จุฬาลงกรณ์มหาวิทยาลัย

ทุนวิจัย

กองทุนรัชดาภิเษกสมโภช

รายงานผลการวิจัย

การย่อยสลายแบบควบคุมของยางธรรมชาติด้วยอนุภาคขนาดไมครอนที่มีไททาเนียมไดออกไซด์

โดย

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เมษายน 2547

Acknowledgement

The authors acknowledge the financial support from Ratchadapisek Sompoj Endowment Fund and partial support from Chulalongkorn University through the Development Grants for New Faculty/Researcher for V. P. Hoven.

บทคัดย่อ

ชื่อโครงการวิจัย การย่อยสลายแบบควบคุมของยางธรรมชาติด้วยอนุภาคขนาดไมครอนที่มีไททาเนียมไดออกไซด์

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เดือนและปีที่ทำวิจัยสำเร็จ เมษายน 2547

งานวิจัยนี้ศึกษาการย่อยสลายแบบโฟโตออกซิเดทีฟของยางธรรมชาติที่มีไทเทเนียมไดออกไซด์ภายใต้รังสีอัลตราไวโอเลตและแสงแดด โดยติดตามการย่อยสลายของยางธรรมชาติที่ไม่ได้ผ่านการวัลคาไนซ์ทั้งในภาวะที่เป็นสารละลายและของแข็งโดยการวิเคราะห์น้ำหนักโมเลกุลแบบเฉลี่ยโดยตัวเลขด้วยเจลเพอมิเอชันโครมาโทกราฟี และติดตามการย่อยสลายของยางธรรมชาติที่ผ่านการวัลคาไนซ์โดยการศึกษาสมบัติเชิงกล จากการศึกษาพบว่าสัดส่วนการลดลงของน้ำหนักโมเลกุลของยางธรรมชาติในภาวะสารละลายเพิ่มขึ้นเมื่อมีปริมาณไทเทเนียมไดออกไซด์เพิ่มขึ้น ในทางกลับกันการย่อยสลายของยางธรรมชาติในภาวะของแข็ง (ทั้งในรูปที่ผ่านการวัลคาไนซ์และไม่ผ่านการวัลคาไนซ์) เป็นส่วนกลับกับปริมาณไทเทเนียมไดออกไซด์ที่เติมลงไปซึ่งแสดงให้เห็นว่าไทเทเนียมไดออกไซด์ทำหน้าที่หลักเป็นตัวทำให้เสถียรแทนที่จะเป็นสารเร่งปฏิกิริยาด้วยแสง ผู้วิจัยเชื่อว่าการรวมตัวกันของอนุภาคไทเทเนียมไดออกไซด์เป็นสาเหตุสำคัญที่ทำให้ประสิทธิภาพในการเร่งปฏิกิริยาด้วยแสงของมันมีค่าต่ำ จากผลการวิเคราะห์ด้วยเอสอีเอ็มพบว่าไทเทเนียมไดออกไซด์ที่เติมลงไปในแผ่นยางธรรมชาติมีแนวโน้มในการเกิดการรวมตัวกันเป็นอนุภาคที่มีขนาดเส้นผ่านศูนย์กลาง 1-2 ไมโครเมตร ซึ่งเป็นขนาดที่ใหญ่เพียงพอที่สามารถสะท้อนแสงยูวีได้ การปรากฏรอยแตกหักทั่วพื้นผิวของยางธรรมชาติทั้งที่มีและไม่มีไทเทเนียมไดออกไซด์บ่งชี้ว่าการย่อยสลายของยางธรรมชาติส่วนใหญ่ไม่ได้เกิดขึ้นเพียงแต่ที่ผิวรอยต่อระหว่างไทเทเนียมไดออกไซด์กับยางธรรมชาติเท่านั้น ข้อมูลน้ำหนักโมเลกุลแบบเฉลี่ยโดยความหนืดแสดงให้เห็นว่าไม่สามารถควบคุมการย่อยสลายของยางที่ไม่ได้ผ่านการวัลคาไนซ์ได้ด้วยอนุภาคขนาดไมครอนของไทเทเนียมไดออกไซด์ การเติมอนุภาคขนาดไมครอนของไทเทเนียมไดออกไซด์เพิ่มการย่อยสลายแทนที่จะชะลอการย่อยสลายตามที่คาดไว้ในเบื้องต้น

Abstract

Project Title Controlled degradation of natural rubber by microparticles containing titanium dioxide

Name of the Investigators Vipavee P. Hoven, Yasuyuki Tanaka, Narisa Na Lumpoon, Jittima Deeprasertwong

Year 2004

Photooxidative degradation of natural rubber by of titanium dioxide (TiO_2) under accelerated ultraviolet light and sunlight was investigated. Degradation of unvulcanized natural rubber both in solution phase and solid phase was determined by following number-average molecular weight using gel permeation chromatography. The degradation of vulcanized natural rubber was determined as a function of mechanical properties. Extent of molecular weight reduction of natural rubber in solution phase was increased when the amount of TiO_2 was increased. In contrast, the degradation of natural rubber in solid phase (both as vulcanized and unvulcanized form), was inversely proportional to the amount of TiO_2 incorporated indicating that TiO_2 plays a major role as a stabilizer instead of a photocatalytic agent. The agglomeration of TiO_2 is believed to account for its poor photocatalytic activity. As demonstrated by SEM analysis, TiO_2 filled in solid natural rubber tended to aggregate into particles having the diameter of 1-2 μm which are large enough to reflect UV light. The appearance of fracture all over the surface of natural rubber sheets despite the presence of TiO_2 after UV exposure suggested that the degradation of natural rubber in solid phase did not predominantly occur at the interface between TiO_2 and natural rubber. According to viscosity-average molecular weight data, controlled degradation of unvulcanized natural rubber cannot be achieved by TiO_2 microparticles. An incorporation of TiO_2 microparticles insignificantly increase the extent of degradation instead of delaying the degradation as originally expected.

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CHAPTER I

INTRODUCTION

1.1 Statements of Problem

The global consumption of vulcanized elastomers has grown to a yearly production level of about 17.2 million tons. Approximately 40% of that is natural rubber with the remaining 60% consisting of various synthetic rubbers. Vulcanization is required to give rubber its characteristics such as high elasticity and strength. Once rubbers are cross-linked, they do not melt or dissolve. The presence of these networks thus creates a tremendous problem at the end of a product's life. The recycling and reutilization of cross-linked elastomers are difficult preposition because of these three dimensional chemical network.

Wastes from natural rubber products have become increasingly problematic due to their non-degradability in environment. Gloves are non-recycled garbage after being used. While expired tires are usually discarded by an incineration which in turn causes air pollution. The development of natural rubber that can degrade under ambient sunlight irradiation is believed to be an environmental-friendly approach for disposal of natural rubber wastes. In addition, such a concept offers an alternative to value-added rubber products that can be used for some applications requiring a short lifetime rubber such as soil cover sheet used in agriculture.

Titanium dioxide (TiO_2) is a well-known inorganic pigment. It cannot only exhibit a protective effect but also behaves as an oxidation catalyst sensitizing the photochemical breakdown of organic matters. As a result of its chemical inertness, non-photocorrosivity and nontoxicity, TiO_2 is considered as one of the most suitable photocatalyst used for waste treatment and controlled degradation of polymers.

This research aims to control degradation of natural rubber by incorporating TiO_2. The photocatalytic degradation under accelerating condition is investigated. The ability of TiO_2 to enhance the durability or to catalyze the photo-oxidation of natural rubber in solution and unvulcanized natural rubber sheet is monitored by following molecular weight decay as a function of time and TiO_2 composition. To assess the feasibility of developing photodegradable vulcanized natural rubber, mechanical properties of vulcanized natural rubber incorporated with TiO_2 are investigated. The chemical composition and morphology of the degraded natural rubber are characterized by FT-IR and SEM, respectively.

An attempt to incorporate microparticles containing TiO_2 is also carried out. The microparticles are prepared by complex coacervation of gelatin and gum arabic, which are natural water – soluble polymers. It is anticipated that the polymer matrix would act as a protecting coating that can prevent the premature degradation of natural rubber. And the degradation can be triggered when encapsulated TiO_2 is released due to the swelling of microparticles in the presence of water, oxygen and UV light. Microparticles are characterized by scanning electron microscopy (SEM) and electron dispersive X-ray (EDX). Oxidative degradation of unvulcanized rubber is studied under ultraviolet light (accelerated condition) and sunlight by following viscosity-average molecular weight using solution viscometry method. Degradation of vulcanized rubber containing TiO_2 microparticles under ultraviolet light and sunlight is monitored by determination of mechanical properties.

1.2 Objectives

1. To study the degradation of natural rubber in solution and as a solid form in the presence of TiO_2 under ultraviolet light
2. To study an effect of TiO_2 composition on the rate of natural rubber degradation
3. To determine an ability to control degradation by incorporating TiO_2 microparticles

1.3 Scope of the Investigation

1. Literature survey for related research work
2. To study the degradation of natural rubber in the presence of TiO_2 in solution by following number-average molecular weight using gel permeation

chromatography (GPC) after exposure to UV light under accelerated condition

3. To prepare unvulcanized natural rubber sheets filled with TiO_2 or TiO_2 microparticles
4. To study the degradation of unvulcanized natural rubber sheet filled with TiO_2 by following number-average molecular weight using gel permeation chromatography (GPC) and the degradation of unvulcanized natural rubber sheet filled with TiO_2 microparticles by following viscosity-average molecular weight using solution viscometry after exposure to UV light under accelerated condition and sunlight
5. To prepare vulcanized natural rubber sheets filled with TiO_2 or TiO_2 microparticles
6. To determine mechanical properties of vulcanized natural rubber sheets filled with TiO_2 or TiO_2 microparticles after exposure to UV light under accelerated condition and sunlight according to ASTM method.
7. To summarize the results

CHAPTER II

THEORY AND LITERATURE REVIEWS

2.1 Natural Rubber [2,3]

On tapping the *Heavea brasiliensis* tree, natural rubber latex exudes, which has a rubber content between 25 and 40 percent by weight. The variation is due to factors such as the type of tree, the tapping method, the soil conditions, and the season. The latex is normally called 'field' latex, and its average rubber content is 30 percent by weight. This material is not utilized in its original form due to its high water content and susceptibility to bacterial attack. It is necessary to preserve and concentrate it, so that the end product is stable and contains 60 percent or more of rubber. All the important processes of fabrication of latex articles begin with latex that has a 60 percent minimum rubber content. Extensive blending of the concentrated latex ensures a consistent high quality material meeting national and international specifications.

Latex concentrate is differentiated by the method of concentration and the type of preservative used. In addition to the general-purpose type of latex, there are special forms such as double centrifuged latex, creamed/centrifuged latex and modified types such as prevulcanized latex. Three methods of concentration are employed, centrifugation, evaporation and creaming; centrifugation is the preferred method and accounts for 95 percent of total production. Details of the preservation systems used in centrifuged concentrate are given in Table 2.1. The predominant lattices are the HA and LA-TZ types. Latex concentrate prepared by evaporation is usually stabilized by potassium hydroxide, whilst creamed latex is normally preserved with 0.7 percent ammonia.

Table 2.1 Types of preservation system used in centrifuged NR latex concentrate.

Designation	Abbreviation	Preservation system (% by weight)
High or Full Ammonia	HA	0.7 % ammonia
Low ammonia TZ	LA-TZ	0.2% ammonia, 0.025 % zinc oxide, 0.025 % tetramethylthiuram disulphide
Low ammonia pentachlorphenate	LA-SPP	0.2% ammonia, 0.2% sodium pentachlorophenate
Low ammonia boric acid	LA-BA	0.2% ammonia , 0.24% boric acid

Natural rubber is a polymer of isoprene. Isoprene was found to have the formula of C_5H_8, which has the following structure:

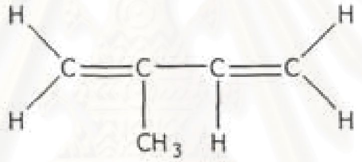


Figure 2.1 Chemical structure of isoprene

The isoprene units are linked together at carbon atom 1 and 4 in a head – to – tail arrangement.

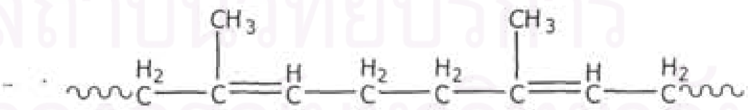


Figure 2.2 Head – to – tail arrangement of polyisoprene

Most commercial natural rubber contains 93-94%wt of cis-1,4-polyisoprene. In this configuration, carbon atoms 1 and 4 are both on the same side of double bond.

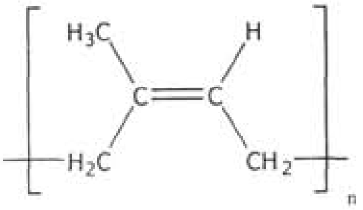


Figure 2.3 Cis – polyisoprene

Molecular weight of natural rubber is about 1.0 – 1.3 x 10^6 with broad molecular weight distribution (MWD). The broad MWD of natural rubber is presumed to derive from the branching and crosslinking by certain special functional groups in rubber molecule. There are two components called sol and gel in natural rubber. The sol phase is a rubber part that dissolves easily in good solvent such as toluene, cyclohexane. The gel phase swells without dissolving. Commercial natural rubber contains 5 – 50% gel phase.

2.2 Natural Rubber Composition

2.2.1 Dispersed Phase

The rubber in natural latex is cis-1,4-polyisoprene with a molecular weight in the region of one million. The molecular weight cannot be known precisely because there is always a proportion of the rubber which is insoluble. This proportion, the gel content, steadily increases as the latex is stored, presumably due to a process similar to the 'storage hardening' which occurs in dry rubber. After about two to three months storage the hardening ceases and the gel content may be as high as 50 percent in toluene. The measurement of gel content is complicated by the fact that the amount of gel is solvent-dependent, which suggests that much of the apparent cross-linking does not involve covalent bond. As a result of storage hardening the rubber in mature latex concentrate has a Mooney Viscosity greater than 100. Increases in rubber hardness, however, do not produce any discernible change in the film-forming properties of latex.

The molecular weight of the 'sol fraction' of the rubber in mature concentrated latex can be determined, for example, by gel permeation chromatography. Results of such measurements are shown in Figure 2.4. For a LA-TZ latex, the rubber from which was dissolved in tetrahydrofuran. The gel content in the solvent was about 40 percent and the average molecular weight ($\overline{M}_w$) of the sol fraction was 880,000.

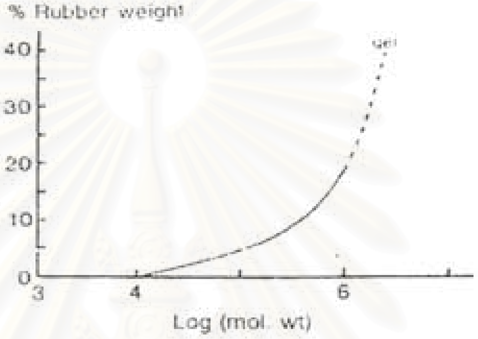


Figure 2.4 The molecular weight distribution of NR latex rubber (LA-TZ).

2.2.2 Non-rubber Materials in the Serum

The non-rubber materials in the serum from latex concentrates comprise a wide variety of chemical species. The major constituents are known to be proteins and their decomposition products, fatty acid soaps, and a range of organic and inorganic salts.

The overall compositions of both HA and LA-TZ lattices are summarized in Table 2.2 for both the latex and the total solid film. These figures can only be regarded as an approximate guide to the composition of natural lattices and much more research needs to be done before a precise composition can be established.

Table 2.2 Overall compositions in percentage by weight of lattices and total solids

	HA		LA-TZ	
	Latex	TSC	Latex	TSC
Rubber	59.67	97.61	59.61	97.62
Protein,etc	1.06	1.73	1.03	1.69
Soaps	0.23	0.38	0.23	0.38
Salts	0.40	0.28	0.38	0.32
Ammonia	0.68	-	0.21	-
Water	37.96	-	38.54	-

2.2.3 Adsorbed Non-rubber Materials

When in the tree, the particles in natural latex are presumed to possess an adsorbed layer of a protein-lipid complex, similar to the membranes of many biological cells. As a consequence of the addition of ammonia to preserve the latex concentrate, the lipid materials are believed to hydrolyze slowly, releasing fatty acid soaps which can later adsorb onto the particle surface. The adsorption of these soaps accounts for the spontaneous rise in mechanical stability when ammoniated concentrate is stored.

Nevertheless, little direct knowledge of the materials adsorbed on the latex particles exists. The surface proteins have never been isolated as such and they are often presumed to be similar to those identified in the serum but they may be different.

2.3 Prevulcanization of Natural Rubber (NR) Latex [4]

2.3.1 Definition and Importance

Prevulcanization of NR latex is defined as a process in which chemical crosslinking of rubber chains takes place inside each particle disperse in aqueous latex serum. Drying of prevulcanized latex produces a crosslinked film without the need for further heating. One of the principle advantages of prevulcanized latex is that effective control of the physical properties can be exercised before manufacturing those articles. For this reason, the prevulcanized NR latex is the most industrially important type of chemically-modified latex. It is especially useful for being directly employed in the dipping operation in small to medium sized factory. It is also applied in other fields such as adhesives, latex foam, carpet backing and textile combining.

2.3.2 Sulfur Prevulcanization

Mineral sulfur is widely used as an ingredient to provide crosslink between rubber chains in the vulcanization process. In sulfur prevulcanization, vulcanized latex is prepared by heating NR latex, mixed with the dispersions of sulfur and an accelerator at 50-80°C. Accelerator employed in latex mixture is usually ultra-fast dithiocarbamate, such as zinc diethykdithiocarbamate (ZDEC), due to the fact that reaction in latex proceeds much more rapidly than that in dry rubber at the same temperature with the same vulcanizing ingredient. The speed of the prevulcanization reaction seems to be associated primarily with the presence of non-rubber constituents which also act as accelerator in latex. Chemical network structure of sulfur vulcanized rubber can be presented in Figure 2.5.

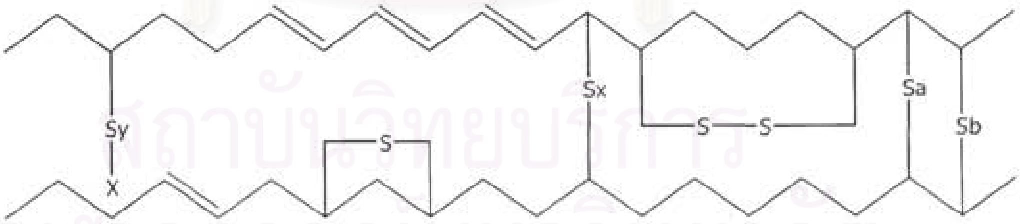


Figure 2.5 A diagrammatic representation of network structure of sulfur vulcanized rubber (x, y, a and b = 1-9, x = accelerator fragment).

2.4 Vulcanization [5]

Useful rubber articles, such as tires and mechanical goods, cannot be made without vulcanization. Unvulcanized rubber is generally not very strong, does not maintain its shape after a large deformation and can be very sticky. In short, unvulcanized rubber can have about the same consistency as chewing gum.

2.4.1 Definition of Vulcanization

The term *vulcanization* is generally applied to rubbery or elastomeric materials. These materials forcibly retract to their approximately original shape after a rather large mechanically imposed deformation. Vulcanization can be defined as a process which increases the retractile force and reduces the amount of permanent deformation remaining after removal of the deforming force. Thus, vulcanization increases elasticity while it decreases plasticity. It is generally accomplished by the formation of a crosslinked molecular network. (Figure 2.6)

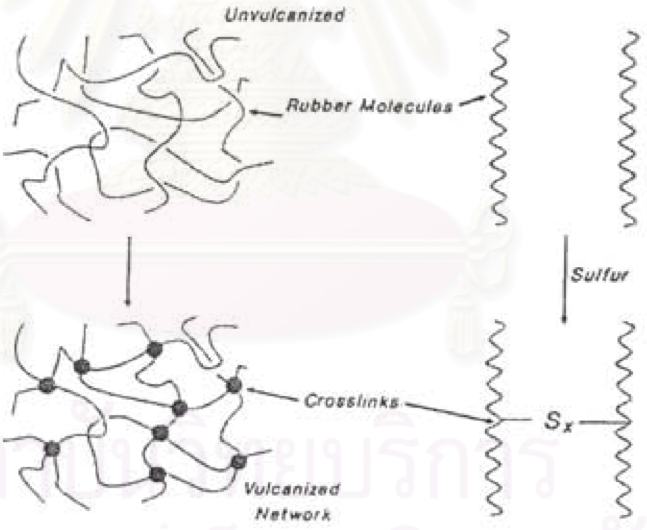


Figure 2.6 Network formation after vulcanization

2.4.2 Effects of Vulcanization on Vulcanizate Properties

At the molecular level, vulcanization causes profound chemical changes. The long rubber molecules (molecular weight usually between 100,000 and 500,000) become linked together with junctures (crosslinks) spaced along the polymeric chains, with the average distance between junctures corresponding to a molecular weight between crosslinks of about 4,000 to 10,000. As a result of this network formation, the rubber becomes essentially insoluble in any solvent and it cannot be processed by any means which require it to flow, e.g., in a mixer, in an extruder, on a mill, on a calendar, or during shaping, forming, or molding. Thus it is essential that vulcanization occurs only after the rubber article is in its final form.

Major effects of vulcanization on use-related properties are illustrated by the idealization of Figure 2.7. It should be noted that static modulus increases with vulcanization to a greater extent than does the dynamic modulus. The dynamic modulus is a composite of viscous and elastic behavior, whereas static modulus is largely a measure of only the elastic component of rheological behavior.

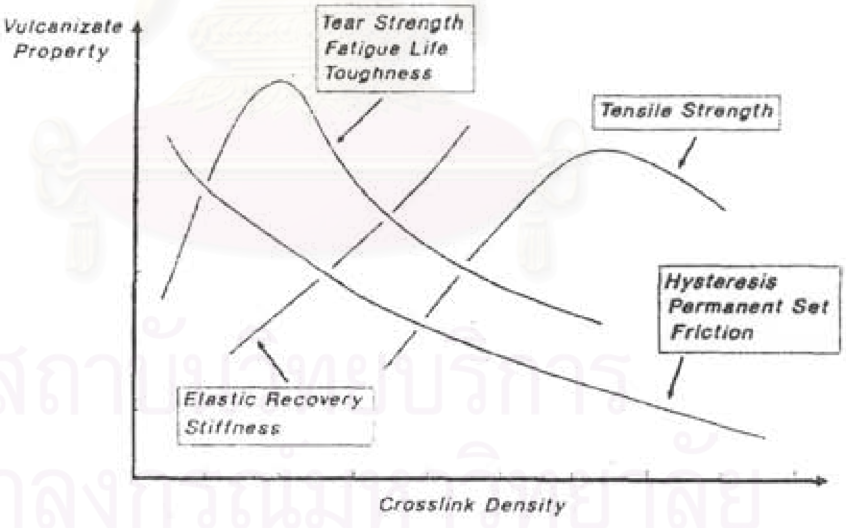


Figure 2.7 Mechanical properties as a function of the extent of vulcanization

Hysteresis is reduced with increasing crosslink formation. Hysteresis is the ratio of the rate-dependent or viscous component to the elastic component of deformation resistance. It is also a measure of deformation energy which is not stored (or borne by the elastic network) but which is converted to heat. Vulcanization then causes a trade-off of elasticity for viscous or plastic behavior. Tear strength, fatigue life, and toughness are related to the breaking energy. Values of these properties increase with small amounts of crosslinking but they are reduced by further crosslink formation. Properties related to the energy-to-break increase with increases in both the number of network chains and hysteresis. Since hysteresis decreases as more network chains are developed, the energy-to-break related properties are maximized at some intermediate crosslink density.

It should be noted that the properties given in Figure 2.7 are not only functions of crosslink density. They are also affected by the type of crosslink, the type of polymer and the type and amount of filler.

Reversion is a term generally applied to the loss of network structures by non-oxidative thermal aging. It is usually associated with isoprene rubbers vulcanized by sulfur. It can be the result of too long of a vulcanization time (overcure) or of hot aging of thick section. It is most severe at temperatures above about 155 °C. It occurs in vulcanizates containing a large number of polysulfidic crosslinks. Though its mechanism is complex, a good deal about the chemical changes which occurs during the reversion of natural rubber has been deduced.

Sometimes the term *reversion* is applied to other types of non-oxidative degradation, especially with respect to rubbers not based on isoprene. For example, thermal aging of SBR, which can cause increased crosslink density and hardening, has been called reversion because it can be the result of overcure.

2.4.3 Sulfur Vulcanization [4]

Sulfur is the main curing agent for most crude rubbers that contain enough double bond in their macromolecules. The sulfur-only vulcanization proceeds via a polar or ionic mechanism, where species of the type RS_x^+ (R = rubber chain) added onto the double bond. Sulfur is combined in the vulcanization network of rubber similar to the network structure of sulfur-prevulcanized latex as illustrated in Figure 2.5.

Since the vulcanization of rubber by heating with sulfur alone is a relatively slow process and exhibits a poor efficiency, it is necessary to add accelerators to increase the rate of vulcanization. These accelerators are usually complex sulfur-containing organic compounds such as tetraalkylthiuram disulfide, zinc dialkyldithiocarbamate, and related compounds, as well as a few non-sulfur compounds such as aryl guanidines. Many accelerators function best in the presence of activators, like zinc oxide (ZnO) and stearic acid. Due to the importance of solubility of the accelerator and activator, a rubber-soluble soap, e.g., the zinc salt of a long chain fatty acid, is usually interacted with molecular sulfur (S_8) to form a sulfurating reagent or zinc perthio-salt (XS_xZnS_xX). This salt reacts with the rubber hydrocarbon (RH) to give a rubber-bound intermediate (RS_xX) which subsequently reacts with a molecule of rubber hydrocarbon (RH), or itself, to give polysulfide crosslink, and more accelerator is regenerated. The polysulfide ($RS_{x-1}R$) in turn can lose sulfur to give monosulfidic and disulfidic crosslinks, or can give cyclic sulfide with loss of crosslink. With a large accelerator: sulfur ratio, most of the polysulfidic is transformed into monosulfide crosslink, and the undesirable cyclic sulfide formation is suppressed. The general mechanism of the accelerated sulfur vulcanization is shown in Figure 2.8.

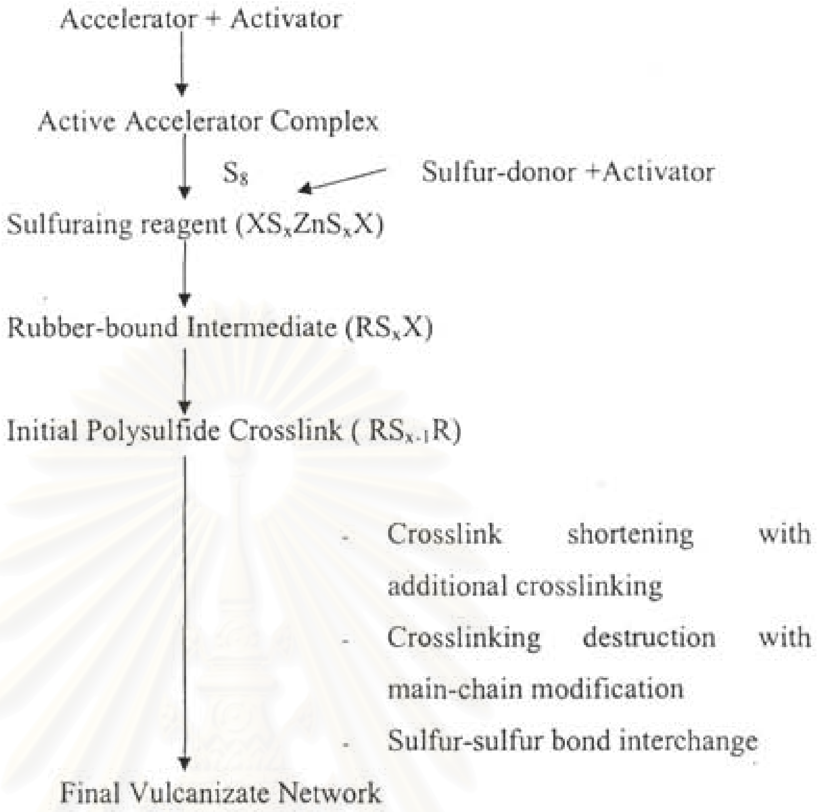


Figure 2.8 General mechanism of accelerated sulfur vulcanization (R = rubber chain, H = allylic proton and X = accelerator).

2.5 Molecular Weight of Polymer [6]

Molecular weight of polymer is generally very high, ranging from about 25,000 g/mol to 1,000,000 g/mol or higher. Polymers differ from small–sized compounds in that they are polydispersed or heterogeneous in molecular weight. When one discusses the molecular weight of a polymer, one is actually involved with its average molecular weight.

2.5.1 Molecular Weight Average

There are three molecular weight averages in common use.

1. Number – average molecular weight, $\overline{M}_n$

Number–average molecular weight involves a count of the number of molecules of each species divided by the total number of molecules. $\overline{M}_n$ was defined as:

$$\overline{M}_n = \frac{\Sigma N_i M_i}{\Sigma N_i}$$

Where N_i is the number of moles whose weight is M_i.

The methods for measuring $\overline{M}_n$ are those that measure colligative properties of solution–vapor pressure lowering (vapor pressure osmometry), freezing point depression (cryoscopy), boiling point elevation (ebulliometry) and osmotic pressure (membrane osmometry). The most common methods are membrane osmometry and vapor pressure osmometry. Vapor pressure osmometry, which measures vapor pressure indirectly by measuring the change in temperature of a polymer solution on dilution by solvent vapor. It is generally useful for polymers with $\overline{M}_n$ below 10,000 – 15,000. Membrane osmometry is limited to polymers with $\overline{M}_n$ above about 20,000 – 30,000 and below 50,000.

2. Weight – average molecular weight, $\overline{M}_w$

The principal method of determining the weight – average molecular weight is light – scattering that is greater for larger – sized molecules than for smaller – sized molecules $\overline{M}_w$ is defined as:

$$\overline{M}_w = \frac{\Sigma N_i M_i^2}{\Sigma N_i M_i}$$

The lower limit of $\overline{M}_w$ by the light scattering method is close to 5,000 – 10,000. Below this molecular weight, the amount of scattered light is too small to measure accurately.

3. Viscosity – average molecular weight, $\overline{M}_v$

Solution viscosity measures the viscosity – average molecular weight. Viscosity, like light scattering, is greater for the larger – sized polymer molecules. $\overline{M}_v$ was defined as:

$$\overline{M}_v = \left(\frac{\Sigma N_i M_i^{a+1}}{\Sigma N_i M_i} \right)^{1/a}$$

Where a is a constant. $\overline{M}_v$ depends on a as well as on the distribution of molecular weight species. For many polymers $\overline{M}_v$ is 10 – 20% below $\overline{M}_w$.

For a polydisperse polymer with the differences between the various average molecular weights increasing as the molecular – weight distribution becomes broader. Distribution of molecular weights in a typical polymer sample is shown in Figure 2.9

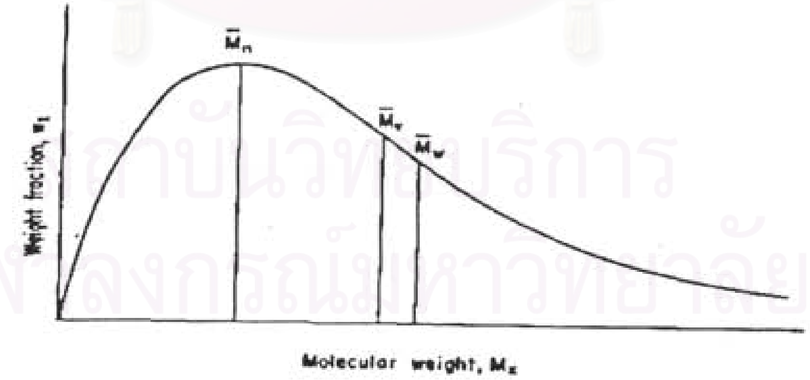


Figure 2.9 Distribution of molecular weights in a typical polymer sample

2.5.2 Molecular Weight Measurement [7]

Size exclusion chromatography (SEC), also referred to gel permeation chromatography (GPC) is the method most widely used today for determining the molecular size and molecular weight distribution.

Gel permeation chromatography (GPC) makes use of the size exclusion principle. The size of the molecule, defined by its hydrodynamic radius, can or cannot enter small pores in a bed of cross-linked polymer particles, the most common form of the stationary phase. The smaller molecules diffuse into the pores via Brownian motion (See Figure 2.10) and are delayed. The larger molecules pass by and continue in the mobile phase.

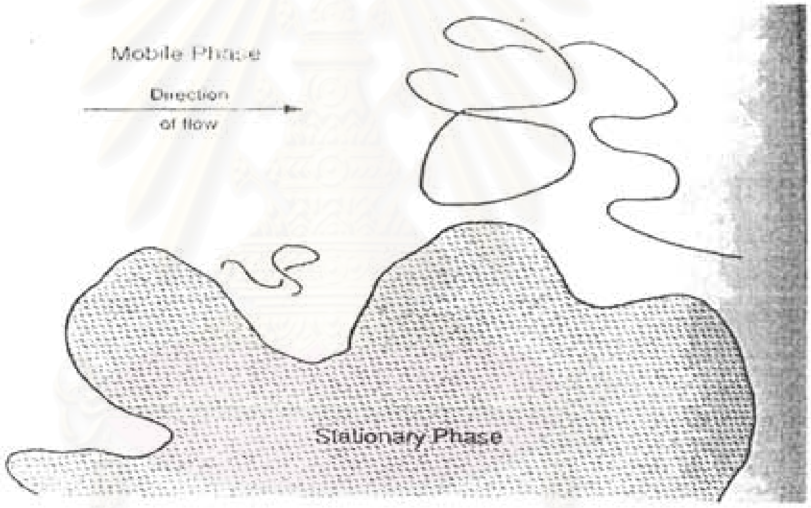


Figure 2.10 The size exclusion effect.

The instrumentation most commonly used in GPC work is illustrated in Figure 2.11. The stationary phase consists of small, porous particles. While the mobile phase flows at a specified rate controlled by the solvent delivery system, the sample is injected into the mobile phase and enters the columns. The length of time that a particular fraction remains in the columns is called the *retention time*. As the mobile phase passes the porous particles, the separation between the smaller and the larger molecules becomes greater (see Figure 2.12). While separation of polymer chains according to size remains the most important experiment, there are many other aspects, as described below.

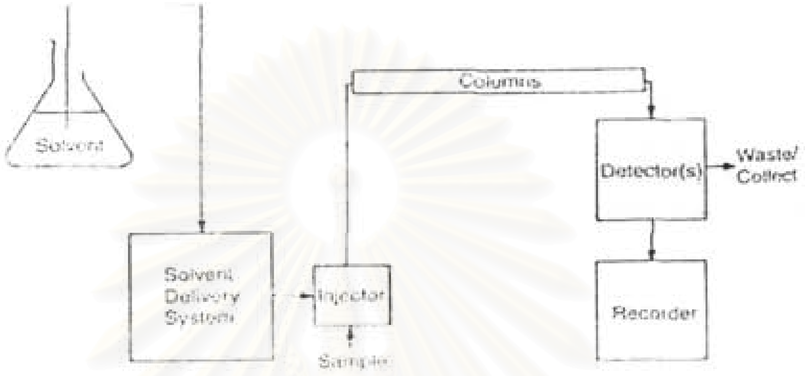


Figure 2.11 An illustration of the modules that make up GPC instrumentation.

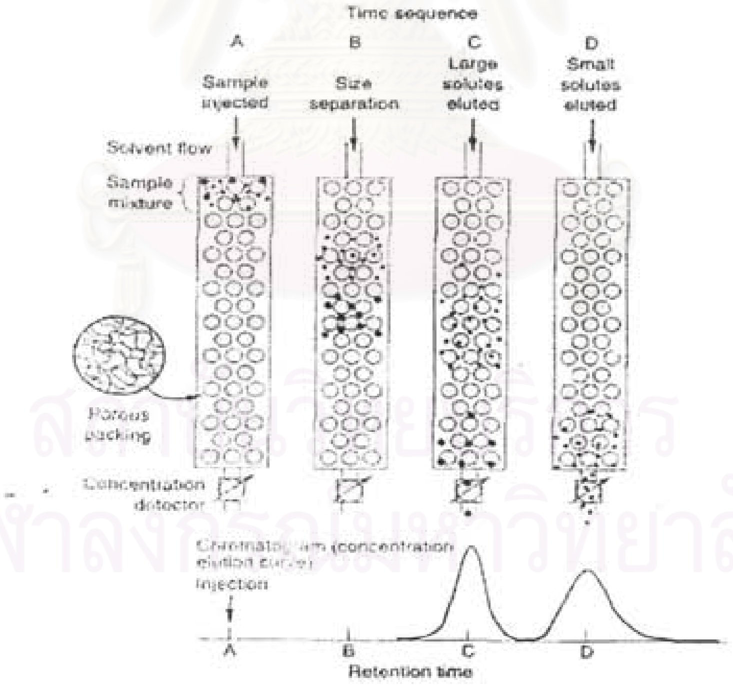


Figure 2.12 Illustration of the GPC experiment.

With the exception of proteins and a very few other macromolecules, most polymers exhibit some form(s) of heterogeneity. The most important is the molecular weight distribution (MWD), sometimes called a molar mass distribution, or polydispersity index (PDI), equal to $\overline{M}_w/\overline{M}_n$. Another type of heterogeneity involves a distribution of chemical composition, including statistical, alternating, block, and graft copolymers. Still another type of heterogeneity relates to functionality, particularly end groups. Macromolecules with terminal functional groups are usually called telechelics or macromonomers. Molecular architecture provides yet another type of heterogeneity, dictated by the shape of the chain. While most synthetic polymers form random coils, an increasing number of polymers are rod shaped, or form rings. Many polymers are branched. Each of these types of heterogeneity must be taken into account when measuring molecular weight by relative methods.

There are two very popular relative methods of characterizing polymers with one or more of the above heterogeneities. Gel permeation chromatography (GPC), also known as size exclusion chromatography (SEC) or gel filtration chromatography, is one of several chromatographic methods available for molecular weight (molar mass) and molecular weight distribution. While GPC has its greatest value for measuring the molecular weight and polydispersity of synthetic polymers, a closely related method, high performance liquid chromatography (HPLC) is more useful for separating and characterizing polymers containing functional groups, such as proteins and pharmaceutical polymers containing special active group. Both of these methods depend on distribution coefficients.

2.6 Degradation of Polymer [8]

Degradation may happen during every phase of a polymer's life such as during its synthesis, processing and use. Macromolecules are composed of monomeric units that are joined by chemical bonds to each other. The monomeric units contain chemical bonds, which either are in the main chain of macromolecule or connect various atoms or side groups to it. The dissociation energy of carbon – carbon bonds in the middle is 75 – 85 kcal/mol. The most important types of energy that causes degradation are that of the ultraviolet (UV) of sunlight. The wavelength is 300 nm and energy is about 95 kcal/mol, which is higher than most bond dissociation energy in polymers. UVB radiation that is in the range of 290 – 315 nm, is important in the degradation of polymers.

Chain scission and crosslinking lead to a change of molecular weight distribution. Oxidation and other chemical reactions in the side chains also, cause changes in chemical composition, which may result in discoloration. The dissociation energies of the various bonds in the polymer may determine the course of degradation. Table 2.3 shows bond dissociation energies of various single bonds.

Table 2.3 Bond dissociation energies of various single bonds

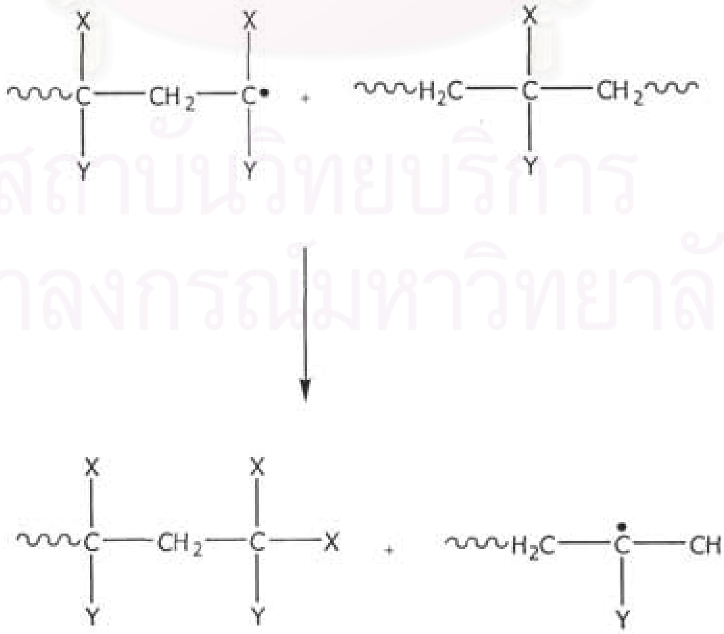
Bond	Bond dissociation energies (kcal/mol)	Bond	Bond dissociation energies (kcal/mol)
$C_2H_5 - H$	99	$C_6H_5 - CH_3$	94
$n\text{-}C_3H_7 - H$	98	$C_6H_5CH_2 - Cl_3$	72
$t\text{-}C_4H_9 - H$	91	$CH_3 - Cl$	84
$CH_2 = CHCH_2 - H$	82	$C_2H_5 - Cl$	81
$C_6H_5 - H$	103	$CH_2 = CHCH_2 - Cl$	65
$C_2H_5CH_2 - H$	83	$CH_3 - F$	108
$C_2H_5 - CH_3$	83	$CH_2H_5 - F$	106
$n\text{-}C_3H_7 - CH_3$	83	$HO - OH$	51
$t\text{-}C_4H_9 - CH_3$	81	$t\text{-}C_4H_9O - OH$	36

2.6.1 Random Chain Scission and Crosslinking

Typical examples for degradation processes with random chain scission character are hydrolysis, thermal degradation and degradation by radiation. Degradation by UV radiation usually occurs by a mechanism involves free radical formation, as follows:

a) Initiation by main chain scission is a necessary condition of depolymerization because this process produces the terminal active site capable of depropagation. In initiation by random chain scission, two macroradicals are formed with different terminal groups.

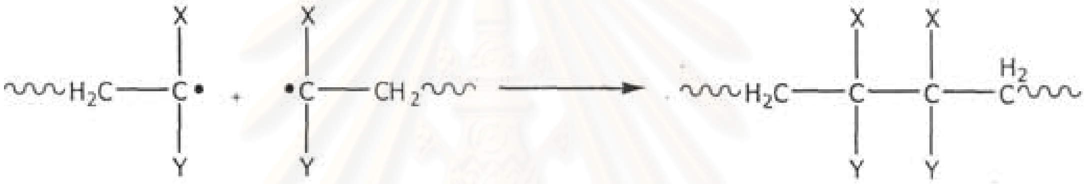
b) The terminal radicals formed in the initiation step or in the depropagation steps must be stable enough not to participate in various side reactions such as chain transfer. A very common way of chain transfer is H - abstraction from another macromolecule.



c) Termination can be a uni–or bimolecular reaction for example:

Disproportionation:

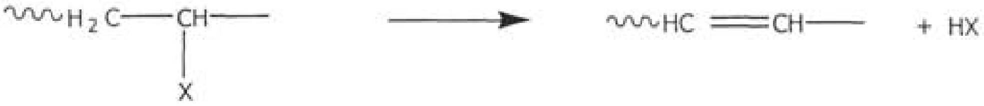
or *recombination:*



The termination products are of high molecular weight, they can participate in further reactions.

2.6.2 Degradation without Chain Scission

A very important type of polymer degradation consists of those processes, which take place without scission of the main polymer chain; characteristic of this kind of degradation is the participation of side groups in the reaction. For example, vinyl polymers of structure (-CH_2 – CHX-)$_n$ where X is an electronegative group. HX elimination is the most common form of degradation.



The elimination of side groups from polymer likes the elimination of HX from low molecular weight compounds, usually proceeds via a nonradical mechanism. Reactions of the polymer side groups are important not only with respect to degradation but also for intentional alteration of some polymers such as preparation of poly(vinyl alcohol) from poly(vinyl acetate) that is carried out by alcoholysis of the acetate groups by methanol.

2.6.3 Oxidative Degradation [9]

Although all polymers degrade at high temperatures in the absence of air, degradation is almost always faster in the presence of oxygen. Oxidation if hydrocarbons is normally auto-accelerating, i.e. the rate is slow or even negligible at first but gradually accelerates, often to a constant value. The addition of an initiator normally removes the slow auto-accelerating induction time and antioxidants and stabilizers extend it.

Ground state oxygen is unusual in that it exists in the triplet state, i.e, it is a diradical (I). Although excited singlet oxygen (II) can be important as an autooxidation initiator under certain circumstances, oxygen normally reacts with organic compounds in a radical chain reaction involving the ground state.

$\dot{O}-\dot{O}$

(I)

$O=O$

(II)

Each cyclical sequence of reactions (III) and (IV) absorbs one molecule of oxygen and leads to the formation of hydroperoxide.

$$R\bullet + O_2 \longrightarrow ROO\bullet \qquad \text{(III)}$$

$$ROO\bullet + RH \longrightarrow ROOH + R\bullet \qquad \text{(IV)}$$

Since reaction (III) is a radical pairing process it has a low activation energy and occurs with high frequency. The second step (IV) on the other hand involves the breaking of a carbon-hydrogen bond and has a higher activation energy. In most polymers at normal oxygen pressures, the rate of this step in the chain reaction determines the overall rate of oxidation.

The radical chain reaction can be initiated by any radical generators. Initiation normally occurs by thermolysis or photolysis of the hydroperoxide formed in the chain reaction.

$$2ROOH \longrightarrow RO\bullet + H_2O + \bullet OH \qquad (V)$$

$$ROOH \xrightarrow{h\nu} RO\bullet + \bullet OH \qquad (VI)$$

Since both the alkoxyl and hydroxyl radical are efficient hydrogen abstracting agents, they effectively inject new radicals into the radical chain (III), (IV) by reaction (VII).

$$\begin{array}{c} RO\bullet \\ OR \\ HO\bullet \end{array} \xrightarrow{RH} \begin{array}{c} ROH \\ OR \\ H_2O \end{array} + R\bullet \qquad (VII)$$

2.6.4 Photodegradation

Polymers have different photodegradative sensitivities to ultraviolet light at different wavelengths, as shown in Table 2.4. The maximum sensitivity of several polymers is in the range of 290 and 400 nm.

Tables 2.4 Wavelength of ultraviolet radiation at which various polymers have maximum sensitivity.

Polymer	Wavelength (nm)	kcal/mol
Styrene – acrylonitrile copolymer	290, 325	99, 88
Polycarbonate	295, 345	97, 83
Polyethylene	300	96
Polystyrene	318	90
Poly(vinyl chloride)	320	89
Polyester	325	88
Vinyl chloride – vinyl acetate copolymer	327, 364	87, 79
Polypropylene	370	77

2.6.4.1 Photo-oxidation

The term 'weathering' is used as a comprehensive description of all possible changes which may occur in polymers upon outdoor exposure. It thus embraces not only changes in mechanical behavior (tensile strength, impact strength, etc.) but also aesthetically undesirable changes such as discoloration, loss of gloss. Although moisture and humidity can have secondary effects in weathering, the primary process occurring is photo-oxidation or perhaps more accurately, photo-initiated oxidation, since, as has already been seen, the effect of light is primarily on the generation of free radicals. Light has relatively little effect on the propagating steps of the radical chain reaction.

The nature of the initiating reaction in the photo-oxidation of polymers has aroused considerable scientific controversy in recent years since 'pure' polymers do not normally contain functional groups capable of acting as sensitizing species. For example, pure hydrocarbons show no UV absorption in the spectral region found in sunlight (i.e. > 285 nm) and yet all the commercial polymers photo-oxidize readily.

It was noted that a variety of oxygen-containing groups are formed during the processing of polymers even under nominally oxygen-free conditions, due to oxygen dissolved in the polymer. By far the functional groups that are easily detected are the group of carbonyl compounds absorbing in the IR in the region 1710-1735 cm^{-1}. Some of these compounds have strong absorbance in the sun's special region and show characteristics luminescence associated with the excitation to the triplet state. The triplet states of carbonyl compounds are highly chemically reactive species and can undergo transformation in polymers as shown below

The alkyl radicals produced can react with oxygen as in reaction (III). Polymers have to be processed very severely before applicable quantities of carbonyl compounds appear since they are formed by thermolysis or photolysis of hydroperoxides. Polymers which have been subjected to very severe processing in order to produce carbonyl compounds in the polymer chain photo-oxidise much more rapidly than mildly processed polymers.

2.6.4.2 Sensitization by Pigments

A photosensitizer usually has a high absorption coefficient for ultraviolet light. The excited compound both decomposes into free radicals and initiates degradation or oxidation of polymer or transfers the excitation energy to polymer or oxygen. A good sensitizer should be easily admixed with polymer and must not decompose thermally or in the dark. Examples of photosensitizer are polycyclic aromatic compounds, quinones, nitrogen containing chromophores, inorganic metal oxides and salts such as zinc oxide (ZnO) and titanium dioxide (TiO_2).

2.7 Titanium (IV) oxide, titanium dioxide (TiO_2) [10, 11]

Pigments are widely used in polymer materials to provide characteristics to suit a particular commercial application. Inorganic and organic pigments are used primarily to impart color to the polymer while others such as silica is used to impart haze or act as an antiblocking agent. In many cases pigments can have a marked influence on the thermal and photochemical stability of the polymer material . For example, by absorbing and/or screening light energy, they can exhibit a protective effect or alternatively they may be photoactive and sensitize the photochemical breakdown of the polymer. One of the most widely used pigments in this regard is titanium dioxide, often referred to as simply "Titania".

The ability of TiO_2 to catalyze the photo-oxidation of polymer systems has received much attention in terms of their mechanistic behavior. In this regard much of the information originates from work carried out on TiO_2 in polymers, coatings and model systems. To date there are three current mechanisms of the photosensitized oxidation of polymers by TiO_2 .

1. The formation of an oxygen radical anion by electron transfer from photoexcited TiO_2 to molecular oxygen. A recent modification of this scheme involves a process of ion-annihilation to form singlet oxygen which then attacks any unsaturation in the polymer.

$$TiO_2 + O_2 \xrightarrow{h\nu} TiO_2^{+\bullet} + O_2^{-\bullet} \qquad (I)$$

$$(I) \longrightarrow TiO_2 + {}^1O_2 \qquad \text{(ion-annihilation)}$$

$$(I) + H_2O \longrightarrow TiO_2 + HO\bullet + HO_2^{\bullet}$$

$$RCH_2{=}CHR' + {}^1O_2 \longrightarrow RCH{=}CHCH(OOH)R'$$

2. Formation of reactive hydroxyl radicals by electron transfer from water catalyzed by photoexcited TiO_2. The Ti^{3+} ions are reoxidised back to Ti^{4+} ions to start the cycle over again.

$$H_2O \xrightarrow{(TiO_2)h\nu} H + e'(Aqu) + HO\bullet$$
$$[Ti^{4+}] + e' \longrightarrow [Ti^{3+}]$$
$$[Ti^{3+}] + O_2 \longrightarrow [Ti^{4+}]$$

3. Irradiation of TiO_2 creates an exciton (p) which reacts with the surface hydroxyl groups to form a hydroxyl radical. Oxygen anions which are also produced which are adsorbed on the surface of the pigment particle. They generate active perhydroxyl radicals.

$$TiO_2 \xrightarrow{h\nu} e' + (p)$$
$$OH^- + (p) \longrightarrow HO\bullet$$
$$Ti^{4+} + e' \longrightarrow Ti^{3+}$$
$$Ti^{3+} + O_2 \longrightarrow [Ti^{4+}.......O^{2-}]adsorbed$$
$$[Ti^{4+}.......O^{2-}]adsorbed + H_2O \longrightarrow Ti^{4+} + HO^- + H_2O$$

TiO_2 exists in three morphological crystalline forms, modifications; anatase, brookite and rutile. Brookite is rare and orthorhombic. The other two are tetragonal but are not isomorphous. They are also of different crystal habit; rutile forms slender, prismatic crystals that are frequently twinned, but anatase usually occurs in near regular octahedral. Structure of rutile and anatase are shown in Fig. 2.13. A summary of the crystallographic properties of the three varieties is shown in Table 2.5.

Brookite is the least stable and has never been used commercially as a pigment. Anatase and rutile exhibit different photo-activities when incorporated into a number of commercial polymers and coatings. Differences in the photo-activities of the two modifications of titania depends markedly upon the manufacturing history of the TiO_2. Anatase is generally more photo-active than rutile type. During the weathering of commercial polymers and coatings containing white pigments such as TiO_2, oxidation occurs at the surface layers of the material which eventually erodes away, leaving the pigment particles "chalking". TiO_2 pigments absorb strongly in the near UV region with anatase having a cut-off point at 340 nm and rutile at 370 nm.

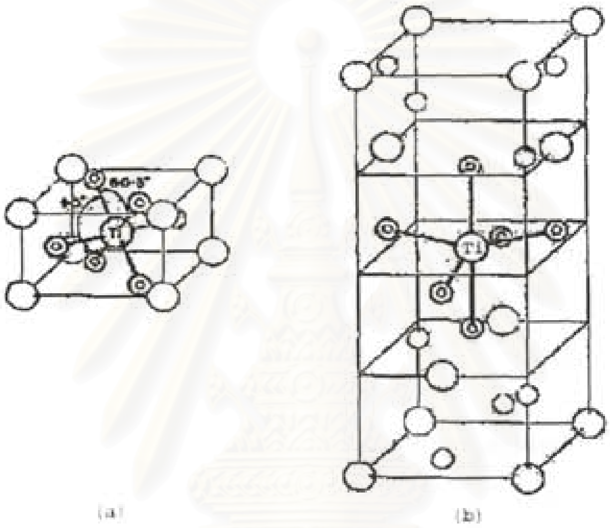


Figure 2.13 Structures of titanium dioxide (a) rutile, (b) anatase. [12]

Table 2.5 Crystallographic properties of anatase, brookite and rutile.

Mineral	Anatase	Brookite	Rutile
Crystalline	tetragonal	Orthorhombic	tetragonal
Optically	uniaxial, negative	Biaxial, positive	uniaxial, positive
Density, g/ml	3.9	4.0	4.23
Hardness, Moh's scale	5½ - 6	5½ - 6	6 - 6½
Unit cell	$D_{4a}{}^{19}4TiO_2$	$D_{4h}{}^{15}8TiO_2$	$D_{4h}{}^{14}2TiO_2$
Dimensions, Å			
A	3.758	9.166	4.584
B	-	5.436	-
C	9.514	5.135	2.953

2.8 Literature Review

Cho and Choi [13] investigated the solid-phase photocatalytic degradation of poly(vinyl chloride) (PVC)-TiO_2 composite film under the ambient air. TiO_2-embeded PVC showed highly enhanced photo-degradation. Irradiating the composite film for 300 hours under air reduced its average molecular weight by two-thirds and weight by 27%. The SEM images of the irradiated composite films showed the development of cavities around the embedded TiO_2 particles and implied that active oxygen species which were photo-generated on TiO_2 surface desorb and diffuse across a few micrometers to react with the polymer matrix.

Chen and coworkers [14] investigated titanium dioxide mediated photo-catalytic degradation of polyvinyl alcohol (PVA) under UV lamps. The results indicated that the optimum dosage of TiO_2 in the photo-degradation of PVA was 2.0 g/l. For extremely few of TiO_2, the degradation rates were lower because that the limiting factor for the low rate was the lack of required amount of the catalyst. In superfluous TiO_2, the UV was diffused by TiO_2 particles. The results also indicated that it was more effective for PVA to be degraded under acidic or alkaline condition.

Under different pH conditions, the main pathways of producing hydroxyl radical are probably different, therefore, producing rate of hydroxyl radical are different. As well as TiO_2 concentration, there was an optimum peroxide concentration on the rate of PVA destruction.

Allen and coworkers [10] studied thermal and photochemical activities of nano and micron particle grade anatase and rutile TiO_2 in monomodal metallocene polyethylene and alkyd paint film. Photo-oxidation studies on PE containing nano-particle and pigmentary grade. TiO_2 showed that in general the former are more photo-active with anatase and rutile forms exhibiting high activity. Photo-oxidation studies showed a clear demarcation between nano-particle and pigmentary grade. TiO_2 with the anatase form was more active. SEM analysis showed the formation of pits and holes formed as a consequence of oxidation of the polymer at the particle surface and subsequently spreading out from the particle.

Gesenhues [15] studied the effect of photodegradation catalyst and ultraviolet protection of TiO_2 on photodegradation of poly(vinyl chloride) with and without moisture. Moisture or water was an accelerator to oxidation reaction because the surface of TiO_2 can release hydroxyl radicals, which are more active oxidizing species than oxygen anions.

Allen and Katami [11] studied the degradation of linear low density polyethylene with TiO_2 pigments under ultraviolet light and heat. At 90°C and under ultraviolet light, all pigments (rutile, anatase) were oxidative degradation catalysts. Oxidative catalytic property of pigment was enhanced at wavelength of 365 nm. Rutile can scatter ultraviolet light at 254 nm. It does behave as UV screener and stabilize the polymer.

Angulo–Sanchez, Ortega–Ortiz and Sanchez-Valdes [16] reported the photodegradation of low–density polyethylene (LDPE) films formulated with titanium (IV) oxide acetylacetonate (TAc) and titanium dioxide pigment (TiO_2). Number–average molecular weight ($\overline{M}_n$) of LDPE with TAc decreased rapidly at short ultraviolet exposure with a tendency to level off later. LDPE with TiO_2 behaved in a similar way but showed higher values of $\overline{M}_n$ for the same exposure time. Molecular weight results suggested that there was some chain recombination at short exposure time. Elongation at break decreased when the time of ultraviolet exposure increased.

Kurian and coworkers [17] studied the degradation of natural rubber latex thread under ultraviolet radiation. The thread samples were exposed to ultraviolet radiation in the region of 290 – 350 nm for 24, 48 and 96 hours. Tensile strength of thread samples decreased when UV exposure time increased. The tensile strength of the thread having zinc diethyl dithiocarbamate (ZDEC) and zinc mercaptobenzothiazole (ZMBT) combination is lower than the thread having zinc dibutyl dithiocarbamate (ZDBC)/ZMBT, and ZDBC/ZDEC. Ultraviolet light caused considerable deterioration of the tensile strength of the thread.

Menon, Pillai and Nando [18] studied thermal degradation of natural rubber vulcanizates modified with phosphorylated cashew nut shell liquid. Thermal degradation of natural rubber occurred at 200-475°C. Degradation of natural rubber in air showed the two–stage decomposition. The first stage of degradation occurred in the temperature range of 300-420 °C. The second stage occurred in temperature range of 460–560°C. Under nitrogen atmosphere, the degradation occurred only in the temperature range of 300–420°C.

Phetphasit and Phinyocheep [19] studied degradation of purified natural rubber. There were better degradation results for natural rubber which was purified by the elimination of proteins, than the unpurified natural rubber. This may be due to the presence of non-rubber constituents which act as antioxidant, or the presence of microgels, which retard the oxidative degradation in the system. It was found that the radical initiator $K_2S_2O_8$, propanol and the temperature played important roles in the degradation .

Riyajan and coworkers [20] studied controlled photodegradation of natural rubber glove by encapsulated benzophenone (BP) and 2,6-di-*t*-butyl-*p*-cresol toluene (BHT). The efficiency of controlling photodegradation was improved by encapsulated

BP or BHT/BP. It was clearly observed that the photodegradation of NR in the presence of BP was faster than that of BHT/BP. It was found that the optimum ratio of BP:BHT for both raw and cured NRs was 1:2. It can be explained that BP accelerated photodegradation of NR films, while BHT retarded the degradation. In the case of cured NR, the encapsulated BHT/BP can effectively control the photodegradation better than the unencapsulated BHT/BP, especially, at the initial stage.

CHAPTER III

EXPERIMENTAL

3.1 Materials

1. High-ammonia natural rubber (HANR) latex
: Thai Rubber Latex and Cooperation (Thailand) Co., Ltd
2. Titanium (IV) oxide (TiO_2)
: Analytical grade; Riedel-de Haen and Degussa P25
3. Sulfur
: Chemical grade; Kijphaiboon Co.Ltd.
4. Zinc oxide
: Chemical grade; Kijphaiboon Co.,Ltd
5. Zinc diethyl dithiocarbamate (ZDEC)
: Chemical grade; Kijphaiboon Co.,Ltd
6. Potassium Laurate
: Chemical grade; Kijphaiboon Co.,Ltd
7. Potassium hydroxide
: Chemical grade; Kijphaiboon Co.,Ltd
8. Toluene
: Analytical grade; Carlo Erba
9. Methanol
: Analytical grade; Merck
10. Tetrahydrofuran
: Analytical grade; Lab-Scan
11. Gelatin from porcine skin
: Chemical grade; Fluka
12. Gum Arabic
: Chemical grade; Fluka
13. Formaldehyde solution

: Analytical grade; Lab-Scan
14. Soybean oil was obtained commercially

3.2 Equipments

1. Ultraviolet light
: Phillip, UVB 290-315 nm, 40 watt
2. UV Simulator Machine
: Q. Panel Company, 160 watt
3. Hot Plate
: Corning
4. Analytical Balance
: Mettler , model AB204-S
5. Centrifuge
: MSE, model Centaur 2
6. Mechanical Stirrer
: IKA Labortechnik, model RW 20DZM.n
7. Fourier Transform Infrared Spectrophotometer (FT-IR)
: Perkin Elmer, Spectrum One
8. Scanning Electron Dispersive X-ray Microscopy (SEM-EDX)
: JEOL, model JSM-5800LV
9. Gel Permeation Chromatrography (GPC)
: Waters, model 150-CV, PLgel column, RI detector
10. Tensile Tester
: LLOYD , model LLOYD500,UK
11. Mastersizer S
: Malvern , model Mastersizer S, UK
12. X-ray Diffractometer
: JEOL, model JDX-8030
13. Attenuated Total Reflection Infrared Spectrophotometer (ATR-IR)

: Bruker, model Vector 33

14. Ubbelhode Viscometer

: Sibata, model 2613-001

3.3 Procedure

3.3.1 Preparation of Microparticles Containing TiO_2 Powder

Gelatin and gum arabic solution 5%(w/v) were prepared separately at 47°C by dissolving 2.5 g gelatin or gum arabic in 50 mL deionized water. TiO_2 powder (1.5 g) was mixed with 10 mL soybean oil in 600 mL beaker at room temperature. Gelatin solution 5%(w/v) 50 mL at 47°C was added into the mixture. The emulsion was homogenized at 14,000 rpm for 2 min. Gum arabic solution 5%(w/v) 50 mL at 47°C was added into the suspension. pH of the suspension was reduced to 3.5 by 10% acetic acid followed by an addition of 80 mL warm water (47°C). The suspension was homogenized at 14,000 rpm for 30 min. The system was cooled down to 5°C and left for 30 min before 3 mL formaldehyde was added. 10% NaOH was added to the suspension to elevate pH to 8.5. After agitation continued for 30 min, the temperature was increased to 50°C. Microparticles were subjected to freeze–drying for 1 day before characterized by scanning electron microscopy.

3.3.2. Purification and Determination of Gel Content of Natural Rubber

HANR latex 5 mL was poured into a glass mold and covered with aluminum foil. The latex was dried in the dark at ambient temperature for 2 days. The dried latex sheet was dissolved in toluene. The solution was kept without stirring in the dark at ambient temperature for 3 days. The gel fraction collected as a bottom fraction by vacuum filtration. The solution fraction of rubber was collected as a sol fraction, which was later precipitated with an excess amount of methanol. The dried solid rubber obtained after precipitation was called fractionated rubber.

3.3.3 Degradation of Natural Rubber Solution in the Presence of TiO_2 under Accelerated Condition

The rubber solution (5.0×10^{-3} g/mL) was prepared by dissolving 1.0 g of fractionated rubber in 200 mL toluene, which was stirred for 2 days in the dark at ambient temperature. TiO_2 powder was added into 100 mL beaker containing 30 mL rubber solution and a magnetic stirrer to obtain 0.5, 1, 10, 20 %w/w. The solution was kept stirring continuously while exposed to ultraviolet light for a desired period of time. The solution was then centrifuged and filtered to separate TiO_2 powder. Solid rubber was obtained by precipitating the rubber solution in an excess amount of methanol and dried under vacuum for 24 h.

3.3.4 Degradation of Unvulcanized Natural Rubber Sheet Filled with TiO_2 or TiO_2 Microparticles under Accelerated Condition

TiO_2 powder or TiO_2 microparticles was mixed with 100 g HANR latex by stirring for 2 h. The mixture was poured into a glass mold and covered with aluminum foil. The latex was dried in the dark at ambient temperature for 2 days. The rubber sheets were tested for degradability by UV simulator machine and sunlight for a desired period of time. The irradiated rubber sheet was dissolved in 200 mL toluene. The solution was kept without stirring in the dark at ambient temperature for 2 days. The solution was then filtered by vacuum filtration to remove TiO_2 powder along with the gel fraction. After the removal of TiO_2 or TiO_2 microparticles, the solid rubber was obtained by precipitating the rubber solution in an excess amount of methanol and dried under vacuum for 24 h.

3.3.5 Molecular Weight Determination of Natural Rubber by Gel Permeation Chromatography

15.0 mg of irradiated solid rubber was dissolved in 5 mL of tetrahydrofuran (THF) and shaken for 24 h. Rubber solution was then subjected to molecular weight determination using Gel Permeation Chromatography fitted with PL gel column. The column set was calibrated using polystyrene standard. Tetrahydrofuran was used as the solvent with a flow rate of 1 mL/min at 30°C.

3.3.6 Molecular Weight Determination of Natural Rubber by Solution Viscometry

The stock rubber solution (2.1×10^{-3} g/mL) was prepared by dissolving fractionated rubber 0.2 g in 100 mL dried toluene, which was stirred for 2 days in the dark at ambient temperature. 6 mL of the stock rubber solution and 2 mL toluene (1.6×10^{-3} g/mL) were added into Ubbelhode tube at 25°C. The time at which the solution moved down with a predetermined distance was measured. The same procedure was repeated for each concentrations by a stepwise addition of 2 mL toluene to obtain rubber concentration of 1.3×10^{-3}, 1.1×10^{-3} , 9×10^{-4} and 8×10^{-4} g/mL, respectively. Viscosity–average molecular weight (M_v) was determined using Mark–Houwink equation where $K = 50.2 \times 10^{3}$ mL/g, $a = 0.667$, $T = 25°C$.

3.3.7 Preparation of Vulcanized Natural Rubber Sheet filled with TiO_2

Pre-vulcanized natural rubber latex was prepared from concentrated HANR latex having 60% dry rubber content (DRC). Ingredients used for sulfur pre-vulcanization were obtained in dispersion form. Each ingredient was prepared by grinding its original form in water for 24 h in a ball mill. The formulation is shown in Table 3.1

Table 3.1 Formulation for sulfur pre-vulcanization

Ingredient	Composition (phr)
60 % HANR	100
10 % Potassium hydroxide	0.50
20 % Potassium laurate	0.25
50 % Sulfur	0.75
50 % Zinc diethyl dithiocarbamate (ZDEC)	1.00
50 % Zinc oxide (ZnO)	1.00

Sulfur, ZDEC and ZnO in the form of 50% dispersion were added to a 1-L beaker containing HANR latex at 60°C under continuous stirring for 2 h. 25% TiO_2 dispersion was then added into the latex mixture. The pre-vulcanized latex was filtered to remove non-dispersed material and left overnight in the dark at ambient temperature.

A test tube with 2-cm diameter was dipped into the pre-vulcanized latex for 45 sec to obtain compounded rubber sheet with the thickness of 0.1-0.2 mm. The compounded rubber sheet was dried in the dark at ambient temperature. The vulcanized sheets were prepared by heating the compounded sheet at 100°C for 1 h. The vulcanized sheets were exposed to UV for a desired period of time (4-24 h). Photooxidative degradation was studied by monitoring mechanical properties.

3.3.8 Mechanical Testing

The tensile strength and elongation at break of vulcanized rubber sheets were measured using a tensile tester according to ASTM D 412-87. The condition for tensile testing is illustrated in Table 3.2. A dumbbell test piece (type C) has a dimension as shown in Figure 3.1.

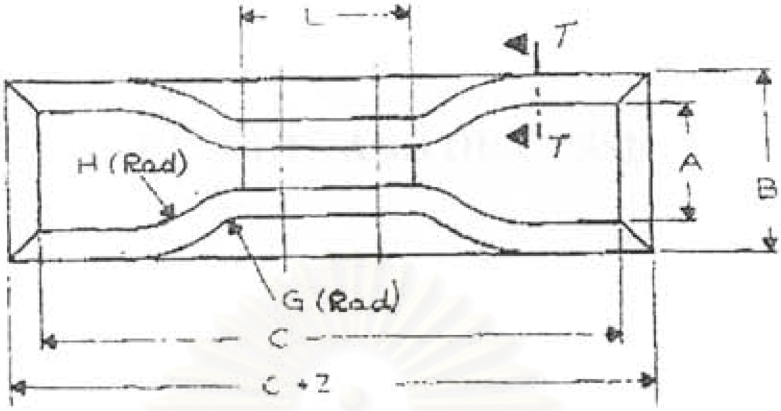


Figure 3.1 Schematic of tensile specimen.

Table 3.2 Dimension of dumbbell test pieces (type C) prepared for mechanical testing

Dimension	(mm)
(A) Width of ends	25 ± 1
(C) Overall length (minimum)	115
(G) Transition radius outside	14 ± 1
(H) Transition radius inside	25 ± 2
(L) Length of narrow portion	33 ± 2

Table 3.3 The condition for tensile testing

Temperature	25 °C
Humidity	60%
Crosshead speed	500.00 mm/min
Gauge length	20.0 mm

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Preparation of Microparticles Containing TiO_2

Microparticles were prepared by microencapsulation utilizing phase separation from an aqueous solution system. When pH is lower than 4.8, 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 TiO_2 powder during coacervation process. For this experiment, the speed of 14,000 rpm was chosen. After being recovered by freeze-drying, TiO_2-containing particles were characterized by SEM-EDX. As can be seen from SEM micrograph (Figure 4.1), a particle with an average diameter of 30 μm appeared as agglomeration of smaller particles. From the micrograph in Figure 4.2 with higher magnification, each agglomerated particle consists of smaller particles with an average diameter of 0.3 – 0.5 μm. This data agree with the previous work reported earlier by Palmieri and coworkers about the fact that freeze-drying is not an effective drying process.[21] 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 contain TiO_2. It is also plausible that some particles are uncoacervated excess of colloidal polymers without TiO_2. In order to estimate the amount (%w/w) of 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.

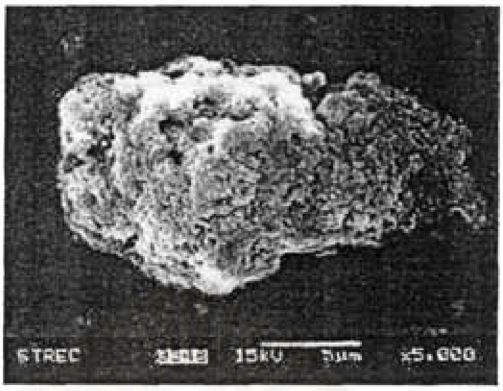


Figure 4.1 SEM micrograph of an agglomerated microparticle containing TiO_2 obtained after freeze-drying (x 5,000).

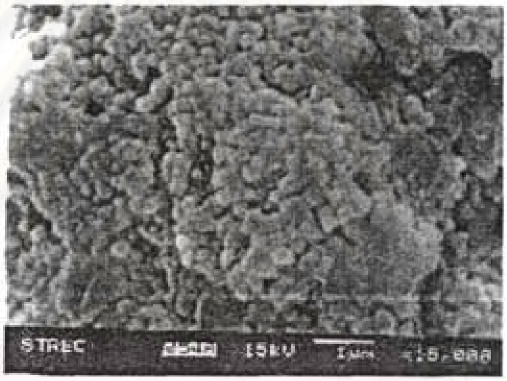


Figure 4.2 SEM micrograph of an agglomerated microparticle containing TiO_2 obtained after freeze-drying (x 15,000).

The existence of TiO_2 in the microparticles was also confirmed qualitatively by EDX data as indicated in Figure 4.3. A characteristic peak of titanium appeared around 4.25 eV. The atomic composition result indicated that the particles contained 0.1% of titanium. The principal crystalline structure of TiO_2 used in this study was proven to be anatase as confirmed by X–ray diffractogram structure shown in Figure 4.4. This form of TiO_2 is the most active form that exhibits oxidative catalytic behavior.

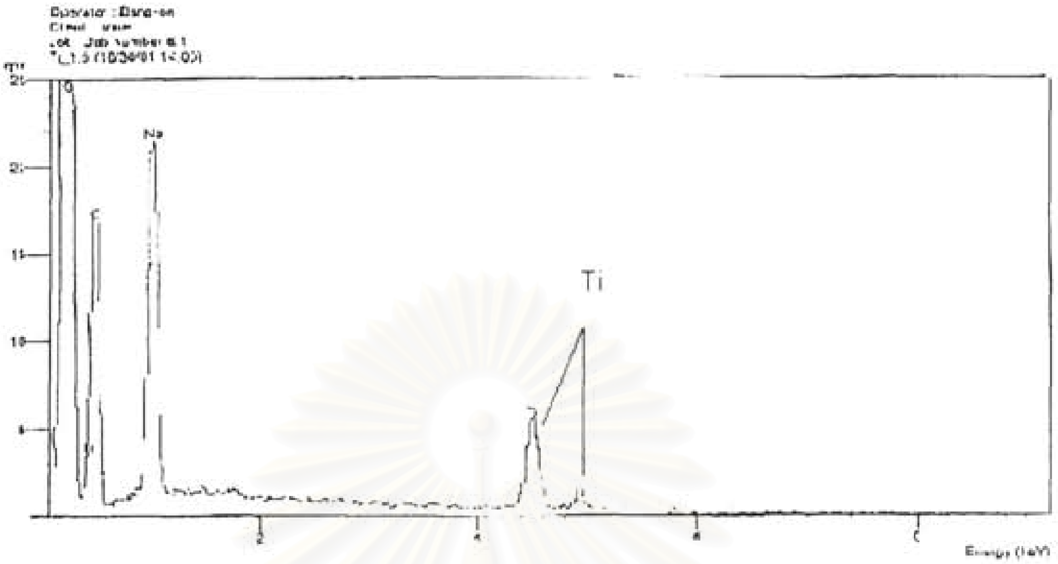


Figure 4.3 EDX of encapsulated TiO_2 microparticles

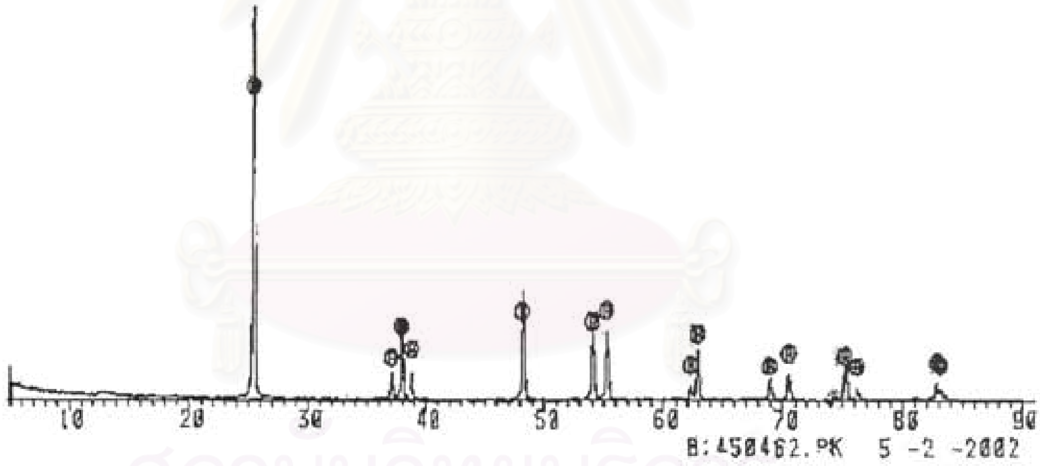


Figure 4.4 X-ray diffractrogram of TiO_2

4.2 Degradation of Natural 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. 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 4.5 shows number-average molecular weight ($\overline{M}_n$) of natural rubber after exposed to UV light for 5-150 min. Initial molecular weight ($\overline{M}_n$) 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. $\overline{M}_n$ 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.

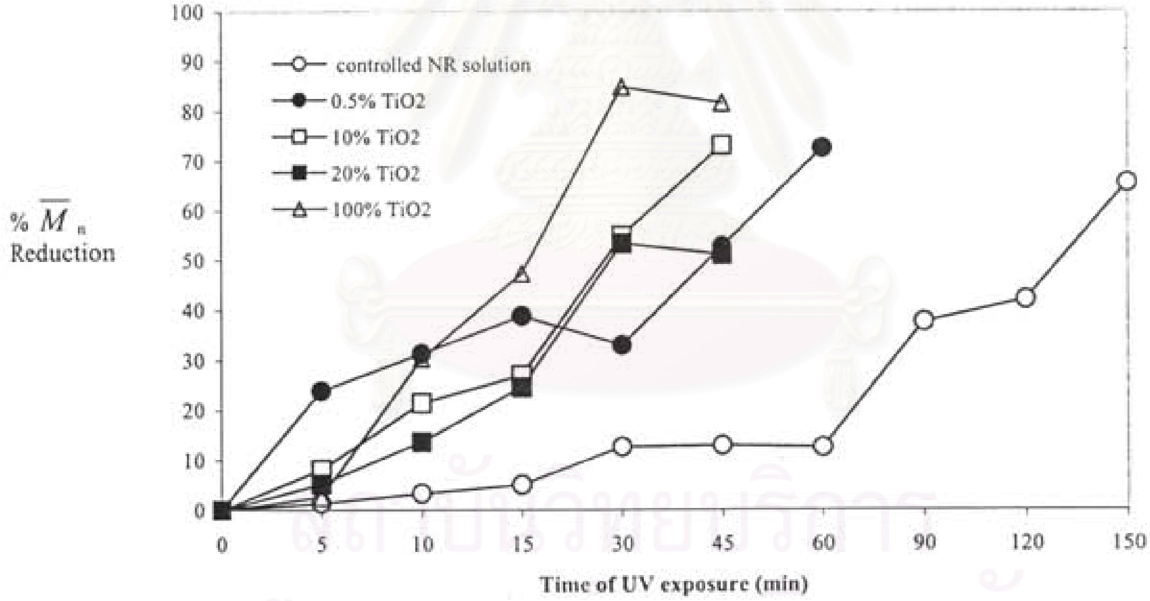


Figure 4.5 % Reduction of number-average molecular weight of natural rubber solution after UV exposure under accelerated condition.

Figure 4.5 also 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% decreased while that of the rubber solution containing 0.5 %w/w TiO_2 was only 53% reduced. The rate of degradation seems to depend upon the exposure time. The rubber solution containing 0.5 %w/w TiO_2 showed a 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. This is probably implied that TiO_2 was not distributed evenly during the first 10 minutes. TiO_2 powder may agglomerate and resulted in an 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 4.6 (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 4.6 (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.

4.3 Degradation of Unvulcanized Natural Rubber Sheets Containing TiO_2

The effect of TiO_2 on oxidative degradation of natural rubber in solid phase was also investigated. As shown in Figure 4.7, $\overline{M}_n$ of natural rubber sheet containing 0.5 %w/w TiO_2 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.

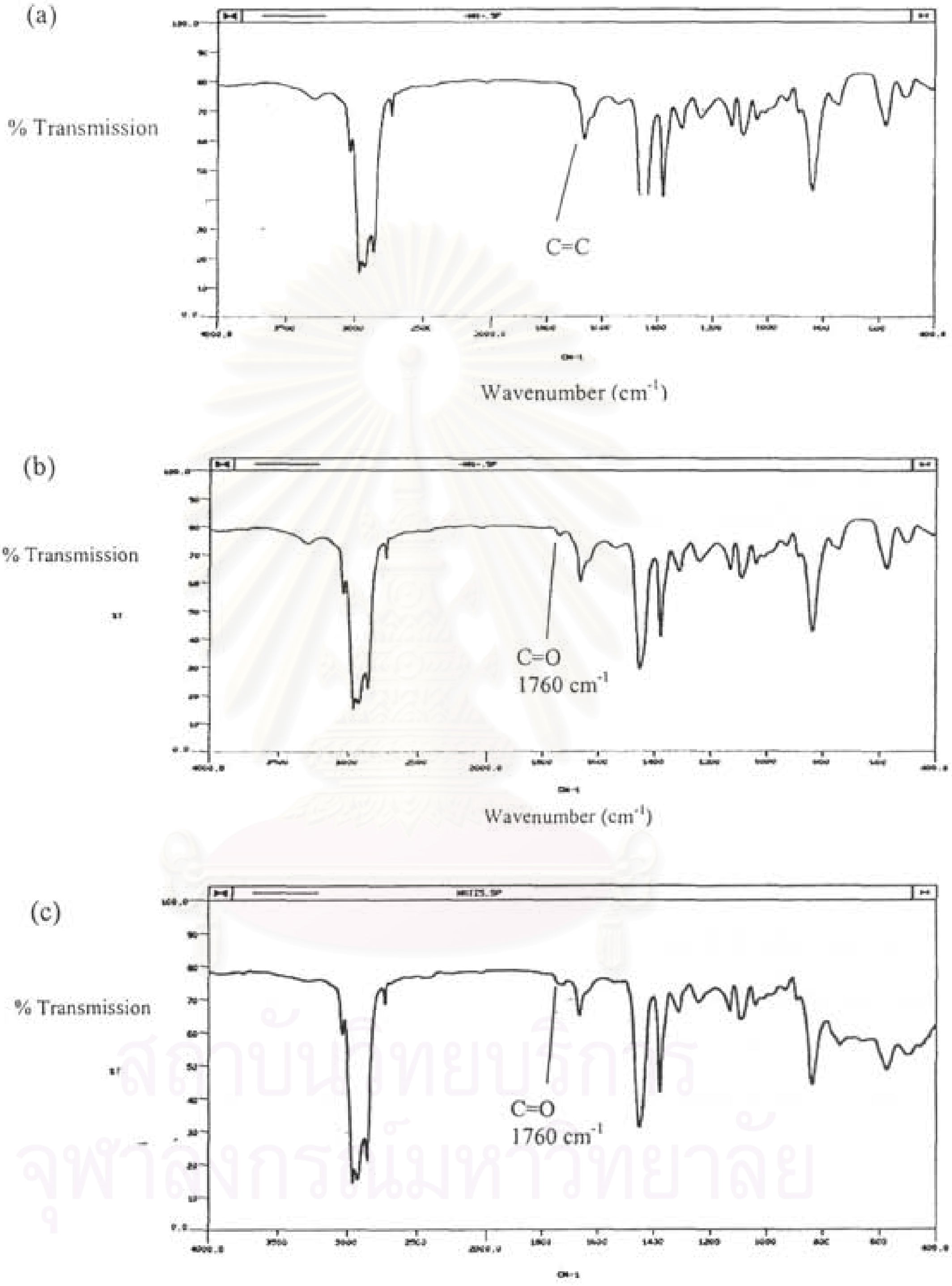


Figure 4.6 FT-IR spectra of (a) controlled natural rubber solution before UV exposure, (b) controlled natural rubber solution without TiO_2 and (c) natural rubber solution with TiO_2 after UV exposure for 30 min under accelerated condition.

Interestingly, no solid rubber can be precipitated from the solution after 12 h of UV exposure implying that the degradation was so extensive that the molecular weight of natural rubber became very low. The degradation of natural rubber sheets containing TiO_2 was less extensive than the controlled natural rubber when the amount of TiO_2 added was more than 0.5 %w/w. More importantly, the rate of degradation was declined when the amount of TiO_2 was increased.After 8 h of UV exposure, $\overline{M}_n$ of natural rubber sheet containing 10 %w/w TiO_2 was only 3% decreased, while those of natural rubber sheets containing 1% and 5 %w/w TiO_2 were 28% and 27 % decreased, respectively.

This data clearly indicated that TiO_2 acts as a stabilizer rather than a photocatalyst when a certain amount of TiO_2 was incorporated (> 0.5 %w/w). Sensitizing effect of TiO_2 was suppressed due to two possible reasons. Firstly, agglomeration of TiO_2 in solid phase reduced interfacial area between TiO_2 and natural rubber matrix. Photooxidative species generated on TiO_2 surface which include oxygen anion and hydroxyl radical cannot sufficiently desorb from TiO_2 surface to natural rubber matrix. Consequently, photocatalytic process was inhibited. Secondly, the higher amount of TiO_2, the better it can scatter out the incident light. As a result, the TiO_2-natural rubber sheet was somewhat protected from degradation by UV irradiation.

Stabilizing efficiency of TiO_2 was directly proportional to the amount of TiO_2. After 12 h of UV exposure, $\overline{M}_n$ of natural rubber with 10 %w/w TiO_2 was only 22% decreased, whereas that of natural rubber sheet comprising 1 %w/w TiO_2 was 45% reduced. According to Figure 4.8, a similar trend was observed when natural rubber sheets filled with TiO_2 were exposed to sunlight for 20 h.

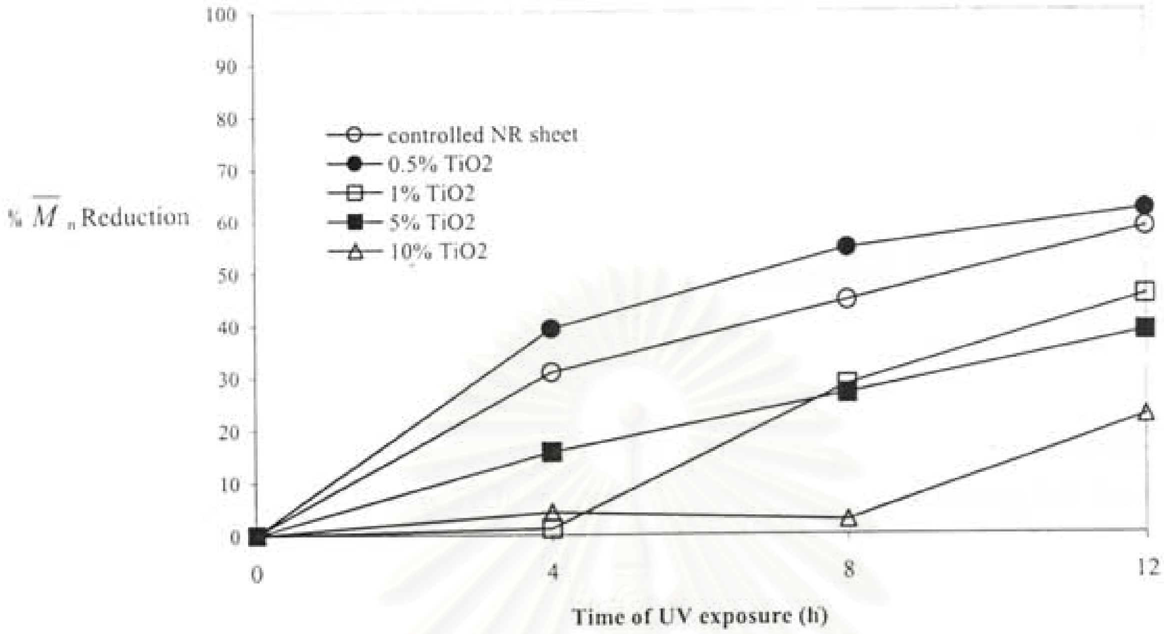


Figure 4.7 % Reduction of number-average molecular weight of natural rubber sheet as a function of time after UV exposure under accelerated condition.

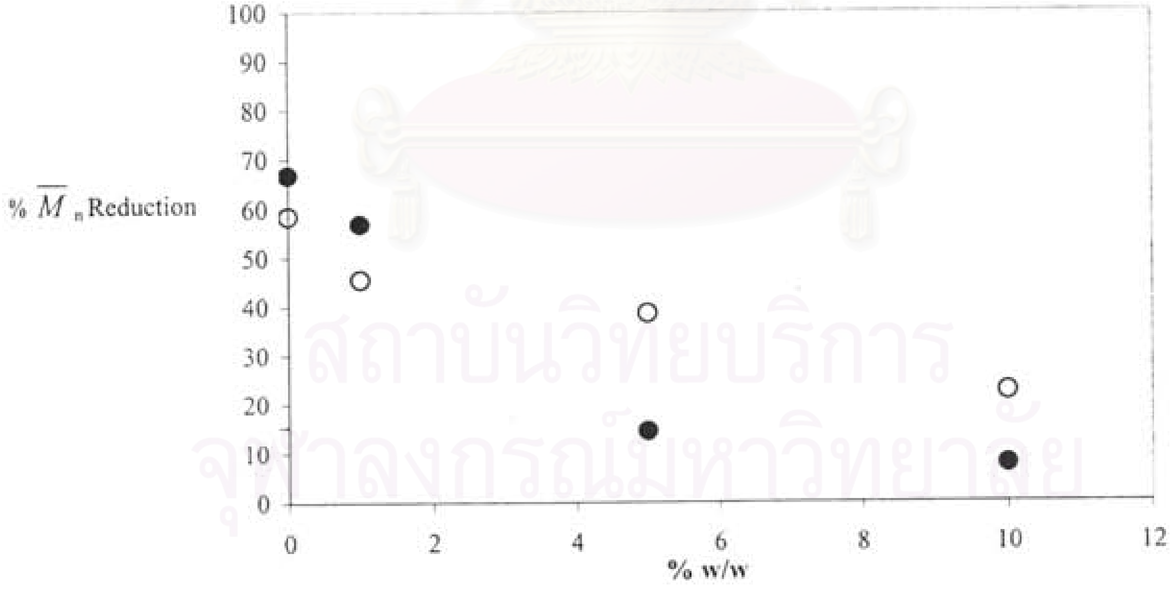
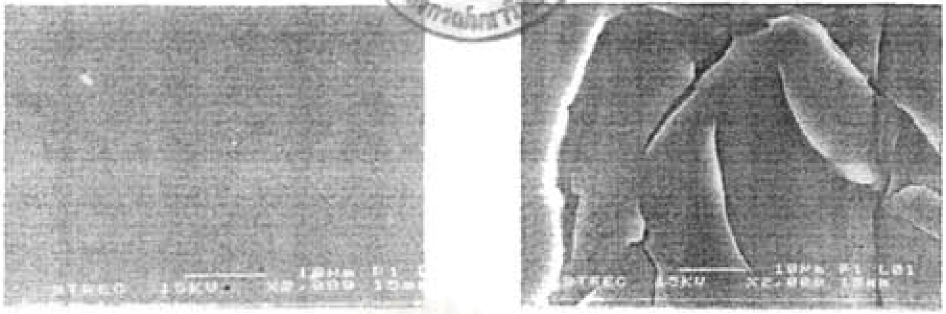


Figure 4.8 % Reduction of number-average molecular weight of natural rubber sheet as a function of TiO_2 after 12 h of UV exposure (○), 20 h of sunlight exposure (●).

SEM micrographs in Figure 4.9 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 be able to reflect the UV light having the wavelength in the range of 290-315 nm (0.29-0.32 µm). It is worth noting that TiO_2 particles do not homogeneously appear on the surface of the surface of natural rubber sheets containing 0.5 %w/w. Some area is lack of TiO_2 particles. In contrast, TiO_2 particles appeared all over the surfaces of natural rubber sheets containing 20 %w/w. Presumably, stabilizing effect of TiO_2 can also be demonstrated by the appearance of the surface of natural rubber sheets. If the surface crack is regarded as a sign of degradation, the extent of degradation of natural rubber sheet containing 20% w/w TiO_2 is apparently less than that containing 0.5 %w/w TiO_2 and the controlled natural rubber sheets.

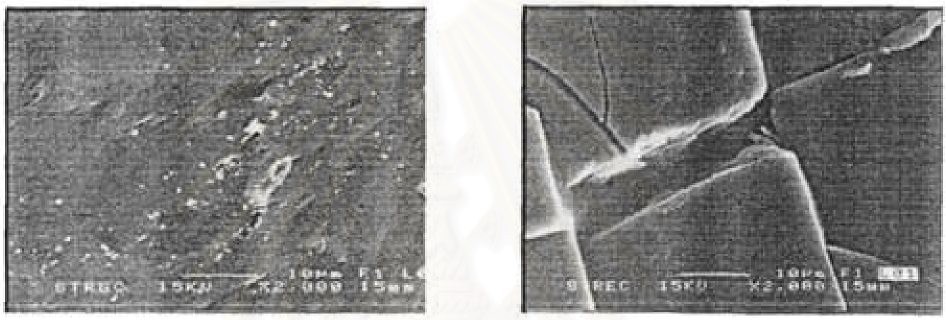
The other evidence that can be used to support the assumption that TiO_2 incorporated in natural rubber sheet helps reflecting the light and stabilizes the sheet is the opacity of the unvulcanized natural rubber sheets filled with TiO_2. Figure 4.10 shows the physical appearance of unvulcanized natural rubber sheets 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.

To determine the influence of TiO_2 particle size on an efficiency of photo-catalytic degradation, natural rubber sheets with 0.5% and 1% w/w TiO_2 were prepared from two different sizes of TiO_2. 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. The percentages reduction of $\overline{M}_n$ of natural rubber sheets are shown in Figure 4.11. After 8 h of UV exposure, $\overline{M}_n$ of natural rubber sheet with 0.5% w/w TiO_2-Degussa-P25 was 33% reduced but that of natural rubber sheet with TiO_2-Riedel was 54 % decreased. Difference in catalytic efficiency between two types of TiO_2 was reduced when the amount of TiO_2 was increased to 1% w/w. This data suggested that the catalytic activity of TiO_2 -Degussa P25 whose size supposed to be very small was not better than that of TiO_2-Riedel.



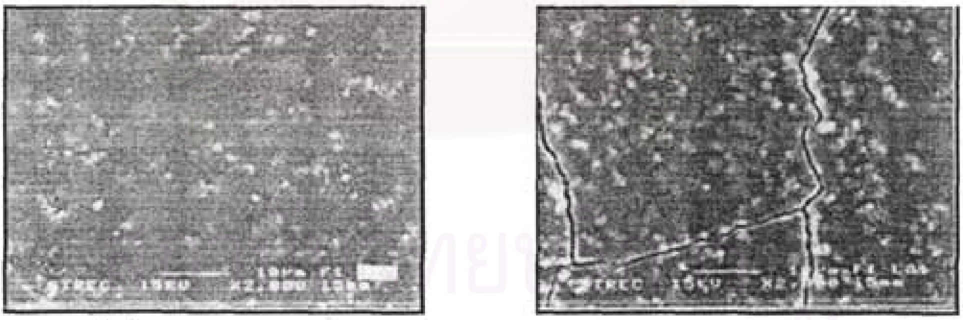
Unvulcanized NR before UV exposure

Unvulcanized NR after UV exposure for 8h



Unvulcanized NR with 0.5% TiO_2 before UV exposure

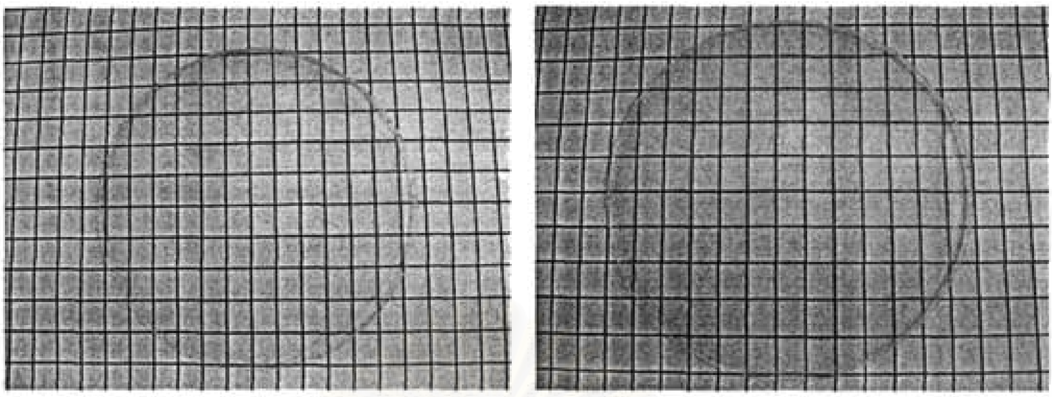
Unvulcanized NR with 0.5% TiO_2 after UV exposure for 8h



Unvulcanized NR with 20% TiO_2 before UV exposure

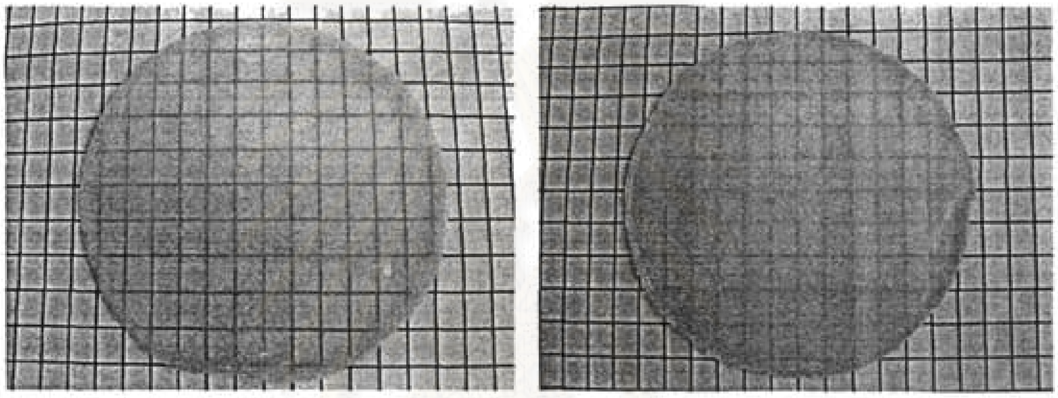
Unvulcanized NR with 20% TiO_2 after UV exposure for 8 h

Figure 4.9 SEM micrographs of unvulcanized natural rubber sheets with and without TiO_2 before and after UV exposure under accelerated condition.



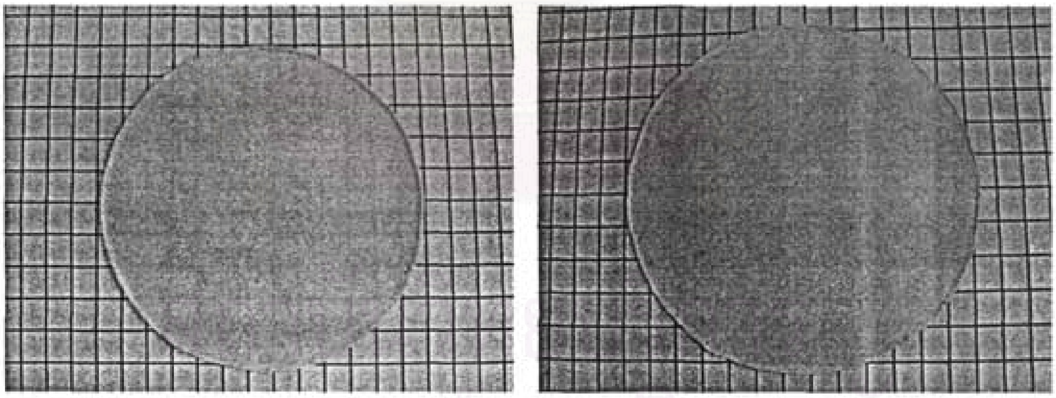
Unvulcanized NR

Unvulcanized NR with 0.1 % TiO_2



Unvulcanized NR with 0.5 % TiO_2

Unvulcanized NR with 1% TiO_2



Unvulcanized NR with 5 % TiO_2

Unvulcanized NR with 10 % TiO_2

Figure 4.10 Physical appearance of unvulcanized natural rubber sheets with and without TiO_2 before UV exposure.

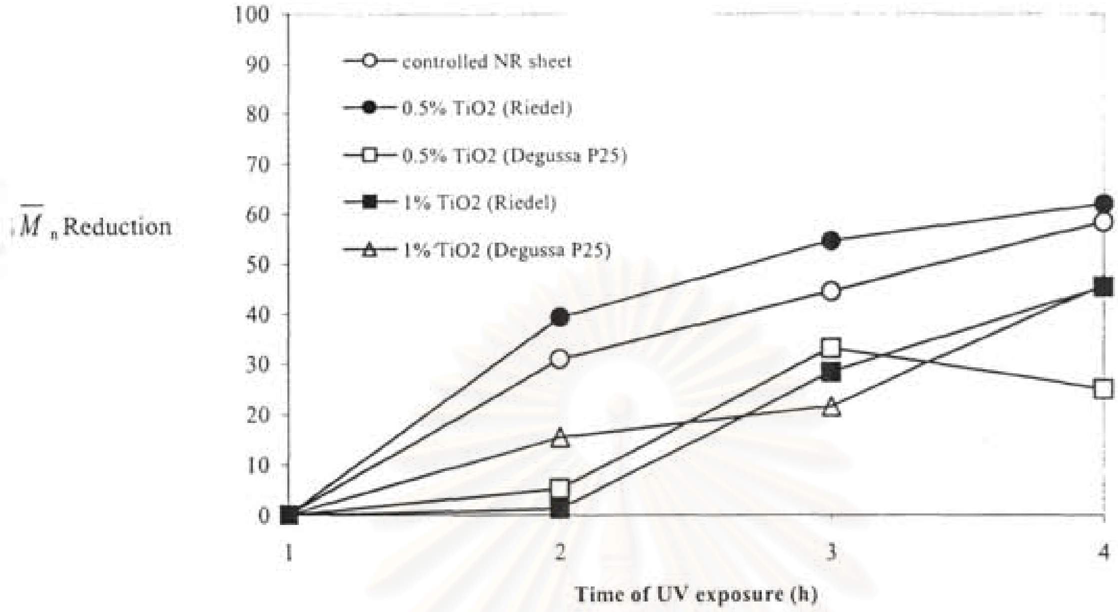


Figure 4.11 % Reduction of number-average molecular weight of natural rubber sheets containing TiO_2-Riedel or TiO_2-Degussa P25 after UV exposure under accelerated condition.

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 4.12. This implies that the TiO_2-Degussa P25 is highly susceptible to agglomeration in solution. Perhaps, this is the reason why TiO_2–Degussa P25 was not so effective in catalyzing photodegradation of natural rubber. The aggregation of both TiO_2–Riedel and TiO_2–Degussa P25 in natural rubber matrix was demonstrated by SEM micrographs. (Figure 4.13) The average aggregated size of TiO_2-Degussa P25 appears slightly larger than that of TiO_2 – Riedel. This evidently agrees well with the data obtained from particle size analysis.

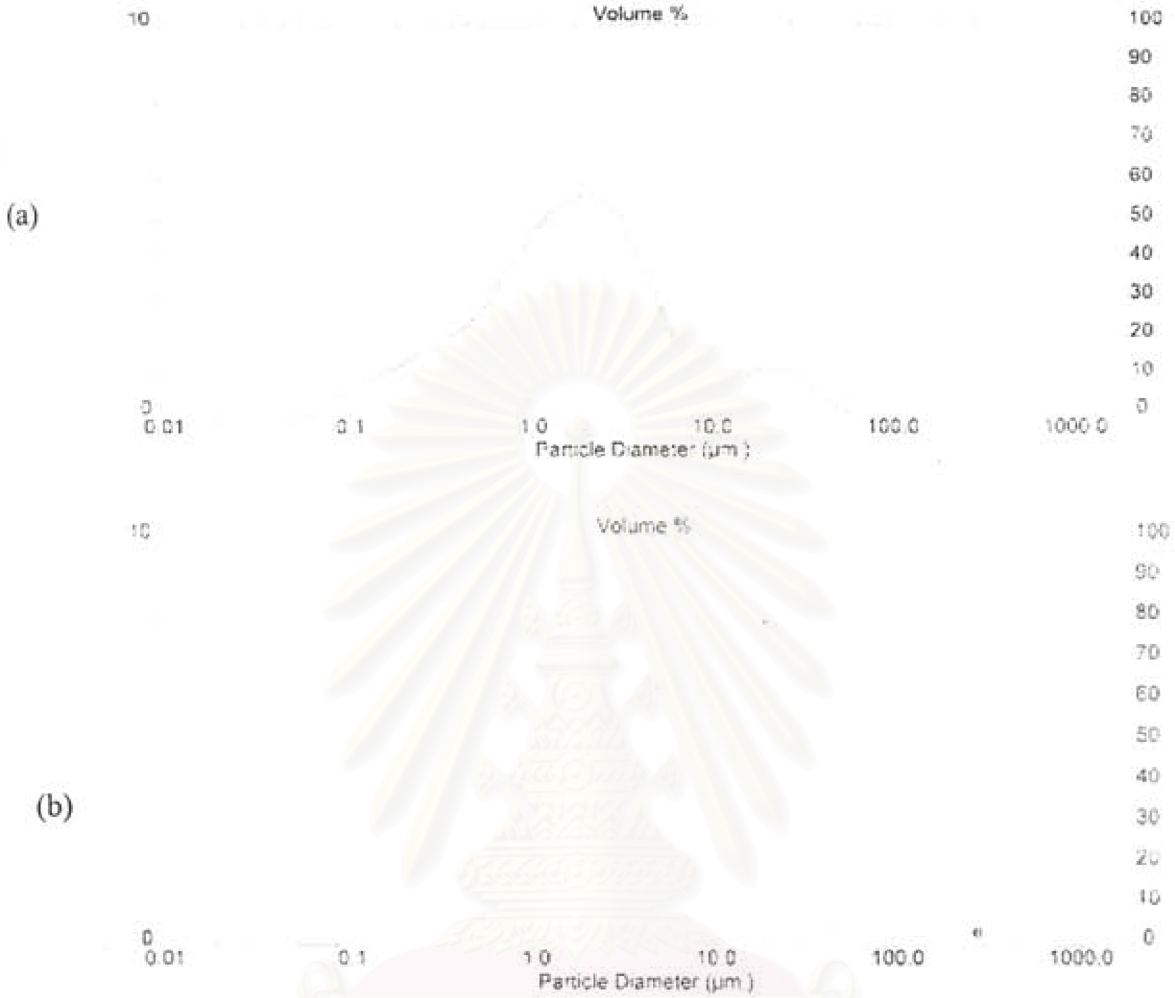
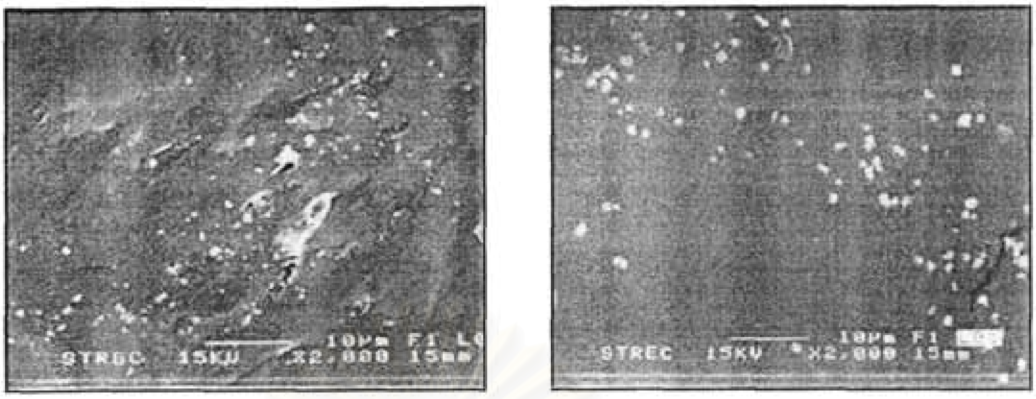


Figure 4.12 Particle size distribution of (a) TiO_2-Riedel and (b) TiO_2-Degussa P25.



(a) (b)

Figure 4.13 SEM micrographs of natural rubber sheets with (a) 0.5% w/w TiO_2 -Riedel and (b) 0.5% w/w TiO_2-Degussa P25.

4.4 Degradation of Unvulcanized Natural Rubber Sheets Containing TiO_2 Microparticles

Because the degradation of natural rubber in solid phase is most efficient in the presence of 0.5%w/w TiO_2, we desire to conduct a comparative study to investigate the degradation of natural rubber sheet containing 0.5%w/w TiO_2 microparticles. From Figure 4.14, viscosity-average molecular weight of natural rubber, natural rubber containing TiO_2 powder and natural rubber containing TiO_2 microparticles were reduced after 1 h exposure. Marginally greater extent of degradation was observed for natural rubber sheets containing 0.5%w/w TiO_2 powder (50% decreased) and 0.5%w/w TiO_2 microparticles (45% decreased) as compared to the controlled natural rubber without TiO_2 (40% decrease). Interestingly, it was observed that the extent of degradation of natural rubber containing TiO_2 microparticles became greater than the one containing TiO_2 powder after 2 h. This indicated that the encapsulation of TiO_2 suppressed the rate of degradation as compared to the direct addition of TiO_2 powder only at an early stage. We explain the degradation of natural rubber containing TiO_2 powder being lower than the one containing TiO_2 microparticles as a result of ultraviolet reflection of TiO_2 powder as previously described.

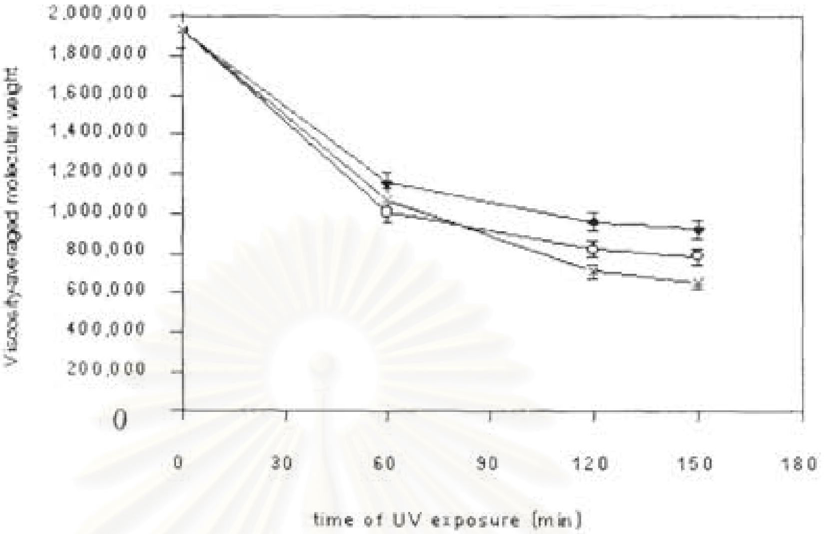


Figure 4.14 Viscosity-average molecular weight of natural rubber sheets after exposed to UV light for 120 min: natural rubber (◆), natural rubber + 0.5%w/w TiO_2 powder (○), natural rubber + 0.5%w/w TiO_2 microparticles (×).

A similar trend of degradation after exposure to sunlight (Figure 4.15) was observed for natural rubber sheets containing 0.5%w/w TiO_2 powder and 0.5%w/w TiO_2 microparticles. The sheets containing TiO_2 powder seem to be more stable than the ones containing TiO_2 microparticles due to more efficient UV reflection of TiO_2 powder than the encapsulated TiO_2 especially after long exposure. The molecular weights of all samples were unexpectedly decreased to approximately the same value (M_v = 80,000) after 4 days of exposure. We would like to comment that all samples were unvulcanized. It is then possible to observe such a trend due to the damage of natural rubber by a combination of heat and sunlight. Hence, the extent of degradation became independent of TiO_2 incorporation. Due to the insignificant difference between natural rubber sheets containing 0.5%w/w TiO_2 powder and 0.5%w/w TiO_2 microparticles, we desire not to conduct any further experiments using TiO_2 microparticles in vulcanized natural rubber which will be discussed in the next section.

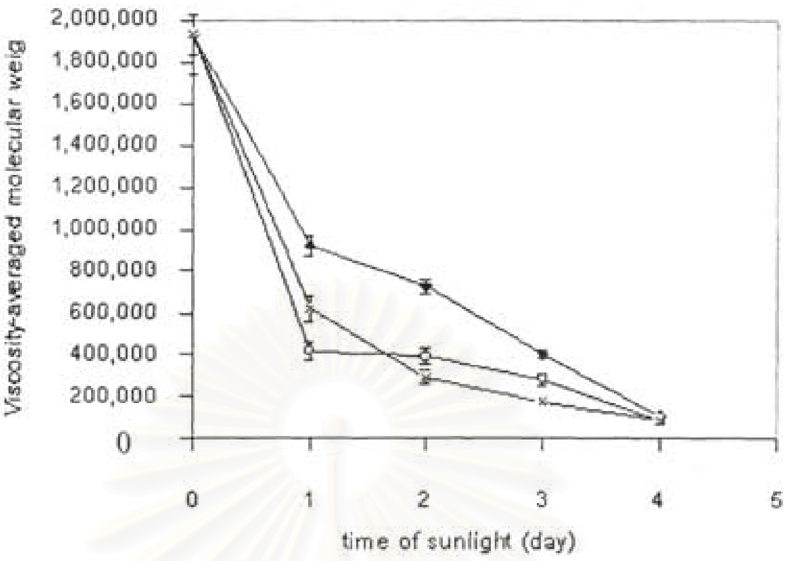


Figure 4.15 Viscosity-average molecular weight of natural rubber sheets after exposed to sunlight for 1 – 4 days : natural rubber (◆), natural rubber + 0.5%w/w TiO_2 powder (O), natural rubber + 0.5%w/w TiO_2 microparticles (×).

4.5 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 4.16 and 4.17 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 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.

Figure 4.16 obviously indicated that the higher content of TiO_2 increased the stability of vulcanized natural rubber sheet. 12 h and 20 h of UV exposure time were required to reduce the original tensile strength (21 MPa) to about 2 MPa for 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.

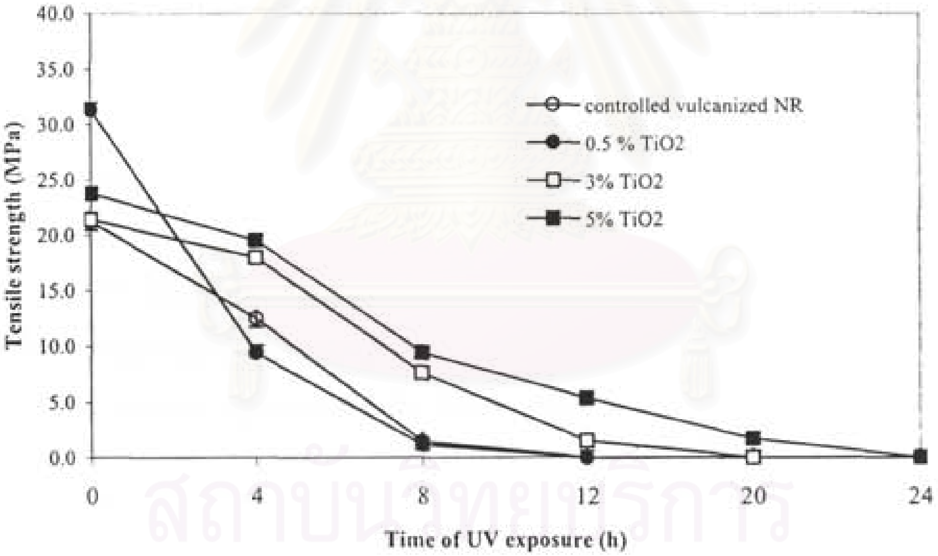


Figure 4.16 Tensile strength of vulcanized natural rubber sheet after exposed to UV under accelerated condition.

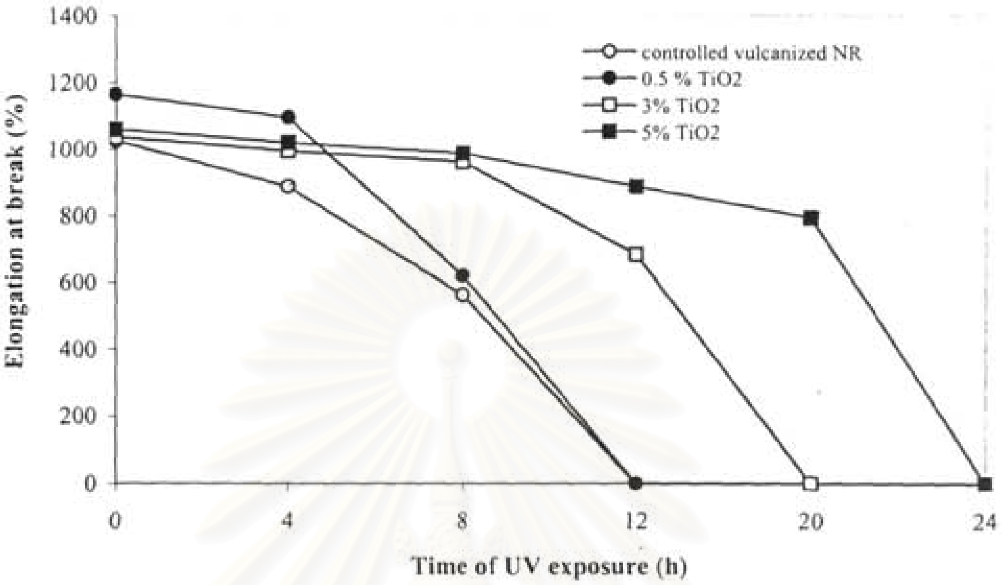
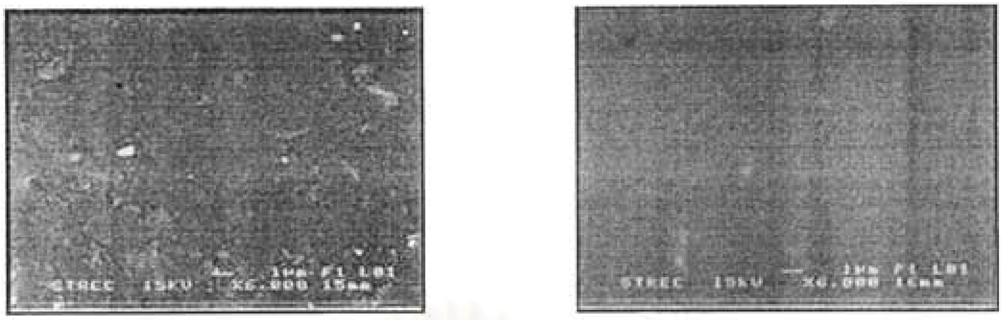


Figure 4.17 Elongation at break of vulcanized natural rubber sheet after exposed to UV under accelerated condition.

The vulcanized natural rubber sheets were analyzed by SEM. Figure 4.18 demonstrated the surface morphology of natural rubber sheets containing TiO_2 before and after UV exposure. These micrographs suggested that the controlled vulcanized rubber sheet showed the greater extent of degradation as compared with those containing TiO_2. Some cavities began to appear on 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 TiO_2 after UV exposure for 12 h.

Degraded natural rubber sheets were also characterized by ATR-IR. The results are shown in Figure 4.19. As expected, ATR-IR spectra of both vulcanized natural rubber with and without TiO_2 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.

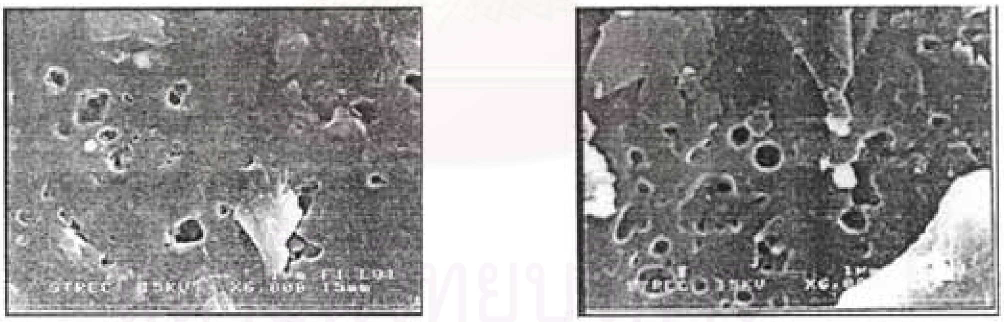


Vulcanized NR
before UV exposure

Vulcanized NR with 3% w/w TiO_2
before UV exposure

Vulcanized NR
after UV exposure for 8h

Vulcanized NR with 3% w/w TiO_2
after UV exposure for 8h



Vulcanized NR
after UV exposure for 12h

Vulcanized NR with 3% w/w TiO_2
after UV exposure for 12h

Figure 4.18 SEM micrographs of vulcanized natural rubber sheets with and without TiO_2 before and after UV exposure under accelerated condition.

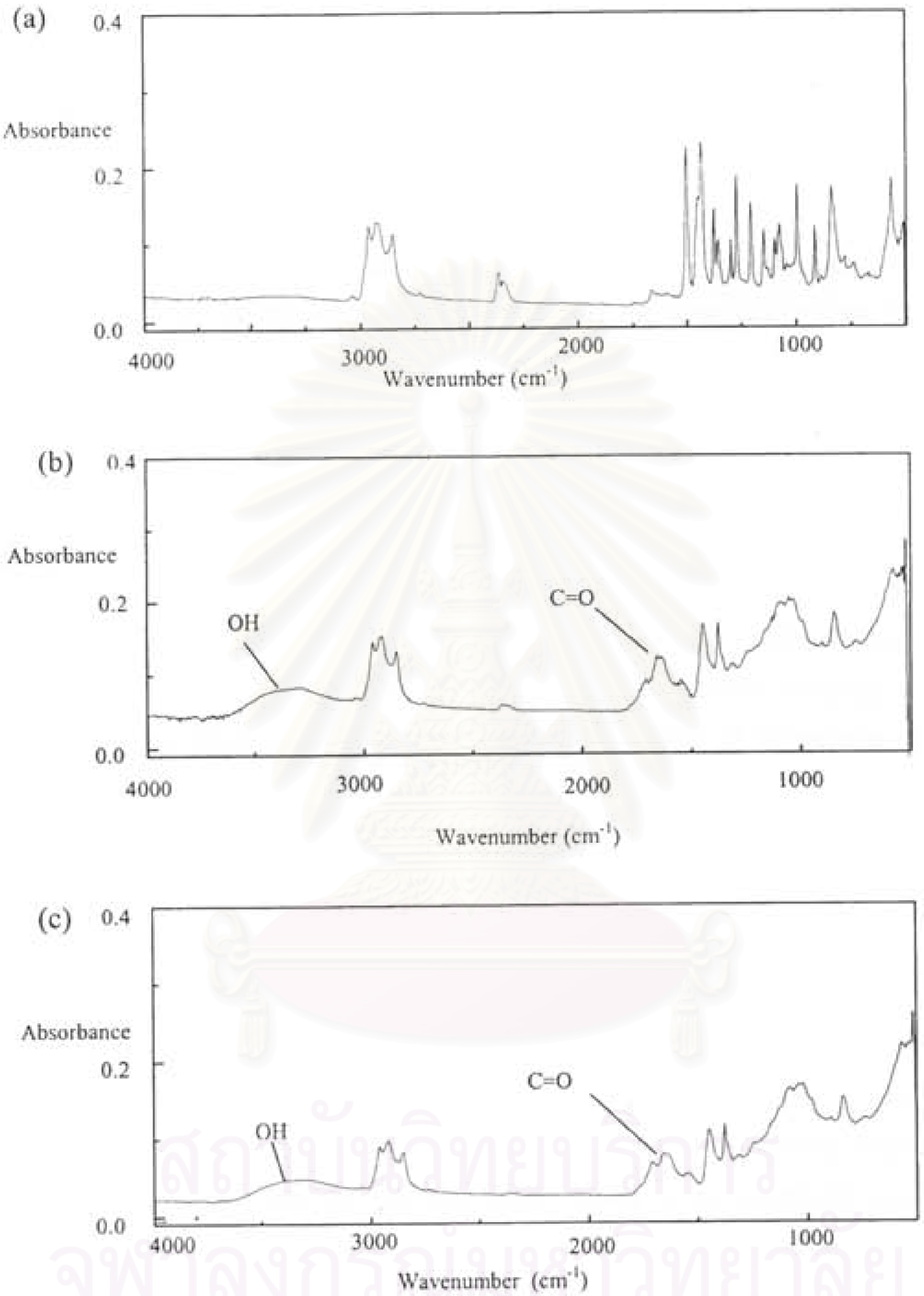


Figure 4.19 ATR-IR spectra of (a) controlled vulcanized natural rubber sheet before UV exposure, (b) controlled vulcanized natural rubber sheet after 8 h UV exposure and (c) vulcanized natural rubber with 0.5 %w/w TiO_2 after 8 h UV exposure.

CHAPTER V

CONCLUSIONS AND SUGGESTION

TiO_2 – encapsulated microparticles recovered by freeze – drying were agglomerated having 30 μm. in diameter. SEM-EDX suggested that there was 0.1% atomic concentration of titanium within the particles. X – ray diffraction confirmed that TiO_2 is in the form of anatase, which was the most active form of TiO_2 to accelerate oxidation. The ash content indicated that there is 1.1 % w/w of titanium dioxide in particles.

Photodegradation of natural rubber in the presence of TiO_2 under UV light was investigated. The extent of degradation of unvulcanized natural rubber in solution phase is varied as a function of UV exposure time and the content of TiO_2 under accelerated condition. FT-IR spectrum of degraded natural rubber solution showed a peak corresponding to carbonyl group indicating that a decay of molecular weight is a consequence of photo-oxidative degradation. The extent of degradation of natural rubber in solid phase (both unvulcanized and vulcanized sheets) is proportional to UV exposure time. Unlike the degradation of natural rubber in solution phase, the degradation of natural rubber in solid phase is inversely proportional to the amount of TiO_2 incorporated. The higher content of TiO_2 added, the greater stability against degradation of natural rubber is observed. This outcome suggests that TiO_2 acts as a stabilizer rather than a sensitizer. As demonstrated by SEM and particle size analyses, TiO_2 tended to aggregate into larger particles having a diameter of 1-2 μm which can reflect the UV light ($\lambda \sim 0.29–0.32$ μm). As a consequence of particle agglomeration, the interfacial area between TiO_2 and rubber matrix is also decreased leading to the lower photocatalytic efficiency.

The incorporation of TiO_2 in the form of microparticles do not significantly delay the degradation as initially expected. The control release of solid TiO_2 in the solid matrix of natural rubber may not be easily achieved. The controlled degradation of natural rubber by TiO_2 microparticles is thus not successful.

The appearance of surface fracture of both unvulcanized and vulcanized natural rubber sheets implied that the degradation of natural rubber in solid phase do not predominantly occur at the interface between TiO_2 and natural rubber matrix. This research study strongly suggests that the distribution of TiO_2 throughout the matrix is a key factor in controlling the degradation and stability of natural rubber.

Although the degradation of natural rubber cannot be successfully controlled by TiO_2 incorporation, TiO_2 can be used as a nontoxic agent that can effectively enhance the natural rubber stability against the photo-oxidative degradation in solid phase. Besides, TiO_2 can be very useful for some applications requiring low molecular weight natural rubber. Natural rubber can be effectively degraded in solution within a short period of time. Since the degradation is carried out under heterogeneous condition, TiO_2 can be easily removed at the end of the process.

To achieve sensitizing role of TiO_2 as well as to improve an efficiency of photo-catalytic degradation of natural rubber in solid phase, it is necessary to prevent TiO_2 from agglomeration when being incorporated in natural rubber matrix. Another alternative is to use TiO_2 having the size in nanometer that can be distributed well in order to increase the interfacial area between TiO_2 and the natural rubber matrix, and thereby enhancing the extent of photooxidative degradation.

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APPENDIX

Table A.1 Number-average molecular weight of natural rubber solution

Time of UV exposure (min)	NR		0.5% w/w		10% w/w		20% w/w		100% w/w	
	$\overline{M}_n$	% Reduction	$\overline{M}_n$	% Reduction	$\overline{M}_n$	% Reduction	$\overline{M}_n$	% Reduction	$\overline{M}_n$	% Reduction
0	206989	0	285693	0	183255	0	284569	0	158232	0
5	204158	1.4	217453	23.9	168523	8.0	269863	5.2	154126	2.6
10	200239	3.3	196258	31.3	143985	21.4	245896	13.6	110258	30.3
15	196618	5.0	174852	38.8	133786	27.0	214628	24.6	83459	47.3
30	180983	12.6	145896	32.9	82842	54.8	132985	53.3	24053	81.5
45	180500	12.8	135419	52.6	49442	73.0	139450	51.0	29262	
60	181226	12.4	78925	72.4						
90	129339	37.5								
120	120256	41.9								
150	71686	65.4								

Table A.2 Number-average molecular weight of unvulcanized natural rubber sheets containing 0-0.5 %w/w TiO_2

Time of UV exposure (h)	NR		0.1% w/w		0.5% w/w	
	$\overline{M}_n$	% Reduction	$\overline{M}_n$	% Reduction	$\overline{M}_n$	% Reduction
0	182910	0	249022	0	214991	0
4	126310	30.9	178135	28.47	104845	39.2
8	101557	44.5	86735	53.47	97843	54.5
12	76058	58.4	ND	ND	81719	62.0

Table A.3 Number-average molecular weight of unvulcanized natural rubber sheets containing 1-10 %w/w TiO_2

Time of UV exposure (h)	1% w/w		5% w/w		10% w/w	
	$\overline{M}_n$	% Reduction	$\overline{M}_n$	% Reduction	$\overline{M}_n$	% Reduction
0	161586	0	246421	0	241510	0
5	159683	1.2	207396	15.8	231153	4.3
10	115701	28.4	180411	26.8	234974	2.7
15	88100	45.5	151540	38.5	187355	22.4

Table A.4 Number-average molecular weight of unvulcanized natural rubber sheets as a function of TiO_2 after 12 h of UV exposure

% w/w of TiO_2	Initial $\overline{M}_n$	Final $\overline{M}_n$	% Reduction of $\overline{M}_n$
0	182910	76058	58.4
1.0	161586	88100	45.5
5.0	246421	151540	38.5
10.0	241510	187355	22.4

Table A.5 Number-average molecular weight of unvulcanized natural rubber sheets as a function of TiO_2 after 20 h of sunlight exposure

% w/w of TiO_2	Initial $\overline{M}_n$	Final $\overline{M}_n$	% Reduction of $\overline{M}_n$
0	247439	82256	66.8
1.0	322766	139361	56.8
5.0	246421	210986	14.4
10.0	241510	223098	7.62

Table A.6 Tensile strength of vulcanized natural rubber sheets after UV exposure under accelerated condition

Time to UV exposure (h)	1^{st} Experiment	2^{nd} Experiment	3^{rd} Experiment	Tensile strength average (MPa)	Standard deviation
NR					
0	22.2	21.7	19.8	21.2	1.3
4	13.0	11.8	12.7	12.5	0.6
8	1.6	1.0	1.8	1.5	0.4
NR + 0.5 %w/w TiO_2 powder					
0	32.4	30.7	30.9	31.3	0.9
4	9.8	8.6	10.0	9.5	0.8
8	1.3	1.0	1.2	1.2	0.2
NR + 3.0 %w/w TiO_2 powder					
0	22.0	21.5	20.5	21.4	0.9
4	18.5	17.4	18.0	18.0	0.6
8	7.5	7.0	8.4	7.6	0.7
12	1.7	1.3	1.6	1.5	0.2
NR + 5.0 %w/w TiO_2 powder					
0	23.4	23.7	24.1	23.7	0.4
4	20.0	19.0	19.5	19.5	0.5
8	10.0	8.9	9.5	9.5	0.6
12	5.3	6.0	4.9	5.4	0.6
24	1.7	1.5	1.9	1.7	0.2

Table A.7 Elongation at break of vulcanized natural rubber sheets after UV exposure under accelerated condition

Time to UV exposure (h)	1st Experiment	2nd Experiment	3rd Experiment	Elongation at break (%)	Standard deviation
NR					
0	1056	1011	1009	1025	26.2
4	899	867	900	889	18.8
8	570	544	574	563	16.3
NR + 0.5 %w/w TiO_2 powder					
0	1150	1165	1180	1165	15.0
4	1110	1080	1097	1096	15.0
8	640	620	603	621	18.5
NR + 3.0 %w/w TiO_2 powder					
0	1050	1040	1019	1036	15.8
4	1010	990	987	996	12.5
8	970	967	950	962	10.8
12	697	660	698	685	21.7
NR + 5.0 %w/w TiO_2 powder					
0	1080	1060	1038	1059	21.0
4	990	1046	1030	1020	26.5
8	988	998	978	988	10.0
12	880	915	870	888	23.6
24	780	800	801	794	11.8

PUBLICATION AND PRESENTATION

National Presentation

Na Lumpoon, N.; Tanaka, Y.; Hoven, V. P. " Controlled Degradation of Natural Rubber by Microparticles Containing Titanium Dioxide" *The 2nd Thailand Materials Science and Technology Conference*, August 6-7, 2002, Bangkok, Thailand.

International Presentation

Deeprasertkul, J.; Hoven, V. P. "Photodegradation of Natural Rubber in the Presence of Titanium Dioxide" *8th Pacific Polymer Conference*, November 24-27, 2003, Bangkok, Thailand.

International Publication

Hoven, V. P.; Deeprasertkul, J.; Tanaka, Y. "Photodegradation and Stability of Natural Rubber in the Presence of Titanium Dioxide" *Manuscript In Preparation* and to be submitted to *Polym. Degrad. Stabil.* or *Photochem and Photobio A: Chem.*