

CHAPTER IV

RESULTS AND DISCUSSION

Photocatalytic degradation of unvulcanized rubber in the presence of titanium dioxide (TiO_2) was studied under ultraviolet light (accelerated condition) and sunlight by following number-average molecular weight using gel permeation chromatography. Degradation of vulcanized rubber containing titanium dioxide under accelerated condition was monitored by determination of mechanical properties. The chemical composition and morphology of the degraded natural rubber are characterized by FT-IR and SEM, respectively.

4.1 Degradation of Rubber Solution in the Presence of TiO_2

Oxidative degradation of natural rubber in the presence of TiO_2 was studied under accelerated condition after exposure to UV light having wavenumber in the range of 290-315 nm (UVB) to which most polymer are sensitive. The principle crystalline structure of TiO_2 used in this study is anatase. Particle size of TiO_2 determined by Malvern Mastersizer was approximately 4 μm in diameter. The particle size distribution is illustrated in Figure 4.1. Sol fraction of natural rubber dissolved in toluene was exposed to UV light and kept stirring in order to have TiO_2 dispersed evenly throughout the solution.

Figure 4.2 shows number average molecular weight (\bar{M}_n) of natural rubber after exposed to UV light for 5-150 min. Initial molecular weight (\bar{M}_n) of controlled natural rubber was about 160,000 -290,000. Molecular weight of natural rubber containing TiO_2 was decreased approximately 25-50% within 15 min of exposure. The molecular weight of natural rubber in the presence of TiO_2 decreased more rapidly than that of the controlled sample. The molecular weight continued to

decrease as the exposure time was increased. This data suggested that the degradation in solution can be effectively accelerated in the presence of TiO_2 .

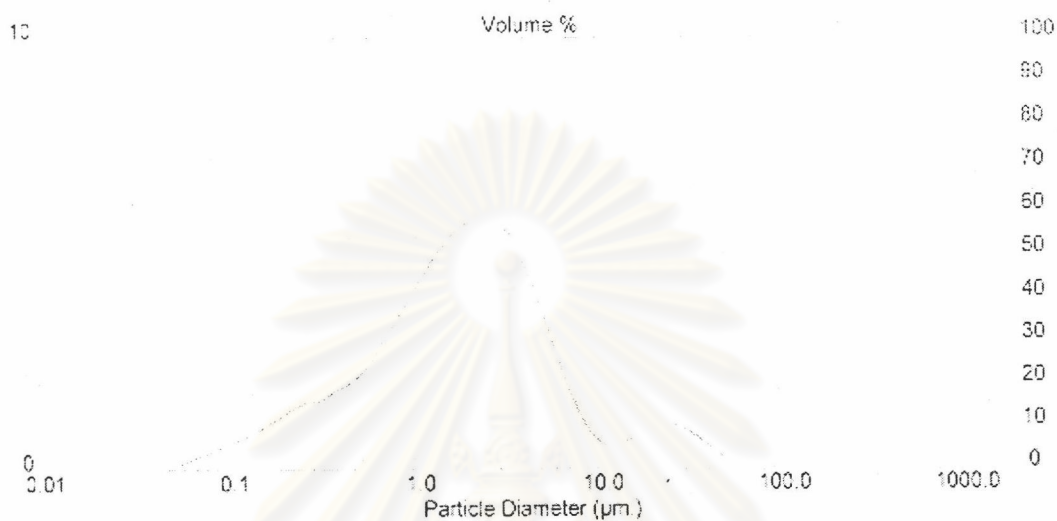


Figure 4.1 Particle size distribution of titanium dioxide (TiO_2)

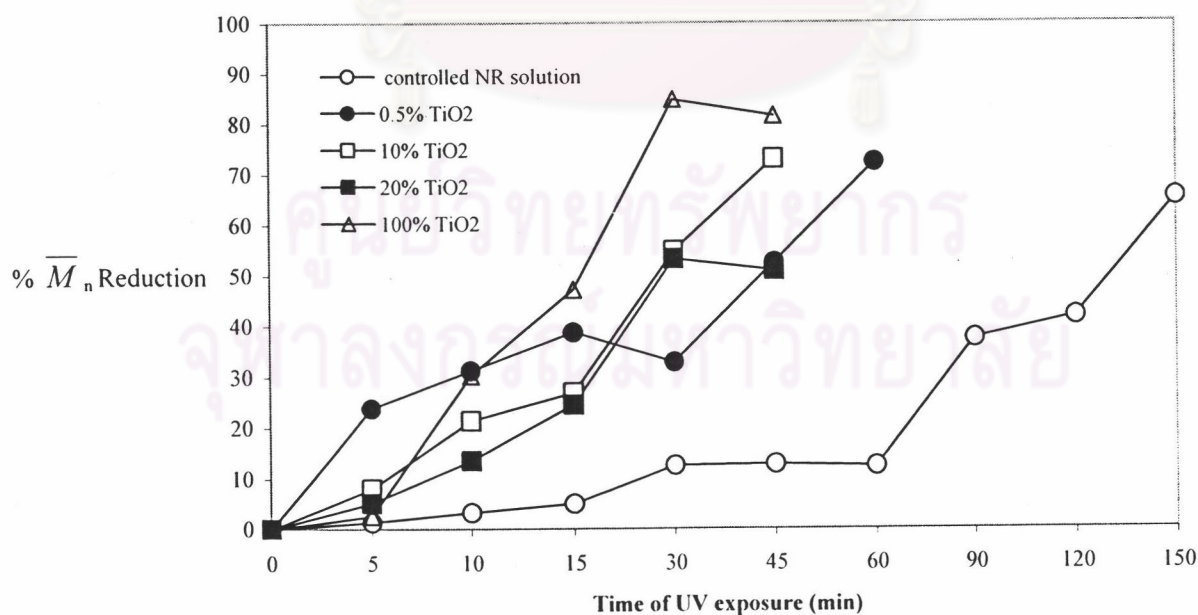


Figure 4.2 % Reduction of number-average molecular weight of natural rubber solution after UV exposure for 5 – 150 min under accelerated condition

The degradation of natural rubber solution as a function of TiO_2 was also determined. Figure 4.2 indicated that the extent of degradation is proportional to the amount of TiO_2 added. After 45 min exposure, molecular weight of natural rubber solution containing 10% w/w TiO_2 was about 73% decayed while that of rubber solution containing 0.5 % w/w TiO_2 was only 53% reduced. The rate of degradation also depends upon the exposure time. The rubber solution containing 0.5 % w/w TiO_2 showed higher rate of molecular weight reduction than that of the rubber solutions containing 10, 20 and 100% w/w TiO_2 within the first 10 min exposure. This is probably implied that TiO_2 was not distributed evenly during the first 10 minutes. TiO_2 powder may be agglomerated and resulted in increased size of TiO_2 particles. These agglomerates may diffuse UV light and protect natural rubber from degradation. After 10 min, the particle size of TiO_2 agglomerates should be reduced due to a better distribution throughout natural rubber solution. Thus, higher % TiO_2 tended to give a greater extent of degradation when exposure time was increased.

IR spectrum of controlled natural rubber in Figure 4.3 (a) showed a peak at 1660 cm^{-1} as an indication of C=C stretching. IR spectra of natural rubber and natural rubber containing TiO_2 powder after exposure to UV light for 30 min are shown in Figures 4.3 (b) and (c), respectively. Both IR spectra showed peaks at 1760 cm^{-1} indicating the existence of carbonyl group which should be a composition of products from oxidative degradation. This data suggested that natural rubber even without TiO_2 showed some extent of degradation.

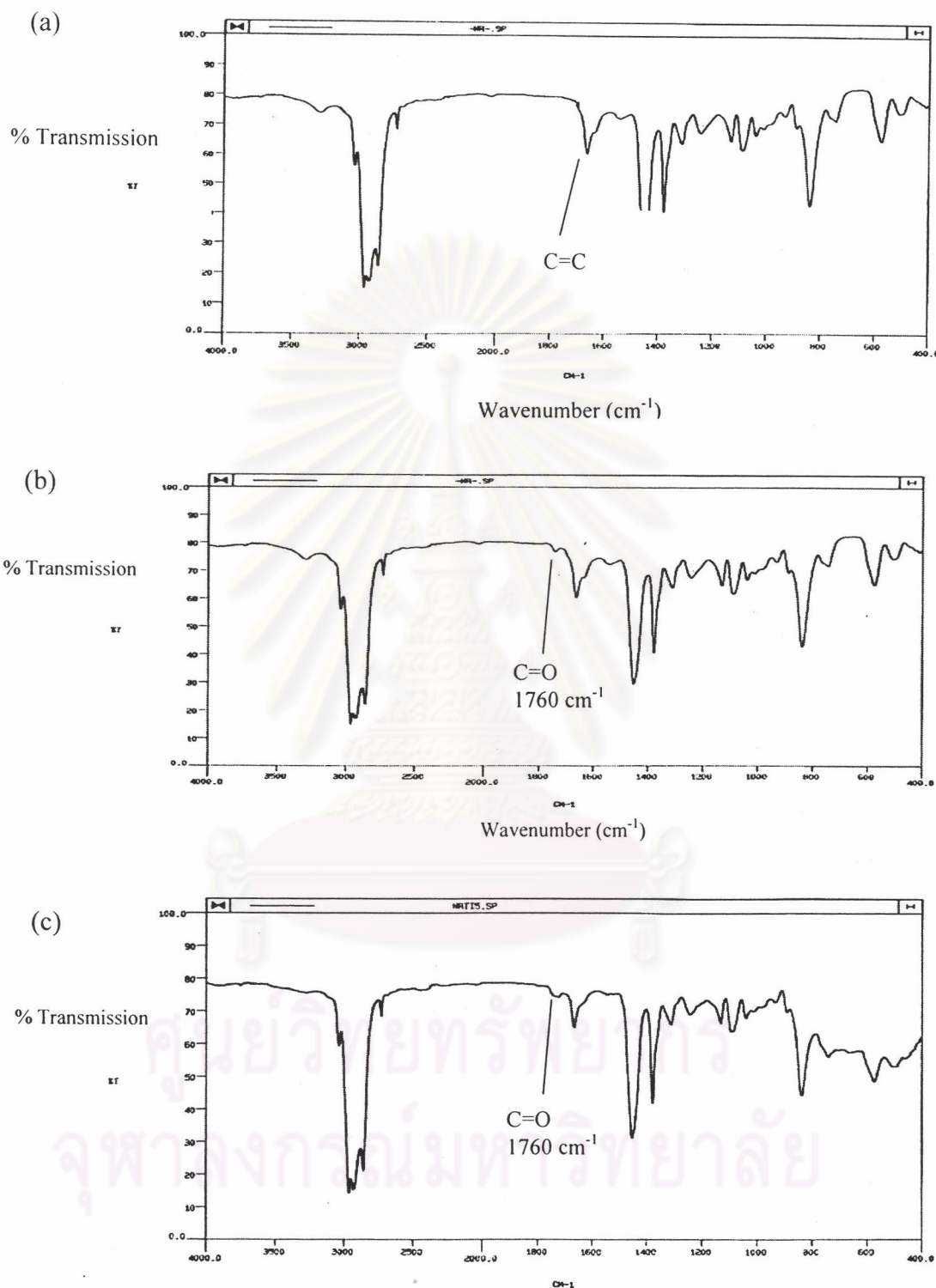


Figure 4.3 FT-IR spectra of (a) controlled natural rubber solution before UV exposure, (b) controlled natural rubber solution without TiO_2 and (c) natural rubber solution with TiO_2 after UV exposure for 30 min under accelerated condition

4.2 Oxidative Degradation of Natural Rubber Sheets containing TiO₂

The effect of TiO₂ on oxidative degradation of natural rubber in solid phase was also investigated. As shown in Figure 4.4, the molecular weight of natural rubber sheet containing 0.5 % w/w TiO₂ was approximately 39% decreased within 4 h of UV exposure whereas that of controlled natural rubber sheet was only 31% reduced. The molecular weight continued to decrease when time of UV exposure was increased. Interestingly, no solid rubber was precipitated out from solution after 12 h of UV exposure implying that the degradation was so extensive that the molecular weight of natural rubber was too low to be precipitated.

The degradation of natural rubber sheets containing TiO₂ was less extensive than the controlled natural rubber when the amount of TiO₂ added was more than 0.5 % w/w. More importantly, the rate of degradation was declined when the amount of TiO₂ was increased. After 8 h of UV exposure, molecular weight of natural rubber sheet containing 10% w/w TiO₂ was only 3% decreased, while those of natural rubber sheets containing 1% and 5 %w/w TiO₂ were 28% and 27 % decreased respectively.

This data clearly indicated that TiO₂ behaves as a stabilizer rather than a photocatalyst when certain amount of TiO₂ was incorporated (> 0.5 %w/w). Sensitizing effect of TiO₂ was suppressed due to two reasons. Firstly, agglomeration of TiO₂ in solid phase reduced interfacial area between TiO₂ and rubber matrix. Photooxidants generated on TiO₂ surface which include oxygen anion and hydroxyl radical cannot sufficiently desorb from TiO₂ surface to rubber matrix. Consequently, a photocatalytic process was inhibited. Secondly, the higher amount of TiO₂, the better it can scatter out the incident light. As a result, TiO₂ somewhat protected the rubber sheet from degradation by UV irradiation.

Stabilizing efficiency of TiO₂ was directly proportional to the amount of TiO₂. After 12 h of UV exposure, molecular weight of natural rubber with 10% w/w TiO₂ was only 22% decreased, whereas that of natural rubber sheet comprising 1 %

w/w TiO_2 was 45% reduced. According to Figure 4.5, a similar trend was observed when natural rubber sheets were exposed to sunlight for 20 h.

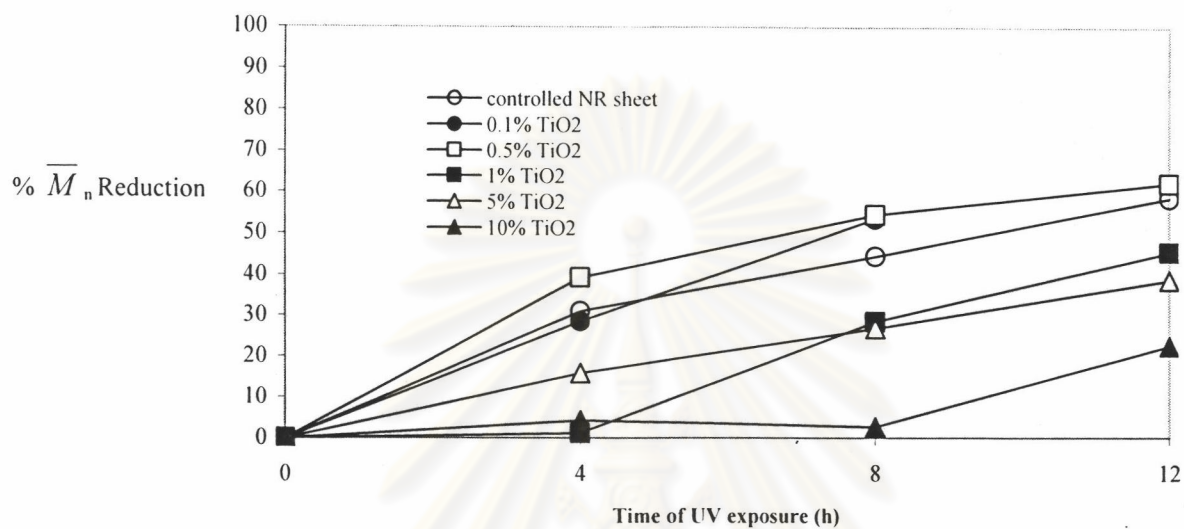


Figure 4.4 % Reduction of number-average molecular weight of natural rubber sheet as a function of time after UV exposure under accelerated condition

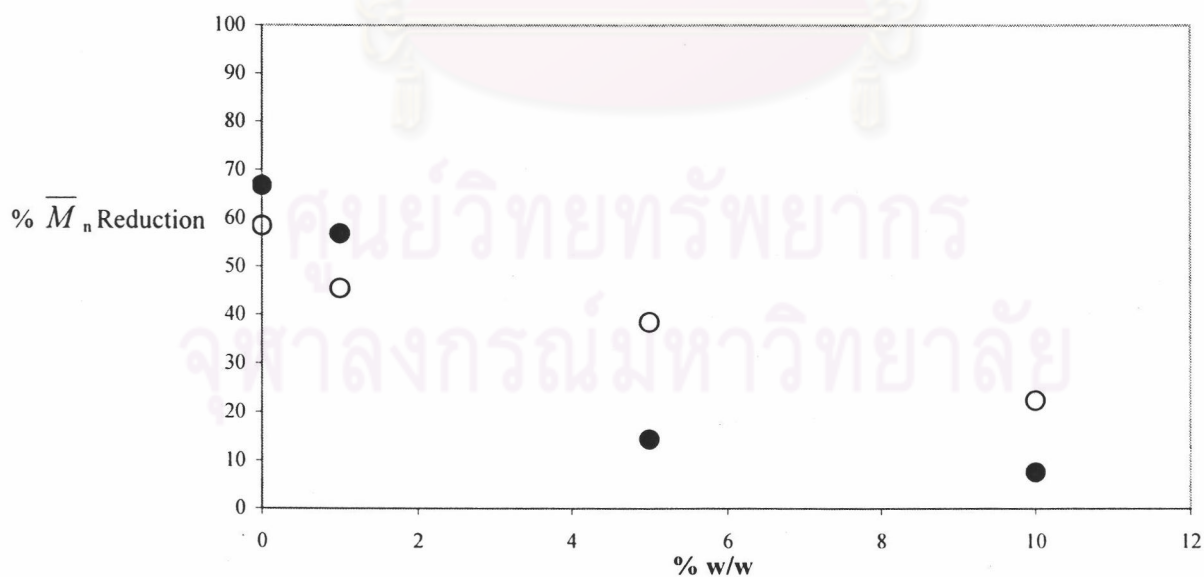
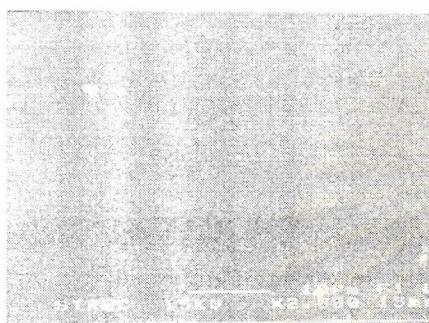


Figure 4.5 % Reduction of number-average molecular weight of natural rubber sheet as a function of TiO_2 after 12 h of UV exposure (○), 20 h of sunlight exposure (●)

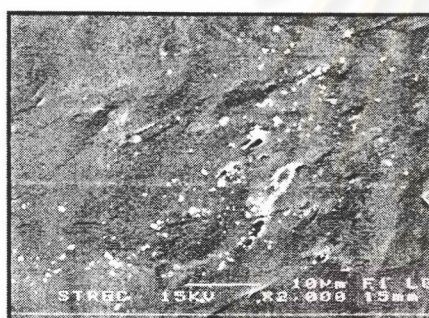
SEM micrographs in Figure 4.6 showed that the aggregated size of TiO_2 embedded in natural rubber sheet was about 1-2 μm in diameter which is large enough to reflect UV light having the wavelength in the range of 290-315 nm (0.29-0.32 μm).



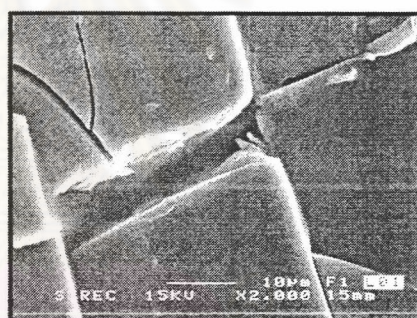
Controlled unvulcanized natural rubber sheet



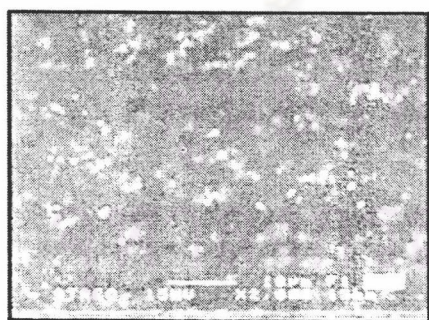
Unvulcanized natural rubber sheet after UV exposure for 8 h.



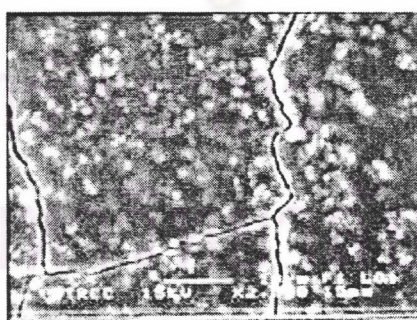
Controlled unvulcanized natural rubber sheet with 0.5% w/w TiO_2



Unvulcanized natural rubber sheet with 0.5% w/w TiO_2 after UV exposure for 8 h.



Controlled unvulcanized natural rubber sheet with 20% w/w TiO_2



Unvulcanized natural rubber sheet with 20% w/w TiO_2 after UV exposure for 8 h.

Figure 4.6 SEM micrographs of unvulcanized natural rubber sheets with and without TiO_2 before and after UV exposure under accelerated condition

Stabilizing effect of TiO_2 can also be demonstrated by surface appearance of natural rubber sheets as shown in SEM micrographs (Figure 4.6). If the surface crack is regarded as a sign of degradation, the extent of degradation of natural rubber sheets containing 20% w/w TiO_2 is apparently less than those containing 0.5 % w/w TiO_2 and the controlled sheets. Another evidence that can be used to support the assumption that TiO_2 incorporated in natural rubber sheet helps reflecting the light and stabilizes the sheet is the whitening of the unvulcanized natural rubber sheets filled with TiO_2 . Figure 4.7 showed the physical appearance of unvulcanized natural rubber sheet containing different amount of TiO_2 as compared with the controlled rubber sheet. Obviously, the sheets became less transparent as the higher content of TiO_2 was incorporated.

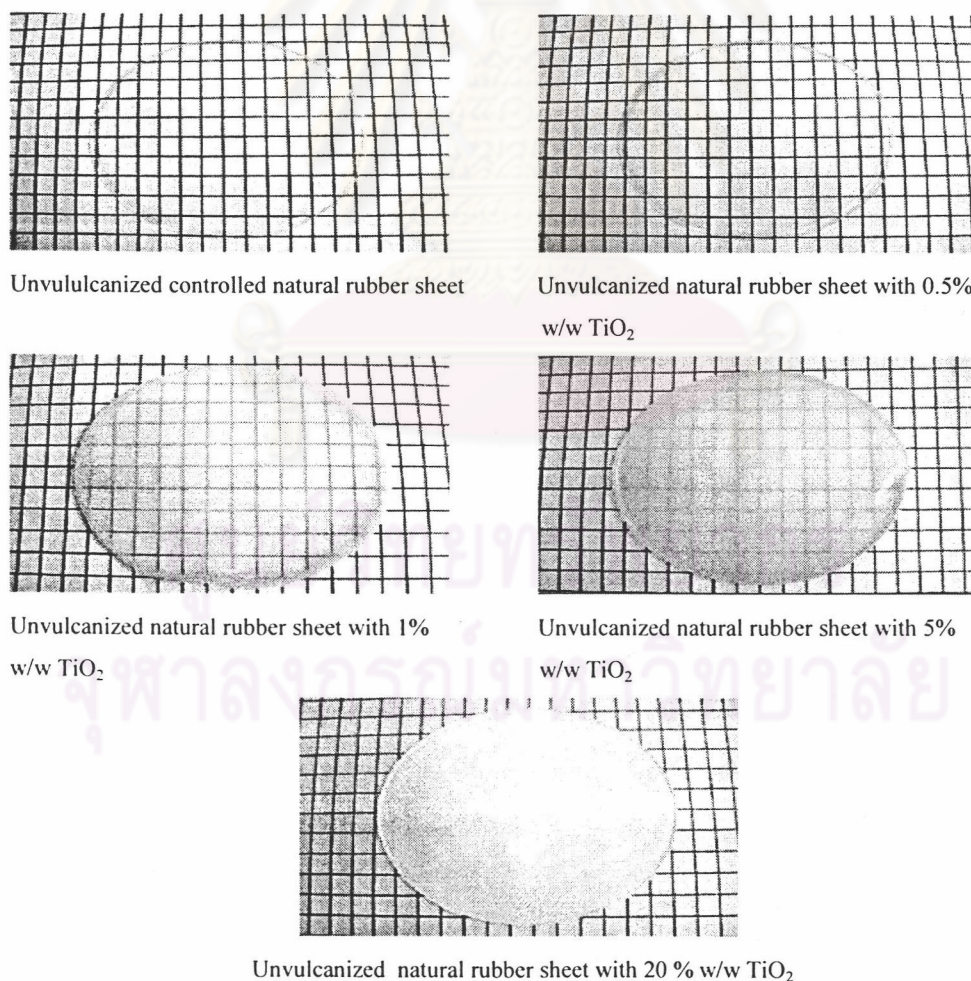


Figure 4.7 Physical appearance of unvulcanized natural rubber sheets with and without TiO_2 before UV exposure

To determine the influence of TiO₂ particle size on an efficiency of photocatalytic degradation, natural rubber sheets with 0.5% and 1% w/w TiO₂ were prepared from two different sizes of TiO₂. The first one purchased from Riedel having a diameter of 1 μm . The other one supplied by Degussa P25 has a diameter of 20 nm. Reduction of the number-averaged molecular weight of natural rubber sheets was shown in Figure 4.8. After 8 h of UV exposure, molecular weight of natural rubber sheet with 0.5% w/w TiO₂ (Degussa-P25) was 33% reduced but that of natural rubber sheet with TiO₂ (Riedel) was 54 % decreased. Difference in catalytic efficiency between two types of TiO₂ was reduced when the amount of TiO₂ was increased to 1% w/w. This data suggested that the catalytic activity of TiO₂ (Degussa P25) whose size supposed to be very small was not better than that of TiO₂ (Riedel).

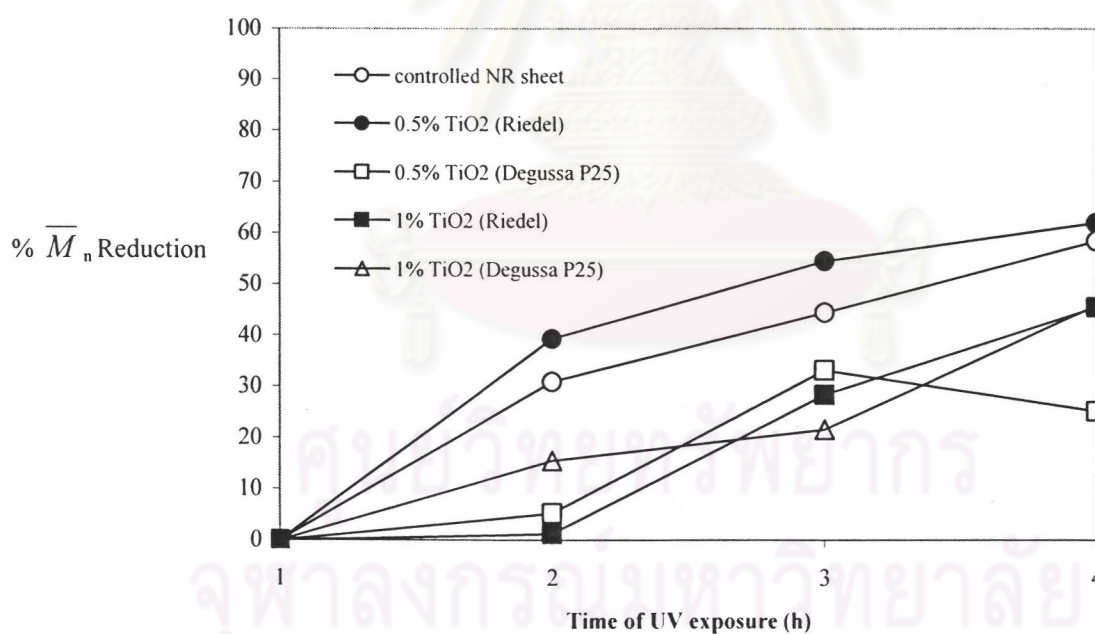


Figure 4.8 % Reduction of number-average molecular weight of natural rubber sheet containing TiO₂ (Riedel) or TiO₂ (Degussa P25) after UV exposure under accelerated condition

As determined by Malvern Mastersizer, it turned out that the aggregated size of TiO_2 - Degussa P25 and TiO_2 - Riedel was about 6 and 4 μm , respectively. Their particle size distributions are shown in Figure 4.9. This implies that the TiO_2 - Degussa P25 was more susceptible to agglomerate in solution than the TiO_2 - Riedel. Perhaps, this is the reason why TiO_2 - Degussa P25 was not so effective in catalyzing photodegradation of natural rubber.

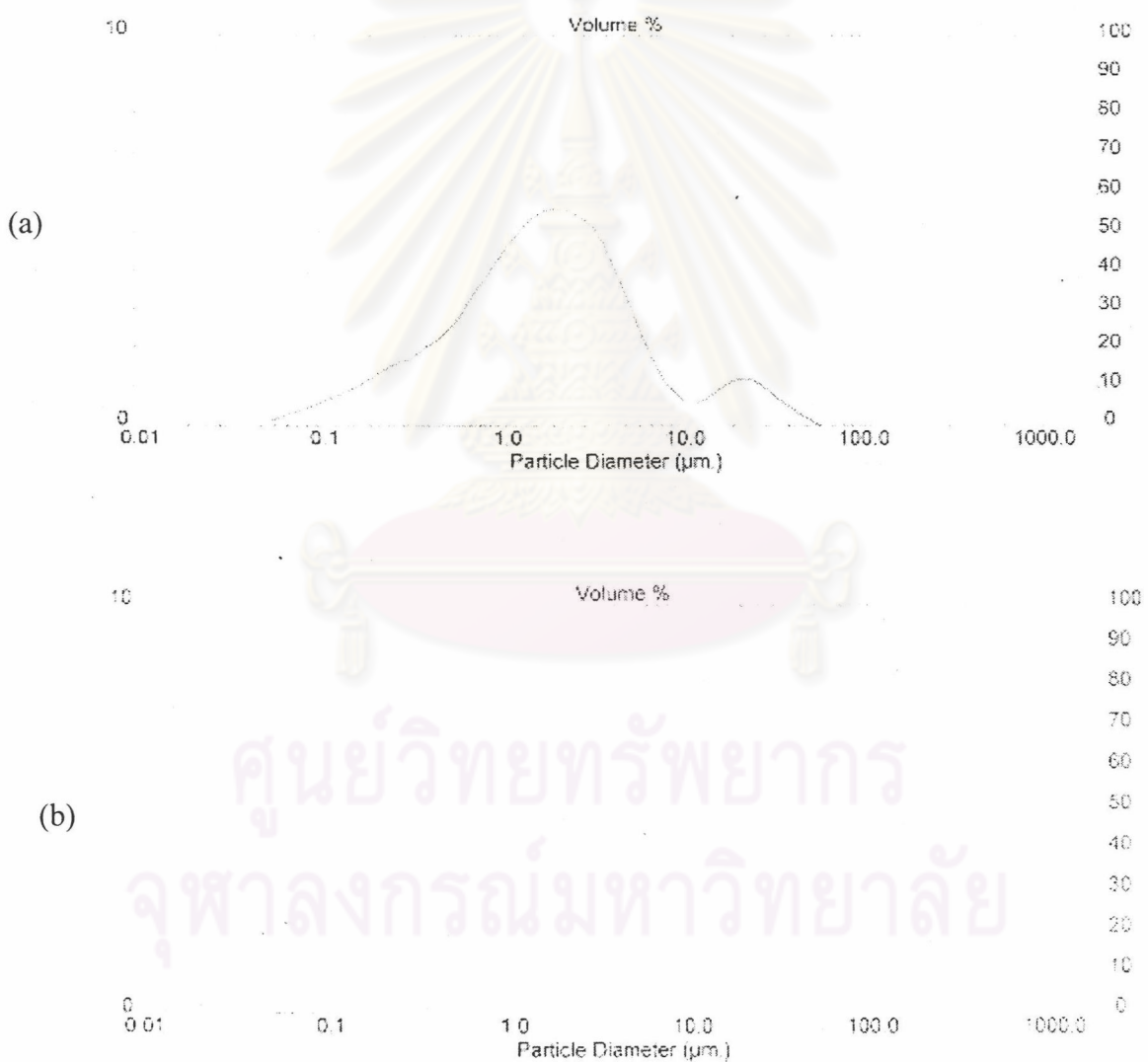


Figure 4.9 Particle size distribution of (a) TiO_2 (Riedel) and (b) TiO_2 (Degussa P25)

The aggregation of both TiO_2 – Riedel and TiO_2 – Degussa P25 in natural rubber matrix was also demonstrated by SEM micrographs. (Figure 4.10)

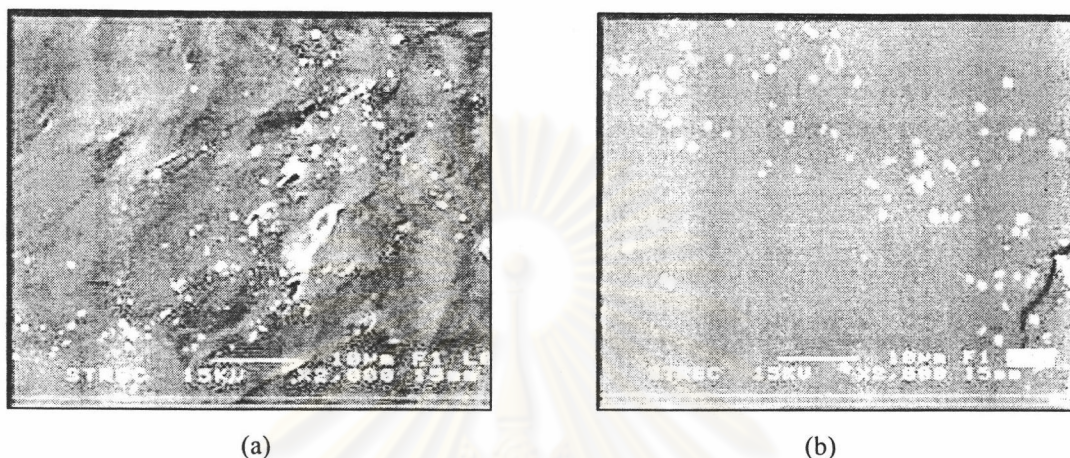


Figure 4.10 SEM micrographs of unvulcanized natural rubber sheets with (a) 0.5% w/w TiO_2 (Riedel) and (b) 0.5% w/w TiO_2 (Degussa P25)

4.3 Oxidative Degradation of Vulcanized Natural Rubber Sheets containing TiO_2

Vulcanized natural rubber sheets containing 0.5-5% w/w TiO_2 were exposed to UV under accelerated condition for 4-24 h. Figure 4.11 and 4.12 illustrate the tensile strength and elongation at break of vulcanized natural rubber sheets after UV exposure, respectively. All samples showed a decrease in tensile strength and elongation at break as the time of UV exposure was longer.

The tensile strength of vulcanized natural rubber sheet without TiO_2 was decreased from 21.2 MPa to 1.5 MPa within 8 h of UV exposure, whilst 12 h of exposure was required to achieve the similar degree of tensile strength reduction for the vulcanized rubber sheet containing 3% w/w TiO_2 . Considering the elongation at break, the reduction from 1025 % to 563 % took place within 8 h of UV exposure for controlled vulcanized rubber sheet. Vulcanized natural rubber sheet containing 3 %w/w TiO_2 showed the similar reduction with longer UV exposure.

The degradation of vulcanized natural rubber sheet as a function of the amount of TiO_2 was also monitored. Figure 4.11 obviously indicated that the higher content of TiO_2 increased the stability of vulcanized natural rubber sheet. UV exposure time of 12 h and 20 h caused the reduction the tensile strength from 21 MPa to about 2 MPa for the vulcanized rubber sheet containing 3.0 % w/w and 5.0 % w/w TiO_2 , respectively. This result agrees very well with what was observed in the case of unvulcanized rubber sheets. However, neither the stabilizing role nor the catalytic role of TiO_2 was clearly seen if only small amount of TiO_2 was incorporated into natural rubber sheet. The tensile strength and elongation at break of vulcanized natural rubber sheets containing 0.5% w/w TiO_2 was insignificantly different from that of the controlled vulcanized natural rubber sheet. The results from mechanical properties clearly indicated that the stabilizing role of TiO_2 outweighed the photocatalytic character of TiO_2 in solid phase degradation of natural rubber.

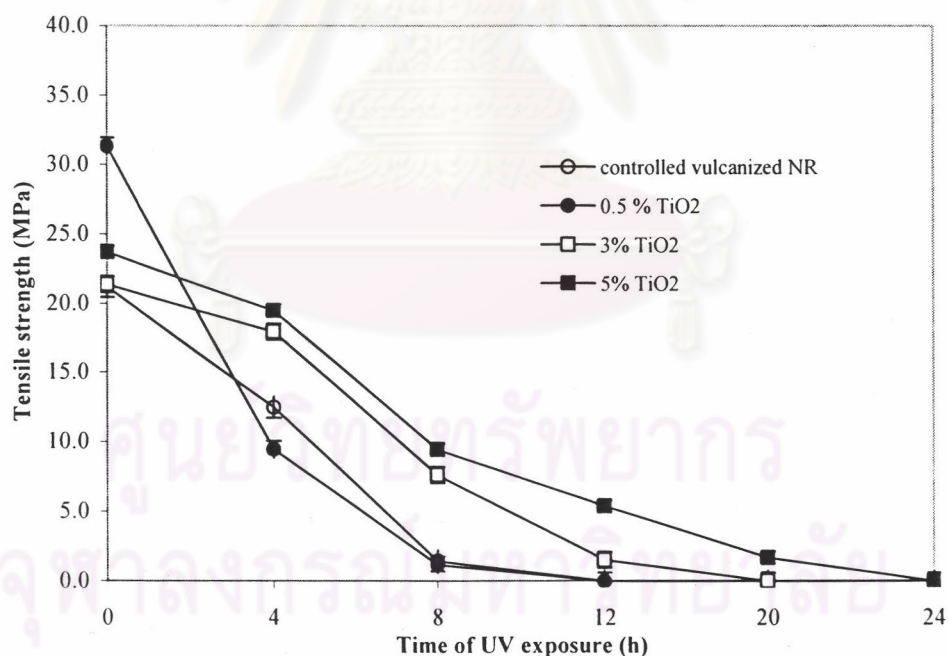


Figure 4.11 Tensile strength of vulcanized natural rubber sheet after exposed to UV under accelerated condition

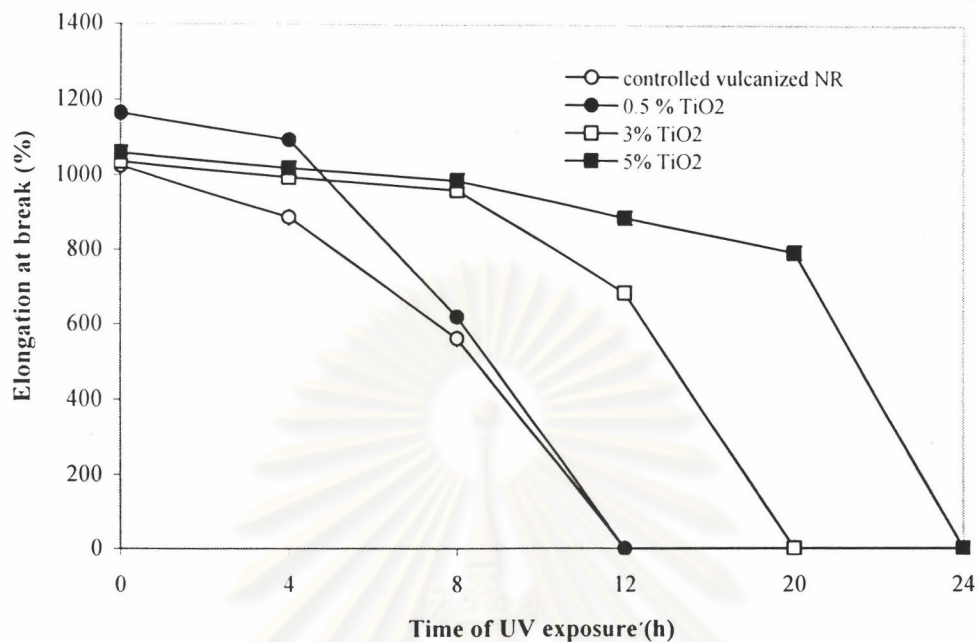


Figure 4.12 Elongation at break of vulcanized natural rubber sheet after exposed to UV under accelerated condition

The vulcanized natural rubber sheets were analyzed by SEM. Figure 4.13 demonstrated the surface morphology of natural rubber sheets containing TiO₂ before and after UV exposure. These micrographs suggested that the controlled vulcanized rubber sheet showed a greater extent of degradation as compared with those containing TiO₂. Some cavities began to appear in the surface of the controlled sheet indicating the deterioration of polymer matrix after UV exposure for 8 h. Unlike the controlled sheet, the holes and pits began to appear on the surface of vulcanized rubber sheet containing TiO₂ after UV exposure for 12 h.



Controlled vulcanized natural rubber sheet

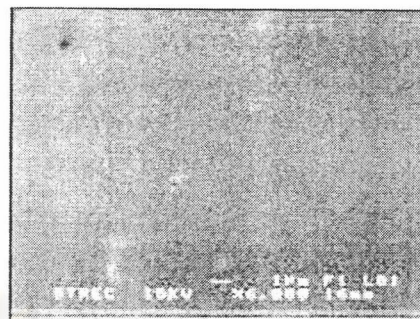
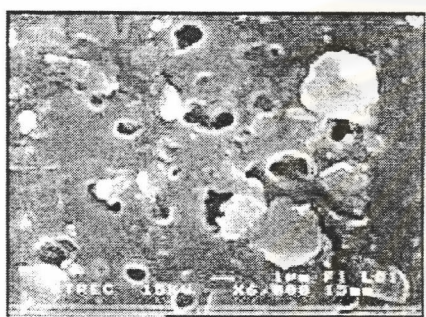
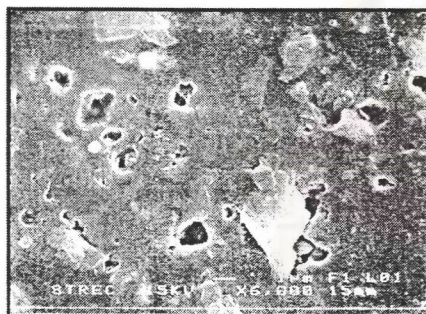
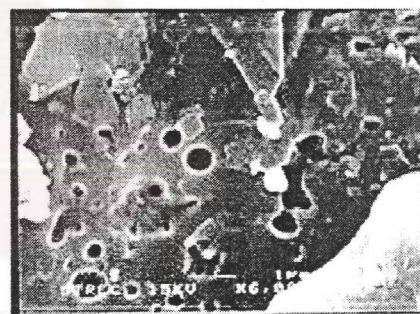
Controlled vulcanized natural rubber sheet
with TiO₂Controlled vulcanized natural rubber sheet,
after UV exposure for 8 hVulcanized natural rubber sheet with 3% w/w
TiO₂ after UV exposure for 8 hControlled vulcanized natural rubber sheet,
after UV exposure for 12 hVulcanized natural rubber sheet with 3% w/w
TiO₂ after UV exposure for 12 h

Figure 4.13 SEM micrographs of vulcanized natural rubber sheets with and without TiO₂ before and after UV exposure under accelerated condition.

Degraded natural rubber sheets were also characterized by ATR-IR. The results are shown in Figure 4.13. As expected, ATR-IR spectra of both vulcanized natural rubber with and without TiO₂ after UV exposure exhibited carbonyl peaks in the region of 1700 –1760 cm⁻¹ and hydroxyl stretching in the region of 3500-3000 cm⁻¹ which are the characteristic peaks of oxidized products.

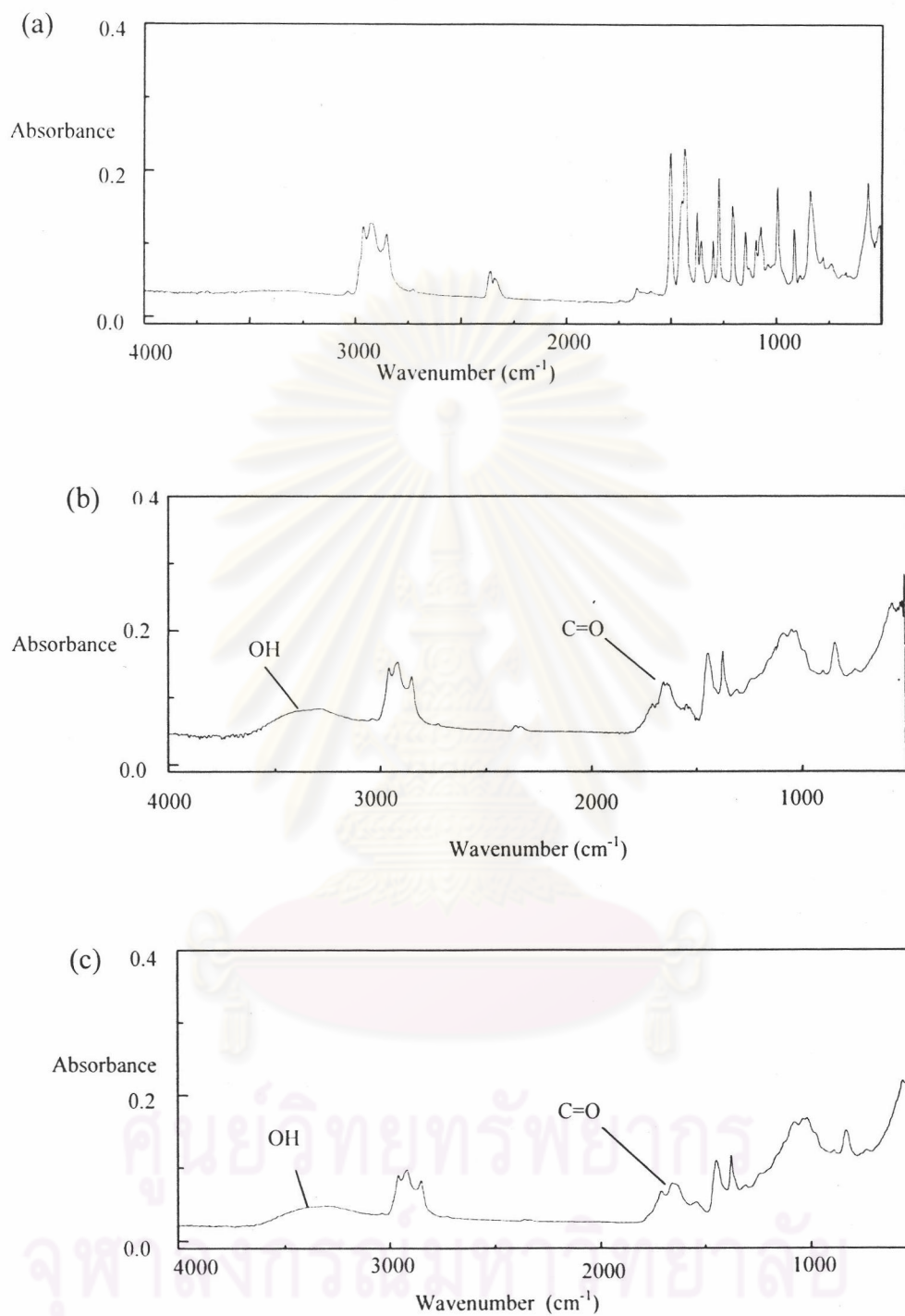


Figure 4.14 ATR-IR spectra of (a) controlled vulcanized natural rubber sheet before UV exposure, (b) controlled vulcanized natural rubber sheet after 8 h UV exposure and (c) vulcanized natural rubber with 0.5 %w/w TiO_2 after 8 h UV exposure