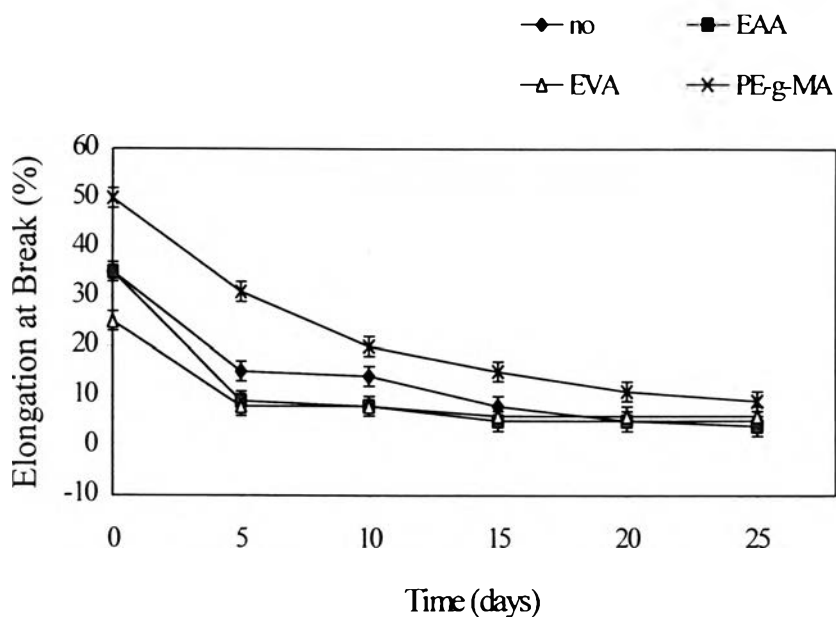
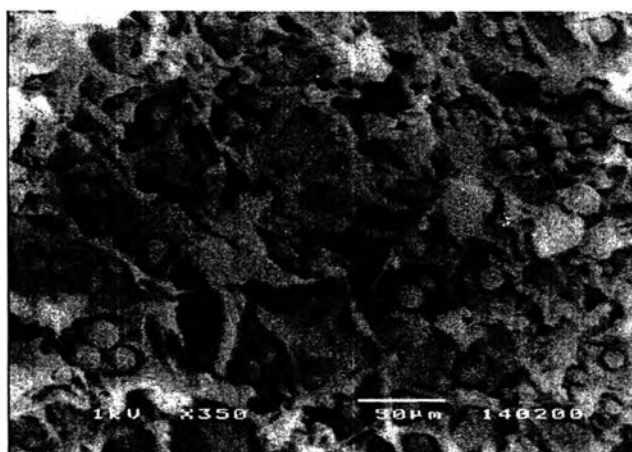


Figure 4.15 Elongation at break of the PE containing 1 wt% of zinc stearate, 5 wt% of natural rubber and 20 wt% of starch with various types of compatibilizers during incubation at 75°C.

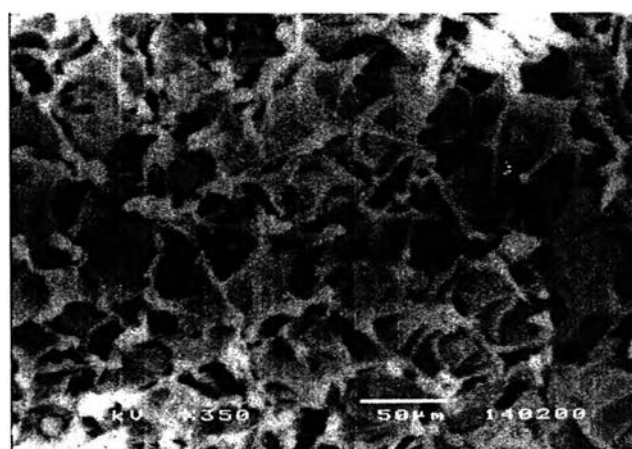
4.2 Enzymatic Degradation

4.2.1 Microstructure

The microstructures of HDPE/starch blends before and after enzyme treatment are shown in Figure 4.16. It can be seen that starch was removed from the PE matrix after enzyme treatment. Starch was hydrolyzed leaving the blends with porous structure.



(a) before enzyme treatment



(b) after enzyme treatment

Figure 4.16 Microstructure of granular starch-filled PE matrix.

4.2.2 Effect of Starch Content

Figure 4.17 shows the percentage of starch hydrolysis as a function of time. It was found that the rate of starch hydrolysis increased with increasing incubation time and became constant after incubation for 6 hours. The percentage of starch hydrolysis also increased as starch content increased. It can be explained by the scheme in Figure 4.4. It is supposed that as the starch content increases, there are more sites on the surface for starch hydrolysis to occur. In addition, with more starch embedded in the PE, there are the more gaps between the starch granules and the PE matrix. This facilitated enzyme to penetration into the inner parts of the specimen resulting in higher starch hydrolysis.

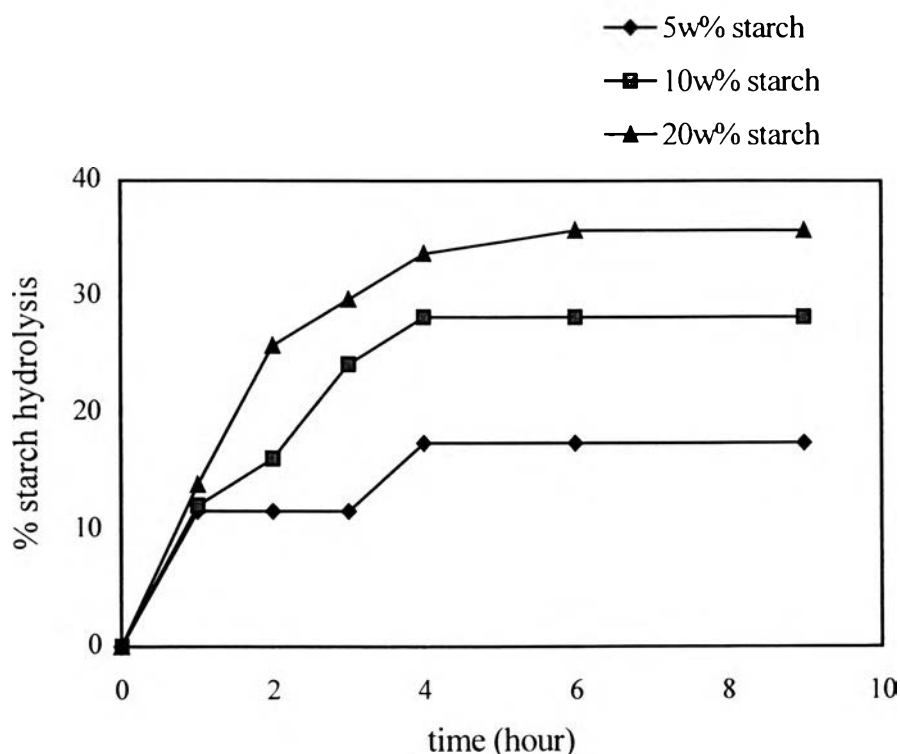


Figure 4.17 Percentage of starch hydrolysis of granular starch-filled PE matrix during enzyme treatment.

4.2.3 Effect of Preheat Treatment

The effect of compatibilizers and preheat treatment at 75°C for 8 days before enzyme treatment for each compatibilizer used is presented in Figure 4.18. Compatibilizers had only a slight effect on the percentage of starch hydrolysis. The extent of starch hydrolysis for the preheated specimen increased significantly with up to 50% comparing with unpreheated blends. This is evidently because the thermooxidation taking place during incubation led to a deterioration of the film samples. The easier access of the enzyme to the starch granules led to higher starch removal.

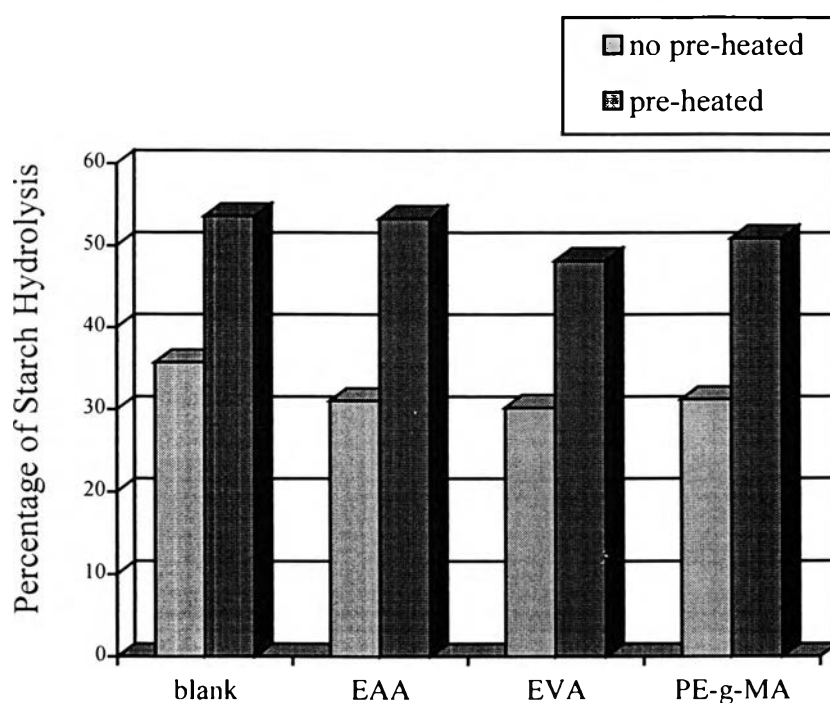


Figure 4.18 Effect of compatibilizer and preheat treatment at 75°C for 8 days on the percentage of starch hydrolysis.