A STUDY OF MORPHOLOGY OF VULCANIZED NATURAL RUBBER PARTICLES BY USING PHASE TRANSFER/ BULK POLYMERIZATION/ TRANSMISSION ELECTRON MICROSCOPIC (TEM) TECHNIQUE

CHUTAMAST LERTHITITRAKUL

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CHUTAMAST LERTHITITRAKUL: A STUDY OF MORPHOLOGY OF VULCANIZED NATURAL RUBBER PARTICLES BY USING PHASE TRANSFER/ BULK POLYMERIZATION/ TRANSMISSION ELECTRON MICROSCOPIC (TEM) TECHNIQUE. THESIS ADVISORS: PRAMUAN TANGBORIBOONRAT, Ph.D., KRISDA SUCHIVA, Ph.D., 93 p. ISBN 974-665-031-9

Phase transfer/ bulk polymerization/ TEM technique was used to provide direct evidence of the morphology of latex particles vulcanized by sulphur and peroxide systems. Firstly, the crosslinked latex was characterized mainly by measuring the swelling ratio of sheet. The maturation stage in sulphur prevulcanization caused an increase in crosslink reaction in the initial step but it did not affect the crosslink density of final prevulcanized latex sheet. When comparing latex with different nitrogen content, it was found that protein in NR latex could accelerate the sulphur vulcanization reaction. Addition of sodium dodecyl sulfate did not influence the sulphur- and peroxide-prevulcanization reactions even though it caused the increment of the amount of negative charge on NR particle. Multicentrifuged, "residue-free-sulphur-prevulcanized" latex was also prepared. Only a small amount of the residual chemicals in the serum was detected. When the morphology of peroxide-prevulcanized latex particles was studied by using SEM, the micrographs of fractured latex sheet showed the discrete crosslinked rubber particles and the clear membrane around them. Conversely, SEM of fractured prevulcanized and residue-free-sulphur-prevulcanized latex sheets revealed indistinct appearance of rubber particle boundary. Under TEM, semi-IPNs type Semi-I of network structure of NR chains in rubber particle containing PS was observed in both types of all crosslinked particles. Moreover, inhomogeneous network structure inside each particle was observed in peroxide-prevulcanizate while the rubber network in sulphur-prevulcanized and γ-radiation-vulcanized NR particles was uniform.

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จุฑามาศ เลิศฐิติตระกูล: การศึกษาโครงสร้างสัณฐานของอนุภาคยางธรรมชาติชนิดวัลคาไนซ์โดยใช้เทคนิคเฟสทรานเฟอร์/ พอลิเมอไรเซชันแบบบัลค์/ กล้องจุลทรรศน์อิเลคตรอนแบบส่องผ่าน (A STUDY OF MORPHOLOGY OF VULCANIZED NATURAL RUBBER PARTICLES BY USING PHASE TRANSFER/ BULK POLYMERIZATION/ TRANSMISSION ELECTRON MICROSCOPIC (TEM) TECHNIQUE). คณะกรรมการควบคุมวิทยานิพนธ์: ประมวล ตั้งบริบูรณ์รัตน์, Ph.D., กฤษฎา สุชีวะ, Ph.D. 93 หน้า. ISBN 974-665-031-9

เทคนิคเฟสทรานเฟอร์/ พอลิเมอไรเซชันแบบบัลค์/ กล้องจุลทรรศน์อิเลคตรอนแบบส่องผ่าน (TEM) เป็นเทคนิคที่ใช้ในการศึกษาเพื่อให้ได้หลักฐานโดยตรงของโครงสร้างสัณฐานของอนุภาคยางธรรมชาติที่ทำการเชื่อมโยงเป็นร่างแหโดยใช้ระบบกำมะถันและเปอร์ออกไซด์ โดยตอนแรกได้ทำการตรวจสอบลักษณะน้ำยางที่ภายในอนุภาคมีการเชื่อมโยงเป็นร่างแหโดยนำน้ำยางมาเตรียมเป็นแผ่นแล้ววัดอัตราการบวมตัวของแผ่นยาง ผลการทดลองพบว่าขั้นตอนการบ่มในระบบการเชื่อมโยงที่ใช้กำมะถันทำให้การเชื่อมโยงเกิดมากขึ้นในช่วงแรกแต่ไม่มีผลต่อความหนาแน่นของโครงสร้างร่างแหของแผ่นยางที่ได้จากน้ำยางเมื่อสิ้นสุดกระบวนการ เมื่อนำน้ำยางที่มีปริมาณไนโตรเจนต่างกันมาผ่านกระบวนการเชื่อมโยงด้วยกำมะถันพบว่าโปรตีนในน้ำยางธรรมชาติสามารถเร่งปฏิกิริยาการเชื่อมโยงได้ ในขณะที่การเติมโซเดียมโดเดคซิลซัลเฟตไม่มีผลต่อการเชื่อมโยงโมเลกุลด้วยระบบกำมะถันและเปอร์ออกไซด์ถึงแม้ว่ามีผลให้ประจุลบบนอนุภาคยางธรรมชาติเพิ่มขึ้น เมื่อนำน้ำยางที่เชื่อมโยงด้วยกำมะถันมากำจัดสารเคมีที่เหลือโดยวิธีการเซนติฟิวส์หลายครั้งพบว่าสารเคมีที่ตกค้างในซีรั่มมีปริมาณน้อย ผลของการศึกษาโครงสร้างสัณฐานที่ผิวของอนุภาคยางที่เชื่อมโยงด้วยเปอร์ออกไซด์บริเวณรอยหักของแผ่นยางด้วยกล้องจุลทรรศน์อิเลคตรอนแบบส่องกราด (SEM) พบว่าอนุภาคยางอยู่แยกกันและสังเกตเห็นเมมเบรนอยู่รอบอนุภาคยางอย่างชัดเจน เมื่อเปรียบเทียบกับอนุภาคยางที่เชื่อมโยงด้วยกำมะถันและรังสีแกมมา เมื่อใช้กล้องจุลทรรศน์อิเลคตรอนแบบส่องผ่าน (TEM) ในการศึกษาโครงสร้างภายในของอนุภาคยางพบว่าร่างแหของสายโซ่ยางในอนุภาคยางที่มีพอลิสไตรีนอยู่ภายในมีลักษณะเป็นแบบ Semi-IPNs ชนิด Semi-I โดยอนุภาคยางที่เชื่อมโยงด้วยเปอร์ออกไซด์มีโครงสร้างร่างแหที่ไม่สม่ำเสมอภายในแต่ละอนุภาค ในขณะที่อนุภาคยางที่เชื่อมโยงด้วยกำมะถันและรังสีแกมมานั้นแสดงโครงสร้างร่างแหที่มีความสม่ำเสมอตลอดทั้งอนุภาคในทุกอนุภาค

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LIST OF ABBREVIATIONS

NR	=	Natural rubber
RVNR	=	γ-Radiation vulcanized natural rubber
DPNR	=	Deproteinized natural rubber
RV-DPNR	=	γ-Radiation vulcanized-deproteinized natural rubber
DP-RVNR	=	Deproteinized-γ-radiation vulcanized natural rubber
DRC	=	Dry rubber content
TSC	=	Total solid content
ZDEC	=	Zinc diethyldithiocarbamate
t-BuHP	=	*tert*-Butyl hydroperoxide
t-BPIB	=	*tert*-Butyl peroxyisobutyrate
TMTD	=	Tetramethylthiuram disulphide
BHAC	=	Benzyldimethylhexadecylammonium chloride
SDS	=	Sodium dodecyl sulfate
CTC	=	Critical transfer concentration
BPO	=	Benzoyl peroxide
PS	=	Polystyrene
AFM	=	Atomic force microscopy
SEM	=	Scanning electron microscopy
TEM	=	Transmission electron microscopy
semi-IPNs	=	Semi-interpenetrating polymer networks

CHAPTER I

INTRODUCTION

Vulcanization of natural rubber (NR) latex is mainly performed by sulphur, peroxide or radiation. Among the three methods, it exists a direct evidence that irradiation of NR latex using γ-ray leads to the formation of homogeneous crosslink inside latex particle [1-3]. However, from the economic point of view, γ-radiation vulcanized (RV) NR latex has not been widely attracted due to its high cost.

Sulphur-prevulcanized NR latex is normally used to prepare dipping products in industry although, up until present, chemical mechanism of the prevulcanization is not well understood and still controversial [4]. The previous works [5] reported that all NR particles, in sulphur and radiation prevulcanizates, show homogeneous network structure. Whereas in peroxide cured NR latex, only small latex particle has this appearance while the large particle shows inhomogeneous structure. Recently, atomic force microscopy (AFM) has been applied for the study of surface morphology of sulphur crosslinked NR latex film. AFM images show film morphology which correlates with sulphur-prevulcanized latex particle having an unvulcanized core surrounded by a highly crosslinked shell [6,7]. However, it is noted that the description of structure of prevulcanized NR latex particle in the aforementioned works, is deduced from the study of latex film. Direct evidence of the particle morphology and actual mechanism of latex prevulcanization have not clearly been elucidated. Therefore, the phase transfer/ bulk polymerization/ transmission electron

microscopic (TEM) technique [1-3], which has been successfully used in the study of RVNR latex particle, will be extended to study of morphology of sulphur and peroxide vulcanized NR latex particles in this thesis.

1.1 Prevulcanization of Natural Rubber (NR) Latex

1.1.1 Definition and Importance

Prevulcanization of NR latex is defined as a process in which chemical crosslinking of rubber chains takes place inside each particle dispersed in aqueous latex serum. Drying of prevulcanized latex produces a crosslinked film without the need for further heating [8]. One of the principal 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 [9].

1.1.2 Types of Prevulcanization

NR latex can be normally prevulcanized by sulphur, sulphur-donor, peroxide or irradiation treatment [10,11]. The rate of vulcanization differs with the use of various vulcanizing ingredients in each system and the extent of crosslink has a profound effect on the final vulcanizate properties [10].

1.1.2.1 Sulphur Prevulcanization

Mineral sulphur is widely used as an ingredient to provide crosslink between rubber chains in the vulcanization process. In sulphur prevulcanization, vulcanized latex is prepared by heating NR latex, mixed with the dispersions of sulphur and an accelerator at 50-80°C. Accelerator employed in latex mixture is usually ultra-fast dithiocarbamate, such as zinc diethyldithiocarbamate (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 [11,12].

Chemical network structure of sulphur vulcanized rubber can be presented in Figure 1.1 [10].

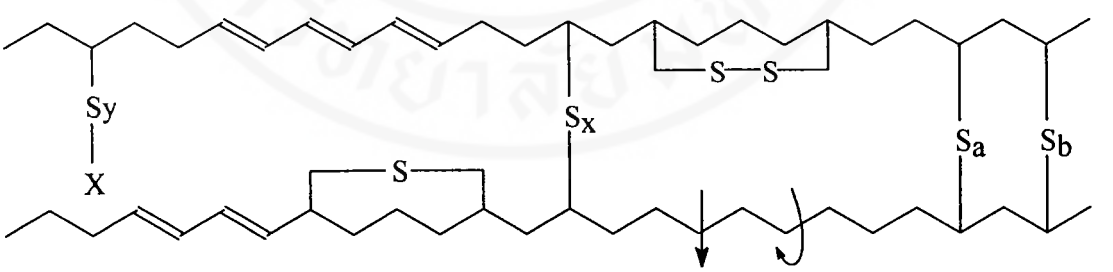


Figure 1.1: A diagrammatic representation of network structures of a sulphur vulcanized rubber (x, y, a and b = 1-9, x = accelerator fragment, curly arrow denotes a cis-trans isomerized double bond, and downward arrow denoted mainchain scission)

The formed crosslinks may be a monosulphide, disulphide, or polysulphide, however pendant sulphide, or cyclic monosulphide and disulphide possibly take place.

In addition, the accelerator providing sulphur can be also used for vulcanizing NR latex without the presence of elemental sulphur. The sulphurless system is generally referred to formulation in which compound contains a sulphur-donor such as tetramethylthiuram disulphide (TMTD) [13].

1.1.2.2 Peroxide Prevulcanization

The peroxide vulcanized NR in both solid and latex forms occurs through the formation of carbon-carbon (C-C) crosslink between the primary rubber macromolecules as illustrated in Figure 1.2 [10].

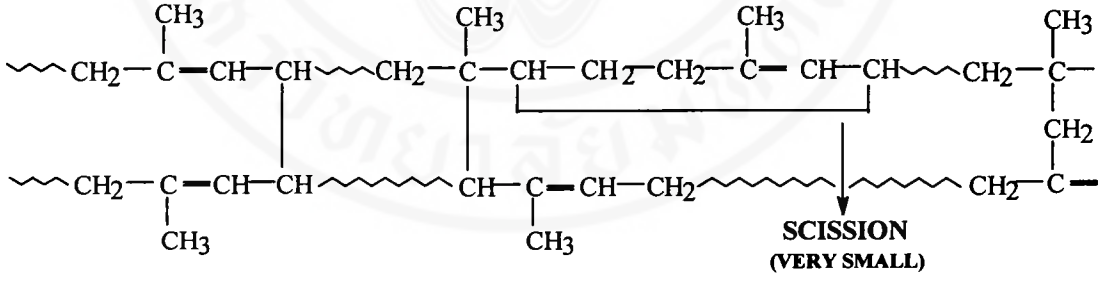


Figure 1.2: Simple representation of structure of a peroxide vulcanized rubber

The crosslinking of NR latex by free radicals generated from peroxide and hydroperoxide systems has been known for many years [14]. In more recent works various improvements of the process have been indicated. Said et al. [15] investigated the peroxide vulcanization of NR latex using fructose-activated hydroperoxide and fructose-activated peroxyester systems. These systems are found

to be effective at temperature above 50°C and the effectiveness of the systems is further enhanced in the presence of a ferric ion complex. The kinetics of *tert*-butyl peroxyisobutyrate (*t*-BPIB) decomposition in fructose/ *t*-BPIB system during vulcanization of NR latex were also studied [16]. The rate coefficients, for *t*-BPIB decomposition and crosslink formation, are generally found to increase with increasing fructose concentration and temperature.

1.1.2.3 γ-Radiation Prevulcanization

High energy radiation can be used to vulcanize dry natural rubber but the energy dose required is high and the cost tends to be prohibitive. The energy dose used in latex, however, is much lower with possibility of crosslinking that the free radicals generated in aqueous phase of the latex by interaction between the high-energy radiation and water before absorption of radicals into rubber particle [17]. An effective sensitizer or co-crosslinking agent, which not only considerably reduces the radiation dose required but also has relatively low toxicity and negligible effect upon color is widely used in the system [18,19] and the preferred sensitizer is n-butyl acrylate.

Irradiation of NR latex by gamma radiation from cobalt 60 source [20] causes an ejection of hydrogen atom of the trunk chain, mainly of methylene group in the α-position to double bond, and radical sites are formed. These radical sites are combined into C-C crosslink [21] like in the case of peroxide vulcanization. The properties, such as modulus, tear strength, puncture strength, aging resistance at high temperature, of the radiation vulcanized latex are also very similar to those of the peroxide vulcanized latex.

1.2 Chemical Mechanism of Vulcanization

It is well known that the properties of rubber such as modulus of elasticity, tensile strength and resistance to degradation by oxidation can be greatly enhanced by the vulcanization [22]. However, its chemical mechanism is still unclear and has been studied by many research groups [23,24].

1.2.1 In Solid Rubber

As already mentioned, the sulphur and peroxide vulcanizing systems are the general methods widely used for crosslinking of NR in spite of the fact that their mechanisms are not clearly established.

1.2.1.1 Sulphur Vulcanization

Sulphur is the main curing agent for most crude rubbers that contain enough double bond in their macromolecules. The sulphur-only vulcanization proceeds via a polar or ionic mechanism, where species of the type RS_X^+ (R = rubber chain) added onto the double bond [22,23]. Sulphur is combined in the vulcanization network of rubber similar to the network structure of sulphur-prevulcanized latex illustrated in Figure 1.1 [25].

Since the vulcanization of rubber by heating with sulphur alone is a relatively slow process and exhibits a poor efficiency, it is necessary to add accelerators to increase the rate of vulcanization [26,27]. These accelerators are usually complex sulphur-containing organic compounds such as tetraalkylthiuram disulphide, zinc dialkyldithiocarbamate, and related compounds, as well as a few non-sulphur

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 sulphur (S_8) to form a sulphurating 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 polysulphide crosslink, and more accelerator is regenerated [22,25]. The polysulphide ($RS_{X-1}R$) in turn can lose sulphur to give monosulphidic and disulphidic crosslinks, or can give cyclic sulphide with loss of crosslink. With a large accelerator: sulphur ratio, most of the polysulphide are transformed into monosulphide crosslink, and the undesirable cyclic sulphide formation are suppressed.

The general mechanism of the accelerated sulphur vulcanization is shown in Figure 1.3 [23].

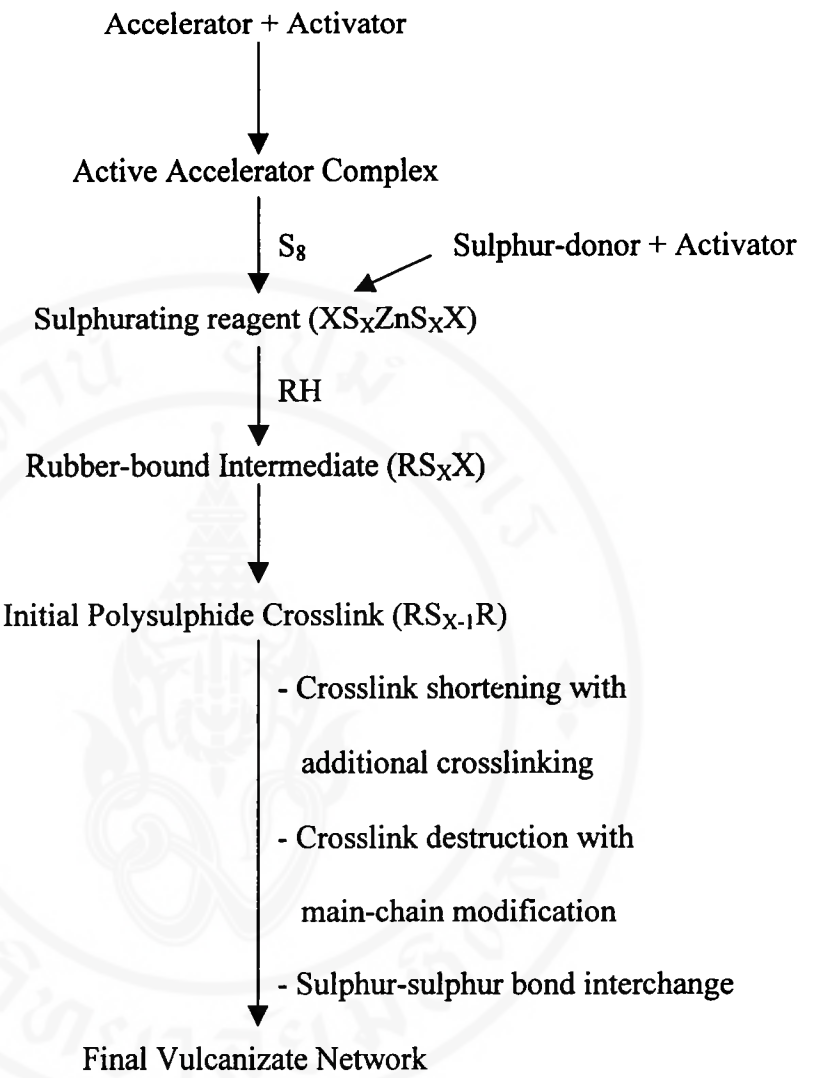
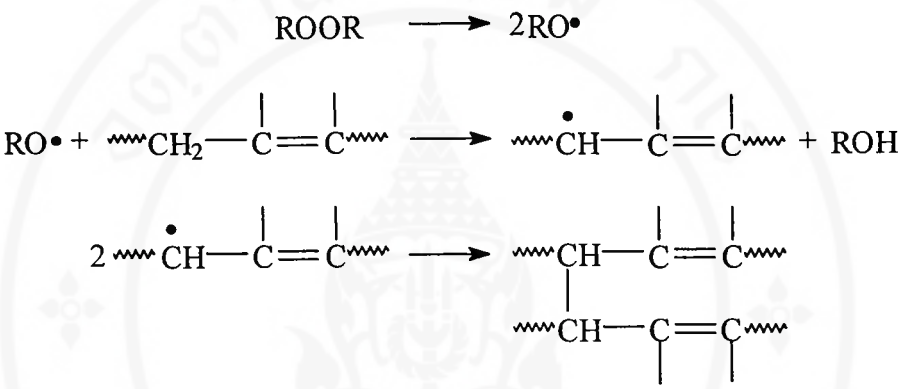


Figure 1.3: General mechanism of accelerated sulphur vulcanization (R = rubber chain, H = allylic proton and X = accelerator)

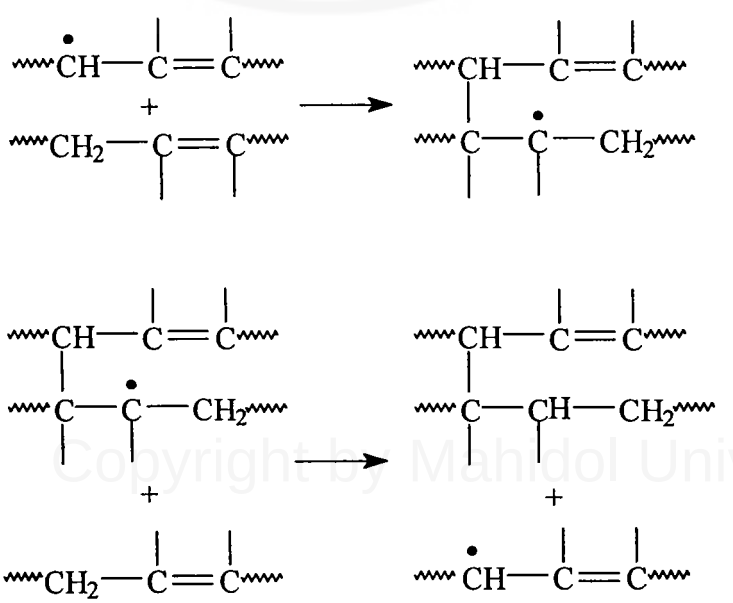
1.2.1.2 Peroxide Vulcanization

Peroxide crosslinking can be used for both fully saturated and unsaturated elastomers [28]. Dialkyl derivatives such as di-*tert*-butyl peroxide or dicumyl peroxide that have a relatively thermally unstable oxygen-oxygen bond in the molecule are normally used in peroxide vulcanization. Upon heating, the peroxide

decomposes and forms peroxy radicals to abstract a hydrogen atom from the rubber molecule, most likely from the allylic positions which give the most stable free radicals. C-C crosslink is formed by coupling of two polymeric radicals [29]. The mechanism can be illustrated as follows [24],



Alternately, crosslink can occur by a chain reaction which involves the addition of polymeric free radicals to double bonds.



Since a crosslink forms without loss of free radical, the process can be repeated until termination by radical coupling occurs. The coupling may be caused by unproductive processes, e.g., a polymeric radical can unite with a radical derived from the peroxide, thus wasting two radicals. If a polymeric radical decomposes to give a vinyl group and a new polymeric radical, the net result is a scission in the chain.

1.2.2 In Natural Rubber (NR) Latex

Due to the presence of water in latex, the molecular mechanisms of vulcanization are likely to differ from those in dry rubber.

1.2.2.1 Sulphur Vulcanization

Although sulphur prevulcanization of NR latex has been widely practiced in industry for many years, and its main features are well-established, remarkably little is known concerning the chemical mechanism by which vulcanizing agents are transported to rubber particles in the aqueous serum of latex [4].

Usually, raw latex is prevulcanized by heating with dispersions of various compounding ingredients such as sulphur, ZnO and zinc dialkyldithiocarbamate at 50-80°C until the required degree of crosslinking is obtained [9]. Previous studies proposed that vulcanizing reagents, which are essentially insoluble in water, must come into contact with the rubber phase and vulcanization reaction may take place upon direct contact between latex particles and vulcanizing reactants [30-32]. Others preferred the premise that reactants must first dissolve in the aqueous serum before diffusing into rubber particles [4]. Gorton and Pendle [33] showed that variation of average particle size of sulphur dispersion over a wide range (number-average particle

diameter = 1.5-13 μm) has no effect on rate or extent of crosslinking. This indicates that sulphur either dissolves in the serum [34] or, possibly, reacts with accelerator (perhaps in the presence of natural serum of the latex) to form some colloidal species (or intermediate species) which are transported to the rubber particle surface and diffused into the particle before crosslinking the rubber molecules therein.

The explanation as mentioned above is confirmed by Porter et al. [4] who suggested that sulphur and ZDEC can dissolve independently in the aqueous phase before migrating to rubber phase. Due to the fact that ZnO is soluble in ammoniated latex, the dissolution depends upon the presence in NR latex of acidic substances which form ammonium ions from ammonia and promote the formation of soluble, positively charged, zinc ammine complexes [35]. These complexes are transported at least as far as surface of rubber particles.

The sequence of events following the arrival of vulcanizing reagents at latex particle surface is of paramount importance in influencing the morphology of rubber particles [6]. The network structure of prevulcanized latex particle is expected to be dependent on the relative rates of diffusion of reagents in the rubber phase and of their reactions with rubber molecules to form crosslinks. When diffusion is much faster than vulcanization reaction, unimpeded diffusion of these reactants into the interior of latex particles occurs followed by crosslinking. This leads to the formation of homogeneous crosslinked rubber particle, irrespective of size. On the other hand, when vulcanization is much faster than diffusion, crosslinking takes place on surface of latex particle before diffusion of reagents into the core. Consequently, a highly crosslinked shell of rubber molecule surrounding an uncrosslinked core is obtained. At present, it seems to be a little direct evidence, which bears on this point, due to

difficulty of separating the effect of diffusion from crosslinking. Recent developments in microscopy, such as AFM [6,36], TEM [37,38], have open up the new scope for experimental techniques to be used in elucidation of chemical mechanism of latex prevulcanization. Evidence from AFM of prevulcanized NR latex films indicates that the rate of crosslinking is much greater than the rate of diffusion. Hence crosslinking occurs rapidly as vulcanizing agents enter the surface of latex particles, and crosslink formed hinder further diffusion of reactants into the interior of particles. A homogeneous vulcanized particle is not achieved by the prevulcanization.

1.2.2.2 Peroxide Vulcanization

The chemical mechanism of peroxide prevulcanization of NR latex is still not fully understood. However, the mechanism, by which crosslinking occurs in dry natural rubber, is believed to be a principle of that occurs in latex. Formation of C-C crosslinks between polyisoprene molecules involves the diffusion of peroxide molecules or radicals generated from decomposition of peroxide in the aqueous serum to rubber latex particle.

The investigation of peroxide prevulcanization of NR latex is initiated by a great concern about the absence of carcinogenic nitrosamines and nitrosatable amines in vulcanized latex [20]. Said et al. [15,16] researched various activated systems in peroxide vulcanization for NR latex and concluded that fructose-activated hydroperoxide system is an effective and suitable prevulcanizing system for NR latex. Prevulcanization rate and efficiency of system increase with increasing fructose concentrations. Therefore, Cudby et al. [5,38] selected the fructose-activated

hydroperoxide system for the study of microstructure of peroxide vulcanized latex film under TEM. The micrographs clearly reveal that the crosslink distribution in peroxide-prevulcanized latex is significantly different from that in latex prevulcanized by using sulphur or radiation. In peroxide cured latex, it can be seen that each large particle is only vulcanized in a layer near its surface, whereas the centre of particle is unvulcanized or poorly vulcanized. By contrast, in sulphur and radiation prevulcanizate all rubber particles are homogeneously crosslinked.

1.3 Surface Structure of Natural Rubber (NR) Latex Particle

Fresh natural rubber (NR) latex consisting of *cis*-1,4-polyisoprene molecules whose molecular weight is in the region of one million is presented in the form of colloidally-stable particles, approximately spherical, with diameter of 0.02-3 μm [10,39]. It is believed that the latex stability is owing to the presence of non-rubber constituents, i.e., protein and lipid, associated with latex particle as an adsorbed complex layer, similar to the membrane of many biological cells [10].

1.3.1 Unvulcanized NR Particle

From the characterization of proteolipids, found as membrane components of unvulcanized NR particles in *Hevea brasiliensis* latex, it was found that they contain 40-50 % of the protein, compared to total proteins in NR latex. The proteolipids are hydrophobic proteins containing 70 % of non-polar amino acids which are closely associated with lipids. Siler et al. [40] proposed that rubber particle surface also

contains a large amount of non-phospholipid phosphate. The membrane of rubber particle has been believed to stabilize NR latex particles [41].

Effect of the addition of small amounts of water-soluble fatty-acid soaps on the mechanical and chemical stabilities of NR latex was reported by Blackley et al. [42,43]. The soap containing approximately eleven carbon atoms causes optimum enhancement of latex stability. It was explained that the strong adsorption of soap anions on the surface of rubber particle makes the indigenous soap anions more effective as the stabilizer for rubber particles. In this case, the alkyl chain should be long enough to be strongly adsorbed at rubber-water interface and also be sufficiently short to modify the nature of indigenous soap acts as a coherent cluster adsorbed at rubber-water interface of latex particle.

Ho [44] applied electrophoresis mobility measurement for characterization of surface structure of NR latex particle. He found that particle has an amphoteric nature with isoelectric point (pI) at pH 3.8. The latex particle possesses negatively charged and negative mobility remains essentially constant above pH 6. Below this pH, negative mobility decreases with decreasing pH until it reaches pI and then mobility becomes positive on further decrease of pH. Positive charges arising from amino acid groups are possibly present in the deep interior of surface layer. The high-ammonia NR latex particle is stabilized mainly by adsorbed long-chain fatty acid soap, the hydrolysis product derived from phospholipid, and polypeptide from hydrolysis of the original protein. The electrophoretic mobility data concur with a model in Figure 1.4.

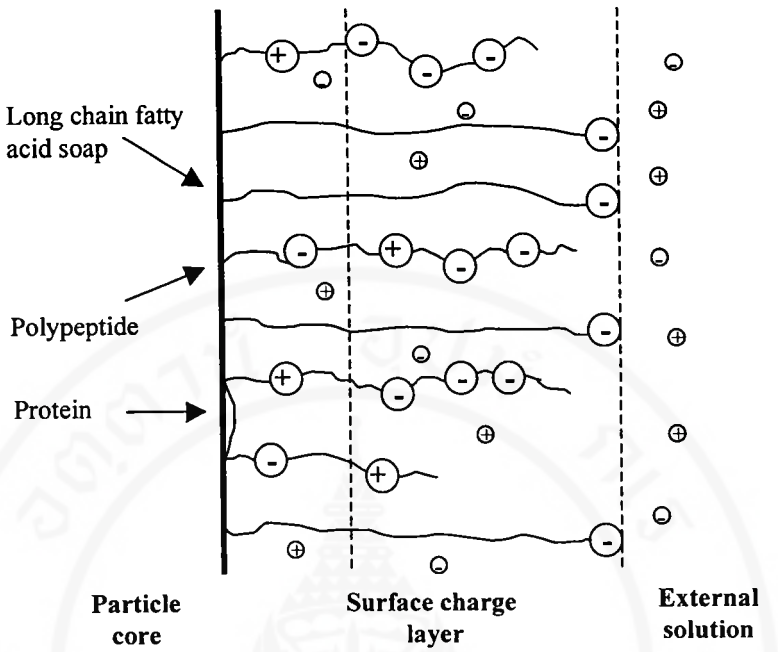


Figure 1.4: A schematic model for an ion-penetrable surface charge layer of long chain fatty acid soap and protein/ polypeptide of finite thickness surrounding the uncharged NR latex particle

This model agrees well with the work of Tangboriboonrat et al. [45] utilizing the phase transfer technique to characterize the surface charge of non-crosslinked NR latex particle (see Section 1.4). From the latter technique, the value of critical transfer concentration (CTC) (see Section 2.6.1) depends on the type of organic solvent used and they explained that NR in contact with "good solvent" shows greatest solvation effect, i.e., extension of the rubber chains. The larger the exposed charge at surface layer, the higher the CTC value.

Although, the aforementioned works attempt to predict the structure of adsorbed non-rubber constituents on the NR latex particle surface, direct elucidation of surface structure is not readily available because the latex is easy to be destable when surface

constituents are removed [44]. Therefore, it is not clear how protein and lipid are arranged at the rubber-water interface of latex particle. It is interesting in using electron microscopic technique for essential corroborating the existence of a real membrane layer of NR latex particles. Gomez et al. [46] confirmed the ultrastructural details of rubber particle membrane by TEM after osmium tetroxide (OsO_4) fixation. TEM micrograph reveals that there is a peripheral electron-dense film approximately 100 Å in thickness, which can be visualized adequately in well stained median sections of rubber particles. The normal rubber particles under OsO_4 fixation are shown as Figure 1.5.

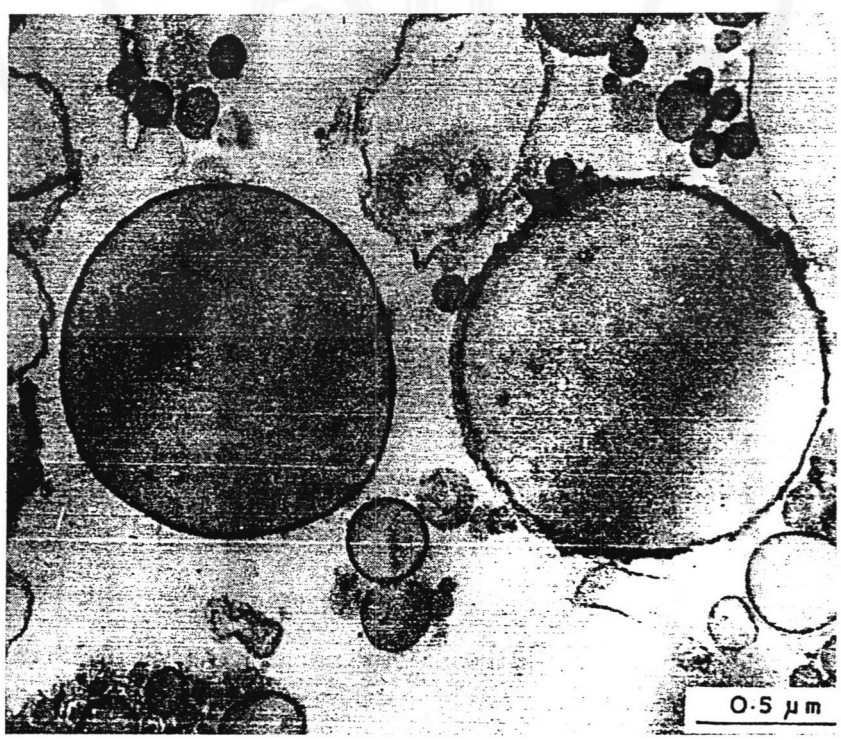
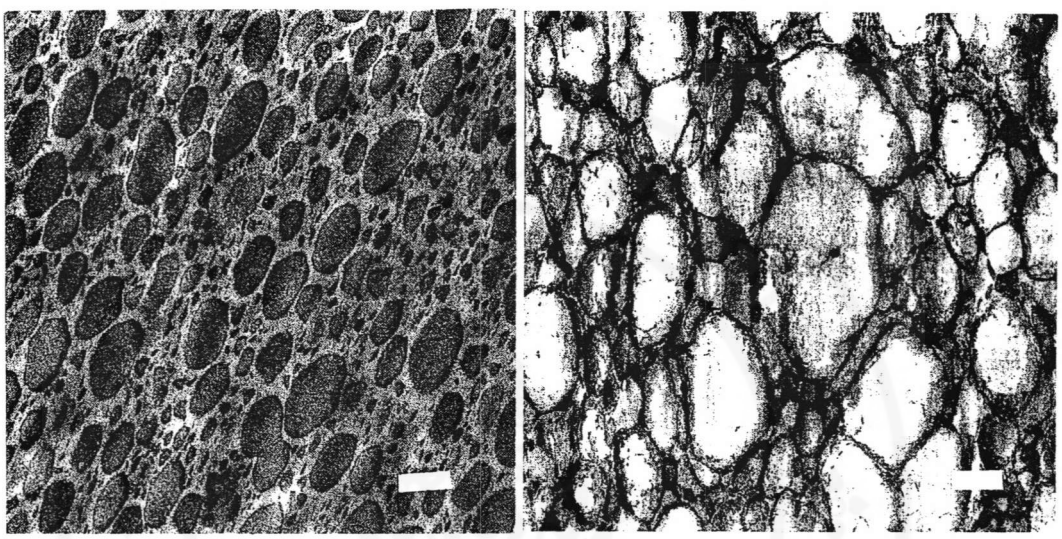


Figure 1.5: Osmium-fixed rubber particles showing characteristic membrane and membrane-associated regions [46]

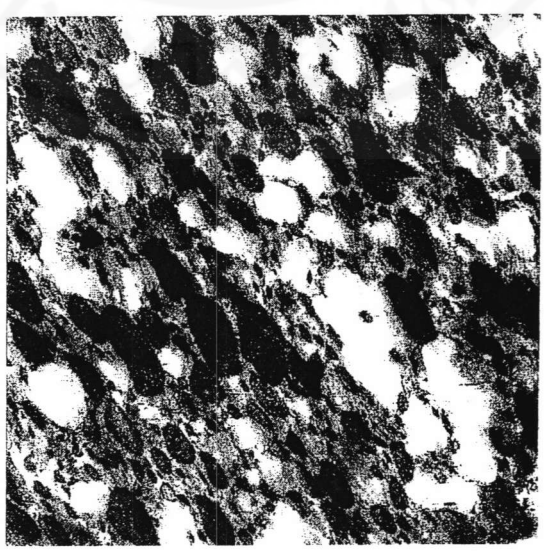
1.3.2 Vulcanized NR Particle

Electron microscopy under fixation technique has been extended to observe the change of rubber particle morphology at various processing stages of sulphur prevulcanization [37]. The results indicated that membranous region as a rigid boundary is observed around particle on complete vulcanization. The behavior of rubber particles during vulcanization can be followed through but resolution of photograph is not adequate to be able to conclude the permeability of vulcanizing agents into rubber particles.

Cook et al. [38] and Cudby et al. [5] applied electron microscopic technique for visualizing the microstructure of various prevulcanized latex films. The results of film formed show chains interpenetration contributing to the strength of film. Moreover, TEM micrographs clearly show that the distribution of peroxide cured rubber is very different from that of sulphur and radiation prevulcanizates in which all latex particles reveal homogeneous network structure as presented in Figure 1.6 (a,c). In Figure 1.6 (b), only small peroxide crosslinked particles have uniformly vulcanized structure while the large rubber particles are vulcanized only in a layer near their surface.



a) sulphur-crosslinked latex film b) peroxide-crosslinked latex film



c) radiation-crosslinked latex film

Figure 1.6: TEM micrographs of microstructure of prevulcanized latex films crosslinked by a) sulphur b) peroxide c) radiation [38]

1.4 Phase Transfer/ Bulk Polymerization/ Transmission Electron Microscopic (TEM) Technique for Morphological Study of Vulcanized NR Particle

Phase transfer technique was previously used by Heim [47] to determine the surface charge of crosslinked synthetic latex particles such as polystyrene, poly (butyl acrylate) and poly (methyl methacrylate). Tangboriboonrat et al. [45,48-49] have extended this technique to study of NR latex both non-crosslinked and crosslinked NR (γ-radiation vulcanized NR (RVNR) and deproteinized natural rubber (DPNR)) latices. This technique involves the titration of negatively charged stabilized latex with an aqueous solution of cationic surfactant, such as benzyldimethylhexadecyl-ammonium chloride (BHAC), in the presence of a non-water miscible organic solvent until end point of titration is reached. At this point, a hydrophobic layer is formed around rubber particle and, hence, particle transfers from the aqueous phase into the organic phase as shown in Figure 1.7.

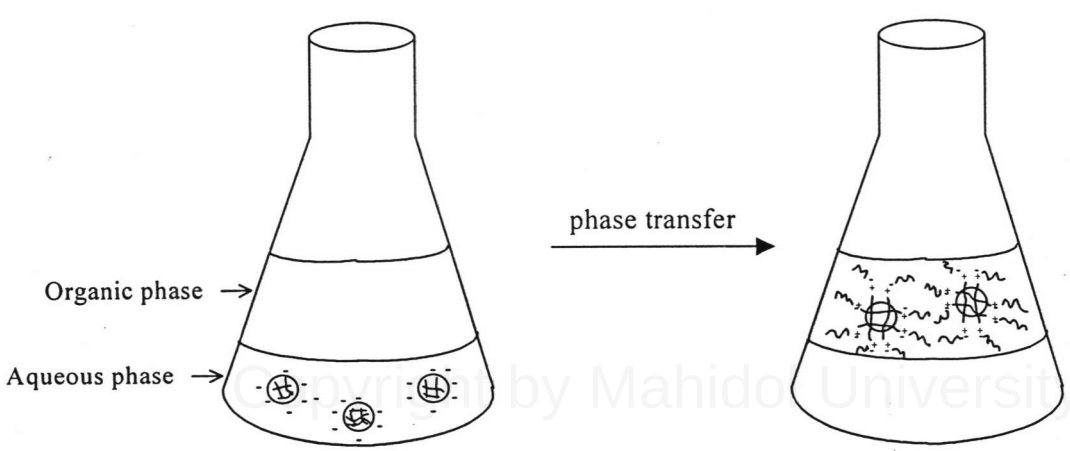


Figure 1.7: Diagram of negatively charged latex particle before and after phase transfer

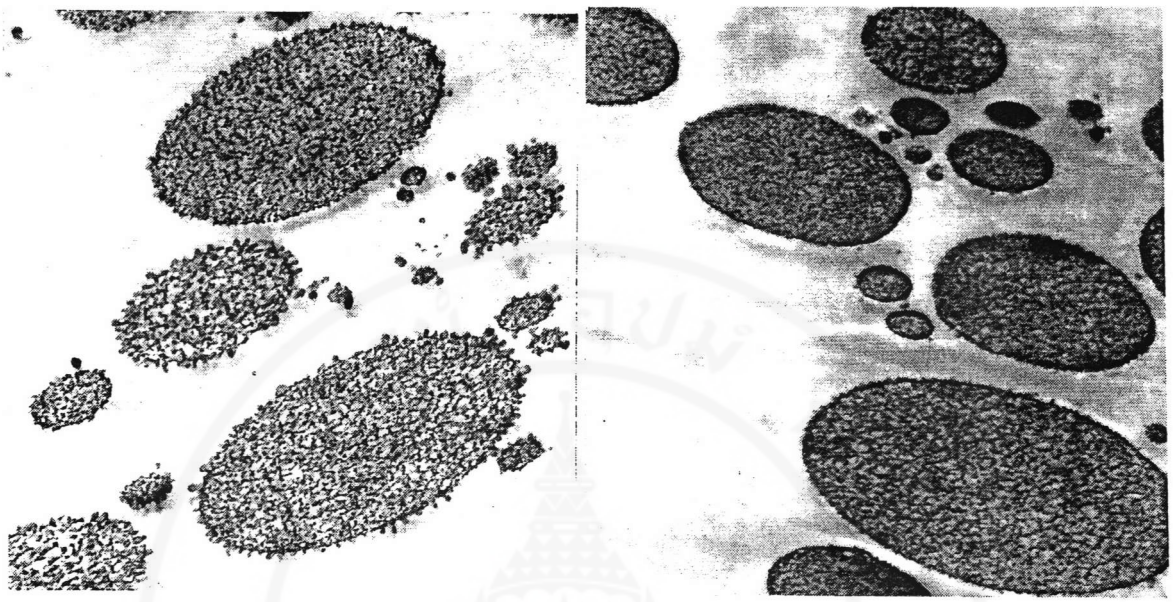
The surface charge of latex particle can be obtained from the amount of added surfactant at the end point, the CTC value is calculated by using the formula indicated in Section 2.6.1.

Besides surface characterization, the phase transfer combined with bulk polymerization has also been systematically investigated. Crosslinked NR latex particle is allowed to transfer and equilibrium swelled in the styrene monomer used as the organic phase. After polymerization of the monomer containing swollen rubber particle, the polymer is sectioned with ultramicrotome and the suitable sample for TEM study is obtained.

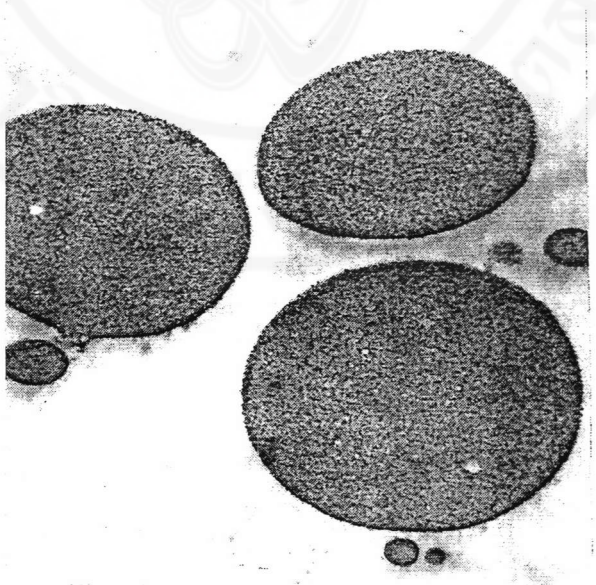
The phase transfer/ bulk polymerization/ TEM technique [1-3] is found to be an effective technique providing direct evidence of interior morphology of crosslinked NR latex particle dispersed in polystyrene (PS) matrix. By using this process, the air, freeze or chemical drying step of rubber latex, normally required before embedding step for specimen preparation, is omitted and, hence, the disturbance of rubber particle structure is minimized.

1.4.1 γ-Radiation Vulcanized Natural Rubber (RVNR) [1,3]

TEM micrographs of RVNR (3%) irradiated with various doses embedded in PS are presented in Figure 1.8. The broad distribution of size and shape of crosslinked rubber particle (dark) containing PS occlusion (light) dispersed in PS matrix (light) is observed. The micrographs reveal the existence of membrane layer around particle derived from protein-lipid complex and the homogeneous crosslinking inside RVNR particle. The extent of crosslink or the dense of network is proportional to total dose used.



a) 4 kGy b) 14 kGy



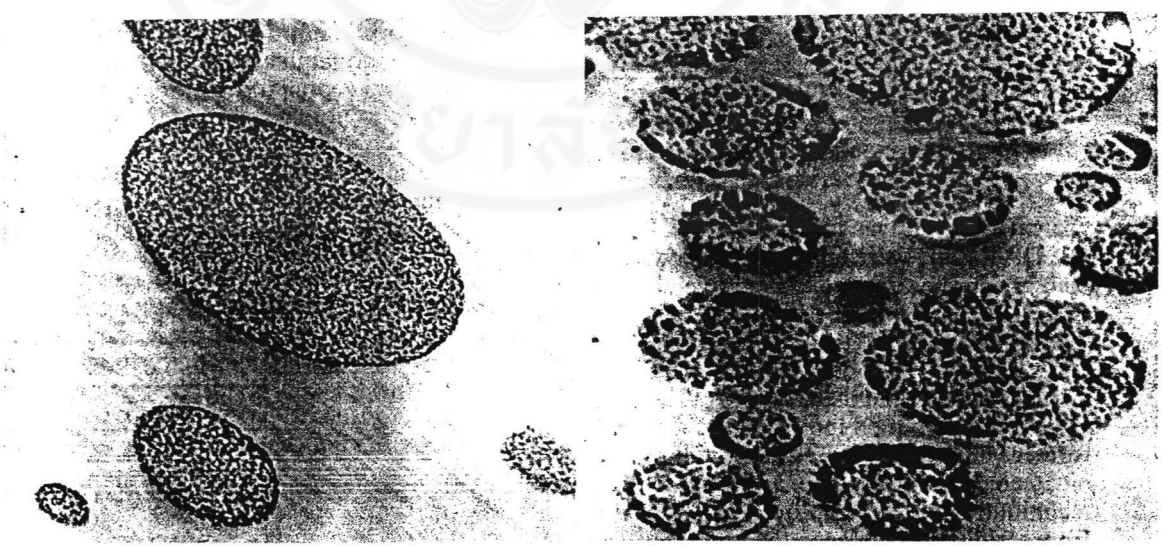
c) 26 kGy

Figure 1.8: TEM micrographs of RVNR irradiated with a) 4 kGy b) 14 kGy c) 26 kGy embedded in PS matrix [1]

1.4.2 Deproteinized Natural Rubber (DPNR) [2]

When concentrated NR latex is chemically modified by using the enzyme alcalase/ sodium dodecyl sulfate (SDS) system, the attained latex is commonly referred to deproteinized natural rubber (DPNR) latex. This enzyme deproteinization technique is very effective in removal of more than half of the original protein from 0.3 to 0.01%. It is of great interest to note that by using this technique, the remaining protein bound to NR particle is still present [50,51].

Two types of crosslinked DPNR latex particles, i.e., γ-radiation vulcanized-deproteinized NR (RV-DPNR), obtained from enzymatic deproteinization of RVNR latex, and deproteinized-γ-radiation vulcanized NR (DP-RVNR), prepared by irradiation of DPNR latex with γ-ray, are studied under TEM and their morphologies are illustrated in Figure 1.9 (a-b).



a) RV-DPNR/ PS b) DP-RVNR/ PS

Figure 1.9: TEM micrographs of crosslinked rubber particles a) RV-DPNR b) DP-RVNR embedded in PS matrix [2]

All micrographs reveal two-phase morphology of rubber particle (dark) dispersed in PS matrix (light). The size distribution of crosslinked NR particle containing PS occlusion was rather broad. From Figure 1.9 (a), RV-DPNR particle seems to be still surrounded by the membrane layer (derived from protein-lipid complex) like in the case of RVNR latex particle in Figure 1.8 (b) which implied that the membrane around RV-DPNR particle is not significantly disturbed. On the other hand, the membrane is clearly broken out in the case of DP-RVNR latex particle as shown in Figure 1.9 (b).

These evidences are very important to experimentally confirm the presence of protein in the membrane of NR particle which can be partly destroyed by using proteolytic enzyme. In addition, the efficiency of enzyme activity decreases in the case of the crosslinked rubber particles.

1.5 Scope of the Present Thesis

A novel technique, the phase transfer/ bulk polymerization/ TEM, was used to provide direct information of morphology of sulphur-and peroxide-prevulcanized NR particles.

In sulphur-prevulcanized latex, the size of vulcanizing agents was measured and compared with that of NR latex before preparing prevulcanized latex. Effect of maturation, NR latex from different suppliers and addition of anionic surfactant (SDS) on the prevulcanization reaction were investigated by determining the swelling ratio of latex sheet. Multicentrifuged called "residue-free-sulphur-prevulcanized" latex was also prepared and the amount of residual ingredients in aqueous serum was

determined. The fractured surface morphologies of prevulcanized and residue-free-sulphur-prevulcanized latex sheet were then studied under SEM. The phase transfer technique was applied and the CTC values of sulphur-prevulcanized latex particles, the concentration of initiator (BPO) and quantity of transferred rubber in styrene monomer were considered. After bulk polymerization of styrene monomer containing transferred NR particles, morphology of rubber particles embedded in PS matrix was studied under TEM.

For peroxide-prevulcanized latex, the swelling ratio of sheets casted from the latex with and without SDS was firstly determined. Then, the CTC and quantity of transferred rubber in styrene were examined after employing the phase transfer technique. The morphology of peroxide-prevulcanized latex particles was studied by using the same technique as in the case of sulphur system.

By using the phase transfer/ bulk polymerization/ TEM technique, the morphologies of NR latex particle crosslinked by using sulphur, peroxide and γ-irradiation systems were compared. Elucidation of crosslinking characteristic of various latex prevulcanizations was attempted in the last part of this research.

CHAPTER II

EXPERIMENTAL

2.1 Apparatus

The apparatus used in the present study are listed in Table 2.1.

Table 2.1: List of apparatus used in the present study

Apparatus	Supplier/ Trade Mark
Ball Mill	Saturn Chemical Co., Ltd.
Circulating Cooling	Renown Technical, THA-CBD I
CHN Elemental Analyzer	Perkin Elmer, 2400 CHN
Fine Coater (gold coating)	JEOL, JFC-1200
Magnetic Stirrer	IKAMAG-Mini-MR
Mechanical Stirrer	Jande & Kunkel, RE-16
Particle Size Analyzer	Malvern, Mastersizer S
Precision Balance	Sartorious, BP 1200
Scanning Electron Microscope	JEOL, JSM-6301F
Supraspeed Centrifuge	Sorvall RC 5C Plus, DuPont
Transmission Electron Microscope	Hitachi, H-300

Table 2.1: (continued)

Apparatus	Supplier/ Trade Mark
Ultramicrotome	Research and Manufacturing Company (RMC), Inc., MT-7
Vacuum Oven	Sheldon (Shel lab)
Vented Air Oven	Memmert, 400UM
Water Bath	Julabo PC

2.2 Reagents

Reagents used in the present study are listed in Table 2.2. Ethyl alcohol was distilled before use while other reagents were used as received.

Table 2.2: Reagents used in this study

Reagents	Supplier	Grade
Acetone	Fluka	Commercial
Aluminium oxide (neutral and basic)	Fluka	Chromatography
Benzoyl peroxide (BPO)	Sigma	Microscope
Benzyldimethylhexadecylammonium chloride (BHAC) hydrate	Fluka	Purum

Table 2.2: (continued)

Reagents	Supplier	Grade
tert-Butyl hydroperoxide (*t*-BuHP)	Fluka	Purum
D(-)-Fructose	Fluka	Bacteriology
Ethyl alcohol	Fluka	Commercial
Glacial acetic acid	Merck	GR
Osmium tetroxide (OsO_4)	Electron Microscopy Sciences	4% Aqueous solution
Potassium hydroxide (KOH)	Merck	GR
Sodium dodecyl sulfate (SDS)	Fluka	GC
Styrene	Fluka	Purum
Sulphur	EMCO Intertrade Co., Ltd.	Commercial
Zinc diethyldithiocarbamate (ZDEC)	EMCO Intertrade Co., Ltd.	Commercial
Zinc oxide (ZnO)	Global Chemical Co., Ltd.	Commercial

2.3 Characterization of Natural Rubber (NR) Latex

Two lots of high ammonia preserved concentrated NR latices were purchased from the Rayong Bangkok Rubber Co., Ltd. (Rayong, Thailand) and from the N.Y. Rubber Co., Ltd. (Chonburi, Thailand). General characteristics of the latices were determined.

2.3.1 Determination of Total Solid Content (%TSC)

%TSC of latex is defined as percentage by weight of concentrated NR latex which is non-volatile at a definite temperature in an open atmosphere. The %TSC of concentrated latex was determined by using the method described in ASTM D1076-97 [52] and calculated by using the following equation:

$$\%TSC = \frac{W_x}{W_t} \times 100 \qquad (2.1)$$

where, W_x = weight of dry NR sample (g)

W_t = weight of NR latex sample (g)

2.3.2 Determination of Dry Rubber Content (%DRC)

%DRC of latex is defined as percentage by weight of concentrated latex which is precipitated by 5% acetic acid. The %DRC of concentrated NR latex in this study was determined by using the method described in ASTM D1076-97 [53] and calculated from equation 2.2.

$$\%DRC = \frac{W_r}{W_t} \times 100 \qquad (2.2)$$

where, W_r = weight of dry coagulum (g)

W_t = weight of NR latex sample (g)

2.3.3 Determination of Nitrogen Content (%N)

Concentrated NR latex was casted onto a petridish and allowed to dry in a vented air oven at 50 ± 2°C. Nitrogen content (%N) of clear rubber sheet obtained was determined by using CHN Elemental Analyzer (Perkin Elmer, 2400 CHN) for both lots of NR latex [54] and semi-micro Kjeldahl method as described in ASTM D 3533-90 only for RB latex [55] (Appendix A).

2.3.4 Measurement of Particle Size

Particle size of NR latex was measured by using a laser diffraction technique (Mastersizer S, Malvern version 2.11) at 25°C (Appendix B). In the measurement, distilled water was added into the chamber of system, flushed into the cell and measured as background. A few drops of NR latex was then added into the chamber containing distilling water, while continuously stirring, until the concentration was in range 10-40%. The measurement was repeated 3 times.

2.4 Vulcanization of Natural Rubber (NR) Latex

Vulcanizing ingredients, i.e., sulphur, zinc diethyldithiocarbamate (ZDEC) and zinc oxide (ZnO), in the form of powder were prepared as 50% aqueous dispersion by ball milling. These ingredients were ground at least 72 h. Size of the vulcanizing ingredients in both unmilled and ball-milled forms was finally measured by using Mastersizer S (Malvern version 2.11) (Appendix B) and procedure was carried out according to the method indicated in Section 2.3.4.

2.4.1 Preparation of Sulphur-prevulcanized NR Latex

The formulations used for preparation of sulphur-prevulcanized NR latex are shown in Table 2.3.

Concentrated NR latex having ≈ 60%DRC was firstly filtered with 250 mesh aluminium screen and then charged in the reaction vessel equipped with a condenser and a thermometer. The latex was stabilized with KOH or KOH+SDS in the Formulations A-B while the addition of the stabilizers was omitted in the Formulation C. Then the aqueous dispersions of vulcanizing ingredients, i.e., sulphur, ZDEC and ZnO were respectively added into the latex at room temperature with continuous stirring. The compounded latex obtained was stirred at 200 ± 20 rpm for 30 min at room temperature in order to ensure homogenization of the ingredients. Then the mixture was undisturbed for 2 h in the dark cabinet for maturing before being heated at 60°C. During that time, each portion (≈ 5 g) of prevulcanized latex was taken at intervals and poured into a petridish. The crosslink density of dried latex sheet was then determined as described in Section 2.5.2. At the end of reaction, the

prevulcanized latex was rapidly cooled to room temperature to prevent further vulcanization. The unmodified latex in the absence of any stabilizer and vulcanizing ingredients was also prepared by using the same procedure as in the previous case.

Table 2.3: Formulations used for sulphur prevulcanization of NR latex [56]

Ingredients	Parts by wet weight (g)		
	A	B	C
Concentrated NR latex (60%DRC)	167.0	167.0	167.0
Stabilizers			
- Potassium hydroxide (KOH) solution (10% w/v)	4.0	4.0	-
- Sodium dodecyl sulfate (SDS) solution (25% w/v)	0.8	-	-
Vulcanizing ingredients			
- Sulphur dispersion (50%)	2.5	2.5	2.5
- Zinc diethyldithiocarbamate (ZDEC) dispersion (50%)	2.0	2.0	2.0
- Zinc oxide (ZnO) dispersion (50%)	0.5	0.5	0.5

2.4.2 Preparation of Peroxide-prevulcanized NR Latex

The formulations used for peroxide prevulcanization of NR latex are given in Table 2.4.

Table 2.4: Formulations used for peroxide prevulcanization of NR latex [20]

Ingredients	Parts by wet weight (g)	
	A	B
Concentrated NR latex (60%DRC)	166.7	166.7
tert-Butyl hydroperoxide (*t*-BuHP) solution (68% w/v)	1.25	1.25
Sodium dodecyl sulfate (SDS) solution (20% w/v)	1.25	-
Fructose solution (25% w/v)	8.5	8.5
Distilled water	22.4	22.4

Peroxide emulsion was firstly prepared by mixing *t*-BuHP (1.25g) with distilled water (11.2 g) [and SDS solution (1.25 g) in Formulation A]. The emulsion was then added, while stirring, to concentrated NR latex at room temperature. 25% Fructose solution (8.5 g) was then added and followed by the rest of water (11.2 g). Prevulcanization was carried out at 60°C in the reaction vessel equipped with a condenser and a thermometer. A portion of latex (≈ 2 g) was also collected at different time intervals for determination of the extent of crosslinking (see Section 2.5.2) by using the same method as used in the case of sulphur prevulcanization. At

the end of heating stage, the vessel was quickly immersed in a water bath at room temperature. The concentrated latex (166.7 g) was also carried out by following the above step and employed as reference.

2.5 Treatment of Prevulcanized Latex

2.5.1 General Characterizations

After prevulcanization, the latex was filtered through 250 mesh aluminium screen. Total solid content of filtered latex was determined by using the procedure mentioned in Section 2.3.1 and its particle size was measured as indicated in Section 2.3.4.

2.5.2 Determination of Crosslink Density [57]

The crosslink density of rubber sheets, casted from both prevulcanized latices at room temperature, was determined by using the swelling method. The dried sheet was cut into a known weight square piece (approximately 0.2 g) and then immersed in toluene (40 ml) at room temperature in the dark cabinet. At equilibrium swelling (≈ 7 days), the weight of swollen rubber piece was recorded after blotting its surface with filter papers. %Swelling ratio was calculated from the following equation:

$$\%\text{Swelling ratio} = \frac{W_{eq} - W_o}{W_o} \times 100 \qquad (2.3)$$

where, W_o = initial weight of dried rubber (g)

W_{eq} = weight of swollen rubber at equilibrium (g)

2.5.3 Preparation of Residue-free-sulphur-prevulcanized Latex

To eliminate residual vulcanizing ingredients, sulphur-prevulcanized NR latex (Section 2.4.1) was centrifuged by using a Supraspeed Centrifuge (Sorvall RC 5C Plus, DuPont) of 4,000 rpm, for 15 min at room temperature. After centrifugation, the upper latex layer was sucked out and collected in 1000 ml beaker and distilled water, the same volume as latex, was added into the centrifuged tube. The whole process was repeated thrice until the absence of latex was observed in the upper layer. The removed latex in each time was combined and the latex obtained was called "residue-free-sulphur-prevulcanized latex".

2.6 Phase Transfer Technique

Prevulcanized or residue-free-sulphur-prevulcanized latices having 6%TSC (15 g) was diluted with distilled water (45 g) in an Erlenmeyer flask. Then a purified styrene monomer (30 g) was added into the flask and the mixture was slowly titrated with aqueous solution of 0.0121 M benzyldimethylhexadecylammonium chloride (BHAC) via a burette, while continuously stir with a magnetic stirrer. At the end point of titration, the mixture became translucent. The agitation was stopped and the phase separation immediately occurred with the appearance of a clear rubber-free serum aqueous lower phase and the upper phase of styrene monomer containing swollen transferred rubber particles.

2.6.1 Critical Transfer Concentration (CTC)

From the concentration and volume of the added cationic surfactant (BHAC) used to attain the end point, the critical transfer concentration (CTC, which is the number of moles of surfactant used per gram of dry latex) of prevulcanized latices was calculated by the following equation [47]:

$$CTC = \frac{V \times C}{10 \times m \times TSC} \qquad (2.4)$$

where,

V = quantity of cationic surfactant used at the titration end point (ml)

C = surfactant concentration (M)

TSC = total solid content of the latex (%)

m = weight of the latex sample (g)

2.6.2 Quantity of Transferred Rubber in Styrene Monomer

When the phase transfer was completed, three parts of the transferred rubbers were noted: swollen rubber in the styrene phase, destabilized and suspended rubber at the interphase and sticked rubber at the inner wall of Erlenmeyer flask.

The swollen rubber in the upper styrene phase and the destabilized rubber suspended at the interphase were centrifuged with Sorvall RC 5C Plus at 4,000 rpm for 4 min. The swollen rubber in styrene monomer was isolated by using a dropper. The rubber was then weighed (≈ 1.0 g) in a petridish and allowed to dry at room

temperature until constant weight. The quantity of transferred rubber in styrene monomer was calculated from:

$$\%\text{Transferred rubber} = \frac{W_1}{W_2} \times 100 \qquad (2.5)$$

where, W_1 = constant weight of dry rubber (g)

W_2 = weight of swollen rubber in styrene monomer before drying (g)

2.6.3 %Conversion of Polystyrene Containing Transferred Rubber

After phase transfer, the styrene monomer containing swollen transferred rubber particles was allowed to equilibrium swell for 24 h at room temperature before being separated from a clear rubber-free serum aqueous phase. Then it was stirred with a magnetic stirrer for 1 min to homogenize swollen rubber particles in styrene and centrifuged by using a Supraspeed Centrifuge (Sorvall RC 5C Plus, DuPont) at 4,000 rpm for 4 min to eliminate the rest of water. The upper phase was separated and various concentrations (i.e. 0.4, 0.6 or 1.0 wt%) of benzoyl peroxide (BPO) were added. A known amount of the mixture was poured into a closed test tube and polymerized at 70°C. At various time intervals, each tube was quickly cooled to room temperature and the residue styrene monomer was removed by evaporating in vacuum oven at room temperature until constant weight was obtained. The %conversion of styrene monomer in the presence of swollen rubber was finally calculated from:

$$\%\text{Conversion} = \frac{W}{W_t} \times 100 \qquad (2.6)$$

where, W_t = weight of sample collected at time t

W = constant weight of sample after removing the remaining monomer by evacuation at room temperature

2.7 Preparation of Specimen for Morphological Study of Prevulcanized NR Particles

2.7.1 Scanning Electron Microscopy (SEM)

The rubber sheets, casted from concentrated, prevulcanized and residue-free-sulphur-prevulcanized latices at room temperature, were immersed in liquid nitrogen about 1 h and then fractured. The sample was placed on double sided sticky tape on a specimen stub and sputtered with gold to prevent charging on the surface. Morphology of surface of the fractured sample was obtained by using a JEOL model JSM-6301F and film for black-white prints (TMX 100, Kodak).

2.7.2 Transmission Electron Microscopy (TEM)

The styrene containing swollen transferred rubber particle, obtained from Section 2.6, was permitted to equilibrium swell for 24 h at room temperature and remaining trace of water was eliminated by centrifuging as previously mentioned. The upper phase isolated and then mixed with 1.0wt% of BPO was poured into a Teflon coated steel mould (10.4×10.4×2.6 cm^3) before being polymerized at 70°C in

an oven for 16 h. After polymerization, the residual styrene was removed by using a vacuum oven at room temperature.

Specimen of rubber particles embedding in PS matrix was finely trimmed with a razor blade under an ultramicrotome (MT-7, RMC) to provide a trapezoidal block face shape. The trimmed block was cut with glass knife in the ultramicrotome to obtain an ultrathin section, which was fit onto a grid and then stained with osmium tetroxide (OsO_4) vapor (2%w/v of the aqueous solution). Transmission electron micrograph of rubber particles embedding in PS was obtained by using a Hitachi model H-300 and electron microscope film (ESTAR thick base 4489, Kodak).

CHAPTER III

RESULTS AND DISCUSSION

I. General Characteristics of Natural Rubber (NR) Latices Used in the Present Study

RB and NY were 2 lots of high ammonia concentrated NR latices supplied by the Rayong Bangkok Rubber and the N.Y. Rubber Co., Ltd., respectively. Their general characteristics were investigated in our study.

I.3.1 Solid Contents

Solid contents, i.e., total solid content (TSC) and dry rubber content (DRC), of both latices, i.e., RB and NY are shown in Table 3.1.

Table 3.1: Solid contents of concentrated NR latices used in this study

Latex	TSC (%)		DRC (%)	
	V_1*	V_2**	V_1*	V_2**
RB	61.6	61.9 ± 0.5	60.1	60.2 ± 0.4
NY	61.7	61.6 ± 0.7	60.2	60.6 ± 0.6

* Values obtained from the suppliers

** Values obtained from our measurements

It can be noted from Table 3.1 that the data obtained in our experiment are not significantly different from those of the suppliers. The %TSC was higher than %DRC by about 1-2 % due to the presence of non-rubber constituents such as protein, fatty acid soap, organic and inorganic salts in NR latex as mentioned in the literature [10].

I.3.2 Nitrogen Content

The data of nitrogen content of RB latex determined by using the CHN elemental analysis and semi-micro Kjeldahl method are shown in Table 3.2. It was seen that the values obtained from both methods were alike and independent of the methods used. Due to its convenience, the CHN elemental analysis was then selected for determining nitrogen content of the NY latex as also shown in Table 3.2.

Table 3.2: Nitrogen content of concentrated NR latices used in this study

	Nitrogen Content (%)	
	RB	**NY**
CHN analysis	0.37 ± 0.01	0.83 ± 0.02
Semi-micro Kjeldahl method	0.37 ± 0.02	-

Since the nitrogen content normally relates to the quantity of proteinaceous substances in NR latex [50], it was reasonably assumed that the amount of proteins in NY latex was higher than that of the RB one.

I.3.3 Particle Size and Their Distribution

The particle size and size distribution of the concentrated NR latices were measured by using Mastersizer S which calculates average particle size based on light diffusion and diffraction principles. From particle size measurement, the average particle size and size distribution, by volume, of both NR latices are shown in Figure 3.1.

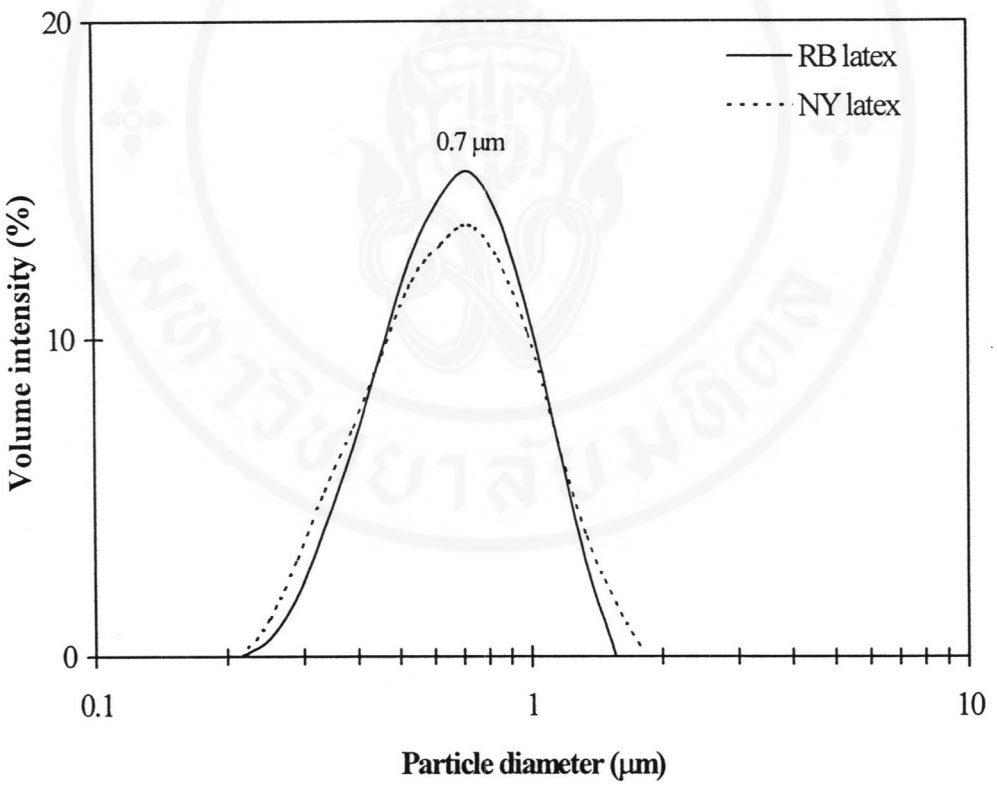


Figure 3.1: Particle size distribution, by volume, of the concentrated NR latices used in this study

The curves in Figure 3.1 could not indicate the meaningful difference between the average particle size by volume of the two latices which was about 0.7 μm. The

broad size distributions were observed in both latices, i.e., the diameter of RB varied from 0.22 to 1.34 μm while that of NY ranged from 0.22 to 1.82 μm. Our results strongly supported that rubber particles in NR latex are naturally polydisperse [10,11].

II. Study of Morphology of Sulphur-prevulcanized NR Latex Particles

The vulcanizing ingredients, i.e., sulphur, ZDEC and ZnO, in powder form were dispersed in distilled water and ground. The size of these ingredients, before and after milling, was determined. After mixing with NY latex, factors affecting the prevulcanization reaction such as effect of maturation and the added surfactant (SDS) were investigated. The fractured surface morphology of sheets casted from prevulcanized latex was observed under SEM. Then the phase transfer/ bulk polymerization/ TEM process was used for the morphological study of sulphur-crosslinked rubber particle embedded in PS. Effect of initiator concentration and quantity of transferred rubber in styrene monomer were also examined.

II.3.1 Size of Vulcanizing Ingredients

Although milling vulcanizing ingredients in water seems to be unnecessary for vulcanization to take place, i.e., their sizes have no effect on the rate or extent of crosslinking, the method is a ubiquitous practice [58].

The size of vulcanizing ingredients in unmilled and ball-milled forms (see Section 2.4) was, therefore, measured by using a particle size analyzer (Mastersizer S, Malvern). The size distribution curves of sulphur, ZDEC and ZnO are displayed in Figures 3.2, 3.3 and 3.4, respectively.

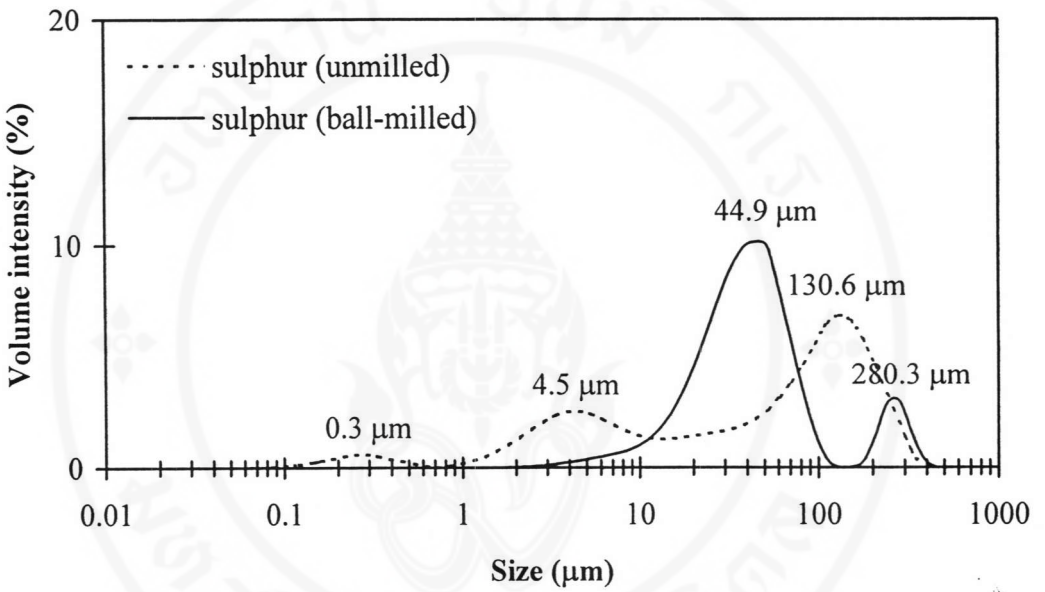


Figure 3.2: Size distribution of sulphur

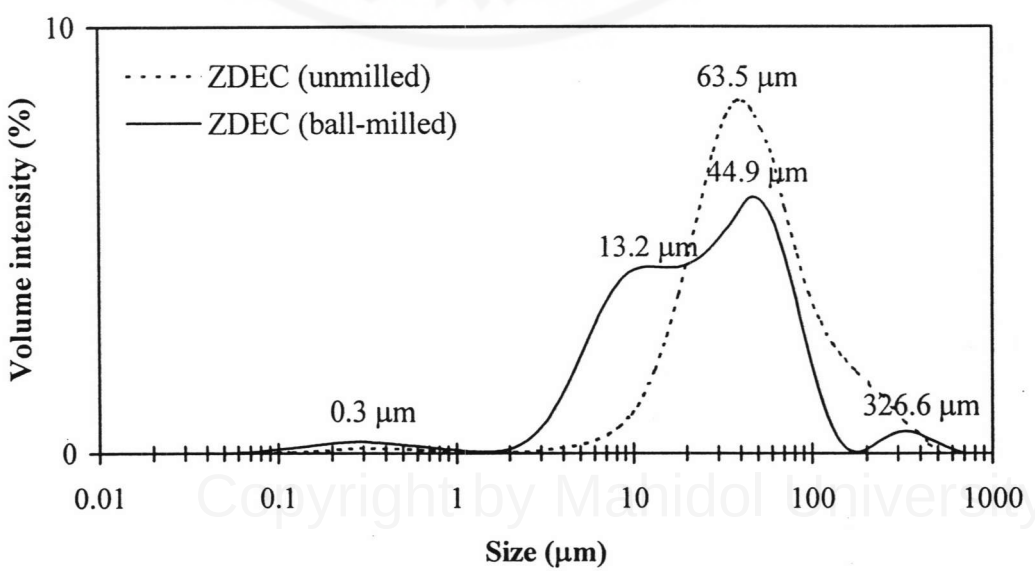


Figure 3.3: Size distribution of zinc diethyldithiocarbamate (ZDEC)

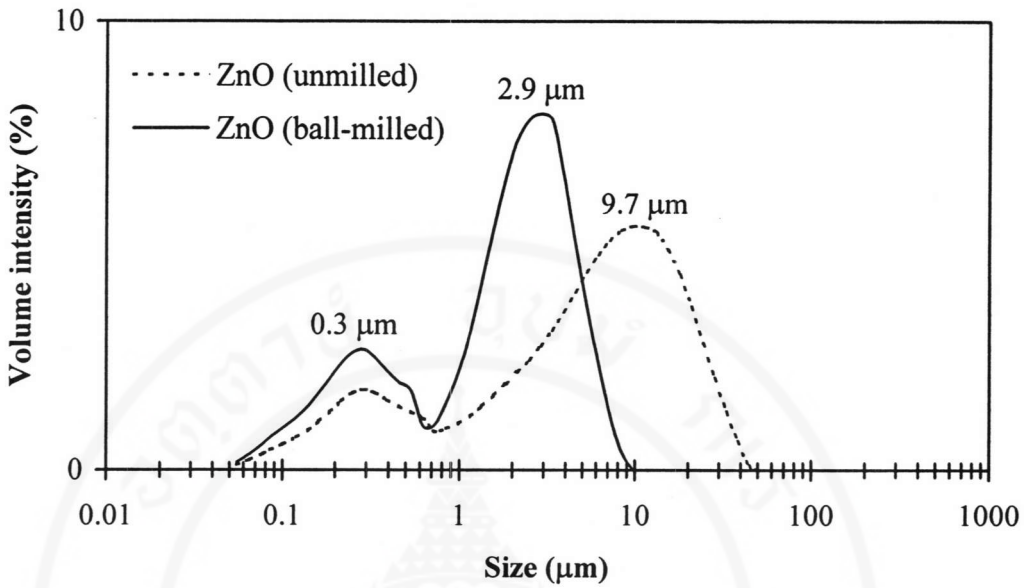


Figure 3.4: Size distribution of zinc oxide (ZnO)

From the results shown in Figure 3.2, it was seen that the average size of sulphur in powder form was about 130.6 μm. After ball milling, its size greatly decreased to about 44.9 μm. Figure 3.3 also shows the decrease of mean diameter of ZDEC from about 63.5 to 13.2 and 44.9 μm after ball milling. For ZnO, its size in powder form was about 9.7 μm and after passing through grinding process, its average size reduced 2.9 μm.

Therefore, the observation in Figures 3.2-3.4 confirms that the sizes of vulcanizing ingredients after ball milling were smaller than those of the original powders. However, their sizes were still very large compared to that of average NR latex particle (0.7 μm).

II.3.2 Study of Factors Affecting Sulphur Prevulcanization

After mixing aqueous dispersion of vulcanizing agents with NY latex, the sulphur prevulcanization was carried out at 60°C. During the reaction, portions of the mixture were collected at different time intervals. Then %swelling ratio, which is inversely proportional to crosslink density, of the sheets casted from the prevulcanized latex were determined. Various factors, i.e., maturation, NR latex from different suppliers and addition of surfactant, affecting the sulphur prevulcanization were investigated. The amount of residual vulcanizing ingredients in the sulphur-prevulcanized latex was also determined.

II.3.2.1 Effect of Maturation [6,12,32]

To study the effect of maturation, 2 experiments, i.e., the sulphur-prevulcanized system heated after maturing for 2 h and the system omitting the maturation stage, were taken place in Formulation A (in Section 2.4.1). The results of swelling ratio (%) of prevulcanized NY latex sheets obtained are shown in Figure 3.5.

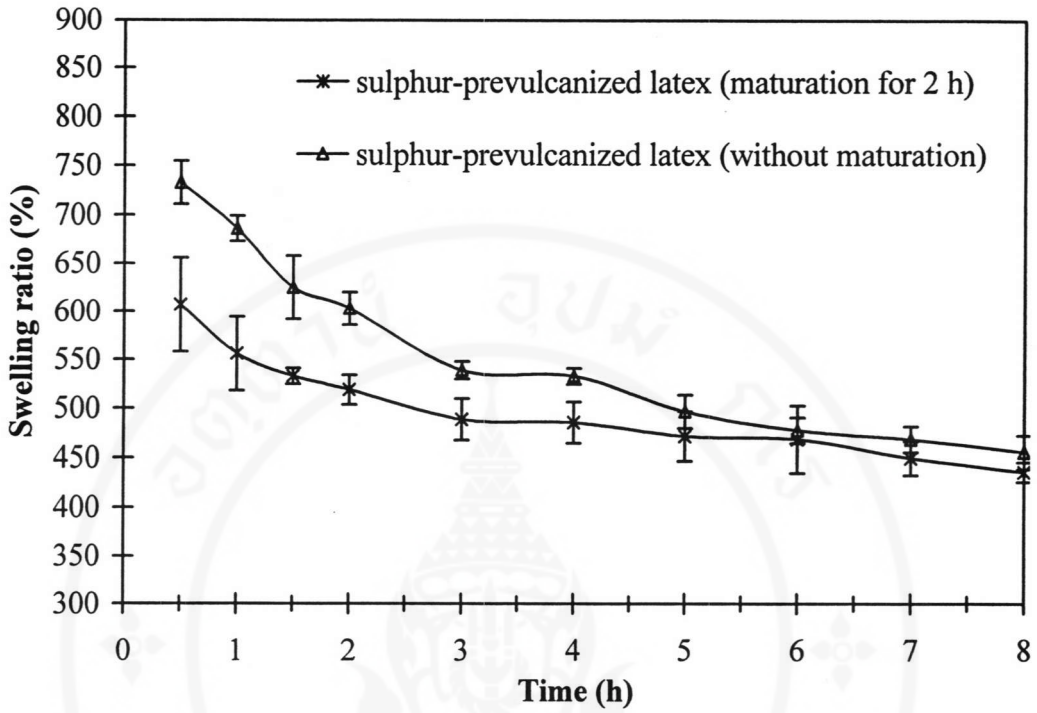


Figure 3.5: Effect of maturation in the sulphur prevulcanization on swelling ratio of sheet casted from prevulcanized NY latex after heating at 60°C

The results showed that the swelling ratio of prevulcanized latex decreased with increasing of reaction time in the beginning and then reached a plateau within 5 h. It was observed that the two curves in Figure 3.5 had the significant difference in the initial period of prevulcanization reaction. Maturing latex for 2 h before being heated provided more crosslink density (less swelling ratio) of latex sheet in the shorter reaction time. It indicated that the maturation stage greatly allowed the maximum dissolution of sulphur-accelerator species, possibly formed as water-soluble surface-active species in the aqueous phase which then migrate to the rubber particles. Consequently, after heating efficient crosslinking of rubber was rapidly produced from the species already present. Indeed, some crosslinking might occur during the

maturation period. However, the equilibrium swelling ratio of the final prevulcanized latex sheet did not depend on maturation because an insignificant difference of the minimum and constant equilibrium swelling ratio, i.e., about 436 ± 10 and 456 ± 17 %, respectively which indicated the fully vulcanized rubber [57] was noted. The sulphur-prevulcanization with maturation stage was selected for using in further experiments.

II.3.2.2 Effect of NR Latex from Different Suppliers

Sulphur prevulcanization of 2 latices, RB and NY, was prepared by using Formulation A (in Section 2.4.1). Their swelling ratios at various reaction times were determined and the results obtained are displayed in Figure 3.6.

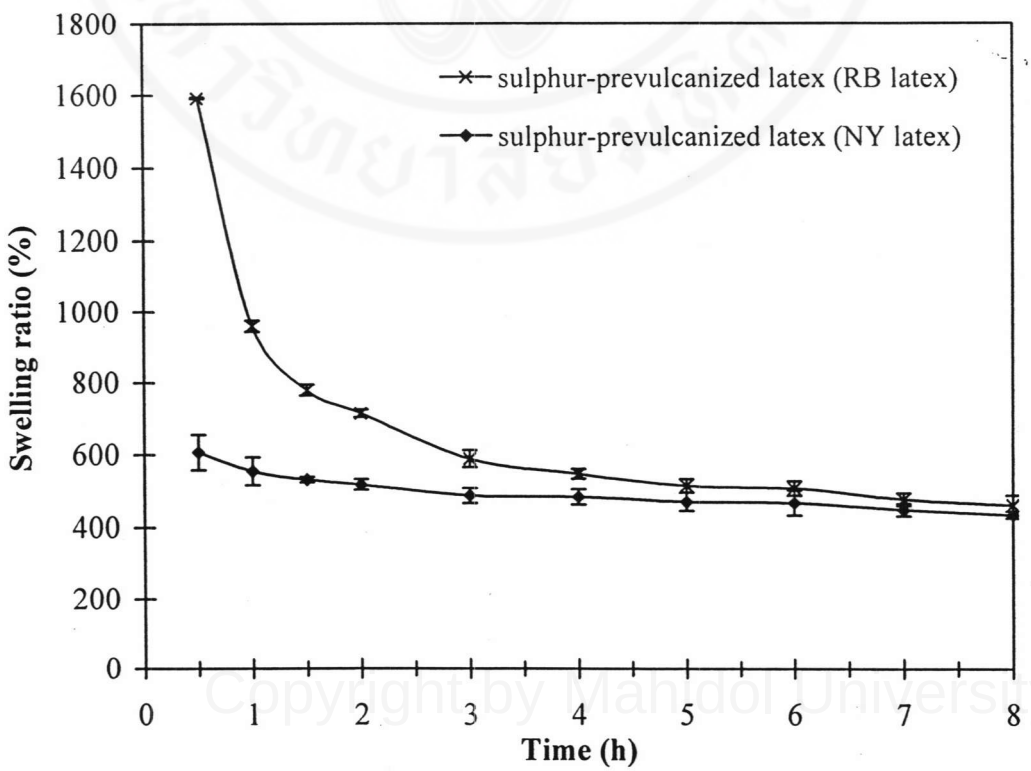


Figure 3.6: Swelling ratio of sheets casted from sulphur-prevulcanized RB and NY latices versus vulcanization times

From Figure 3.6, it was seen that the swelling ratio of prevulcanized RB latex sheet rapidly decreased with increasing of vulcanization time and then approached constant value (463 ± 27%) within 5 h. In the case of NY latex, the low and constant swelling ratio (436 ± 10%) was obtained since the beginning. The results indicated that the rate of prevulcanization of NY was higher than that of RB. It might be explained by considering the effect of non-rubber substances present in the NR latex. It has already been shown (Section I.3.2) that the nitrogen content of NY prevulcanized latex (0.83 ± 0.02%) was greater than that of RB latex (0.37 ± 0.01%). As previously reported by Ghazaly [17] that some non-rubber substances in high-ammonia latex concentrate could accelerate sulphur prevulcanization to a greater extent. Othman [59] precisely found that amino acid, which is the hydrolysis product of NR latex protein, acts as sulphur-cured activator for natural rubber. In addition, Tangboriboonrat [2] has observed that the low amount of remaining proteins in NR latex after enzyme deproteinization causes a decrease of efficiency of vulcanization of latex with γ-ray.

II.3.2.3 Effect of Addition of SDS

In order to better understand the means by which the vulcanization chemicals, originally present as dispersed solids, are transported into the rubber particles, an anionic surfactant, i.e., sodium dodecyl sulfate (SDS) was added to the sulphur prevulcanization system. Blackley et al. [43,60] previously showed that the addition of small amount of fatty acid surfactant having eleven carbon atoms can enhance the stability of NR latex by rearranging the native protein-lipid at rubber surface. It was, therefore, of interest to study effect of SDS on crosslink efficiency of sulphur

prevulcanization of NY (at pH 9) in the present work. Equilibrium swelling ratios of the sulphur-prevulcanized NY latex sheets with and without SDS were determined and compared with that of unmodified NR heated at 60°C for 5 h. The data are plotted with heating time as shown in Figure 3.7.

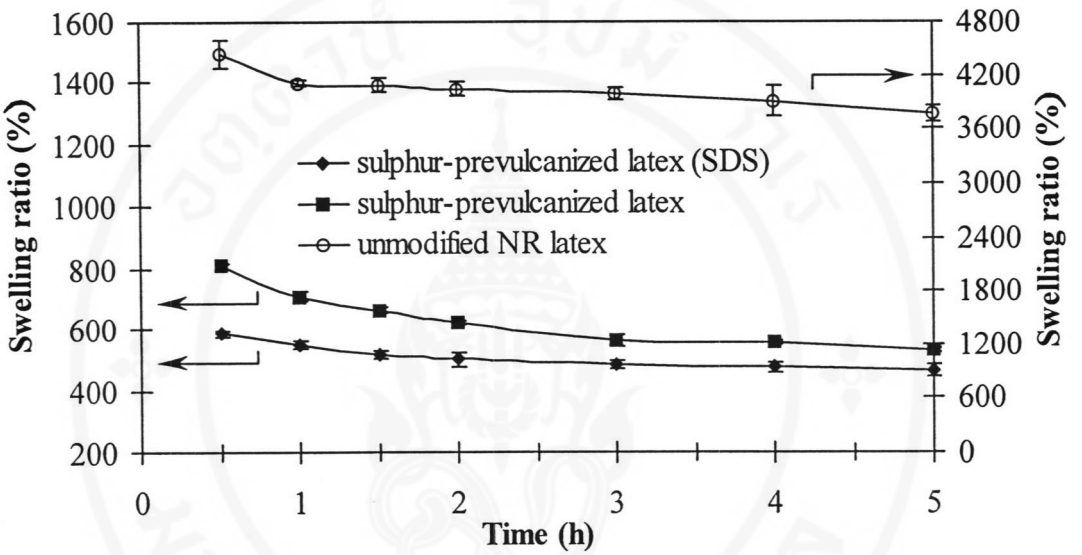


Figure 3.7: Swelling ratio of sulphur-prevulcanized NY latex with and without SDS compared with that of unmodified NR latex heated at 60°C

From Figure 3.7, it was observed that the swelling ratio of both types of sulphur-prevulcanized latex sheets slightly decreased when the prevulcanization time was increased. The constant and minimum value was less than 500% indicating fully crosslinked rubber. The resemblance of two curves of sulphur-prevulcanized latex with and without SDS was noticed. However, the presence of SDS caused an increase in the crosslink density of NR in the initial period. SDS might increase the dissolution of chemicals and accelerate the adsorption of sulphur-accelerator or water-soluble surface-active species on the surfaces of rubber particles.

The effect of addition of surfactant on particle size of prevulcanized latex was also investigated. The particle size distributions of sulphur-prevulcanized latices stabilized by KOH+SDS and by KOH compared with that of unmodified latex are revealed in Figure 3.8.

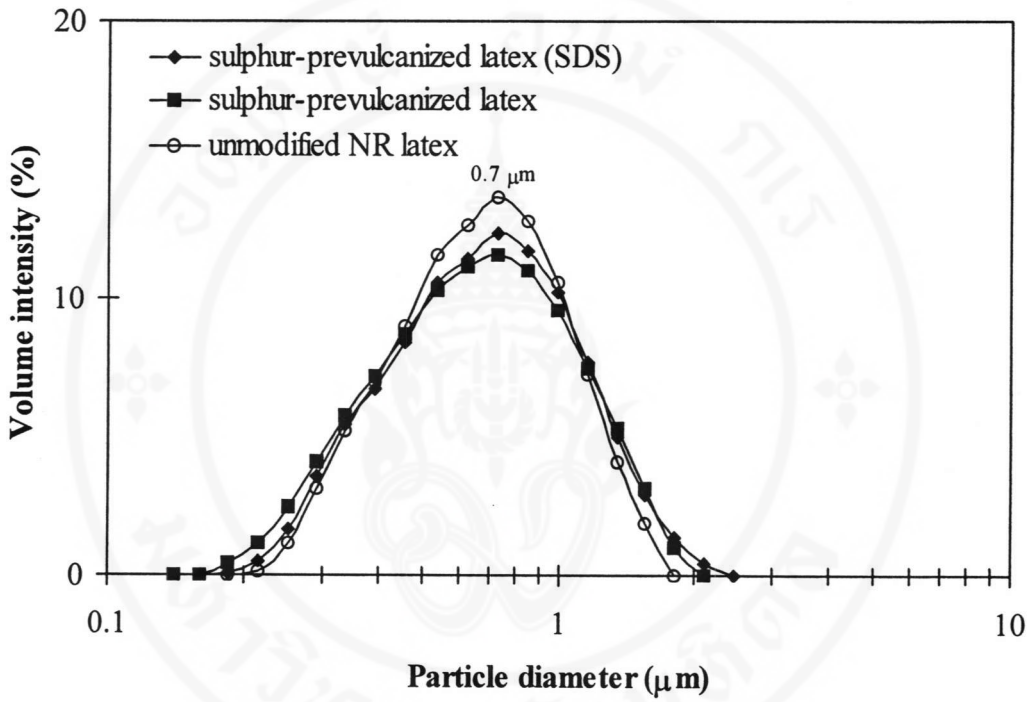


Figure 3.8: Particle size distribution, by volume, of sulphur-prevulcanized latex with and without SDS compared with that of unmodified latex

It was seen in Figure 3.8 that the particle size distributions of both sulphur-prevulcanized latices were slightly broader than that of unmodified latex. This might be explained that KOH and SDS caused an increase in hydrodynamic volume of rubber particles possibly by alteration of arrangement of the indigenous adsorbed anions (possibly derived from protein-lipid complex) on latex particles. The coherent of soap-anion clusters might be redispersed [42] leading to the highly solvated of aqueous serum surrounding NR particles. Between the two types of sulphur-

prevulcanized latex, the particle size of sulphur-prevulcanized latex having SDS was slightly larger than that of the latex adsorbed only with KOH. It insinuated that the presence of SDS assisted in the increment of hydrodynamic volume of crosslinked latex particle as explained above.

The phase transfer technique generally used to indicate the amount of charge on surface particle was applied for the study of sulphur-prevulcanized and unmodified NR latices and the CTC values are shown in Table 3.3.

Table 3.3: CTC values of sulphur-prevulcanized and unmodified NR latices

Sample	CTC ($\times 10^{-5}$)
Unmodified NR latex	4.66 ± 0.15
Sulphur-prevulcanized latex	
- KOH + SDS	4.73 ± 0.02
- KOH	3.60 ± 0.05

From the data obtained, the CTC value of sulphur-prevulcanized latex added with SDS was higher than that of KOH-stabilized system. This was due to an increase in the amount of negative charge on the surface of rubber particle derived from the added SDS as previously reported by Chindaprasert [61]. Unexpectedly, it was found that the presence of only KOH caused a significant decrease in the CTC value compared with the unmodified NR latex. It might be due to the neutralization between KOH and adsorbed long-chain fatty acid soaps, hydrolysis products of lipid, at the latex particle surface. Another possible explanation was the neutralization of

the native surfactants by the species formed from vulcanizing agents notably containing Zn^{2+}ion.

II.3.2.4 Determination of Residue Vulcanizing Ingredients

The quantity of excess vulcanizing ingredients used in the sulphur prevulcanization of NY latex was believed to remain in the aqueous phase. The compounded latex was, therefore, multicentrifuged to eliminate the residues of these chemicals (in Section 2.5.3) and the centrifuged latex obtained was called "residue-free-sulphur-prevulcanized latex". The experiment showed that the amount of residual chemicals of sulphur-prevulcanized latices with and without SDS were 0.52 and 0.63% w/w, respectively. It was noted that the amount of residual chemicals were very small compared with the concentration of vulcanizing ingredients initially added into the concentrated NR latex. This indicated that almost all of the vulcanizing ingredients could diffuse into the rubber particles. The lower amount of residue in the presence of SDS might be due to the improvement of solubility of vulcanizing chemicals in water and/ or of their migration into rubber phase. The data agreed well with the extent of crosslink (Figure 3.7 in Section II.3.2.3).

Next, the phase transfer technique was applied for determining the CTC value of residue-free-sulphur-prevulcanized latex and the data are shown in Table 3.4.

Table 3.4: CTC values of residue-free-sulphur-prevulcanized and unmodified NR latices

Sample	CTC ($\times 10^{-5}$)
Unmodified NR latex	4.66 ± 0.15
Residue-free-sulphur-prevulcanized latex	
- KOH + SDS	4.77 ± 0.03
- KOH	3.62 ± 0.06

It was observed that the trend and the value of CTC of residue-free-sulphur-prevulcanized latex with or without SDS were similar to those of the sulphur-prevulcanized latex before multicentrifugation (see Table 3.3). It might be explained that residual agents did not affect the surface properties of crosslinked latex particle. Therefore, it could be deduced that the mechanism of sulphur prevulcanization involved the water-soluble surface-active species from vulcanizing agents dissolving in the aqueous serum before diffusing into the rubber particles.

II.3.3 Bulk Polymerization of Styrene Monomer Containing Transferred Sulphur-prevulcanized Rubber

Besides using for determination of CTC, the phase transfer technique combined with bulk polymerization has been effectively applied to provide a suitable sample for study of the morphology of rubber particle under TEM [2]. The advantage of this process is that the disturbance of rubber particle structure was minimized because the

air, freeze or chemical drying stage of rubber latex, normally needed in the sample preparation, was omitted.

Before morphological study of sulphur-prevulcanized rubber particle embedded in PS matrix, effect of initiator concentration and quantity of transferred rubber in styrene monomer on bulk polymerization of styrene were investigated in order to accomplish suitable condition for preparation of specimen.

II.3.3.1 Effect of Initiator Concentration

Conversion of the styrene containing swollen transferred sulphur-prevulcanized NR (3% RB latex with SDS, at 70°C) when using various initiator concentrations (0.4, 0.6 or 1.0 wt% of benzoyl peroxide (BPO)) is shown in Figure 3.9.

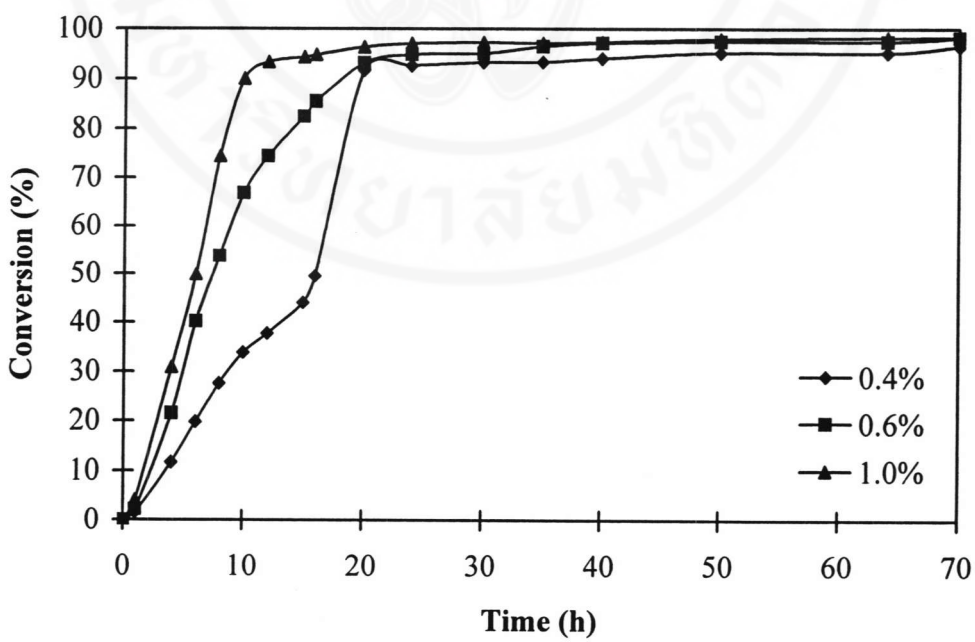


Figure 3.9: Effect of concentration of initiator (BPO) on %conversion of styrene containing transferred sulphur-prevulcanized rubber (3% RB latex with SDS, 70°C)

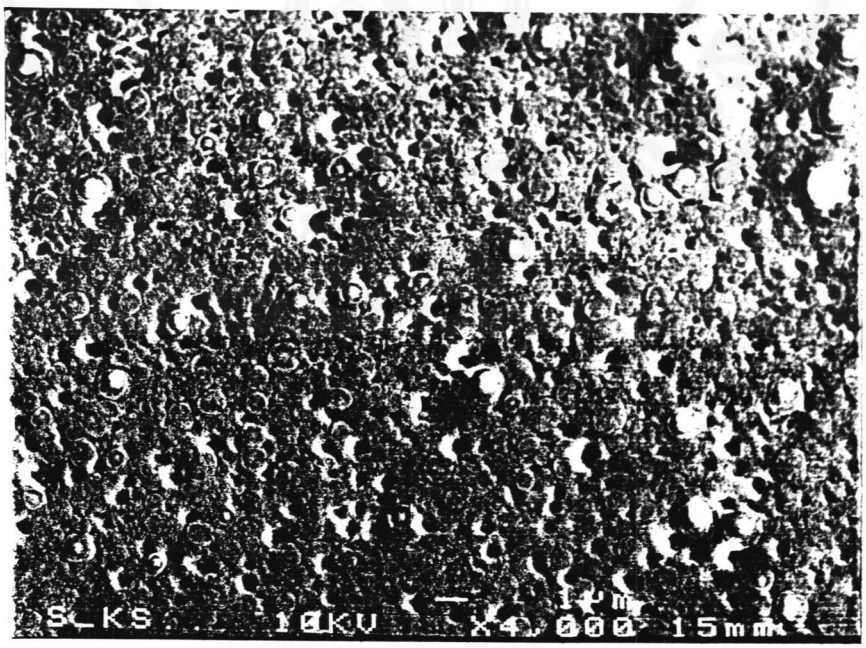
From Figure 3.9, it was observed that the conversion of styrene monomer promptly increased in the initial period of polymerization and then approached a constant value close to 100%. With an increase in the amount of BPO, the rate of polymerization increased and the time required for complete conversion reduced, i.e., within ca. 20 h and 16 h from 0.4 to 1.0%BPO. In the further step, the styrene containing 3%w/w of transferred sulphur-prevulcanized NR polymerized at 70°C for 16 h with 1%BPO were the conditions selected for preparing samples for morphological study of prevulcanized NR particles.

II.3.3.2 Quantity of Transferred Rubber in Styrene Monomer

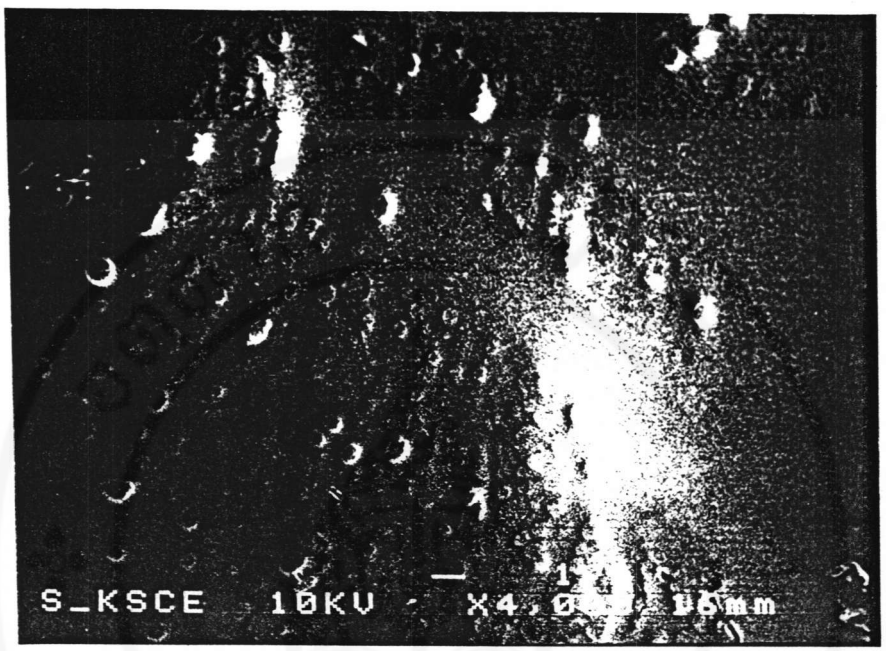
When the phase transfer technique was complete, two parts of rubbers were noted, i.e., the swollen rubber in the upper styrene phase and the destabilized rubber suspended at the interphase. Practically, both parts could not be clearly separated, they were collected together and called "transferred rubber". In our experiment, the quantity of transferred rubber in the styrene monomer was found to be about 80-85% w/w. The remaining rubber was coagulated at the wall of Erlenmeyer flask and magnetic bar. These results agreed well with the values obtained from the phase transfer of γ-radiation vulcanized natural rubber (RVNR) latex (about 80%) reported in the previous study [62].

II.3.4 Scanning Electron Microscopy (SEM) of Fractured Sulphur-prevulcanized NR Latex Sheet

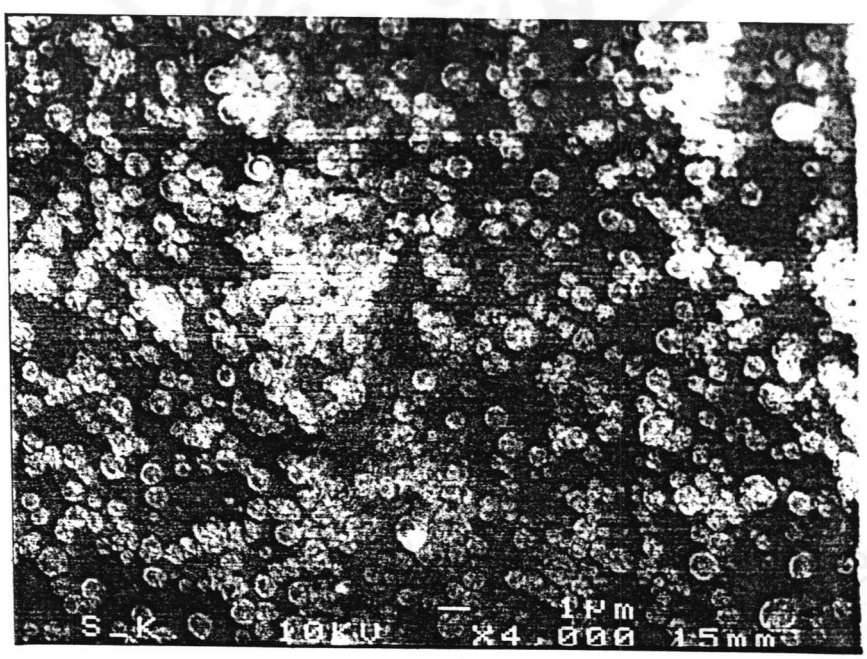
Sulphur-prevulcanized latex having KOH+SDS or KOH was casted to form sheet of 2 mm thickness at room temperature. In addition, the sheet casted from prevulcanized latex after removing residue of vulcanizing ingredients (see Section 2.5.3) called "residue-free-sulphur-prevulcanized latex" was prepared. SEM micrographs of fractured surface of these latex sheets and that of uncrosslinked latex are shown in Figure 3.10 (a-e).



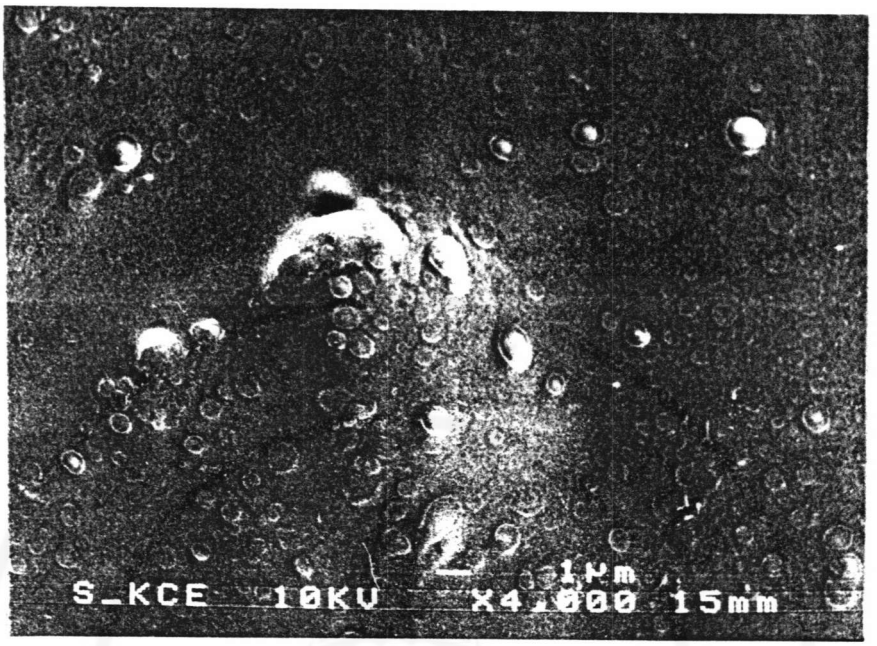
a) sulphur-prevulcanized latex (KOH+SDS)



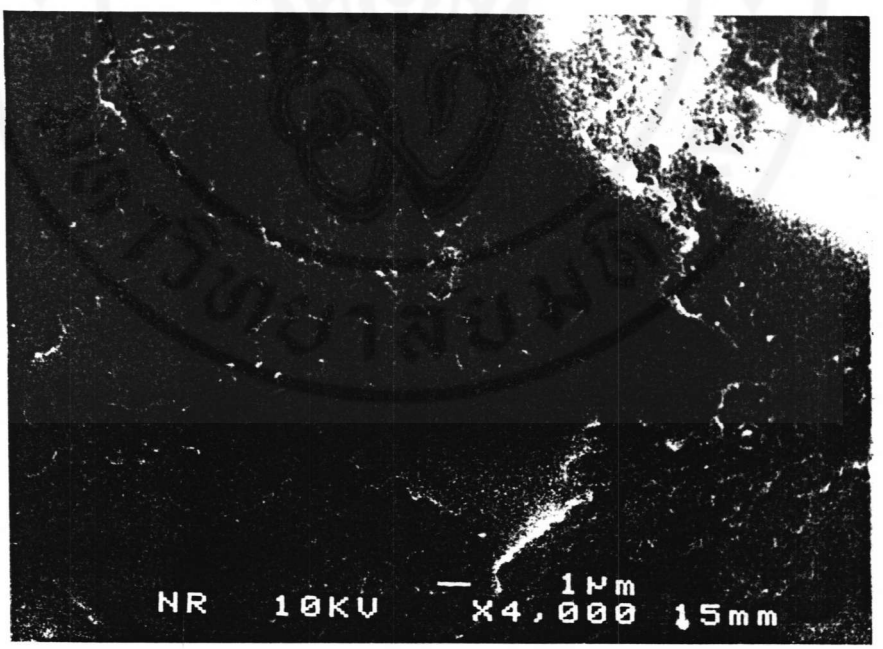
b) residue-free-sulphur-prevulcanized latex (KOH+SDS)



c) sulphur-prevulcanized latex (KOH)



d) residue-free-sulphur-prevulcanized latex (KOH)



e) uncrosslinked NR latex

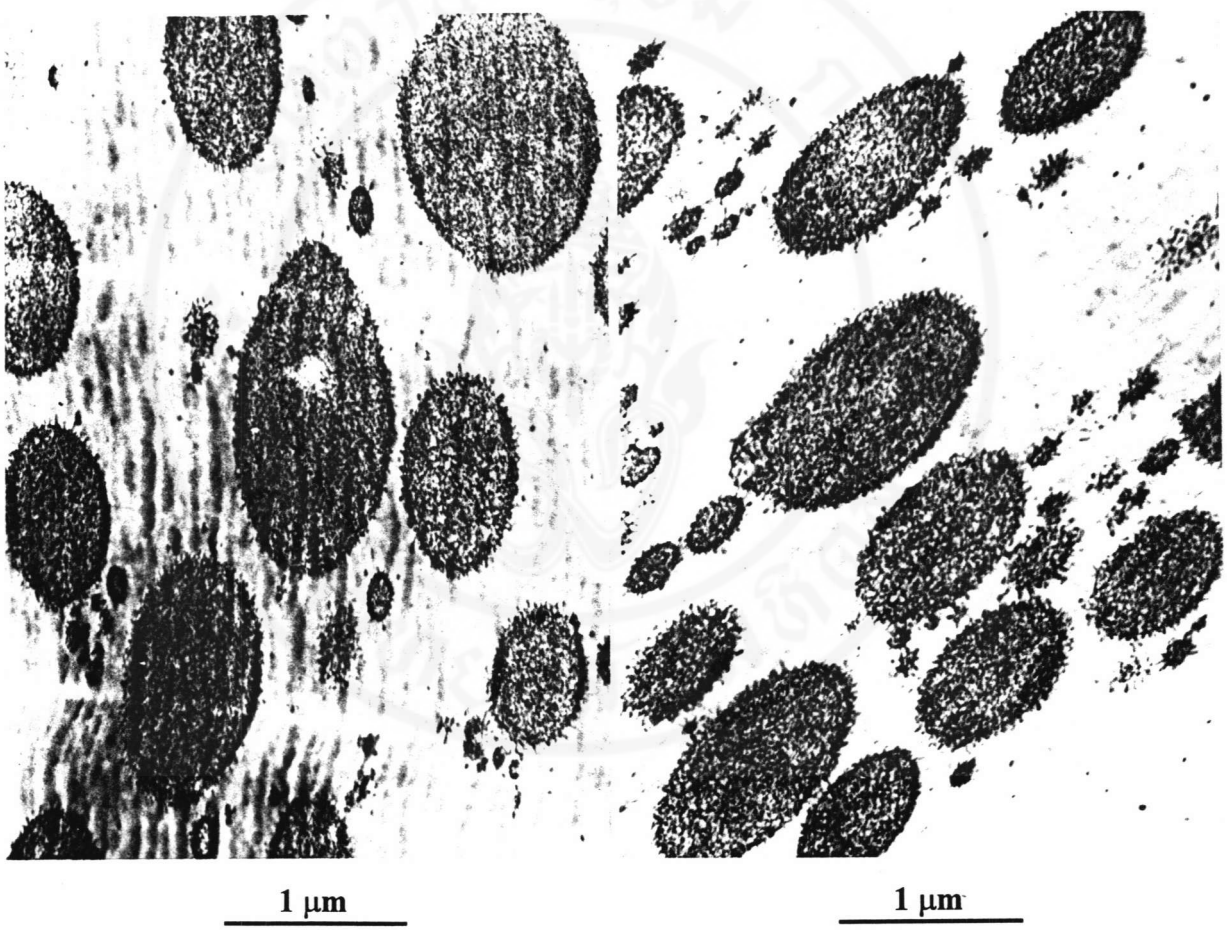
Figure 3.10: SEM micrographs of fractured surface of sheets casted from a) sulphur-prevulcanized (KOH+SDS) b) residue-free-sulphur-prevulcanized (KOH+SDS) c) sulphur-prevulcanized (KOH) d) residue-free-sulphur-prevulcanized (KOH) e) uncrosslinked NR latices

From the micrographs in Figure 3.10 (a-d), it was also observed that most of NR particles were spherical in shape and polydisperse in size. The discrete crosslinked rubber particles were clearly seen in these Figures compared with the structureless feature of sheet casted from the uncrosslinked NR latex in Figure 3.10 (e). This was an evidence that the crosslink of rubber molecules in NR particles really took place and, hence, the harder particles. The highly crosslinked particles could reasonably restrict the interparticle diffusion and entanglement of polymer chains. Moreover, it was of interest to note the presence of membrane layer, derived from protein-lipid complex, around crosslinked particles [1-3]. The membrane seemed to be rigid and possibly retard the coalescence between adjacent particles during the sheet formation [6,63-65].

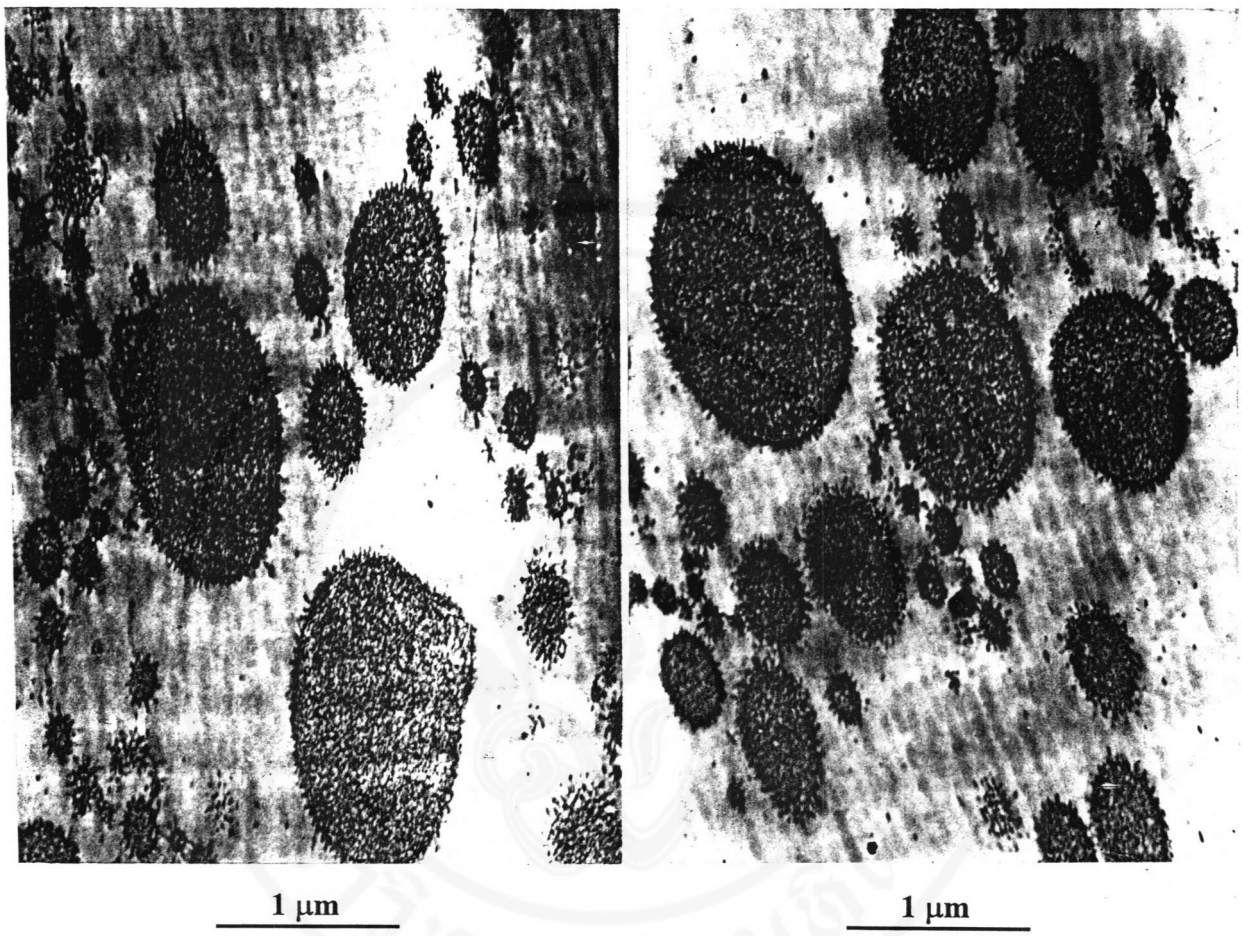
II.3.5 Transmission Electron Microscopy (TEM) of Sulphur-prevulcanized Latex Particle Embedding in Polystyrene Matrix

As previously described, a specimen for morphological study of sulphur-prevulcanized NR particle was obtained after completely polymerizing the styrene containing transferred sulphur-prevulcanized. The sulphur-crosslinked rubber particles embedding in PS matrix were rigid enough to be cut to an ultra-thin section by ultramicrotome and then studied under TEM. By using this method, the direct evidence of actual crosslinked particle structure should be obtained. TEM micrographs of sulphur-prevulcanized latex particles (with and without SDS)

embedded in PS are presented in Figure 3.11 (a-b) while Figure 3.11 (c-d) show those of residue-free-sulphur-prevulcanized latex particles.



a) sulphur-prevulcanized latex (SDS) b) sulphur-prevulcanized latex



c) residue-free-sulphur-prevulcanized latex (SDS)

d) residue-free-sulphur-prevulcanized latex

Figure 3.11: Transmission electron micrographs of an osmium tetroxide-stained sulphur-prevulcanized NR having a) KOH+SDS and b) KOH and residue-free-sulphur-prevulcanized NR having c) KOH+SDS and d) KOH, incorporated in PS matrix

All micrographs showed two-phase morphology of the rubber particles (dark) dispersed in PS matrix (light). The broad distribution of size and the elliptical shape of crosslinked NR particles were clearly seen. The ovoid shape of the particles is

probably a result of the sectioning process wherein the action of the knife edge tends to slightly compress the sample. Inside the rubber particles, the network-like structure was found as previously noticed in the case of RVNR latex [1-3]. The structure was believed to arise from the polymerization of swollen styrene in crosslinked NR particles and could be classified as semi-interpenetrating polymer networks (semi-IPNs type Semi-I) [66]. It was noted that the network of rubber in each sulphur-prevulcanized NR particle uniformly took place as already reported by Cook [38]. However, the present results disagreed with Ho's work which stated that an unvulcanized core surrounded by highly crosslinked shell should be the morphology of sulphur-prevulcanized particle in latex film [6]. The description of structure of prevulcanized NR latex particle in the aforementioned works, is deduced from the study of latex film without providing the direct evidence of particle as done in our work.

It was also of interest to observe in each micrograph that the vulcanization took place in all rubber particles. The mechanism involving dissolution of the reactants in the aqueous phase before diffusing into rubber particles was, therefore, favorable. The equilibrium diffusion of reagents in all particles was produced during the maturation. Then homogeneous crosslink occurred, irrespective of size. This explanation was greatly consistent with the work of Porter cited earlier [4].

The other important observation in the micrograph was a darker ring near the particle surface corresponding to the membrane layer derived from protein- lipid [2]. The hairy-like structure was also noted on rubber surface which might result from uncrosslinked polyisoprene molecules protruding out of the rubber particles as a result of them being swollen by styrene. The presence of SDS (compare Figure 3.11 (a)

with (b)) and elimination of residual reagents (compare Figure 3.11 (a) with (c) and Figure 3.11 (b) with (d)) did not provide obvious differences of the surface structure.

III. Study of Morphology of Peroxide-prevulcanized NR Latex Particles

In peroxide-prevulcanization of NR latex, the formation of carbon-carbon crosslinks between rubber molecules was generated by using the fructose-activated system in conjunction with *tert*-butyl hydroperoxide (*t*-BuHP). Firstly, the swelling ratio of peroxide-prevulcanized latex sheet was examined. Then the surface morphology of the latex sheet was studied by using SEM. The critical transfer concentration (CTC) and quantity of transferred rubber in styrene monomer were determined when the phase transfer was applied. The morphology of peroxide-prevulcanized latex particles embedded in PS was studied under TEM. Effects of SDS on crosslink density and negative charges of rubber particles in the peroxide-vulcanized NR latex were also considered.

III.3.1 Study of Peroxide Prevulcanization of NR Latex

III.3.1.1 Swelling Ratio

The concentrated NR latex (NY latex) was prevulcanized by using the *t*-BuHP/ fructose-activated system at 60°C (Formulation A in Table 2.4). The swelling ratio of sheets casted from the peroxide-prevulcanized NR latex (with and without SDS)

withdrawn at various reaction times were determined to compare with that of unmodified latex sheet as presented in Figure 3.12.

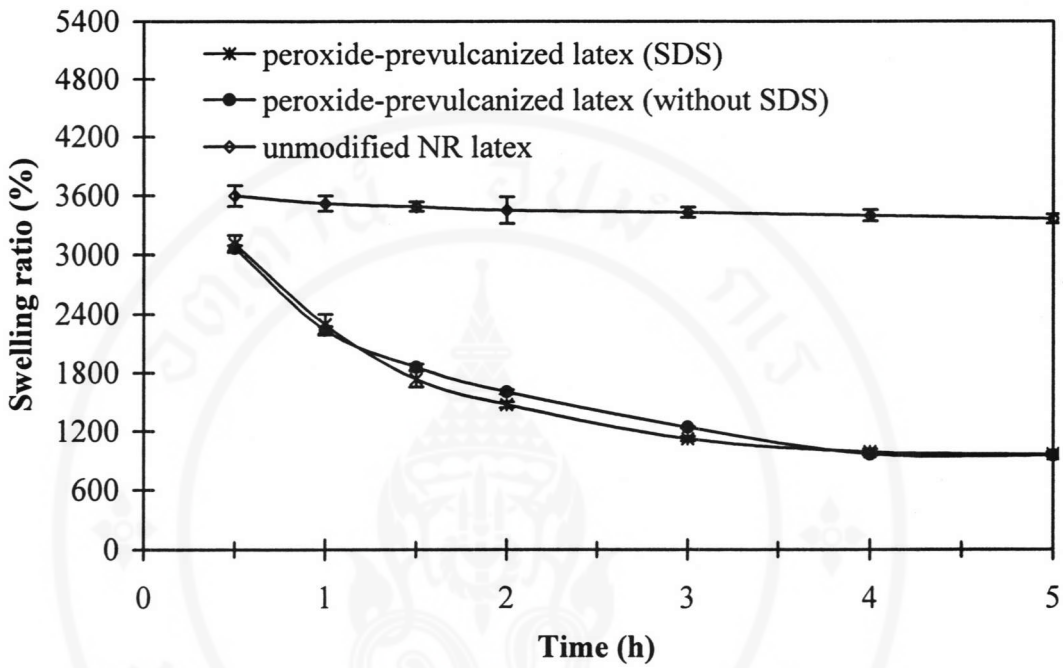


Figure 3.12: Swelling ratio of sheets casted from peroxide-prevulcanized latex (with or without SDS) withdrawn at various vulcanization times at 60°C compared with that of unmodified NR latex

It was observed that %swelling ratio of prevulcanized NR sheet rapidly decreased with increasing of vulcanization time and then approached constant value within ca. 4-5 h. The curves of both vulcanized latex sheet with and without SDS showed the same trend and their constant swelling ratios were 958 ± 17 and 944 ± 11%, respectively. The presence of SDS, therefore, did not affect the peroxide vulcanization reaction of NR latex. From the minimum and constant swelling ratio (about 950%), it was concluded that lightly vulcanized rubber was obtained [57] and the vulcanization time selected for using in the next study was about 5 h.

III.3.1.2 Critical Transfer Concentration (CTC)

The CTC values obtained from the phase transfer technique of the peroxide-prevulcanized and unmodified latices are presented in Table 3.5.

Table 3.5: CTC values of peroxide-prevulcanized and unmodified NR latices

Sample	CTC ($\times 10^{-5}$)
Unmodified NR latex	4.39 ± 0.16
Peroxide-prevulcanized latex	
- SDS	4.70 ± 0.04
- without SDS	4.10 ± 0.03

It was observed in Table 3.5 that the CTC value of peroxide-prevulcanized latex stabilized with SDS was higher than that of unmodified and peroxide-prevulcanized without SDS. This was due to the fact that SDS increased the amount of negative charges on surface of rubber particle as mentioned before (in Section II.3.2.3). Comparing with the unmodified NR, the CTC of peroxide-prevulcanized latex without SDS was slightly lowered. It was possible that the protein-lipid complex around rubber particle surfaces participated in the systematic creation of network structure of rubber molecules inside the particles [2]. The complex could be modified leading to the decrease of negative charge derived from protein-lipid complex. From Tables 3.3 and 3.5, it was deduced that the different interaction taking place on NR particle surface in the two prevulcanization systems. KOH and vulcanizing agents in

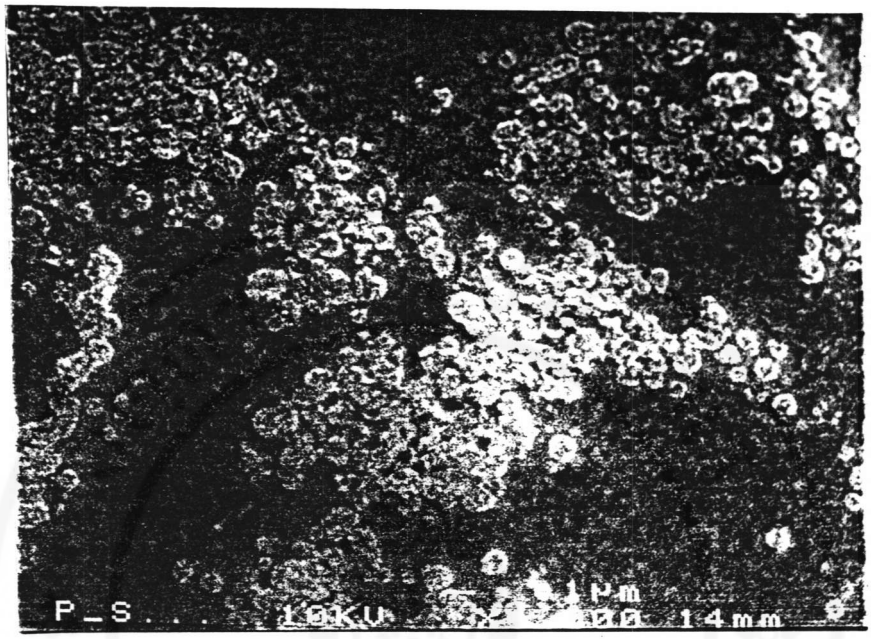
the sulphur system greatly contributed to rubber surface modification as already discussed.

III.3.1.3 Quantity of Transferred Rubber in Styrene Monomer

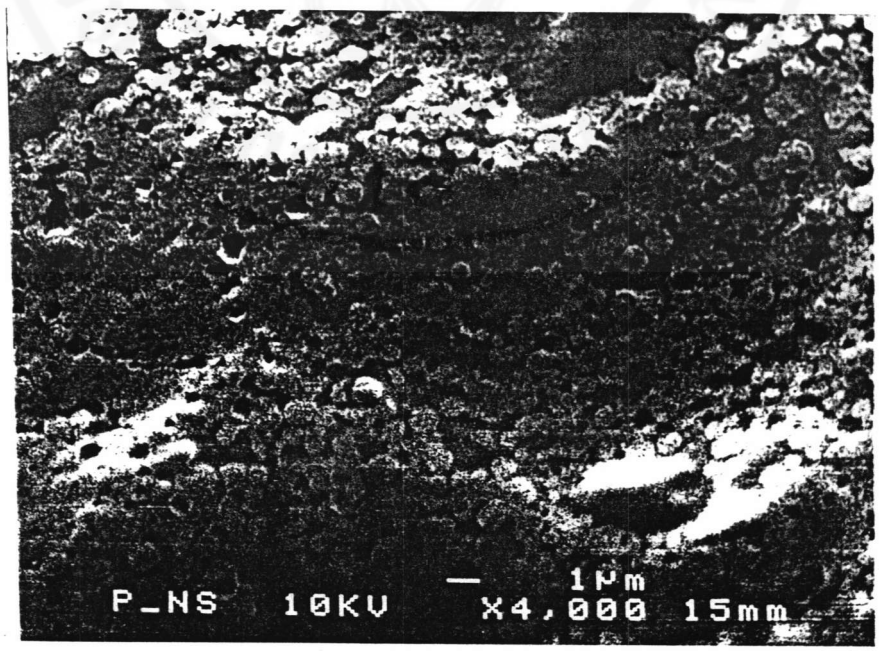
After phase transfer, the styrene containing swollen transferred peroxide-prevulcanized NR was allowed to equilibrium swell for 24 h at room temperature before determining the quantity of rubber in styrene monomer by using the procedure described in Section 2.6.2. About 85%w/w of transferred rubber particles were also accumulated in the styrene phase while the remaining rubber was stuck at the wall of Erlenmeyer flask and magnetic bar. The data showed that the phase transfer of peroxide-prevulcanized latex was completed [62].

III.3.2 Scanning Electron Microscopy (SEM) of Fractured Peroxide-prevulcanized NR Latex Sheet

The morphology of fractured surface of sheet casted from peroxide-crosslinked latex was studied by using the same method as in the case of sulphur-prevulcanized NR. SEM micrographs of peroxide-prevulcanized latex sheet with and without SDS are illustrated in Figure 3.13 (a-b).



a) peroxide-prevulcanized latex (with SDS)



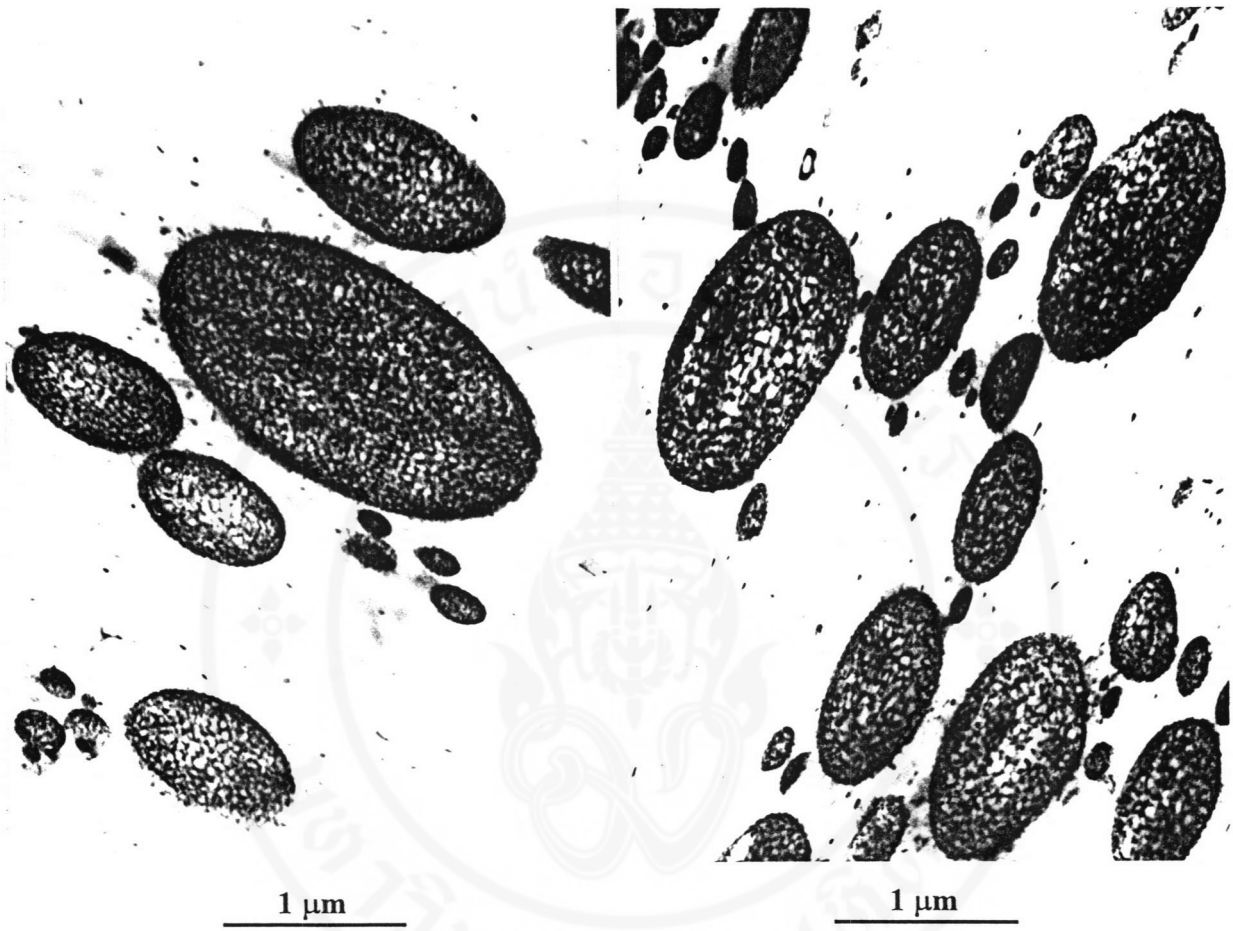
b) peroxide-prevulcanized latex (without SDS)

Figure 3.13: SEM micrographs of surface morphology of sheet casted from peroxide-prevulcanized latex a) with SDS b) without SDS

It was clearly noticed in the micrographs that most of the crosslinked NR particles were sphere and polydisperse in size. The appearance of particle boundary was more distinct than that of sulphur-prevulcanized latex particle. It indicated that peroxide-prevulcanized particles coalesced worse with adjacent particles.

III.3.3 Transmission Electron Microscopy (TEM) of Peroxide-prevulcanized Latex Particle Embedding in Polystyrene Matrix

The morphology of thin section of peroxide-prevulcanized NR particle embedded in PS was also investigated under TEM. The micrographs of peroxide-prevulcanized latex particle with and without SDS are respectively shown in Figure 3.14 (a-b).



a) peroxide-prevulcanized latex (with SDS)

b) peroxide-prevulcanized latex (without SDS)

Figure 3.14: Transmission electron micrographs of osmium tetroxide-stained peroxide-prevulcanized NR embedding in PS a) latex with SDS b) latex without SDS

From the micrographs, the broad size distribution and the elliptical shape of rubber particles (dark) containing small-sized PS subinclusions dispersed in PS matrix (light) were observed. The morphology of peroxide-crosslinked NR particle was generally similar to that of sulphur-vulcanized one (see Section II.3.5). The network

structure thoroughly took place in all sizes of peroxide-prevulcanized latex particles. However, the crosslink density of rubber chains in each particle was not homogeneous, i.e., the dense network was observed near particle surface while the central region of rubber particle had less extent of crosslink density. It was reasonably explained that free radicals from *t*-BuHP were effectively generated at NR particle/ water interface since the peroxide is soluble in NR particle whereas the activator fructose is water soluble [15]. In this case, the prevulcanization reaction was, therefore, faster than diffusion.

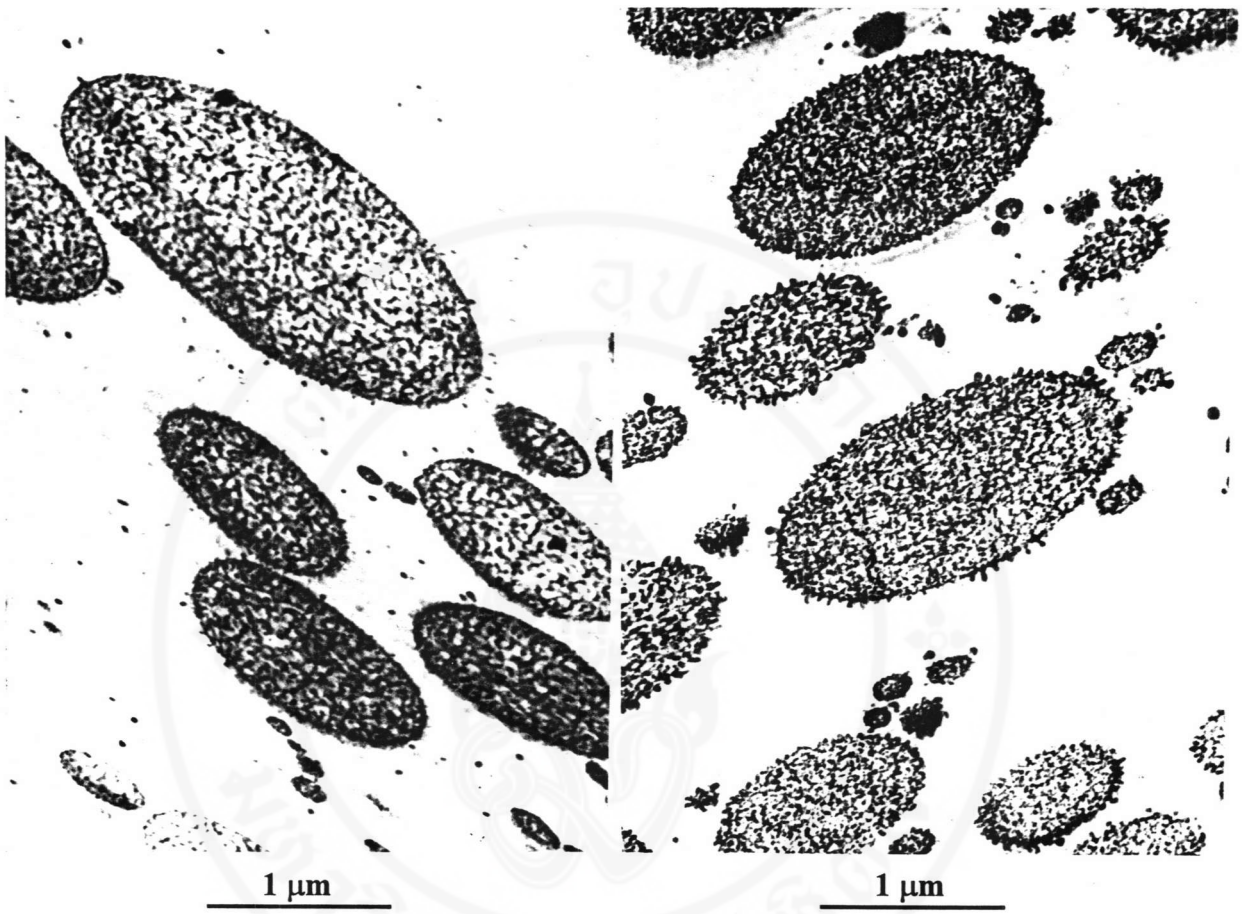
In comparison of Figure 3.14 (a) with (b), it was seen that the network structure of peroxide-prevulcanized particles with and without SDS was quite alike. It insinuated that the vulcanization of NR latex by using peroxide did not depend on the presence of stabilizer in the latex. The morphology agreed well with the value of swelling ratio as presented in Section III.3.1.1.

IV. Comparison of Morphology of Sulphur-prevulcanized, Peroxide-prevulcanized and γ-radiation Vulcanized Natural Rubber Latex Particles

In this part of our study, the morphologies of NR latex particles prevulcanized by using sulphur, peroxide and radiation systems were compared. The phase transfer/ bulk polymerization/ TEM process was the method used to provide direct information of the network structure of latex particles. It was also a tool for an attempt of elucidation of chemical reaction mechanisms of latex prevulcanization.

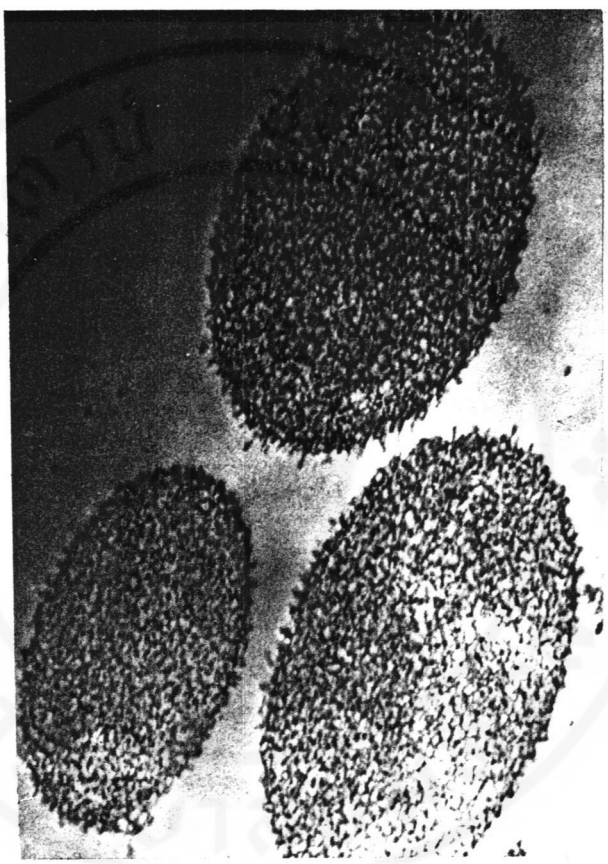
Transmission electron micrographs of sulphur- and peroxide-prevulcanized NR particles (at 60°C for 8 h) incorporated in PS matrix prepared in our experiment, and of γ-radiation vulcanized (RV) NR latex (total dose of 4 kGy) also embedded in PS kindly supported by C. Tiyapiboonchaiya [1], are shown in Figures 3.15 and 3.16.

a) sulphur-prevulcanized NR

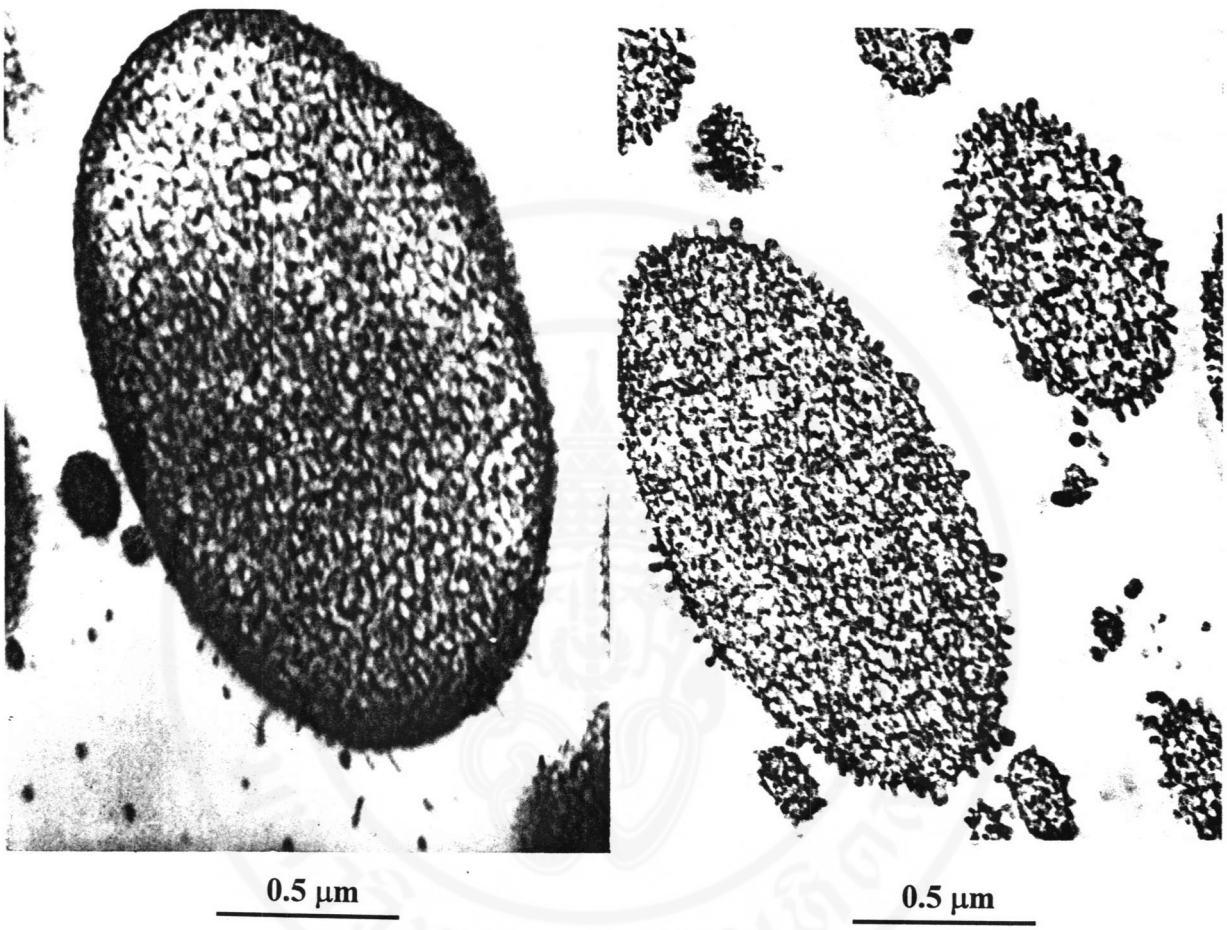


b) peroxide-prevulcanized NR c) RVNR

Figure 3.15: Transmission electron micrographs (×20,000) of NR latex particles prevulcanized by a) sulphur b) peroxide c) γ-radiation and embedded in PS prepared by using phase transfer/ bulk polymerization/ TEM process



a) sulphur-prevulcanized NR



b) peroxide-prevulcanized NR c) RVNR

Figure 3.16: Transmission electron micrographs (×40,000) of NR latex particles prevulcanized by a) sulphur b) peroxide c) γ-radiation and embedded in PS prepared by using phase transfer/ bulk polymerization/ TEM process

As illustrated in Figure 3.15 (a-c), the micrographs revealed the broad size distribution of crosslinked NR particles (dark) dispersed in PS matrix (light). In rubber particles, "semi-IPNs" (Semi-I) structure, was clearly observed [66] in all sizes of particles. Figure 3.16 (a) and (c) shows the uniform network structure within

rubber particles crosslinked by sulphur and γ-ray. The main reason concerned the relative rate of diffusion of the vulcanizing reagents in the rubber phase which was much faster than vulcanization reaction in the former case and the high energy of γ-ray which thoroughly penetrate in the latter case. It was previously found that the crosslink density of RVNR latex particle is proportional to the total dose [1,62]. This was different from the result of the peroxide prevulcanizate in which the inner region of rubber particle showed lower crosslink density than that near the particle boundary. The evidence supported that the free radical was greatly generated at the surface of peroxide-prevulcanized NR particle providing the dense network. The presence of non-rubber substances around rubber particles might play an important role in initiation step [1-3,17]. It could be stated that the peroxide/ fructose prevulcanization system took place from the outer to the inner part of particle. Therefore, the vulcanization was faster than diffusion process of vulcanizing ingredients and this would be the stimulating question remaining open for future research.

Considering the membrane layer around the prevulcanized NR particles, the dark layer around the peroxide-prevulcanized latex particle was clearly seen compared to that of sulphur-prevulcanized and RVNR particles. This indicated that the mechanism of penetration of vulcanizing agents and that of vulcanization in rubber particles in the three systems might be different. As already described in the case of peroxide-prevulcanized latex, *t*-BuHP and fructose encountered in the outer layer of latex particle and, consequently, free radicals were highly generated. Whereas, the vulcanizing agents used for sulphur prevulcanization have to firstly dissolve in the serum and then diffused into latex particle resulting in uniform vulcanization in rubber particle. Moreover, the longer hairy-structures were observed

in sulphur-prevulcanized rubber surface which might be caused from the lower crosslinking between rubber molecules compared to vulcanization in peroxide-prevulcanized rubber. Consequently, a latex composed of homogeneously crosslinked particles and long hairy chains at particle surfaces might be expected to coalescence well and to form a film with optimal physical properties [63].

CHAPTER IV

CONCLUSIONS

From the present study, the following conclusions could be made:

1. In sulphur prevulcanization of concentrated NR latex, the fully vulcanized rubber was produced within 5 h at 60°C. In the initial period of heating, the vulcanization of latex maturated for 2 h was faster than that of the latex without maturation. However, the same values of swelling ratio of sheets casted from both latices were finally obtained.

2. Rate of sulphur prevulcanization of NY latex containing high nitrogen content was greater than that of RB. The non-rubber constituent, i.e., protein could possibly accelerate the prevulcanization reaction.

3. Effect of SDS on sulphur prevulcanization and latex particle size could not be greatly observed. SDS was adsorbed on particle surface causing an increase in the amount of negative charge. It could also act as dispersing agent of aggregated vulcanizing chemicals in water.

4. SEM micrograph clearly showed the discrete sulphur-crosslinked rubber particle in fractured latex sheet. The presence of membrane around rubber particle was also noticed.

5. The phase transfer/ bulk polymerization process could be effectively used to embed sulphur crosslinked NR particles in PS matrix and then ultramicrotomed with minimum disturbance of their morphology. Under TEM, semi-IPNs type Semi-I of uniform network of NR chains in each rubber particle containing PS was observed. The homogeneous crosslink took place irrespective of size indicating that vulcanizing agents dissolved in the aqueous phase before diffusing into rubber particles. A darker ring correlating to the membrane layer derived from protein-lipid and the hairy-like structure around particle surface were also noted.

6. For peroxide prevulcanization using *t*-BuHP/ fructose-activated system, lightly vulcanized rubber was produced. The presence of SDS did not affect the vulcanization reaction of NR latex even though it caused an increase in the negative charge on NR surface and, hence, good distribution of particle in the sheet formed. SEM micrograph of fractured peroxide-crosslinked latex sheet showed the distinct appearance of rubber particle boundary compared with that of sulphur-prevulcanized NR particle.

7. The morphology of peroxide-prevulcanized latex particle was different from that of sulphur-prevulcanized and RVNR particles. TEM of peroxide-prevulcanizate showed inhomogeneous network structure inside each rubber particle, i.e., the dense near particle surface was noticed while the central region of rubber particle had less extent of crosslink density. Prevulcanization reasonably took place at NR particle/ water interface. Together with the observation of membrane layer, it could be deduced that the mechanism of penetration of vulcanizing agents and of vulcanization of rubber particle in the three systems should be different.

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APPENDICES

APPENDIX A

Semi-micro Kjeldahl Method

Apparatus:

1. Digestion apparatus
2. Distillation apparatus

The reagents used for determination of nitrogen content (%N) are illustrated in Table A.

Table A: Reagents used for determination of nitrogen content by semi-micro Kjeldahl method

Sulfuric acid	Conc., 0.01 N
Catalyst mixture	0.65 g
- anhydrous potassium sulfate	15 parts
- copper sulfate pentahydrate	2 parts
- selenium powder	1 parts
Sodium hydroxide solution	67 % w/v
Boric acid solution	2 % w/v

Table A: (continued)

Indicator solution	0.15 % w/v
- methyl red	0.1 g
- methylene blue	0.05 g
- ethyl alcohol	100 ml

Procedure:

1. *Digestion*

Dried rubber about 0.1 g was accurately weighed into a semi-micro Kjeldahl flask. Catalyst mixture about 0.65 g and concentrated sulfuric acid 2.5 ml were then added. The mixture was digested by heating at 350°C until the digest became a clear green color (or colorless with no yellow tint). Normally 4 h was found to be sufficient for the attainment of clear solution.

2. *Distillation*

The Kjeldahl flask with the digest was cooled to approximately room temperature. Distilled water 10 ml was added into the flask and the mixture was transferred to the distillation apparatus containing steam for 30 min. Boric acid solution 10 ml and indicator solution 2-3 drops were added to a 125 ml receiving Erlenmeyer flask. The receiver was placed so that the end of the condenser dipped into the acid solution.

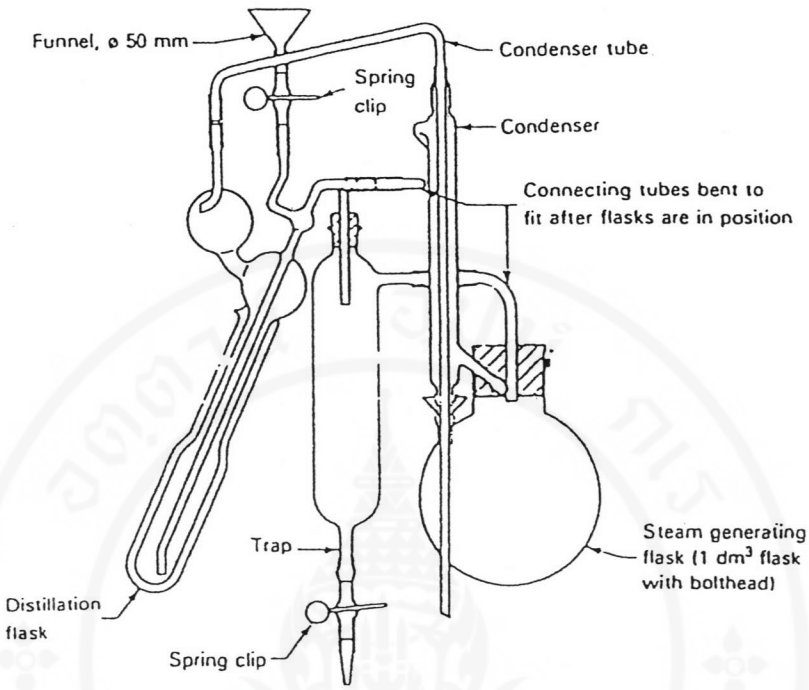

Figure A: Apparatus for the distillation

67% w/v NaOH solution 10 ml and the digest were respectively added to the distillation vessel before rinsing with distilled water not more than 5 ml. The sample showed a distinct change of color to brown or blue. The steam was passed through the distillation apparatus for 8 min until the distillate began to come over. The receiver was lowered until the condenser tip was well below the solution and distillation continued for a further minutes. Finally, the end of the condenser was washed with 3 times of distilled water.

3. *Titration*

The distillate was immediately titrated with standardized 0.01 N sulfuric acid solution. At the end point the color was changed from green to light violet.

A blank determination was carried out by following the above procedure omitting the rubber sample. For determination of %N of each rubber, the experiment was repeated 8 times (3 times in the case of blank).

Calculation:

The nitrogen content was calculated by using the following formula;

$$\%\text{Nitrogen} = \frac{[(V_1 - V_2)M \times 0.0140 \times 100]}{W}$$

where, V_1 = volume of H_2SO_4 required for titration the mixture in receiving flask (ml)

V_2 = volume of H_2SO_4 required for titration of the blank (ml)

M = concentration of H_2SO_4 (M)

W = weight of sample used (g)

0.0140 = millimole mass of nitrogen (mM)

APPENDIX B

Particle Size Measurement

Size of concentrated NR latex and vulcanizing ingredients (sulphur, ZDEC, ZnO) was measured by using Mastersizer S (Malvern version 2.11).

The principle of Mastersizer S is based on laser light scattering both diffusion and diffraction using a He-Ne laser as a light source. The refractive index of suspended material must be different from that of the medium. The Mastersizer S employs two forms of optical configuration to provide its unique specification. The first is a well known optical method, called "Conventional Fourier Optics" is shown diagrammatically in Figure B1. The second is called "Reverse Fourier Optics", used in order to measure size ranging down to 0.05 μm (see Figure B2). Therefore, particle size measurable is in the range of 0.05-900 μm. The surface area of particles can be estimated if the density of material is known and the geometry of particle is assumed as a spherical shape.

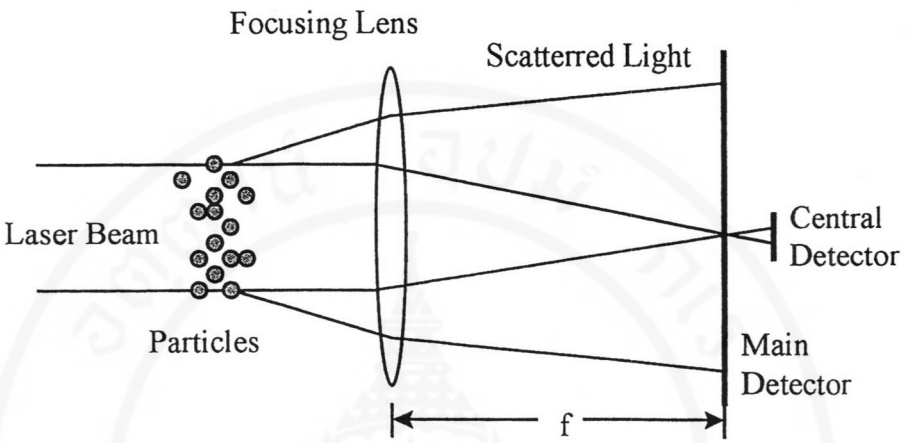

Figure B1: Conventional Fourier Optics

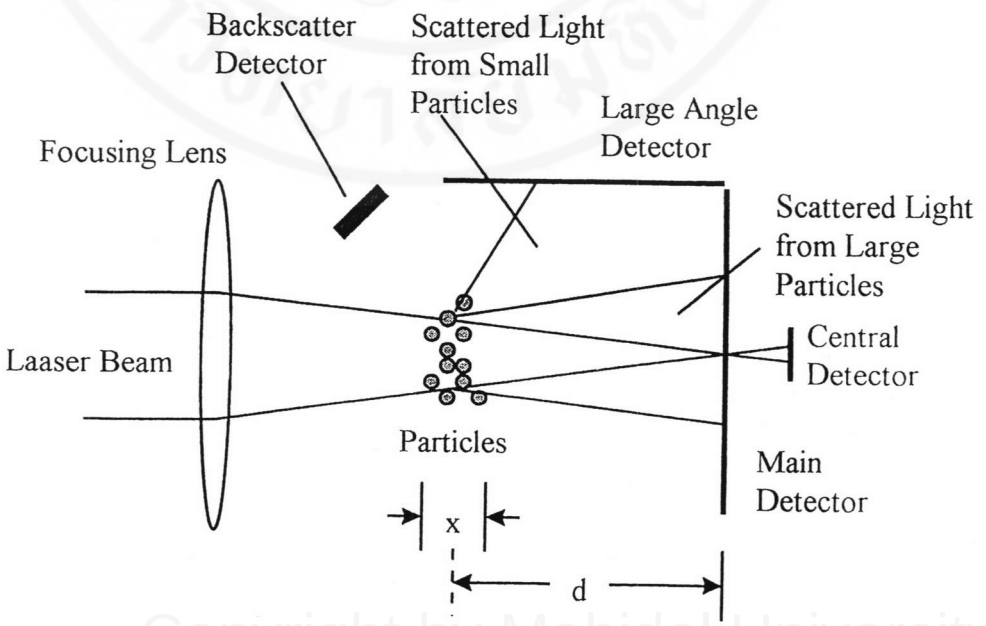

Figure B2: Reverse Fourier Optics of the Mastersizer S

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