

## CHAPTER IV

### RESULTS AND DISCUSSION

This research aimed to study oxidative degradation of natural rubber in the presence of microparticles containing titanium dioxide under ultraviolet light. Microparticles were prepared from gelatin–gum arabic by phase separation from an aqueous solution system. Microparticles were characterized by scanning electron microscopy (SEM) and electron dispersive X-ray (EDX). Oxidative degradation was studied under ultraviolet light (accelerated condition) and sunlight by following viscosity-average molecular weight using solution viscometry method. Degradation of vulcanized rubber containing titanium dioxide microparticles under sunlight was monitored by determination of mechanical properties.

#### 4.1 Preparation of Microparticles Containing Titanium Dioxide Powder

Microparticles were prepared by microencapsulation utilizing phase separation from an aqueous solution system. In this process, the starting materials for formation of a capsule wall are gelatin and gum arabic, which are water–soluble polymers. When pH is lower than 4.8, gelatin becomes polycationic. Gum arabic contains only carboxylic acids in the molecule, and hence, its aqueous solution is polyanion. There is an interaction between polycationic gelatin and polyanionic gum arabic resulting in the formation of a coacervate. We found that very high stirring speed is necessary to achieve even distribution of titanium dioxide ( $\text{TiO}_2$ ) powder during coacervation process. For this experiment, the speed of 14,000 rpm was chosen. After being recovered by freeze-drying  $\text{TiO}_2$ -containing particles were characterized by SEM-EDX. As can be seen from SEM micrographs (Figure 4.1) particles appeared as agglomerated particles with an average diameter of 30  $\mu\text{m}$ . From micrograph in Figure 4.2 with higher magnification

agglomerated particles consist of smaller particles with an average diameter of 0.3 – 0.5  $\mu\text{m}$ . This data agree with the previous work reported earlier by Palmieri<sup>[23]</sup> and coworkers about the fact that freeze-drying is not an effective drying process. It is then difficult to obtain single microparticles since the process cannot break down the particle cluster. It is uncertain to assume that all particles in the agglomerates (Figure 4.2) containing  $\text{TiO}_2$ . It is also plausible that some particles are uncoagulated excess of colloidal polymers without  $\text{TiO}_2$ . In order to estimate the amount (%w/w) of  $\text{TiO}_2$  in the particles quantitatively, it is necessary to determine ash content of the particles. The result suggested that the particles contain 1.13 %w/w.

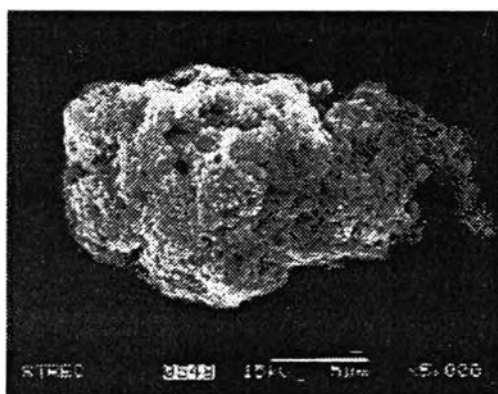


Figure 4.1 SEM micrograph of an agglomerated microparticle containing  $\text{TiO}_2$  obtained after freeze-drying (x 5,000)

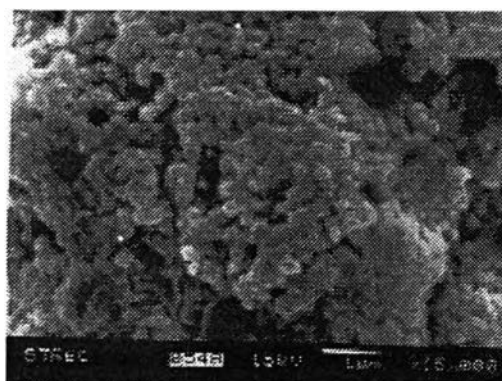


Figure 4.2 SEM micrograph of an agglomerated microparticle containing  $\text{TiO}_2$  obtained after freeze-drying (x 15,000)

The existence of  $\text{TiO}_2$  in the microparticles was also confirmed qualitatively by EDX data as indicated in Figure 4.3. A characteristic peak of titanium appears around 4.25 eV. The atomic composition result indicated that the particles contain 0.1% of titanium.

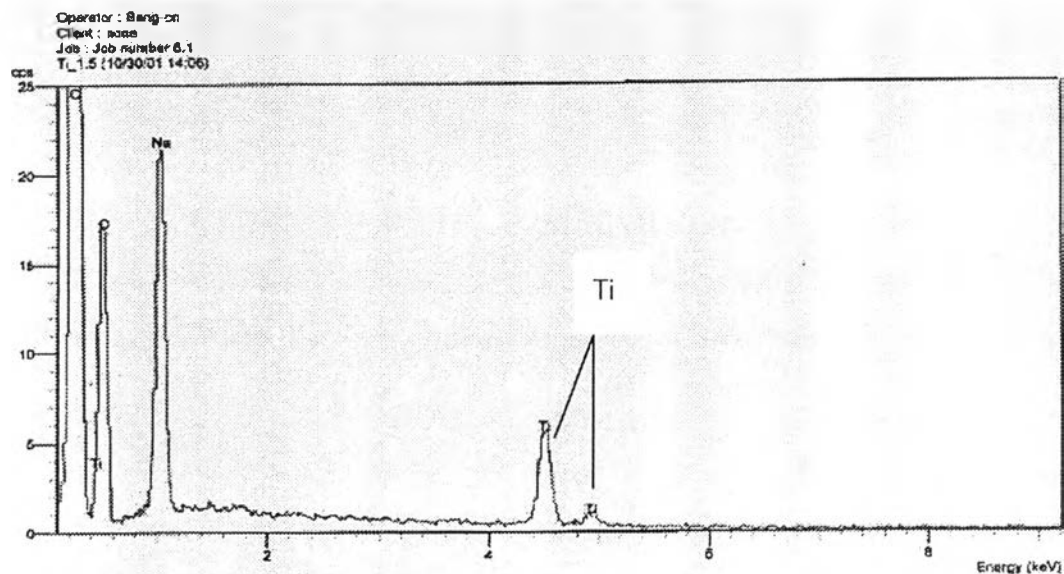


Figure 4.3 EDX of microparticles

#### 4.2 Oxidative Degradation of Natural Rubber

Oxidative degradation studies of natural rubber were divided into 3 parts.

1. The degradation of rubber solution in the presence of  $\text{TiO}_2$  powder was studied after exposed to UV light under accelerated condition by following viscosity – average molecular weight of natural rubber solution.
2. Oxidative degradation of natural rubber sheets containing  $\text{TiO}_2$  powder or  $\text{TiO}_2$  microparticles after exposed to UV light under accelerated condition or to sunlight was studied by following viscosity–average molecular weight of rubber sheets.
3. Oxidative degradation of vulcanized rubber sheets containing  $\text{TiO}_2$  powder or  $\text{TiO}_2$  microparticles after exposed to sunlight was studied by determining tensile properties.

#### 4.2.1 The degradation of rubber solution in the presence of TiO<sub>2</sub> powder after exposed to UV light under accelerated condition

Oxidative degradation of natural rubber in the presence of TiO<sub>2</sub> was studied under accelerated condition after exposed to UV light having wavenumber in the range of UVB (290 – 315 nm) to which most polymers are sensitive. The principal crystalline structure of TiO<sub>2</sub> used in this study was proved to be anatase as confirmed by X-ray diffractogram is shown in Figure 4.4. This form of TiO<sub>2</sub> is the most active form that exhibits oxidative catalytic behavior. Sol fraction of natural rubber dissolved in toluene was exposed to UV light and kept stirring in order to have TiO<sub>2</sub> dispersed evenly throughout the solution. Figure 4.5 showed viscosity - average molecular weight ( $\bar{M}_v$ ) of natural rubber after exposed to UV light for 15 – 120 min.

Initial molecular weight of controlled natural rubber was about 2,000,000. Degradation of natural rubber started within the first 15 min of exposure: molecular weight of controlled rubber decreased 50% to about 1,000,000. As the exposure time was increased, the molecular weight continued to decrease at a slower rate as compared to the first 15 min and the molecular weight seems to level off at approximately 720,000 after 90 min of exposure. The changes in molecular weight promoted during the UV aging can be associated with the breaking process of chain molecules. Molecular weight of natural rubber containing 0.05% w/v TiO<sub>2</sub> powder was about 700,000 (65% decrease) after 15 min exposure. When the exposure time was longer, the molecular weight decreased more rapidly than the controlled sample. The molecular weight continued to decrease as time of exposure and reached about 150,000 after 120 min exposure.

The degradation of natural rubber as a function of the amount of TiO<sub>2</sub> was also determined. Molecular weight of natural rubber exposed to UV light for 60 min is shown in Figure 4.6. The data suggested that the effect of the amount of TiO<sub>2</sub> powder in the solution is quite insignificant. Only slight molecular weight reduction was observed as the amount of TiO<sub>2</sub> was increased from 0.1 to 5%. This first part of degradation studies under accelerated condition suggested that TiO<sub>2</sub> is quite an effective oxidation catalyst for natural rubber degradation.

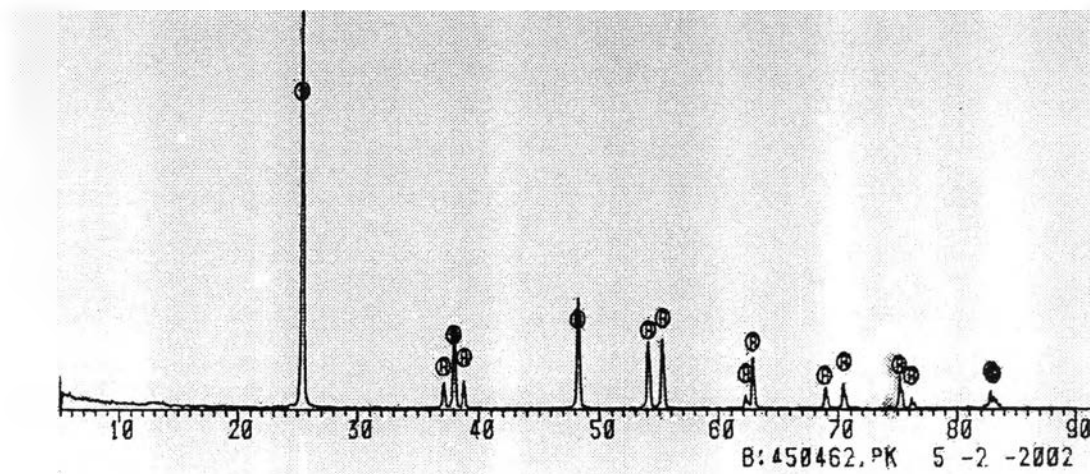


Figure 4.4 X-ray diffractogram of titanium dioxide

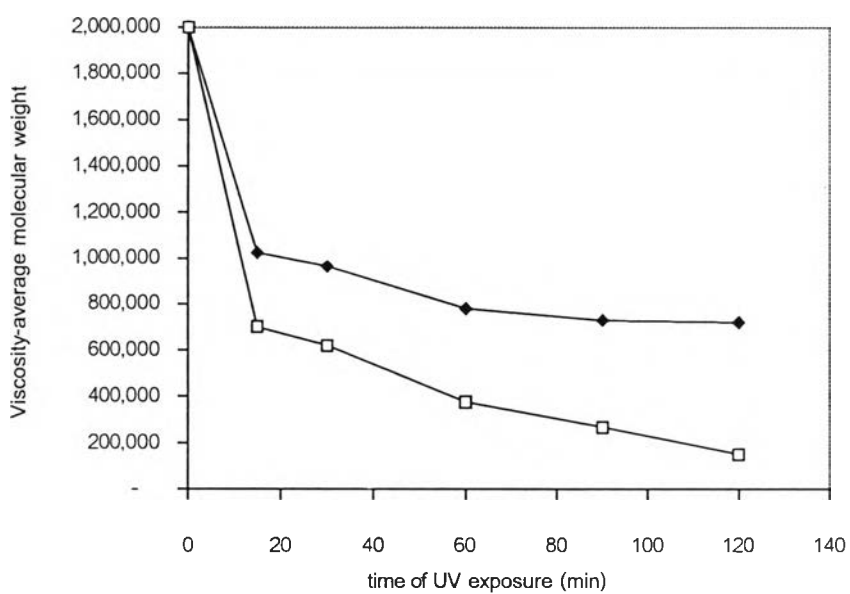


Figure 4.5 Viscosity-average molecular weight of natural rubber after UV exposure for 15 – 120 min under accelerated condition.

(◆ : natural rubber, ○ : natural rubber + TiO<sub>2</sub>)

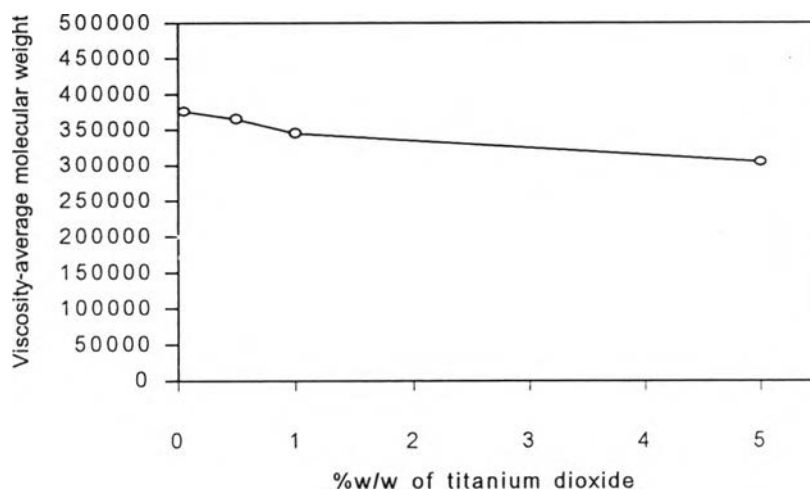


Figure 4.6 Viscosity-average molecular weight of natural rubber containing TiO<sub>2</sub> powder as a function of TiO<sub>2</sub> quantity after UV exposure for 60 min.

IR spectrum of controlled natural rubber is shown in Figure 4.7. The IR spectrum showed peak at  $1660\text{ cm}^{-1}$  as an indication of C=C stretching. IR spectra of natural rubber and natural rubber containing TiO<sub>2</sub> powder after exposed to UV light for 120 min are shown in Figures 4.8 and 4.9. The IR spectra showed peak at  $1760\text{ cm}^{-1}$  as an indication of carbonyl group.

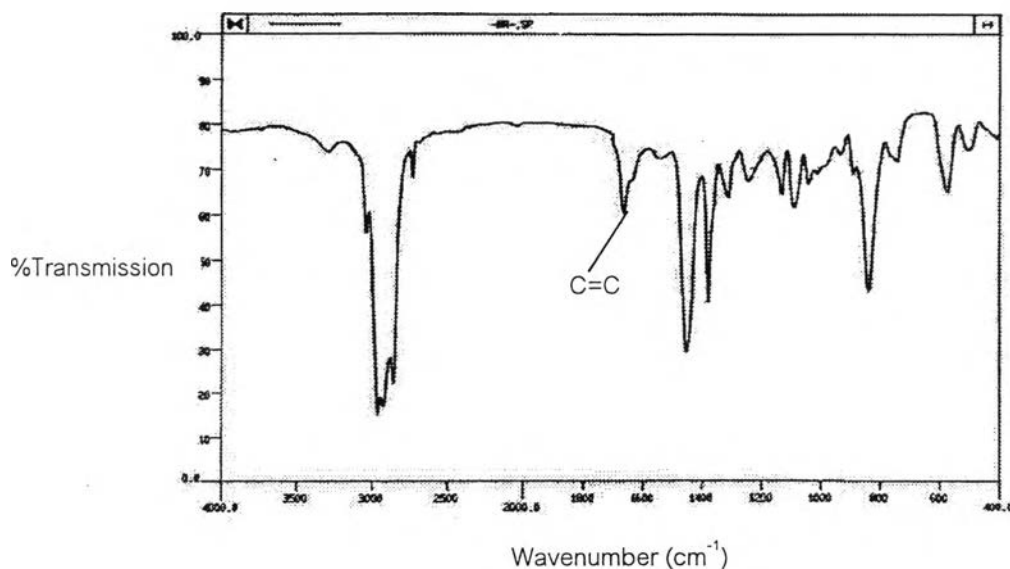


Figure 4.7 FT-IR spectrum of controlled natural rubber solution

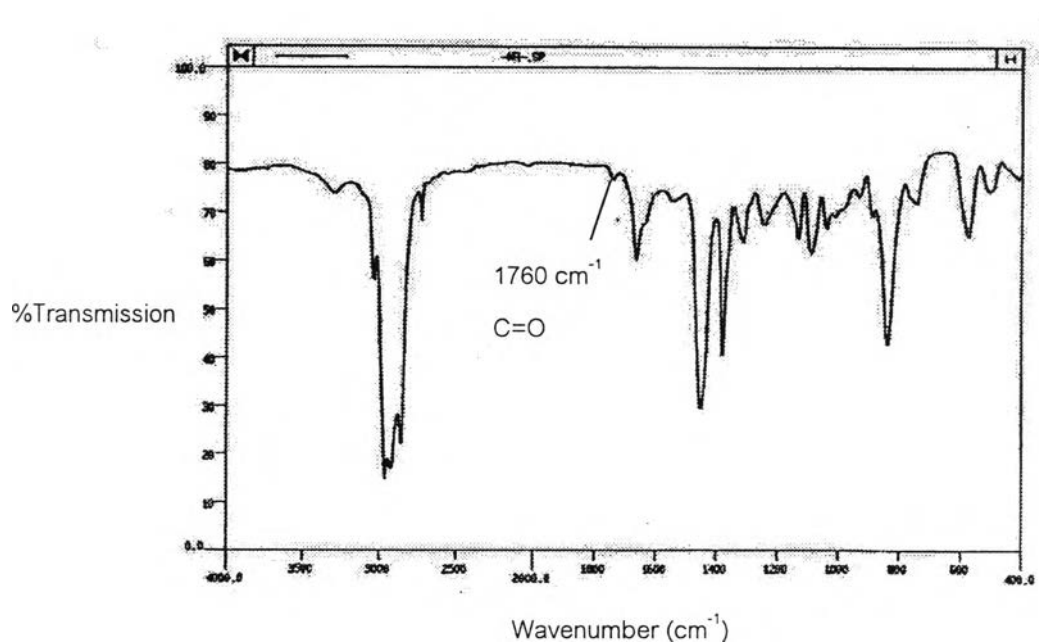


Figure 4.8 FT-IR spectrum of natural rubber solution after UV exposure for 120 min under accelerated condition.

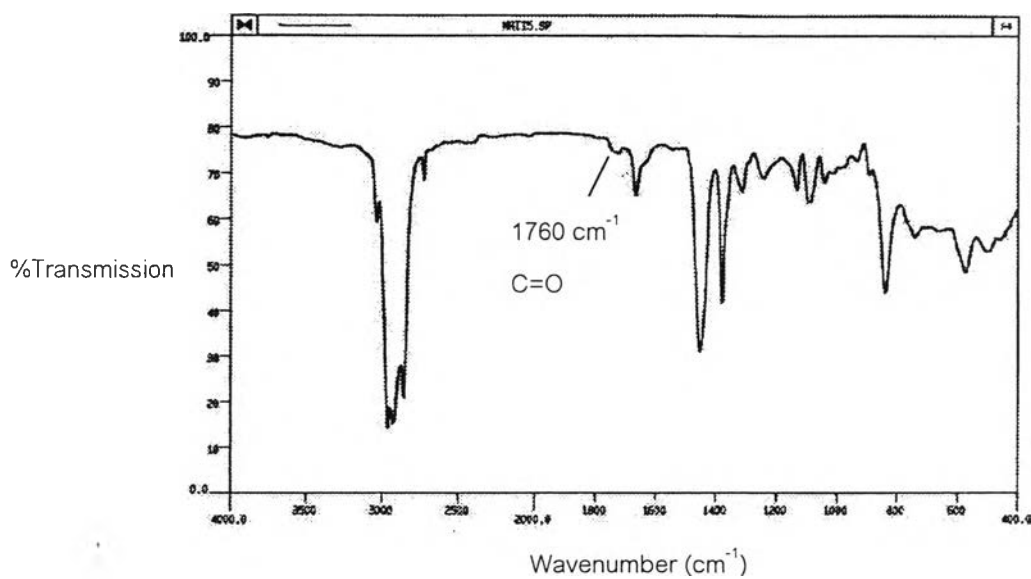


Figure 4.9 FT-IR spectrum of natural rubber solution with TiO<sub>2</sub> powder after UV exposure for 120 min under accelerated condition.

#### 4.2.2 Oxidative degradation of natural rubber sheets containing TiO<sub>2</sub> powder and TiO<sub>2</sub> microparticles

The effect of the amount of TiO<sub>2</sub> powder and TiO<sub>2</sub> microparticles were determined and the results were shown in Figures 4.10 and 4.11, respectively. The data suggested that the degradation of natural rubber sheets were independent of the amount of TiO<sub>2</sub> powder or TiO<sub>2</sub> microparticles. We also suspect that this may be a result of inhomogeneous distribution of TiO<sub>2</sub> powder or TiO<sub>2</sub> microparticles within natural rubber sheet causing ineffective degradation.

For this reason, we desired to compare oxidative degradation of rubber sheets containing 0.5%w/w TiO<sub>2</sub> powder with rubber sheet containing 0.5%w/w TiO<sub>2</sub> microparticles. From Figure 4.12, molecular weight of natural rubber, natural rubber containing TiO<sub>2</sub> powder and natural rubber containing TiO<sub>2</sub> microparticles were reduced after 1 hour exposure. Slightly greater extent of degradation was observed for natural rubber containing 0.5%w/w TiO<sub>2</sub> powder (45% decrease) and 0.5%w/w TiO<sub>2</sub> microparticles (50% decrease) as compared to the controlled natural rubber without TiO<sub>2</sub> (40% decrease). Interestingly, it was observed that the extent of degradation of natural rubber containing TiO<sub>2</sub> microparticles became greater than the one containing TiO<sub>2</sub> powder after 2 hours of exposure. This could indicate that the encapsulation of TiO<sub>2</sub> suppressed the rate of degradation as compared to the direct addition of TiO<sub>2</sub> powder. We explain an initial degradation of natural rubber containing TiO<sub>2</sub> powder being lower than the one containing TiO<sub>2</sub> microparticles as a result of ultraviolet reflection of TiO<sub>2</sub> powder. However, the effect of ultraviolet reflection was outweighed by the catalytic character after longer exposure. We would like to comment that this explanation is only valid based on the fact that extent of degradation is independent of the amount of TiO<sub>2</sub> powder (0.1, 0.5, 1 and 5%w/w) or TiO<sub>2</sub> microparticles (0.5, 1, 3 and 5%w/w).



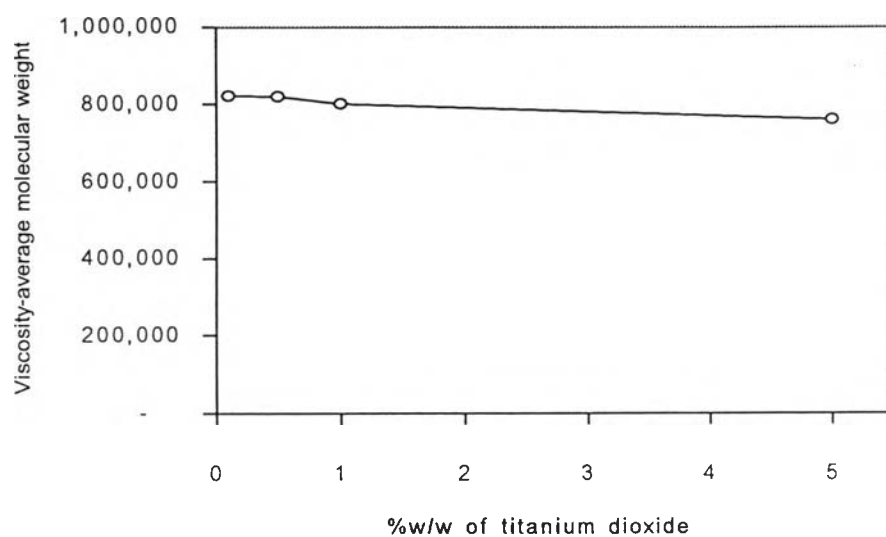


Figure 4.10 Viscosity-average molecular weight of natural rubber sheet containing TiO<sub>2</sub> powder after exposed to UV light under accelerated condition for 120 min.

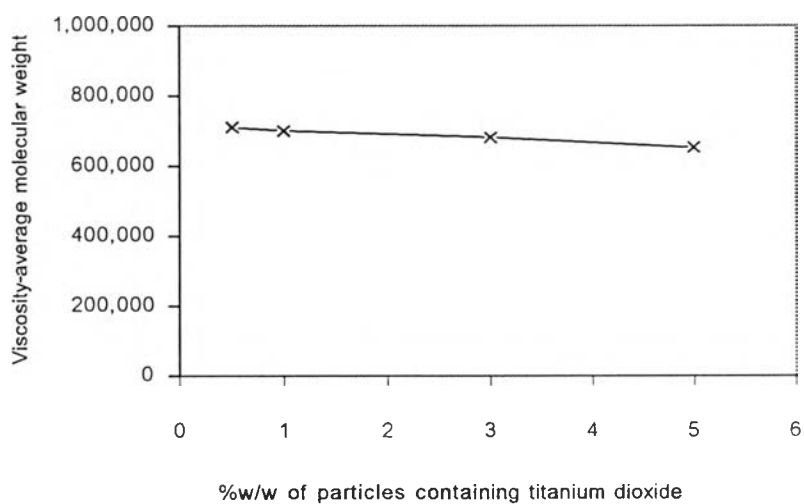


Figure 4.11 Viscosity-average molecular weight of natural rubber sheet containing TiO<sub>2</sub> particles after exposed to UV light under accelerated condition for 120 min.

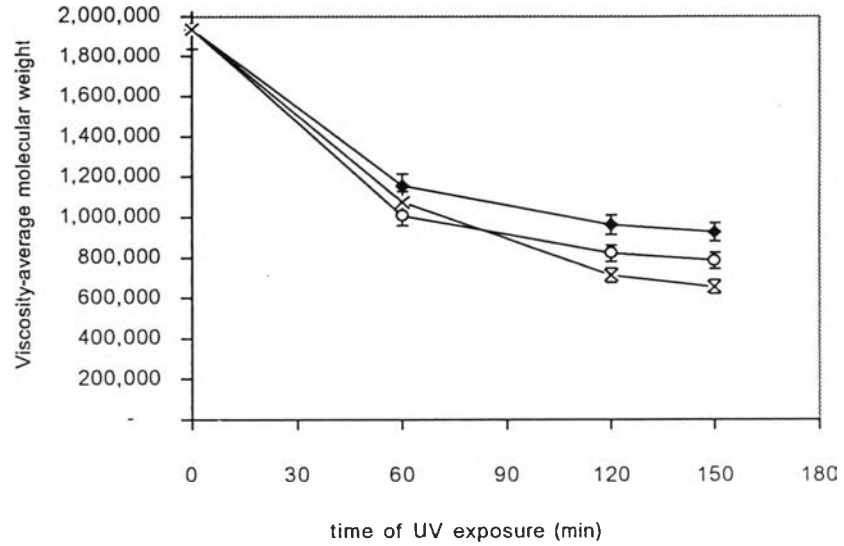


Figure 4.12 Viscosity-average molecular weight of natural rubber sheets after exposed to UV light for 120 min. ( ◆: natural rubber, ○ : natural rubber + 0.5%w/w TiO<sub>2</sub> powder, x : natural rubber + 0.5%w/w TiO<sub>2</sub> particles)

The degradation of natural rubber sheets in the presence of water was shown in Table 4.1. Molecular weight of natural rubber, natural rubber containing TiO<sub>2</sub> powder and natural rubber containing TiO<sub>2</sub> microparticles decreased more rapidly than the samples degraded in dry condition. Molecular weight of natural rubber containing TiO<sub>2</sub> microparticles slightly decreased more than others. These data suggested that water plays a role in controlling degradation to some extent.

Table 4.1 The degradation of natural rubber sheets in the presence of water

NR sample	Dry condition		Soaking in water	
	$\bar{M}_v$	% $\bar{M}_v$ reduction <sup>a</sup>	$\bar{M}_v$	% $\bar{M}_v$ reduction <sup>a</sup>
NR	960,878	50	733,152	62
NR+0.5% TiO <sub>2</sub> powder	821,217	57	589,770	69
NR+0.5% TiO <sub>2</sub> particles	711,560	63	457,214	76

a, The molecular weight reduction was calculated by comparing with the original  $\bar{M}_v$  of ~ 2,000,000

A similar trend of degradation after exposure to sunlight (Figure 4.13) was observed for natural rubber sheets containing 0.5%w/w  $\text{TiO}_2$  powder and 0.5%w/w  $\text{TiO}_2$  microparticles. Initially, the sheets containing  $\text{TiO}_2$  powder seem to be more stable than the ones containing  $\text{TiO}_2$  microparticles due to more efficient UV reflection of  $\text{TiO}_2$  powder than encapsulated  $\text{TiO}_2$ . The reversed trend was evidenced for samples exposed to sunlight for 2 and 3 days. The molecular weights of all samples were unexpectedly decreased to approximately the same value ( $\bar{M}_v = 80,000$ ) after 4 days of exposure. We would like to comment that all samples were uncured rubber. It is then possible to observe such a trend due to the damage of natural rubber by a combination of heat and sunlight after long exposure.

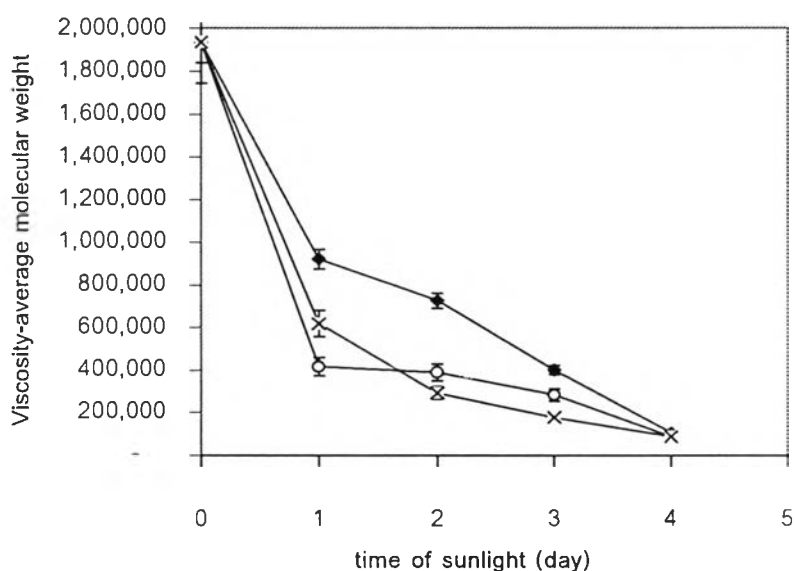


Figure 4.13 Viscosity-average molecular weight of natural rubber sheets after exposed to sunlight for 1 – 4 days. ( ◆ : natural rubber, ◻ : natural rubber + 0.5%w/w  $\text{TiO}_2$  powder, × : natural rubber + 0.5%w/w  $\text{TiO}_2$  particles)

### 4.2.3 Mechanical properties of natural rubber

To determine the effect of  $\text{TiO}_2$  addition on degradation of controlled vulcanized natural rubber sheets, vulcanized natural rubber sheets containing 1%w/w  $\text{TiO}_2$  powder and 1%w/w  $\text{TiO}_2$  particles were exposed to sunlight for 5 to 15 days. Figure 4.14 illustrates the tensile strength of vulcanized natural rubber sheets after sunlight exposure. All samples showed a decrease in tensile strength as the time of sunlight exposure was longer. The reduction of tensile strength of vulcanized natural rubber sheets containing 1%w/w  $\text{TiO}_2$  particles was slightly lower than the controlled vulcanized natural rubber sheets and vulcanized natural rubber sheets containing 1%w/w  $\text{TiO}_2$  powder. This data suggested that the degree of degradation of vulcanized natural rubber sheets containing  $\text{TiO}_2$  powder and  $\text{TiO}_2$  particles were not significantly different from the controlled rubber sheets. Degraded natural rubber sheets were also characterized by ATR-IR as shown in Figures 4.15, 4.16, 4.17 and 4.18. As expected, IR spectra of vulcanized natural rubber, vulcanized natural rubber containing  $\text{TiO}_2$  powder and  $\text{TiO}_2$  particles after exposure to sunlight for 15 days exhibited higher intensity of peaks in the region of  $1700 - 1760 \text{ cm}^{-1}$ . It indicated that higher carbonyl groups at the surface being generated after exposure to sunlight as compared to the controlled rubber sheets before sunlight exposure. The insignificant reduction of tensile strength may be regarded to the fact that insufficient amount of  $\text{TiO}_2$  powder or  $\text{TiO}_2$  particles incorporated causing ineffective degradation especially within cured natural rubber network.

In order to improve the extent of degradation of cured natural rubber, it may be necessary to incorporate greater amount of  $\text{TiO}_2$  powder or  $\text{TiO}_2$  particles.

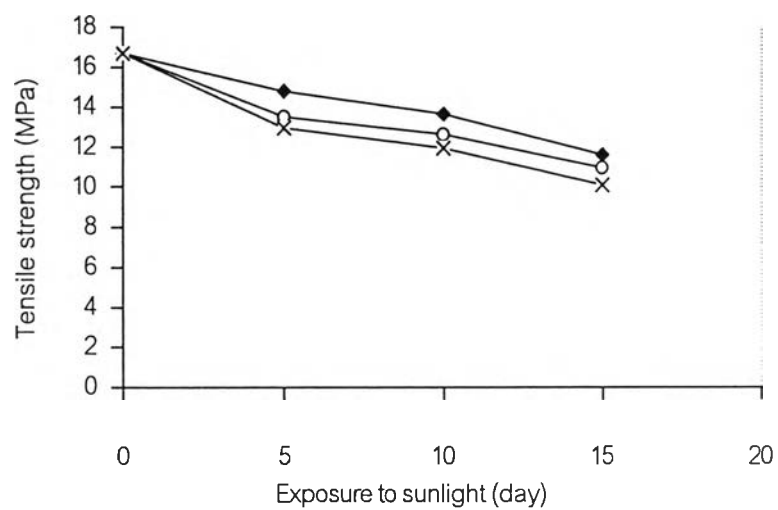


Figure 4.14 Tensile strength of vulcanized natural rubber after exposed to sunlight for 5 - 15 days. (◆ : natural rubber, ○ : natural rubber + 1%w/w TiO<sub>2</sub> powder, X : natural rubber + 1%w/wTiO<sub>2</sub> particles)

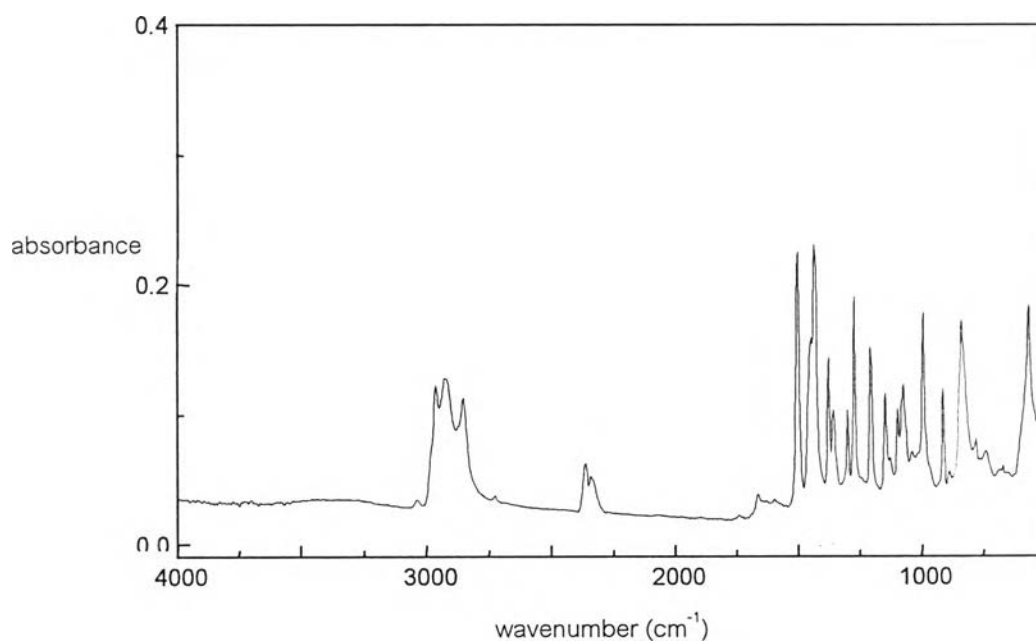


Figure 4.15 ATR-IR spectrum of controlled vulcanized rubber sheet

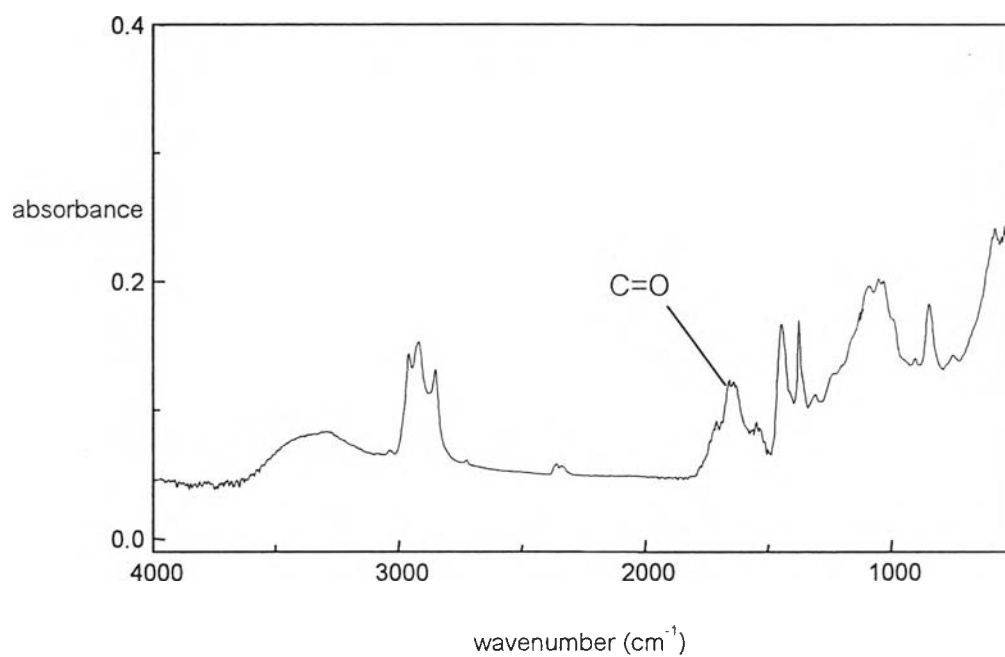


Figure 4.16 ATR-IR spectrum of controlled vulcanized rubber sheet after exposed to sunlight for 15 days

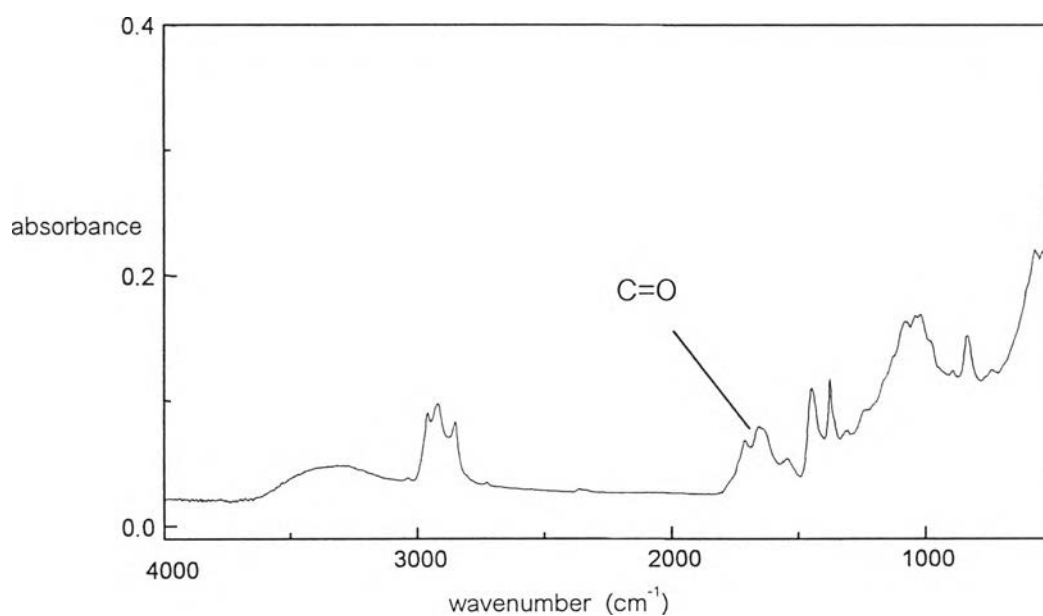


Figure 4.17 ATR-IR spectrum of vulcanized rubber sheet containing 1%w/w TiO<sub>2</sub> powder after exposed to sunlight for 15 days

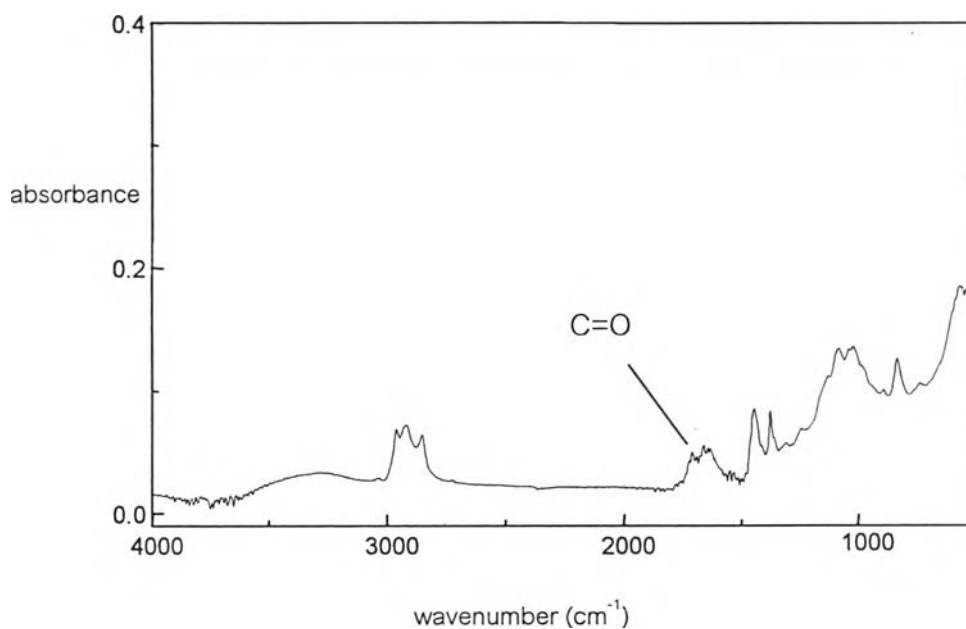


Figure 4.18 ATR-IR spectrum of vulcanized rubber sheet containing 1%w/w TiO<sub>2</sub> particles after exposed to sunlight for 15 day.

The degradation of vulcanized natural rubber sheets in the presence of water was shown in Table 4.2. Tensile strength of vulcanized natural rubber sheet, vulcanized natural rubber sheet containing 1%w/w TiO<sub>2</sub> powder and 1%w/w TiO<sub>2</sub> particles decreased more than the samples degraded in dry condition. Tensile strength of vulcanized natural rubber sheet containing TiO<sub>2</sub> particles slightly decreased more than others. These data suggested that water plays a role in controlling degradation to some extent.

Table 4.2 The degradation of vulcanized natural rubber sheets in the presence of water after exposure to sunlight for 15 days.

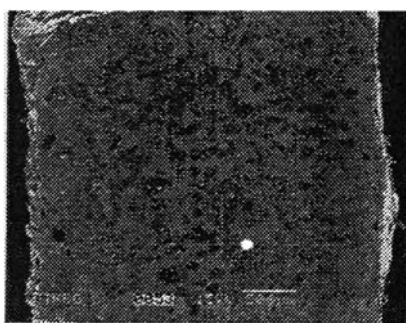
NR sample	Dry condition		Soaking in water	
	Tensile Strength (MPa)	% reduction <sup>a</sup>	Tensile Strength (MPa)	% reduction <sup>a</sup>
NR	11.60	31	11.12	33
NR+1% TiO <sub>2</sub> powder	10.95	34	9.52	43
NR+1% TiO <sub>2</sub> particles	10.10	40	8.78	47

a, The tensile strength reduction was calculated by comparing with the original tensile strength of 16.70.

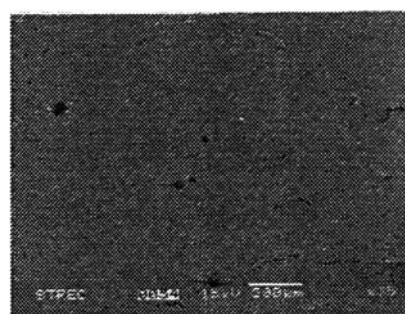
#### 4.2.4 Surface morphologies of vulcanized rubber sheets before and after sunlight exposure.

The vulcanized natural rubber sheets were analyzed by SEM. Figure 4.19 showed surface morphologies of vulcanized natural rubber sheet, vulcanized natural rubber sheet containing TiO<sub>2</sub> powder and TiO<sub>2</sub> particles after exposed to sunlight for 15 days. These micrographs displayed some cavities in surface, probably due to water evaporation during the vulcanization, but the material itself seemed to be homogeneous. Micrograph of natural rubber containing TiO<sub>2</sub> particles (d) displayed some surface fractures, which clearly indicated that the natural rubber sheets have lost some physical integrity after being degraded. However, this lost of physical integrity at the surface is not significant enough to affect bulk mechanical properties.





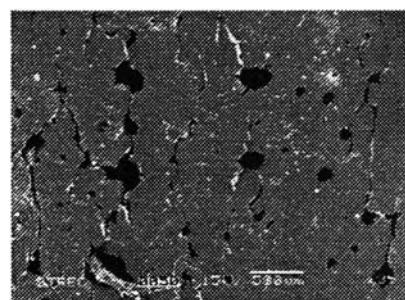
(a) controlled vulcanized natural rubber sheet



(b) controlled vulcanized natural rubber after exposed to sunlight for 15 days



(c) vulcanized natural rubber sheet +  $\text{TiO}_2$  powder after exposed to sunlight for 15 days



(d) vulcanized natural rubber sheet +  $\text{TiO}_2$  particles exposed to sunlight for 15 days

Figure 4.19 Micrographs of vulcanized rubber sheets before and after sunlight exposure