EFFECT OF MATURATION AND STABILIZERS ON PROPERTIES OF NITRILE LATEX GLOVES

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หัวข้อวิทยานิพนธ์	ผลของการบ่มน้ำยางและสารเสถียรที่มีต่อสมบัติของถุงมือยางไนไตรล์
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บทคัดย่อ

การผสมน้ำยาง และการบ่มน้ำยางผสมสูตรเป็นขั้นตอนที่มีความสำคัญในกระบวนการผลิตชิ้นงานจากน้ำยางเลเท็กซ์ โดยการบ่มน้ำยางผสมสูตรไม่เพียงแต่ส่งผลต่อสมบัติของชิ้นงานที่ได้ แต่ยังเป็นตัวกำหนดระยะเวลาที่ใช้ในกระบวนการผลิตและปริมาณของเสียที่เกิดขึ้นอีกด้วย งานวิจัยนี้ทำการศึกษาผลของการบ่มน้ำยางผสมสูตร และระบบของสารเร่งในน้ำยางไนไตรล์ผสมสูตร (NBR latex compound) ที่ส่งผลต่อถุงมือยางไนตรล์ นอกจากนี้ยังศึกษาสมบัติของน้ำยางไนไตรล์ผสมสูตร ได้แก่ ชนิดของสารรักษาเสถียรภาพ และปริมาณอะคริโลไนไตรล์ เพื่อใช้สำหรับเป็นวัตถุดิบทางเลือก โดยสมบัติของน้ำยางไนไตรล์ผสมสูตร และถุงมือยางไนไตรล์ระหว่างการบ่มถูกเก็บตัวอย่างทุก 24 ชั่วโมงจนครบ 96 ชั่วโมง พบว่า ค่าความเป็นกรด-ด่าง (pH) มีค่าลดลงในขณะที่ร้อยละปริมาณก้อนยางจับตัว (%Coagulum) มีแนวโน้มสูงขึ้นเมื่อบ่มน้ำยางไนไตรล์ผสมสูตรเป็นระยะเวลานานมากขึ้น และพบว่าร้อยละการบวมตัว (%Swelling) ของฟิล์มยางลดลงในขณะที่ระดับการเชื่อมโยงน้ำยางผสมสูตรด้วยไซโคลเฮกซาโนน (Cyclohexanone number) มีแนวโน้มเพิ่มมากขึ้น แสดงให้เห็นว่าเกิดการเชื่อมโยงของโมเลกุลยางบางส่วนเพิ่มมากขึ้นเมื่อบ่มน้ำยางไนไตรล์ผสมสูตรเป็นระยะเวลานาน อย่างไรก็ตาม พรีวัลคาไนซ์ รีแลกซ์ มอดุลัส (Prevulcanizate relaxed-modulus, PRM) และสมบัติการรับแรงดึงของถุงมือยางไนไตรล์มีแนวโน้มเพิ่มมากขึ้น ต่อมาหลังจากการบ่มที่ระยะเวลา 48 ชั่วโมงแสดงแนวโน้มลดลง แสดงให้เห็นว่าการบ่มน้ำยางไนไตรล์ผสมสูตรนานเกินไปส่งผลให้ความสามารถในการขึ้นรูปฟิล์มลดลง นอกจากนี้ยังพบว่าการใช้ระบบสารเร่งสูตรควบคุม (สารประกอบไทเอโซล (Thiazole) และ ไดไทโอคาร์บาเมต (Dithiocarbarmate)) ให้สมบัติการรับแรงดึงสูงสุดเนื่องจากการทำงานเสริมกันของทั้งสองสารเร่ง การศึกษาสมบัติของน้ำยางไนไตรล์ผสมสูตรพบว่า แอมโมเนียซึ่งทำหน้าที่เป็นสารรักษาเสถียรภาพในน้ำยางไนไตรล์เกิดการระเหยระหว่างที่ทำการบ่มน้ำยางผสมสูตรในขณะที่โพแทสเซียมไฮดรอกไซด์ไม่ระเหย จึงส่งผลให้น้ำยางผสมสูตรเกรดอะคริโลไนไตรล์สูงซึ่งมีแอมโมเนียเป็นสารรักษาเสถียรภาพ (HAN-NH$_3$) มีค่าร้อยละปริมาณก้อนยางจับตัวเมื่อให้แรงเฉือน (%CMST) และความหนาของถุงมือยางไนไตรล์มากกว่าน้ำยางผสมสูตรเกรดอะคริโลไนไตรล์สูงซึ่งมีโพแทสเซียมไฮดรอกไซด์เป็นสารรักษาเสถียรภาพ (HAN-KOH) นอกจากนี้ยังพบว่าถุงมือยางเกรด HAN-NH$_3$ และ HAN-KOH แสดงระยะเวลาในการซึมผ่าน (Breakthrough time) ของสารเคมีสูงสุดที่ 480 นาที แสดงให้เห็นว่าปริมาณอะคริโลไนไตรล์ที่มากขึ้นส่งผลให้ทนการซึมผ่านสารเคมีเพิ่มมากขึ้นด้วยเช่นกัน การศึกษาผลของปริมาณโพแทสเซียม-

ไฮดรอกไซด์พบว่า ความหนืดของน้ำยางผสมเพิ่มมากขึ้นเมื่อเพิ่มโพแทสเซียมไฮดรอกไซด์จาก 0.0 ถึง 2.0 phr และสมบัติการรับแรงดึงของฟิล์มยางไนไตรล์มีแนวโน้มเพิ่มสูงขึ้นเมื่อเพิ่มปริมาณโพแทสเซียมไฮดรอกไซด์ เนื่องจากในสภาวะที่มีความเป็นด่างสูงส่งผลให้สารเชื่อมโยงมีความสามารถในการทำงานมากขึ้นจึงทำให้มีประสิทธิภาพในการเชื่อมโยงสูงขึ้นเช่นเดียวกัน

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Abstract

Compounding and maturation are ones of the most important steps in rubber latex manufacturing process. These steps affect not only rubber properties, but also processing time and % defective products. In this work, effects of maturation and accelerator systems of acrylonitrile butadiene rubber (NBR) latex on glove properties were studied. Moreover, this research was studied properties of NBR latex compounds including stabilizer types and acrylonitrile (AN) contents for alternative raw materials. Properties of nitrile latex compound and gloves during maturation were monitored every 24 hours until 96 hours. It was found that pH slightly decreased while % coagulum slightly increased with maturation time. As maturation time was increased, % swelling of nitrile latex films reduced while cyclohexanone number had trends to increase. These results corresponded to the increase of crosslinked rubber molecules during long maturation. However, prevulcanizate relaxed-modulus (PRM) and tensile properties had trends to increase and then, after 48 hours maturation time, these properties slightly decreased. These results indicated over-maturation of NBR latex compound could cause poor film formation. Moreover, it was found that control system of accelerators (thiazoles and dithiocarbarmate compound) demonstrated the highest tensile properties due to positive synergistic effect of thiazole and dithiocarbarmate compounds. In order to studied NBR latex properties, it was found that ammonia, stabilizer of NBR latex evaporated during long maturation while potassium hydroxide was not volatile. Thus, high acrylonitrile with ammonia stabilizer grade of compound (HAN-NH_3) showed the higher %coagulum of mechanical stability time (% CMST) and thickness of gloves than high acrylonitrile with potassium hydroxide stabilizer grade of compound (HAN-KOH) compound. It was also found that HAN-NH_3 and HAN-KOH gloves demonstrated the highest breakthrough time (BT) of chemical permeation at 480 minutes. This result indicated that chemical resistance of NBR latex gloves increases with increasing AN content. Effects of stabilizer amount on NBR latex films showed that viscosity of NBR latex compound increased with varying KOH from 0.0 to 2.0 phr. In addition, tensile strength properties increased with increasing amount of KOH due to under higher pH conditions. The curing agents employed may have a high degree of activation for complexes to form, favoring an increased in crosslinking efficiency.

Keywords: Accelerators, Nitrile gloves, NBR latex compound, Maturation time

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Abbreviations

Ac	Accelerator
Ac-free	Accelerator free
Ac1-free	Accelerator1 free
AN	Acrylonitrile
ASTM	American Society for Testing and Materials
BA	Butyraldehyde dianiline
BD	Butadiene
°C	Degree Celsius
$CaCo_3$	Calcium carbonate
CBS	N-Cyclohexyl-2-benzothiazole sulfenamide
%CMST	Percentage of coagulum mechanical stability time
DBTU	Dibutylthiourea
DCBS	Dicyclohexyl-2-benzothiazole sulfenamide
DOTG	Diorthotolyl guanidine
DPG	Diphenyl guanidine
DPTT	Dipentamethylenethiuram
DPTU	Diphenylthiourea
ETU	Ethylene thiourea
HAN-KOH	High acrylonitrile content with potassium hydroxide stabilizers
HAN-NH_3	High acrylonitrile content with ammonia stabilizers
HMT	Hexamethylene tetramine
HNBR	Hydrogenated nitrile butadiene rubber
IIR	Butyl rubber
KOH	Potassium hydroxide
MAN-NH_3 and KOH	Medium acrylonitrile content with ammonia and potassium hydroxide stabilizers
MBS	Morpholine, 4-(2-benzothiazolylthio)
MBT	2-Mercaptobenzothiazole
MBTS	Bis(2-benzothiazole) disulfide
NBR	Nitrile butadiene rubber

Abbreviations (Continued)

NR	Natural rubber
NH_3	Ammonia
PAN	Polyacrylonitrile
PBD	Polybutadiene
PVA	Polyvinyl alcohol
PVC	Polyvinyl chloride
ppm	Parts per million
phr	Parts per hundred rubber
rpm	Revolutions per minute
S	Sulfur
SEM	Scanning electron microscopy
T	Temperature
TBBS	N-tert-butyl-2-benzothiazyl sulfenamide
TMTD	Tetramethyl thiuram disulfide
TMTM	Tetramethyl thiuram monosulfide
TSC	Total solid content
%wt	Percentage of weight
μm	Micrometer
XNBR	Carboxylated nitrile butadiene rubber
ZBDP	Zinc dibutyldithiophosphate
ZBEC	Zinc dibenzyldithiocarbamate
ZDBC	Zinc dibutyldithiocarbamate
ZDMC	Zinc dimethyldithiocarbamate
ZDEC	Zinc diethyl dithiocarbamate
ZIX	Zinc isopropyl xanthate
ZMBT	Zinc salt of mercaptobenzothiazole
Zn^{2+}	Zinc ions
ZnO	Zinc oxide

Chapter 1

Introduction

1.1 Research motivation

Present worldwide demand for the synthetic gloves continues to grow due to viral outbreaks and pandemics which especially increasing demand for disposable medical gloves. In addition, global industrial gloves market to reach such as nitrile food processing gloves and household gloves [1]. The switch from natural rubber (NR) to synthetic rubber has been particularly evident in medical, examination, investigation and diagnosis gloves. The aim has been to avoid the risk of type I hypersensitivity associated with natural rubber [2]. Nitrile butadiene rubber (NBR) gloves are made of a synthetic rubber, and are an alternative ideal when latex allergies are of concern. Therefore, NBR latex has become a popular choice in the gloves industry [3].

Manufacturing process of NBR gloves is a multi-stage process including mainly latex compounding, maturation, dipping, testing and packing. The latex compound maturation is one of the most important aspects in manufacturing latex products. This stage is the mixing step of the latex concentrated with other chemicals. After that the compound latex is mixed with sulfur, a crosslinking substance for rubber molecules [4]. There is an issue of excessive amount of time used for target compound maturation in the production of NBR gloves, which is over the capability of tank stirrer and also lengthen the time used for production of NBR gloves. Moreover, the NBR latex compound formulation, such as acrylonitrile content and stabilizer type influences on production and final properties of NBR gloves. However, properties of NBR gloves must be retained, such as minimum tensile strength at 18.0 MPa and elongation at break at 500% and maximum 300% rubber modulus at 4.5 MPa (ASTM D6319) [5].

In previous work [4], effect of maturation on properties of NR latex compounds was studied. The latex compounds with commercial low ammonia NR latex were prepared. After compounding, the compounds were allowed to mature at 20, 30 and 55°C until 96 hours. To study properties of latex compounds, the samples were taken every 4 hours. It was found that with maturation for 24 hours at 20 and 30°C, viscosity of latex compounds slightly increased but pH and ammonia content slightly decreased with time. For swelling test, the maturation was carried out to 96 hours. The swelling ratio of latex film at 20°C was slightly decreased with time. At 30°C, the swelling ratio was significantly decreased after maturation for 28 hours. This could be the maturation was to allow sulfur to gradually react with rubber. However, for maturation at 55°C, it was found that viscosity of latex compounds increased but swelling ratio reduced quickly within 4 hours after that they became unchanged. These results indicated faster crosslinking reaction with sulfur following with coagulation tendency of compound during maturation. Ammonia content and pH of latex compounds decreased with higher rates at 55°C as compared with those at 20 and 30°C. During maturation the latex particles were swollen due to crosslinking with sulfur, inclusion of compounding ingredients and/or breakdown in colloidal stability of the latex. The changes in average particle diameter of latex would generally be detected. However, Mayers et.al [6] did not find the changes in latex particle size when measuring with angle light scattering photometer. This may be because this technique was not sensitive to detect these changes. Moreover, Silva, K.M. and co-workers [7] studied effect of ammonium laurate soap on NR. NR latex samples with different ammonium laurate soap (surfactant) levels were prepared. It was found that mechanical stability time (MST) of NR latex, foaming height and viscosity were significantly altered. Soap levels above 0.5×10^{-4} moles per 100 g of latex enhanced the mechanical stability time as well as foaming height. Magnitude of the effect depended upon the amount of the added soap. Initial viscosity was decreased by soap addition but a progressive increase and subsequent decrease were observed thereafter. This showed that surfactant affected on stability and properties of NR latex.

Yasin, T. et.al [8] studied effect of acrylonitrile (AN) content on physical properties of electron beam irradiated NBR. It was found the hardness, gel content and tear strength of NBR increased, while the elongation at break, swelling index and tensile strength were decreased with the increase in AN content. This showed that properties of NBR affected on physical properties. Ghazaly, H. M. et.al [9] studied some factors affecting dipped NBR latex films. The pH of the compound was adjusted using various amounts of 5wt% potassium hydroxide (KOH) solution (0.5, 2.5 and 5.2 phr) and then the thin films were prepared by coagulation of the NBR latex compound using coagulant dipping process. It was found that the pH of the compound was adjusted to >12, the mechanical (tensile and tear) properties were found to be better as compared with compounds prepared at pH~9. The tear properties were especially higher when the films were not leached, although the leached films gave a higher tensile strength. This showed that amount of stabilizer (KOH) affected on mechanical properties.

Thus, this research focused on factors affecting the properties of NBR latex gloves including maturation time, accelerator systems, acrylonitrile (AN) contents and stabilizer types. Because maturation allowed prevulcanization of rubber, therefore, over-maturation could cause an increase in coagulation of compounds. Moreover, this caused over the capability of tank stirrer and also lengthened the time used for production. Thus, the study of maturation time of NBR latex compound from 0 until 96 hours was examined. The sample was taken every 24 hours, to study properties of NBR latex compounds. In addition, accelerator systems are important aspects in manufacturing of gloves as they were repoted to have allergic reactions (type IV/ chemical allergy). Hence, the NBR compounds with and without accelerators were examined. Moreover, effects of NBR latex formulations of compound including AN contents (HAN-NH_3 and MAN-NH_3 and KOH grades) and stabilizer types (HAN-NH_3 and HAN-KOH grades), were studied.

1.2 Objectives of the study

1) To understand effects of maturation on properties of NBR latex gloves.

2) To understand effects of NBR compound latex properties, including AN content and stabilizer type on properties of NBR latex gloves.

1.3 Scopes of the study

1) Study effect of maturation time (0-96 hours).

2) Study effect of accelerator system on maturation time.

3) Study effect of NBR latex formulations such as varying AN content and stabilizer type.

4) Study effect of stabilizers amount (KOH) on NBR latex compound properties (0.0-2.0 phr)

5) Preparation of NBR latex compound and NBR gloves using a coagulant hand-dipping process.

6) Characterization of NBR latex compound (pH, viscosity, %total solid content, swelling index and %coagulum) and property examination of gloves (tensile properties, thickness and chemical permeation).

1.4 Benefit of the study

It was expected to find the suitable maturation state of NBR latex compound to reduce tank stirrer and time used for producing industrial NBR latex gloves. Also, the understanding of the effects of accelerator systems, including thiazole and dithiocarbamate compounds, and NBR latex formulations on properties of NBR latex compound. Moreover, alternative raw latex can be applied for industrial NBR latex gloves.

Chapter 2

Theory and Literature Reviews

2.1 Types of rubber gloves

Rubber gloves are protective hand covers worn to reduce human exposure to dangerous or harmful environments. Rubber hand gloves have found their usages in various industrial and medical applications. They are made by using different types of rubber depending upon the requirement of the task. These gloves are of great use when to protect hands from chemicals, hot water, staining, dust, oil substances that need to be cleaned. There are many types of rubber gloves available for various needs [10].

2.1.1 Household gloves

Gloves used around the household are generally called household gloves, have been used for washing dishes, cleaning at home, and are popular with professional cleaners. Many different designs of household gloves have been available in a variety of colors but traditional designs are yellow or pink with long cuffs. The thickness of the gloves and the long cuffs provide excellent protection for all general cleaning tasks and are resistance to be put into water, and provide protection when vacuuming, dusting and polishing. General material used for making household gloves is NR latex occurred the problems with that include allergic reactions and poor protection against such substances as solvents [11].

Figure 2.1 Household gloves [10]

2.1.2 Medical gloves [12-13]

Medical gloves are single used for medical examinations and procedures to prevent cross-contamination between caregivers and patients. Medical gloves are made of different polymers including NR, NBR, polyvinyl chloride (PVC) and neoprene. They come powdered free, or powdered with cornstarch to lubricate the gloves, making them easier to put on the hands. Powder free gloves are being used more often during surgery and other sensitive procedures. Medical gloves can further be divided into surgical and examination gloves.

2.1.2.1 Surgical gloves

Surgical gloves are made of natural or synthetic rubbers intended to be worn by operating room personnel to protect a surgical wound from contamination. Due to the increasing rate of latex allergy among health professionals as well as in the general population, there has been an increasing move to gloves made of synthetic lattices such as vinyl or NBR latex. Sterile surgical gloves (Figure 2.2) are at the top of the range of quality protective gloves and are typically used by surgeons and operating room staffs.

Figure 2.2 Surgical gloves [12]

2.1.2.2 Examination gloves

Examination gloves are disposable devices intended for medical purposes that are worn on the examiner's hand or finger to prevent contamination between patient and examiner. In general examination gloves are available in 3 materials: NR, NBR and vinyl latex. They are ambidextrous (fitting both hands) and are generally thinner than surgical gloves. Performance characteristics of the examination gloves (Figure 2.3) are lower than the surgical glove since they are used for less critical procedures.

Figure 2.3 Examination gloves [12]

2.1.3 Industrial gloves [13]

Industrial gloves serve as an item of protective apparel for workers in factories. Various materials, used in industrial gloves, can be made from NBR, NR latex, neoprene, vinyl, PVC, to ensure maximum protection. Be sure to perform a hazard assessment as gloves made from different materials have different properties and chemical resistances. With the case of latex allergy in place, silk glove liners are tending to be used as a practical and effective solution to the irritating problems of allergic reaction or sensitivity.

Figure 2.4 Industrial gloves [14]

Major technological development has been in the agents, such as waterproofing agents that are added to leather, for example, during the tanning process. Although industrial leather gloves are still used, they have now been superseded in many industrial applications by rubbers, plastics and fabrics. The Figure 2.4 shows the industrial gloves.

2.1.4 Advantages and disadvantages of rubber gloves

There are a variety of glove types available in industry which are designed for use with specific chemicals and chemical families. Each type of gloves has its own advantages and disadvantages. This should be considered carefully before use. Table 2.1 highlights the advantages and disadvantages of each type of gloves.

Table 2.1 Advantages and disadvantages of each type of gloves. [15]

Glove latex materials	Advantages and disadvantages
Natural rubber (NR)	- Good for biological and water-based materials - Little chemical protection - Low cost - Poor for organic solvents and oils - Hard to detect puncture holes - Can cause or trigger latex allergies
Nitrile rubber (NBR)	- Excellent general use glove - Good for solvents, oils, greases and some acids and bases - Clear indication of tears and breaks - Excellent physical properties, long service life - Good alternative for those with latex allergies - Poor for benzene, methylene chloride, trichloro-ethylene and ketones
Polychloroprene (Neoprene)	- Good for acids, bases, alcohols, fuels, peroxides, hydrocarbons, and phenols - Good for most hazardous chemicals - Medium physical properties - Poor for halogenated and aromatic hydrocarbons
Butyl rubber (IIR)	- Specialty gloves, polar organics such as ketone and ester - Poor for gasoline and aliphatic, aromatic, and halogenated hydrocarbons - Expensive

Table 2.1 Advantages and disadvantages of each type of gloves. (continued) [15]

Glove latex materials	**Advantages and disadvantages**
Polyvinyl chloride (PVC)	- Good for acids, bases, oils, fats, peroxides, and amines - Good resistance to abrasions - Very good physical properties - Poor for most organic solvents
Polyvinyl alcohol (PVA)	- Good for aromatic and chlorinated solvents - Good physical properties - Poor for water-based solutions and alcohol - Very expensive
Fluoroelastomer (Viton)	- Good for chlorinated and aromatic solvents - Good resistance to cuts and abrasions - Poor for ketones - Extremely expensive

2.2 Nitrile latex

Nitrile (NBR) latex are copolymers of butadiene (BD) and acrylonitrile (AN) monomers produced by means of an emulsion polymerization reaction initiated by redox catalyst systems. Radical generating activator and other ingredients are introduced into the polymerization vessels. NBR latex have properties intermediate between those of polyacrylonitrile and polybutadiene [16].

2.2.1 Polyacrylonitrile

Polyacrylonitrile (PAN) is a commercially important polymer, produced by a reaction of acrylonitrile monomer with a free radical or an anionic initiator. The polymerization can be carried out in bulk, emulsion, suspension, slurry or solution. The growing acrylonitrile polymer chain occurs in a head-to-tail fashion, attaching to every alternate carbon atom giving a compact and highly polar nitrile unit [17-18].

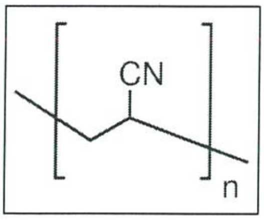


Figure 2.5 Polyacrylonitrile structure

The nitrile group acts as a hydrogen bonding acceptor due to a lone pair on nitrogen atom and has a large dipole moment between electron-deficient carbon atom and electron-rich nitrogen atom, which enable us to use them for relatively strong attractive interactions. Indeed, the strong intermolecular interaction induces the high strength and high resistance for various organic solvents [19].

2.2.2 Polybutadiene

Polybutadiene (PBD) is a homopolymer of 1,3 butadiene and polymerizes by addition of a monomer butadiene unit on an allyl radical resonance structure. The three possible structures are trans-1,4, cis-1,4 and vinyl-1,2 depending on the polymer recipe and polymerization conditions [20]. PBD is a non-polar rubber whose chains are attracted to one another via dispersion forces. It is essentially a rubbery material whose susceptibility to oxidation is high because of the presence of double bonds.

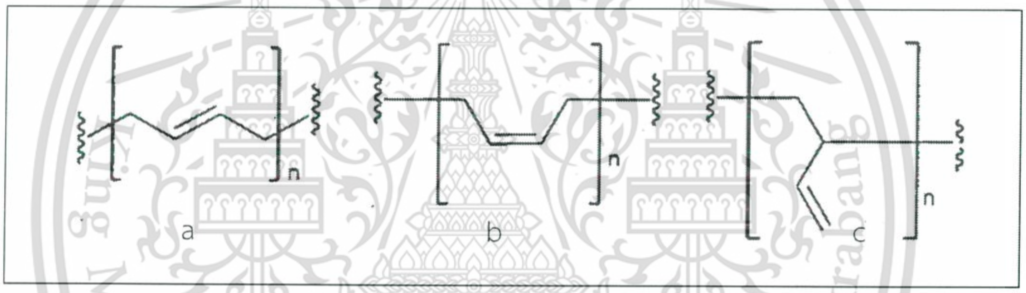


Figure 2.6 Polybutadiene structure: a.) trans-1,4, b.) cis-1,4 and c.) vinyl-1,2 [21]

Reactivity ratios for free radical copolymerization of acrylonitrile (M_1) and butadiene (M_2) are given as $r_1 = 0.03$ and $r_2 = 0.30$ respectively, meaning that normally the polymer composition changes with conversion. However, a charge of butadiene/acrylonitrile of mole ratio 1.67 (azeotropic composition) will give the same copolymer composition as the charge composition. The monomer ratio is probably the most important variable, with the polarity of the copolymer increasing with increasing acrylonitrile content. Structural formula of NBR is illustrated in Figure 2.7.

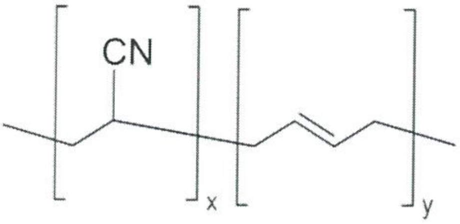


Figure 2.7 NBR structure

2.2.3 Properties and applications of NBR

NBR is actually a complex family of unsaturated copolymers of acrylonitrile and butadiene. By selecting an elastomer with the appropriate acrylonitrile content in balance with other properties, the AN level, by reason of polarity, determines several basic properties. Table 2.2 shows how the AN level influences the NBR properties [22].

Table 2.2 AN level influences the NBR properties. [23]

Low AN content	Property	High AN content
Decrease	Processability	Increase
Decrease	Cure rate with S curing system	Increase
Decrease	Oil, fuel resistance	Increase
Decrease	Compatibility with polar polymers	Increase
Decrease	Low air & gas permeability	Increase
Decrease	Tensile strength	Increase
Decrease	Abrasion	Increase
Decrease	Heat ageing	Increase
Decrease	Cure rate with peroxides	Decrease
Decrease	Compression set	Decrease
Decrease	Resilience	Decrease
Decrease	Hysteresis	Decrease
Decrease	Low temperature flexibility	Decrease

Nitrile latex is used in applicational areas where oil and abrastion resistances and high binding power to polar substrates are required. The main applications are in the textile (non-woven) and paper industries, gloves dipping, surface coating and adhesive [24].

2.2.4 General types of NBR

2.2.4.1 Hot NBR

Hot NBR polymers are polymerized at higher than 25°C. Generally, high temperature polymerization gives a faster reaction This process yields highly branched polymers, higher gel, which make poorer processability. Branching supports good tack and a strong bond in adhesive applications [25].

2.2.4.2 Cold NBR

Cold NBR polymers are polymerized at lower than 25°C, generally reacted at 10°C maximum depending on the balance of linear- to- branched configulation desired. The lower polymerization temperatures yield more linear polymer chains. Cold NBR polymer gains better mixing, processability and slightly lower physical properties as compared with hot NBR polymer. More than 80% of the NBR grades are manufactured by cold polymerization [25].

2.2.4.3 Hydrogenated NBR (HNBR)

Hydrogenated NBR (HNBR) is widely known for its physical strength and retention of properties after long-term exposure to heat, oil and chemicals. Selective hydrogenation of double bonds with maintaining the cyano groups in the side chain is one of the effective methods to improve heat resistance of NBR [26].

2.2.4.4 Carboxylated NBR (XNBR)

Carboxylated NBR (XNBR) is a terpolymer of acrylonitrile, butadiene and a carboxyl group containing monomer such as acrylic or methacrylic acid. Incorporation of carboxyl groups increases intermolecular and intramolecular interactions, resulting in improved properties of the polymer. Owing to the high polarity of carboxyl groups present, they are regarded as polar rubbers. In this execution there are beside the sulfur bridges also carboxyl groups on the double bonds of the butadiene part. These groups can make ionic cross links with zinc ions (Zn^{2+}) to give improved physical properties as compared to a non-carboxylated NBR. The result is a polymer matrix with significantly increased strength, measured by improved tensile, tear, modulus and abrasion resistance. Figure 2.8 shows cross-linking structure of cross- linked XNBR. The degree of caboxylation has significant effect on the latex on the latex dipping performance and on the finished product characteristics [23-26].

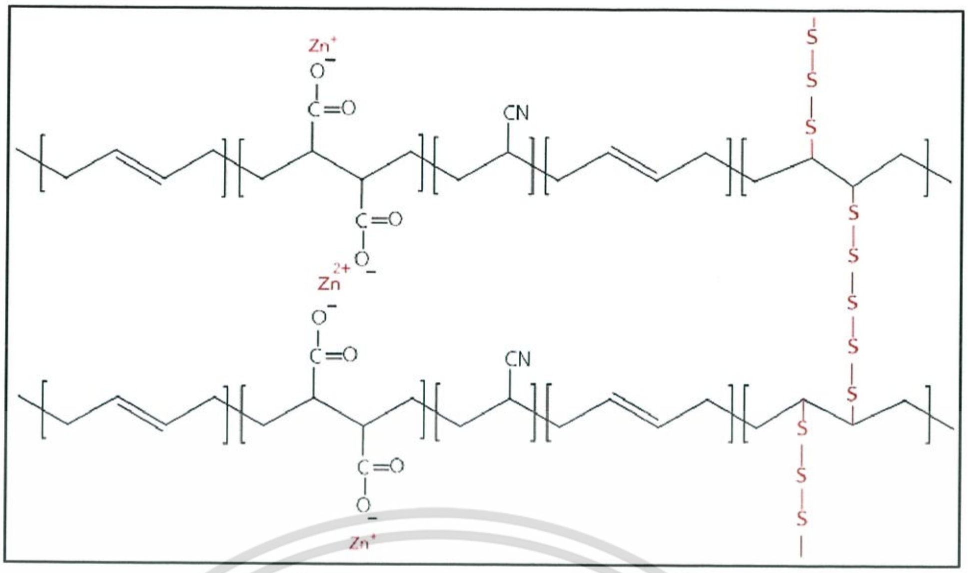


Figure 2.8 Cross-linking structure of cross-linked XNBR [25]

2.3 Emulsion polymerization of synthetic latex [24, 27-28]

Emulsion polymerization has become very important industrially, and today large tonnages of latex and polymers are manufactured by this process. An emulsion polymerization contains four basic ingredients: monomer, water, soap (dispersing agent, emulsifier or surfactant) and catalyst (initiator). The properties of the latex and the polymer or copolymer are very dependent on variation of components. The mechanism of free-radical emulsion polymerization (Figure 2.9) is summarized by the following:

1. Emulsion in aqueous solution above a certain concentration forms micelle (aggregates of molecules).
2. Addition of water insoluble monomer, which forms droplets stabilized by emulsifier. Some monomers are solubilized in micelles.
3. Free radicals are generated by initiator and cause polymerization inside the micelle.
4. Growing polymer particles obtain further monomers by diffusion from monomer droplets.
5. Monomer droplets are used up at 60 percent conversion and polymerization is continued until remaining monomers in polymer particles consumed.

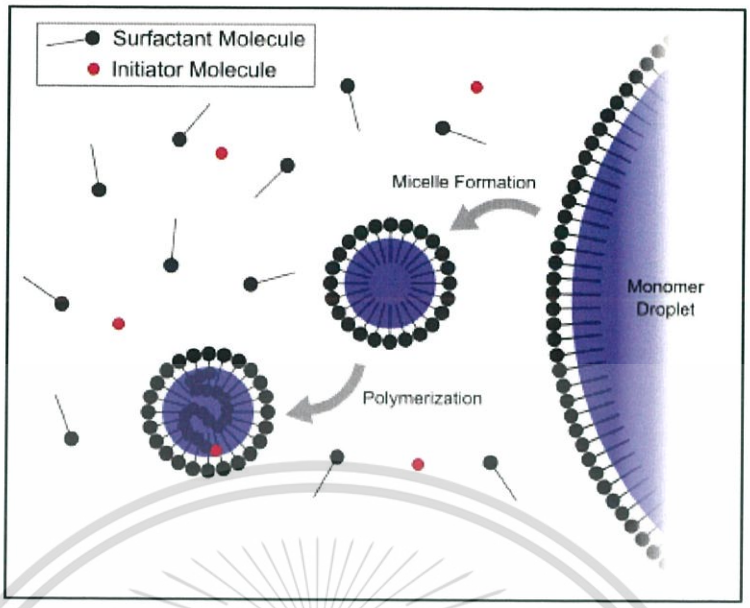


Figure 2.9 Diagram of emulsion polymerization [28]

2.3.1 Soap (Emulsifier)

There are four classes of soaps: anionic, non-ionic, cationic and amphoteric, designated according to their hydrophilic groups. The most commonly used soaps are anionic and non-ionic types. Anionic emulsifiers may be sodium or potassium salts and fatty and rosin acids, alkyl sulphates, sulphonates, sulphosuccinates or alkyl aryl sulphonates. Non- ionic emulsifiers are normally ethylene oxide condensates of long chain alcohols or fatty acids. It is common practice for some applications to use mixture of anionic and non-ionic emulsifiers.

2.3.2 Initiator

A large variety of initiator system is available for use in emulsion polymerization and that used industrially is based on the liberation of free radicals. Both thermal and redox generations of free radicals have been used in emulsion polymerization. Examples of free radical generation by thermal decomposition are given by organic and inorganic peroxides, such as, lauryl peroxide, t- butyl hydroperoxide and ammonium peroxydisulphate. Radicals are produced by redox system using a peroxide or hydroperoxide in conjunction with reducing agent.

2.3.3 Monomers

Typical monomers are those that undergo radical polymerization, are liquid or gaseous at reaction conditions, and are poorly soluble in water. The most important monomers used commercially in emulsion polymerization are styrene, butadiene, alkyl acrylates and methacrylate, vinyl acetate, acrylonitrile, chloroprene, vinyl chloride, vinylidene chloride, ethylene and 2- vinylpyridine, with all being found as constituents of copolymers or terpolymers and, with the exception of acrylonitrile and 2-vinylpryidine, as homopolymers.

2.3.4 Miscellaneous

Other important components of an emulsion polymerization system are the modifier (chain transfer agent) which influences the molecular weight and molecular weight distribution of the polymer, and the electrolyte which can alter the soap efficiency and affect the rate of reaction, particle size and particle size distribution.

2.4 Manufacturing process of rubber gloves

2.4.1 Latex compounding process of rubber gloves

The main objectives of compounding are to obtain the desired processing characteristics and product properties. Compounding processes transform raw latex into a range of materials suitable for applications. These changes are accomplished by addition of a number of ingredients to the concentrated latex according to the required formulation. In general, the main additives added are stabilizers, vulcanizing agents and antioxidants. The stabilizers used for latex compounding are the most important additives because they usually have the greatest influence on latex stability. In compounding, chemicals are normally added in the form of solutions if they are water soluble; if, as is more commonly the case, they are insoluble in water, they are usually added as dispersions in water. The solid is milled to reduce its particle size to a size no greater than that of the largest latex particles [26]. It is generally accepted that the particles in dispersion of solid compounding ingredients should certainly have diameters less than 5 μm, and should preferably have diameters in the range 1-2 μm [29].

2.4.2 Maturation of compound latex

After latex has been compounded it is usual in industrial processes for it to be left to "mature" for a period of time. This process is said to improve the consistency of finished latex products [30]. During this maturation period important changes take place. Absorption of vulcanization ingredients onto, or into, the rubber particle surfaces commences and becomes a continuing process with time and temperature [24]. Some pre-vulcanization may also occur during this "maturation" stage, the extent of which depends upon the length of "maturation" and the temperature at which the latex is stored. A maturation period of at least 24 hours is recommended for latex to be used in industrial processes [30].

2.4.3 Dipping process

The two dipping techniques which are commonly used in the production of examination gloves are straight dipping and coagulant dipping methods. The latter method is more widely used in industry.

2.4.3.1 Straight dipping method

Straight dipping method is the simplest of the dipping processes, the specified former is alternately dipped in the compounded latex and dried until the desired product thickness is obtained. Straight dipping method is used to produce very thin films, for example in the production of condoms [2, 30].

2.4.3.2 Coagulant dipping

Most rubber gloves are fabricated by coagulant dipping method. The process of coagulant dipping takes place in a continuous chain dipping line. The pre-heated, cleaned, formers are firstly dipped in a coagulant tank containing dry coagulant based on calcium nitrate and then the formers are immersed in the latex for a set time until the specified thickness is obtained. After withdrawing it from the latex, the coagulated film is dried. Then the coagulated film is immersed in a water bath to wash out all water leachable materials. This is called ‘wet gel leaching’ or ‘pre-vulcanization leaching’. Once the gloves are done with pre-vulcanization leaching, the manufacturers roll the cuffs to make the gloves easier to remove. Next stage, drying is required to reduce the water content in the gel to the lowest possible value as quickly as possible.

Vulcanization temperature is at around 120 ± 10°C. The vulcanized sample is then given a dry leaching, also called 'post-vulcanization leaching'. After that, the gloves are treatments to prevent adhesion and to facilitate the stripping of gloves from the former. The gloves are stripped from the former manually and turned inside out. After stripping they are fed into tumble driers where complete drying is taken place and sent for inspection and packaging unit. A flow chart of the dipping process is given in Figure 2.10 [31].

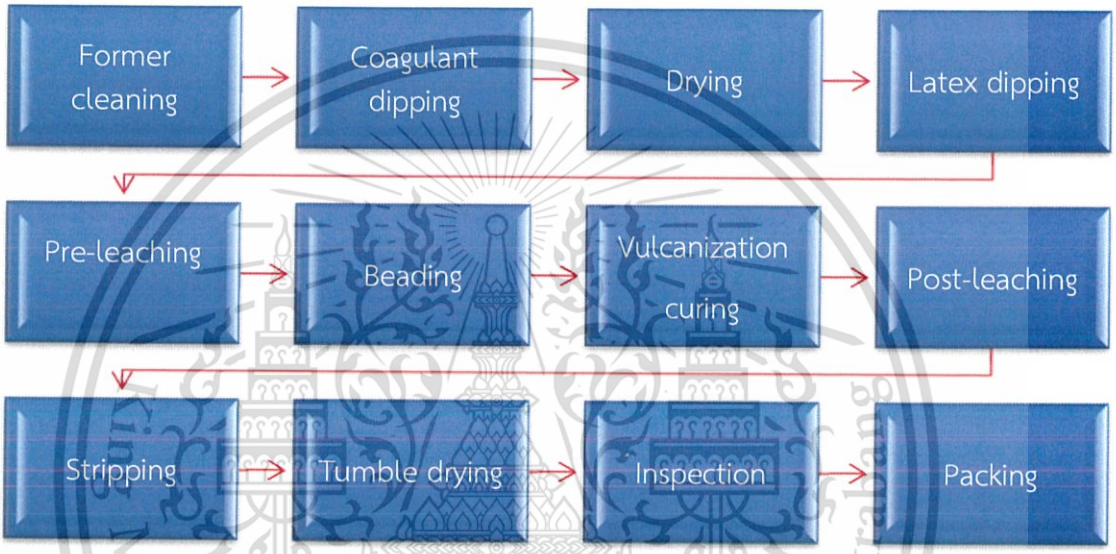


Figure 2.10 Flow chart of the dipping process [31]

2.4.4 Treatment methods of gloves [32]

In the methods, after the gloves are vulcanized, the gloves are treatments for facilitate stripping and wearing. There are several different ways to go about treatment gloves, including powdering, chlorination and polymer coating.

2.4.4.1 Powdering

The powder is applied to surface of gloves that coating on surface of gloves to prevent the gloves from sticking after removal from the formers. Powdering takes place following manufacturing. In the past, gloves had powdered formers, making powder a by-product of manufacturing. Due to an advance in manufacturing technology, gloves are powdered with food-grade cornstarch, before they are taken from their formers and turned inside out. Powdered gloves are not suitable in situations where the powder could interfere with biological and chemical processes.

2.4.4.2 Chlorination

Chlorination is a treatment method for powder free gloves. Manufacturers wash gloves in a chlorine gas or a solution of hypochlorite and hydrochloric acid. Gloves are then rinsed to prevent the chemicals from interacting with the glove further. The solution reduces the surface tackiness of the glove and also gives it a softer texture. This method was developed for NR latex gloves, but new advancements in technology have made the process available for nitrile gloves.

2.4.4.3 Polymer coating

The majority of disposable gloves on the market is now powder free. Applying a polymer coating is a more recent method: Manufacturers use polymers, such as silicones, acrylics and hydrogels, to make gloves easier to wear. The polymer coating has less surface friction than the glove material, which makes it slip on the hand more easily. The polymer is generally applied while the glove is still on the former. Polymer coating is most frequently used on NBR and NR latex.

2.5 Vulcanization

Vulcanization is one of the most important processes for most of rubber technologies. This is a crosslinking process in which individual molecules of rubber (polymer) are converted into a three-dimensional network of inter connected (polymer) chains through chemical crosslinks. During vulcanization the rubber compound is changed to elastic final product (gloves). The part of vulcanizated network is also physical bonds like hydrogen bond, polar or dispersed powers between individual macromolecules [33].

2.5.1 Crosslinker

Colloidal sulfur is normally used with NBR latex. Its effective and fast link in form of crosslinks to rubber macromolecules occurs only in the presence of accelerators and activators. If these are missing, sulfur reacts with rubbers very slowly and it bonds to rubbers in a form of side cyclic structures not in a form of sulfur crosslinks. The range of sulfur usage is generally 0.5-2.5 phr. The crosslinker used for

XNBR is generally 0.8-1.5 phr. Sulfur vulcanization occurs through radical substitution in the forms of polysulfide bridges and sulfur containing intracyclization of the polymer molecules. Figure 2.11 shows the mechanism of rubber crosslinking using sulfur [33-34].

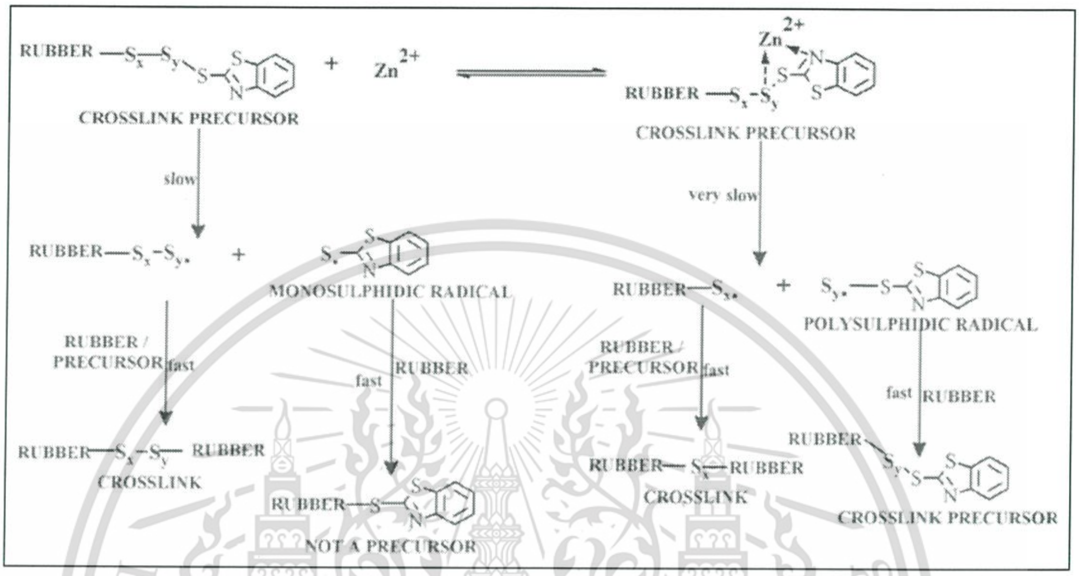


Figure 2.11 Mechanism of rubber crosslinking using sulfur and zinc oxide. [34]

Other chemicals used for crosslinking of polymers are sulfur monochloride, tellurium, selenium, thiuram accelerators, polysulfide polymers, p-quinonedioximes, metallic oxides, organic peroxides, diisocyanates, etc. (mostly for specialized applications). In the case of fully saturated elastomers, organic peroxides are often used for crosslinking.

2.5.2 Accelerator

Accelerators are necessary ingredients of all sulfur curing systems, used semi-ultra or ultra-accelerator. They increase curing ratio, speed of vulcanization and efficiency of the sulfur bonding to rubber macromolecules in form of crosslinks. Accelerator also decreases the quantity of sulfur necessary for vulcanization and thus improving 'aged' properties of the rubber vulcanizates [19]. Presently exclusive organic compounds are used in function of accelerators and evaluated according to their activity in vulcanization process. Most of them contain sulfur and nitrogen atoms in their molecules. Table 2.3 shows classification of accelerators [35].

Table 2.3 Classification of accelerators [35]

Accelerators	Chemical Groups	Vulcanization Speeds
BA, HMT	Aldehyde, Amine	Slow
DPG, DOTG	Guanidine	Slow
MBT, MBTS, ZMBT	Thiazole	Semi ultra fast
ZBDP	Thiophosphate	Ultra fast
CBS, TBBS, MBS, DCBS	Sulfenamides	Fast-delayed action
ETU, DPTU, DBTU	Thiourea	Ultra fast
TMTM, TMTD, DPTT, TBzTD	Thiuram	Ultra fast
ZDMC, ZDEC, ZDBC, ZBEC	Dithiocarbamate	Ultra fast
ZIX	Xanthates	Ultra fast

In addition, accelerators are also classified as primary and secondary accelerators based on compound formulation. Generally, thiazoles and sulfenamide accelerators play a role of being primary accelerators due to their characteristics such as good processing safety, a broad vulcanization plateau and optimum crosslink density as well as desired reversion delay that they offer. The primary accelerators are used at 0.5 to 1.5 phr dosages in most rubber compounds. The basic accelerators such as guanidines, thiurams, and dithiocarbamates etc are used as secondary accelerators to activate the primary accelerators. The use of secondary accelerators increases the speed of vulcanization substantially but at the expense of scorch safety. The dosages of the secondary accelerators are generally between 10- 40% of the primary accelerator. However, dithiocarbamate and thiuram are considered to cause allergic contact dermatitis and unsuited to applications where they come into contact with the body.

2.5.3 Activator

Optimum influence of sulfur vulcanization systems is achieved under participation of activators. For this purpose, inorganic as well as organic compounds are used in practice. These are mostly metal oxides from the inorganic compounds higher fatty acids and their salts, some amines or their derivates and from organic compounds. In general, it is assumed that matters increasing pH of the vulcanization compositions have activation effect. ZnO is used as the activator in latex compounds. In dry rubber compounding normally 4-5 phr of ZnO is used in combination with stearic acid. In latex due to the presence of free fatty acid and due to the addition of soap such as stearate, ZnO alone is used as the accelerator and is used at a lower dosage. Activation effect of ZnO is ascribed mostly to its ability to create complexes generating curing sulfuric fragments with sulfur and accelerators [36]. Moreover, the activators mentioned lead to improve mechanical properties of the vulcanizates. The incorporation of ZnO in XNBR produced an ionic elastomer with increasing mechanical properties what are probably related ionic bonding, to stronger interactions between ZnO particles and rubber matrix [37]. The chemical mechanism of ionic bonding would require one zinc ion to bind two acid groups in Figure 2.12.

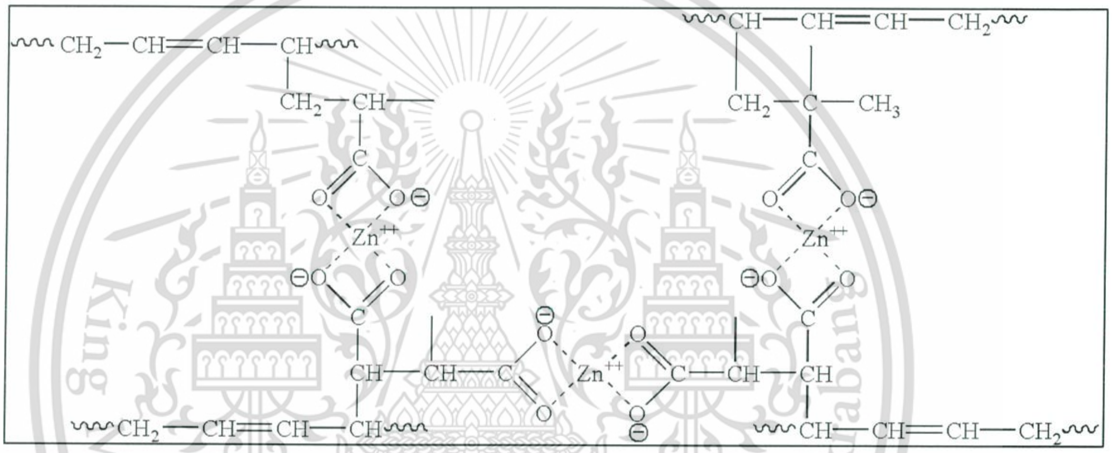


Figure 2.12 Zinc ions providing the crosslinks between the carboxyl groups on the polyacrylic acid polymer chains. [37]

However, ionic crosslinking often increases the stiffness of an article made from the rubber. This is a disadvantage for applications in which a softer rubber is needed. For example, surgical gloves made of soft rubbers can provide greater tactile sensitivity for the wearer.

2.6 Stability for Latex [24, 38]

In all latex processes, a stable colloidal system is maintained until, at the required time, it is made unstable and converted to a solid product. The stability of a polymer latex may be divided into two aspects: mechanicals stability and chemical stability. Mechanical stability is the term used to describe the resistance to those mechanical influences which increase the number and shere force of collisions between particles and hence the tendency of the latex to coagulate. Chemical stability is defined as the ability of the latex to resist the effects of chemical destabilizing agents.

2.6.1 Mechanical stability of synthetic latex

The international test method for the determination of the mechanical stability of synthetic rubber latex is similar in concept to that for NR latex. The same stirring apparatus is used but the stirrer disc has a greater diameter (36.1 mm) and the final stage of the procedure is different. After stirring for an agreed time, the destabilized latex is filtered through 180 μm wire cloth to quantify the amount of coagulum produced. The stirring at 14,000 rpm important with more viscous latex, the test (ISO 2006) is restricted to synthetic rubber latex with a viscosity of 200 mPa.s or less. More viscous latex can be tested but only after dilution to the same viscosity range, providing that such dilution does not reduce the concentration of the latex by more than 10 percent of total solid. This limitation on dilution is set since dilution of latex decreases its stability because the balance of free and absorbed soap is changed.

2.6.2 Chemical stability of synthetic latex

Chemical stability test proposed for synthetic rubber latex are more diverse. One method that has been considered internationally involves the addition of a surfactant and ZnO dispersion to the latex and measurement of the temperature and time taken to initiate coagulation.

2.6.3 Surfactant in latex dispersion

Surfactants are surface active agents with the ability to lower the free energy of a phase boundary and often use to stabilize latexes. Usually they are organic compounds consisting both of hydrophobic and hydrophilic parts, making them amphiphilic. They can influence the structure of the film formed and the structure has an effect of the distribution of the surfactant. There are two important properties influenced by where the surfactant is located in the film, including mechanical strength and adhesion of surfactant. The compatibility of the surfactants depends on their hydrophile-lipophile balance (HLB) and the nature of the polymer. There are three possible ways of a surfactant in latex dispersion including the surfactant dissolves in the polymer, the surfactant phase separates and migrates toward the possible interface of the films and the surfactant remains at the interfaces between latex particles. In case surfactant phase separates and migrates to interfaces of film, it has been recognized as common. Upon aging exudations of surfactants can occur in the interfaces surface-air, surface-substrate and in the interior of the film.

2.7 Literature reviews

The latex compound maturation is one of the most important aspects in processing of gloves [4]. There is an issue of long time used for target compound maturation in the production process of NBR gloves, which is over the capability of tank stirrer and also lengthen the time used for production of NBR gloves. Jose, L. [39] studied optimum cure time of the latex sheets. The latex compound was prepared by different accelerator combinations (ZDC/TMTD, CBS/TMTM and TMTD/ thiocarbanilide). Then latex was kept for 24 hours maturation. Latex films were prepared by casting the compounds in glass dishes. After drying the films at room temperature for 24 hours, they were vulcanized at 120°C, varying the time from 25 to 40 minutes in an air oven. It was found as the cure time of latex films was increased from 25 to 40 minutes, the tensile strength increased and reached a maximum at 30 minutes and then decreased. But the attainment of maximum tensile strength occurred at 27 minutes for the TMTD/ thiocarbanilide compound. This showed that TMTD/ thiocarbanilide combination was a faster accelerator system compared to CBS/TMTM and ZDC/TMT. Tensile strength of latex sheets with CBS/TMTM system and ZDC/TMTD system were found to be comparable. The tensile strength of sheets with TMTD/thiocarbanilide system was superior. This may be due to the more homogeneous distribution of water soluble thiocarbanilide in latex. Moreover, the percentage transmittance of TMTD/thiocarbanilide systems at the wavelength 2000 nm were more than that of CBS/TMTM and ZDC/TMT systems. This also may be due to the homogeneous dispersion of thiocarbanilide in NR latex since thiocarbanilide was soluble in ammonia. NR latex was preserved with ammonia and even at the time of compounding, latex contained approximately 0.2% ammonia in it, which facilitated the dissolution of thiocarbanilide in NR latex.

Porter, M. et.al [40] studied latex prevulcanization and maturation procesed. After compounding, the mixture was stirred slowly for 0.5 hour and allowed to stand for 2 hours before use. In some cases, longer maturation times were used. In experiments, prevulcanizations were carried out in the covered flask immersed in a water bath maintained at 70°C. The latex was subjected to continuously slow stirring and samples were withdrawn at intervals for chloroform number testing and for preparing evaporated films, 0.8 mm thick. The films were removed from the plates, hung in air and, when translucent, were placed in a vacuum desiccator for tensile test. It was found more positive tensile strength on prevulcanization when retaining the 24 hours heating time and increasing the maturation period at room temperature (from 2 to 17 hours) after subsequent compounding. A chloroform number of 4 was reached in 3 hours at 70°C, after which time the tensile strength of a cast film was 17 MPa, shown in Figure 2.13.

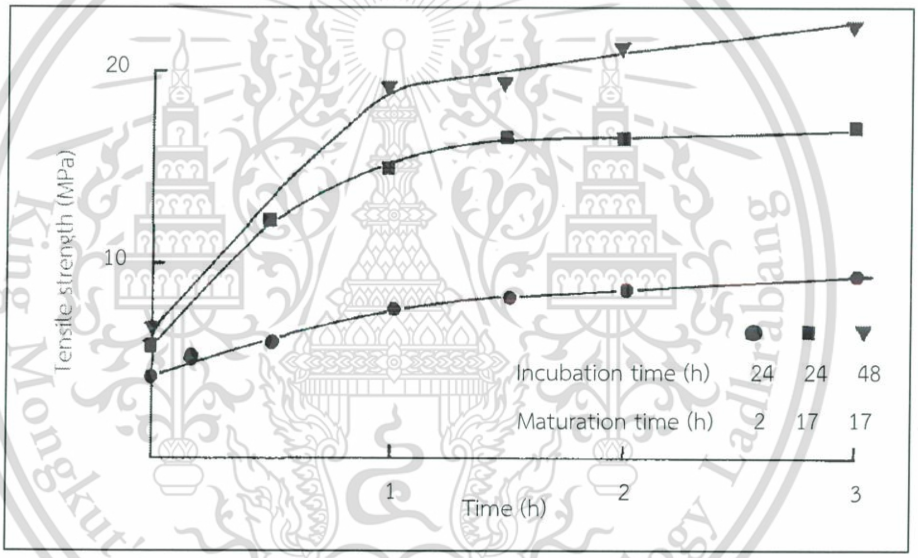


Figure 2.13 Influence of incubation time and maturation time on the development of tensile strength during prevulcanization at 70°C. [40]

However, the limiting crosslink density was higher after 17 hours maturation than after 2 hours maturation. Since the quantity of sulfur in the system was already fixed by the incubation period, this observation implied either that there was a redistribution of sulfur between the aqueous and polymer phases during the maturation period or that longer maturation allowed more accelerator or accelerator complex to enter the rubber phase, producing more efficient crosslinking from the sulfur already present there. Maintaining the 17 hours maturation period but doubling the incubation period increased the initial rate of crosslinking during subsequent prevulcanization indeed, there were indications that some crosslinking was now occurring during the maturation period.

Ruslimie C. A. et. al [41] studied effect of prevulcanization time on the latex particles, surface morphology and strength of epoxidized natural rubber (ENR) latex films. The latex used in the study was ENR and the total solid content was 30% with 25% epoxidation level (ENR25). The latex compounds were prepared using a conventional sulfur acceleration system. ENR25 latex was added into stainless steel vessel and stirred for 10 minutes at room temperature. All the vulcanization ingredients were added into vessel in sequence. The latex compound was kept under slowly stirring at room temperature for at least 30 minutes. The samples were taken every 24 hours to study the prevulcanization time and the ENR25 latex films were prepared by casting technique. It was found from the morphology of unvulcanized ENR25 latex particles showed that the particles size distribution divided to two particles sizes which were large particles (ca 0.7 μm) and small particles (ca 0.1 μm). Morphology of prevulcanized ENR25 latex particles seemed to be deformed and merged as shown in Figure 2.14. The structure of the prevulcanized latex particles was suspected to be reminiscent of the influx of vulcanizing reagents in the rubber particles. The influx of these reagents into the interior of the latex particles was deemed as a prerequisite for crosslinking. It was reported that during prevulcanization, crosslinking activity of rubber molecules had taken place inside discrete rubber particles dispersed in the aqueous phase. Nevertheless, in Figure 2.15 represents light microscopy images of ENR25 films at the air-facing (AF) surfaces taken at 0, 24, 48 and 72 hours of prevulcanization times.

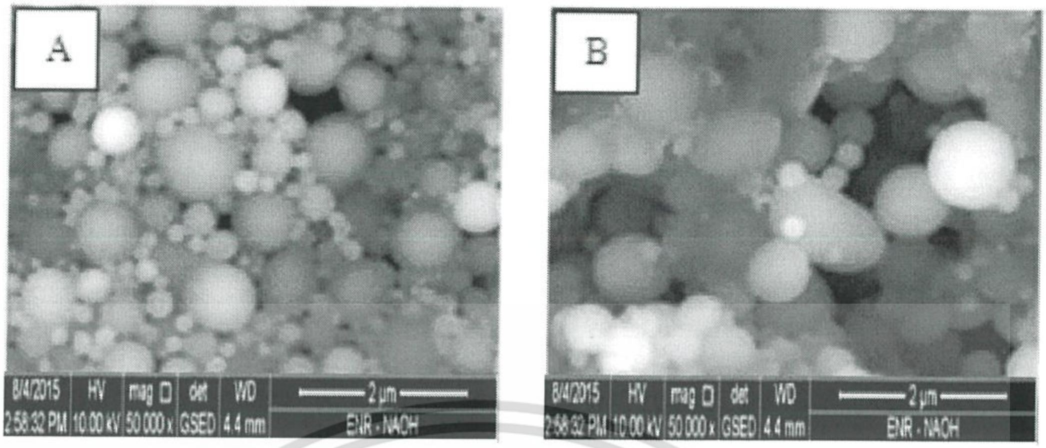


Figure 2.14 ESEM micrograph images showing morphology of latex particles (A) ENR25 and (B) ENR25 latex particles after 72 hours prevulcanization time. [41]

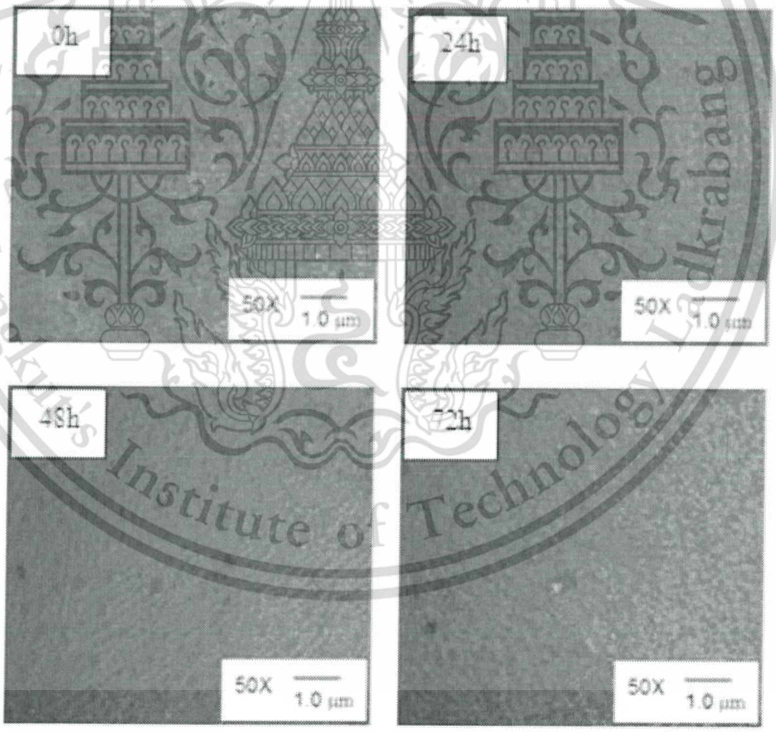


Figure 2.15 Optical light micrographs of vulcanized ENR25 films at various pre-vulcanization times [41]

The films surfaces at the prevulcanization of 0 and 24 hours exhibited smoother and coherence surface while the films surface at 48 and 72 hours prevulcanization showed coarser and more undulating surface. This was because the difference in film formation at the stage where the particle came into close contact with each other prior to coalescence. Hence, it could be suggested that the deformation and merging particles size of ENR25 latex particles at longer prevulcanization time could be attributed to the formation of coarser and more undulating surfaces.

Tensile strength showed increment as prevulcanization time increased. But after 48 hours, tensile strength of films decreased while unvulcanized ENR25 films exhibited the lowest tensile strength as shown in Figure 2.16. This was because increasing prevulcanization time could improved the tensile strength of the ENR25 latex films attributed to denser network chain and restriction in chain mobility. After 48 hours prevulcanization time, tensile strength of films decreased. It was probably a consequence of decreasing ability of latex particles to coalesce and fully integrate as the concentration of crosslinks in the particle increased. The occurrence was caused by poorly coalescing latex particles which inhibited further interparticles coalescence. The results were in agreement where their results reflected that over-matured latex would cause poor film formation and premature rupture latex films.

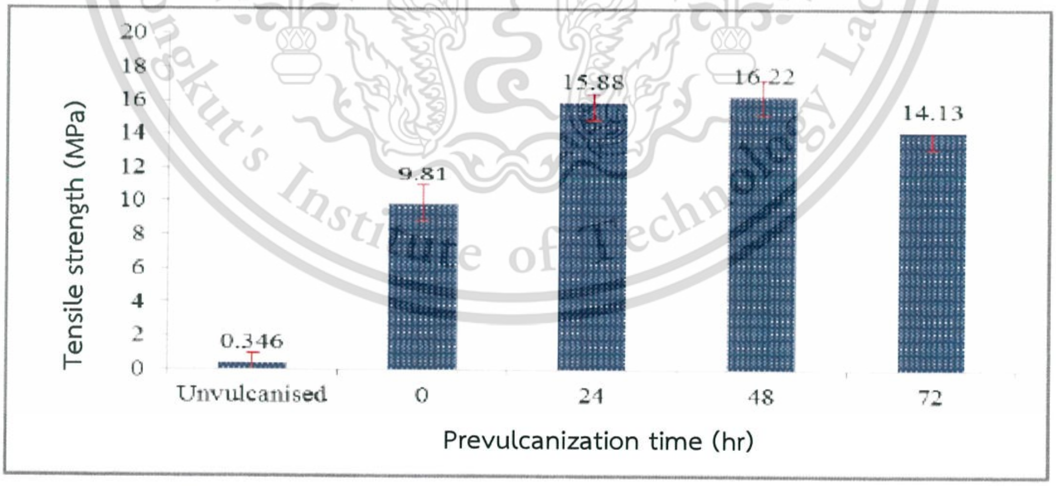


Figure 2.16 Tensile strength of ENR25 films against prevulcanization time [41]

Ghazaly, H. M. et.al [9] studied some factors affecting dipped NBR latex films. The latex compounds were prepared at a total solid content of 30%, containing the various amounts of KOH solution (0.5, 2.5 and 5.2 phr). The dipped films were prepared by the immersion of ceramic plates into 28% of anhydrous calcium nitrate solution.

The ceramic plates were first preheated at 50°C and a latex dwell time of 10 seconds was employed. Wet-gel leaching of the dipped films was done by immersing the wet-gels for 2 minutes into the distilled water, which was kept at 50°C. Drying of the films involved two stages at 50°C and 80°C for 20 minutes each, respectively, and then curing the films undertaken by heating the dried films at 120°C for 20 minutes. The results as the pH increased from 9 to 11, the viscosity of the compound increased but then decreased with a further increase in the pH from 11 to 12 as presented in Table 2.4. The carboxyl groups were susceptible to neutralization, which was accompanied by an increase in the viscosity of the latex (as occurred with alkali-swellable latex), the XNBR latex particles became swollen with water from the aqueous phase.

Table 2.4 Compounds of XNBR latex, recipe and latex viscosity. [9]

Compound ingredient	A (phr)	B (phr)	C (phr)
XNBR	100.0	100.0	100.0
KOH	0.5	2.5	5.2
S	1.0	1.0	1.0
ZDBC	1.0	1.0	1.0
ZnO	2.0	2.0	2.0
pH	9.2	10.9	12.3
Viscosity (cps) Spindle 1, speed 60 r.p.m.	5.0	44.0	16.5

Some of the XNBR latex particles, which have a higher carboxyl content, might even dissolve under the highly alkaline conditions. The dissolved carboxylate chains may subsequently be absorbed onto the latex particles, thus conferring electrostatic and steric stability to the NBR latex. The increase in the viscosity was due primarily to the ionization of the carboxyl acid groups. Subsequent drop in the viscosity was the result of the shielding of ionized carboxylic acid groups by the cations of the alkali and also of a dilution effect. Moreover, it was found that tensile strength and tear resistance of films from compound C (pH of NBR latex compound>12) were higher than films from compound A and B (pH of NBR latex compound <12). This was especially evident when the films were not leached. However, the unleached films showed low tensile strength values. While wet-gel leaching resulted in a dramatic increase in tensile strength values from 25 MPa to about 40 MPa. The elongation at break of the films was in the range of 550% - 600% as presented in Table 2.5.

Table 2.5 Tensile and tear properties of cured-XNBR dipped films [9]

Film (Unaged)	Thickness (mm)	Tensile strength (MPa)	M100 (MPa)	M300 (MPa)	Elongation at break (%)	Tear strength (N/mm)
A/L	0.105	32.0	3.0	6.6	600	4.3
A/U	0.104	23.0	2.5	5.0	580	4.2
B/L	0.100	33.0	3.5	7.3	560	4.2
B/U	0.105	22.0	3.1	6.2	550	4.1
C/L	0.107	42.0	3.2	6.8	620	5.8
C/U	0.108	25.0	3.0	5.6	600	7.5

L: Leached

U: Unleached

The study showed that the amount of stabilizer of compounds (pH) and the leaching protocol had contrasting effects on the tensile and tear properties of the XNBR latex films. It might also be possible that under higher pH conditions, the curing agents employed may have a higher degree of activation for complexes to form, favoring an increase in crosslinking efficiency.

Paakkonen, J. [42] studied surfactants in anionic latex films. Adding surfactants to a carboxylated latex could affect the film being formed. The surfactants being used were anionic sodium dodecyl sulfate (SDS), the cationic dodecyltrimethylammonium bromide (DoTAB) and poly(oxyethylene)(4) lauryl ether (Brij30®), a nonionic surfactant. This study was focusing on DoTAB interacting with 5 and 10%wt latex dispersions. It was found that the high concentrations of DoTAB, with time crystallized at the surface of the films (Figure 2.13) suggesting that the molecules migrated towards the air-film surface. The reason was the incompatibility between positively charged surfactant and negatively charged latex. The phase separation tended to expel the surfactants towards domains of pure surfactants within the film. In these domains the surfactant could crystallize. However, SDS demonstrated the surfactants could be observed at the air surface but age did not affect the structure indicating no movement of surfactant in dry films. For Brij30® no apparent free form of surfactants could be found, neither did the surface change with time.

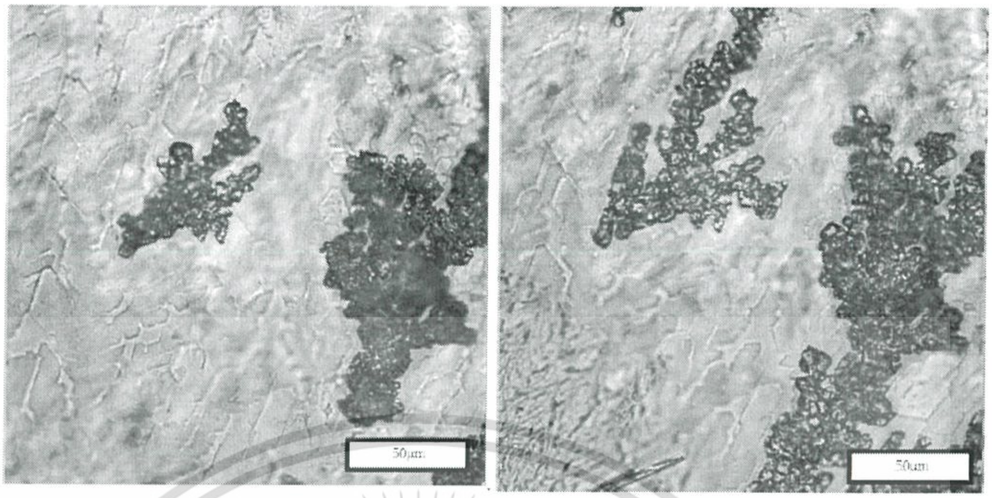


Figure 2.17 Images taken with light microscope, 50x objective at different ages of a film consisting of 5%wt latex, 15 mM DoTAB a.) 24 hours and b.) 48 hours [42]

The work and results reported in this research showed types of surfactants affecting on film formation, when the films were dried and during aging of the films. Thus, low compatibility between surfactant and latex particles could caused increased the tendency to migrate of surfactant on the surface of film latex and crystallized.

Yasin, T. et.al [8] studied effect of acrylonitrile (AN) content on physical properties of electron beam irradiated NBR. The NBR with different acrylonitrile contents (17.5, 33 and 53 %wt), carbon black 40%wt, ZnO 5%wt and stearic acid 1%wt were mixed for 10 minutes using plastomill operated with 80 rpm at 80°C. Polyfunctional monomers (PFMs) which were diethylene glycol dimethacrylate (2G) and trimethylol propane trimethacrylate (TMPT) were added to the above admixture at 0.02 mol/100 g of rubber. Sheets were prepared using a hot press at 150°C for 5 minutes under 150 kg/cm^2 pressure followed by cold pressing for 2 minutes at the same pressure. The samples were irradiated by an electron beam generated by a Cockrofit-Walton type accelerator (2 MeV, 30 mA). Figure 2.18 shows the effect of irradiation dose on tensile strength of NBR possessing 17.5%, 33% and 53% AN contents. NBR having 33% AN content has relatively the highest tensile strength at all irradiation doses. The constancy in tensile strength was observed when increasing in irradiation doses. The constancy at high dose may be attributed to high degree of crosslinking, resulting in hindering of orientation process.

The elongation at break (%) of the samples was dependent upon the crosslink density. As the number of crosslinks between polymer chains increased, the chains could not move relative to each other as easily and consequently elongation at break decreased as shown in Figure 2.19

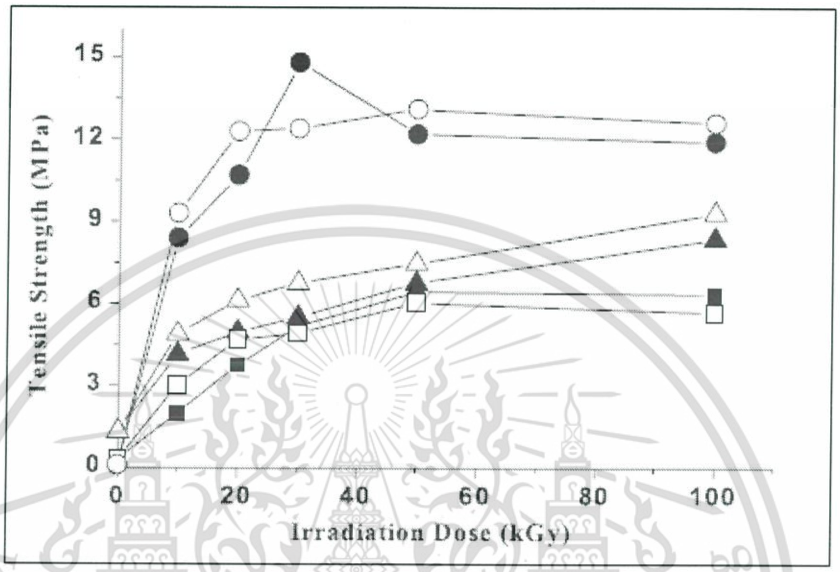


Figure2.18 Effect of irradiation dose on tensile strength of NBR with different acrylonitrile contents. ■ 17.58% AN (2G); ● 33% AN (2G); ▲ 53% AN (2G); □ 17.5% AN (TMPT); ○ 33% AN (TMPT); △ 53% AN (TMPT). [8]

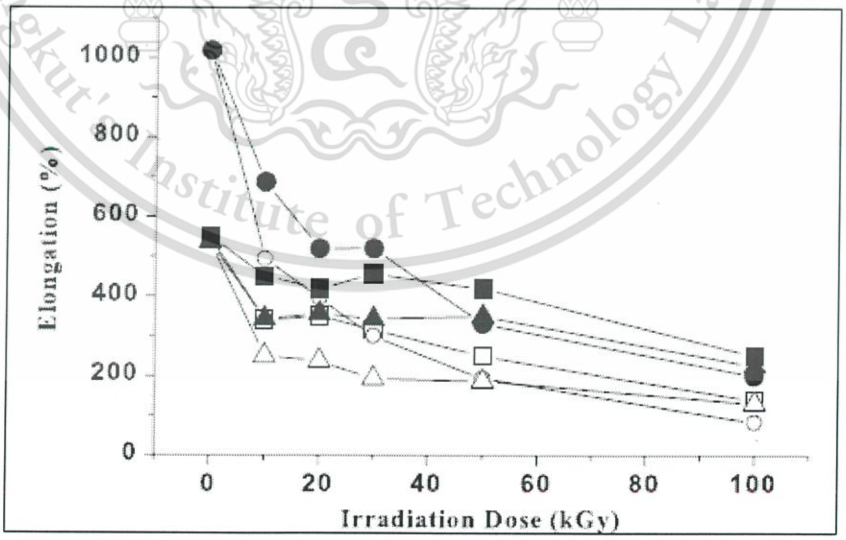
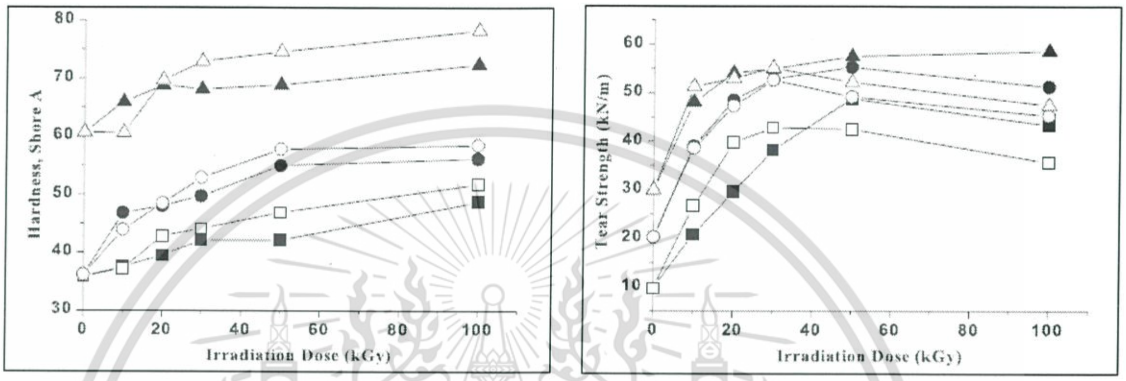


Figure 2.19 Effect of irradiation dose on elongation at break (%) of NBR with different acrylonitrile contents. ■ 17.5% AN (2G); ● 33% AN (2G); ▲ 53 % AN (2G); □ 17.5% AN (TMPT); ○ 33% AN (TMPT); △ 53% AN (TMPT). [8]

Moreover, the hardness (Shore A) values of NBR vulcanizate depended very much upon the acrylonitrile content of the rubber. It increased with correspondingly increasing in AN content as shown in Figure 2.20 This tendency was positively a consequence of the effect of acrylonitrile content of the rubber. The increased in hardness with increasing dose was brought about by an increase in crosslinking of NBR.



A B

Figure 2.20 Effect of irradiation dose on (A) hardness shore A, (B) tear strength of NBR with different acrylonitrile contents. ■ 17.5% AN (2G); ● 33% AN (2G); ▲ 53% AN (2G); □ 17.5% AN (TMPT); ○ 33% AN (TMPT); △ 53% AN (TMPT). [8]

The tear strength of NBR having different AN contents was found to increase with correspondingly increasing in AN content or the irradiation dose. By considering the Thomas equation, the increase in dose favorably affected the stress of NBR having different acrylonitrile contents. Therefore, the tear strength increased up to the value at which the decrease in the strain became appreciable as illustrated as Figure 2.20 (B). It was confirmed that grade of nitrile rubber (AN content) affected on physical properties of NBR.

The purpose of this study was to determine the optimum maturation time and studied effects of accelerator systems on properties of NBR latex gloves. Moreover, the effects of NBR latex formulations of compound such as AN contents and stabilizer types, were studied. In previous work, the maturation time was one of the most important aspects in manufacturing latex products. There was an issue of excessive amount of time used for target compound maturation in the production of NBR gloves, which was over the capability of tank stirrer and also lengthens the time used for production of NBR latex gloves. Therefore, in this study, the maturation time of NBR latex compound from 0 until 96 hours was examined. The samples were taken every 24 hours, to studied properties of NBR latex compound. Furthermore, previous work [8, 9, 42] showed that stabilizer, surfactant and acrylonitrile contents affected on production and properties of final product. So, grades of NBR latex compound (HAN-NH_3, HAN-KOH and MAN-NH_3 and KOH) were focused on properties of NBR latex gloves.

Chapter 3

Research methodology

3.1 Chemicals and materials

1. Latex of acrylonitrile butadiene copolymer (NBR): high acrylonitrile content grade with ammonia stabilizer (HAN-NH_3), Zeon (Japan) Co., Ltd.

Table 3.1 Specification of NBR latex, grade HAN-NH_3 [43]

Property	Value
Modified acrylonitrile/butadiene/copolymer, %wt	43
Water, %wt	57
Acrylonitrile, ppm	<100
1,3-Butadiene, ppm	<100
Methacrylic acid, ppm	<5,000
%Total solid content	43.0 - 45.0
pH	8.4 - 9.0
Brookfield viscosity (No.1, 60 rpm), mPa.s	Max 100
Coagulum content (200 mesh), %wt	0.05
Surface tension, mN/m	25.0 - 31.0

2. Latex of acrylonitrile butadiene copolymer (NBR): high acrylonitrile content grade with potassium hydroxide stabilizer (HAN-KOH), Zeon (Japan) Co., Ltd.

Table 3.2 Specification of NBR latex grade HAN-KOH [44]

Property	Value
Modified acrylonitrile/butadiene/copolymer, %wt	43
Water, %wt	57
Acrylonitrile, ppm	<100
1,3-Butadiene, ppm	<100
Methacrylic acid, ppm	<5,000

3. Latex of acrylonitrile butadiene copolymer (NBR): medium acrylonitrile content grade with ammonia and potassium hydroxide stabilizer (MAN-NH_3 and KOH), BST (Thailand) Co., Ltd.

Table 3.3 Specification of NBR latex grade MAN-NH_3 and KOH [45]

Property	Value
Carboxylated butadiene acrylonitrile, %wt	40-50
Water, %wt	50-60
Acrylonitrile, ppm	Max 40
%Total solid content	44-46
pH	8.0-8.7
Brookfield viscosity, mPa.s	Max 300
Coagulum content, %wt	0.01
Surface tension, dynes/cm	20.0-50.0

4. Standard zinc oxide (ZnO) dispersion: Ansell (Thailand) Co., Ltd.
5. Sulfur: Utids Enterprise (Thailand) Co., Ltd
6. Accelerator 1 (Thiazoles compound): Lanxess Co., Ltd.
7. Accelerator 2 (Dithiocarbamates compound): Performance Additive Co., Ltd.
8. Coagulant solution (powder): Ansell (Thailand) Co., Ltd.
9. Antioxidant A: Rashing Gmbh Co., Ltd.
10. Stabilizer A: Thanodom Trading Co., Ltd.
11. Stabilizer B: Connell Bros. Co. (Thailand), Ltd.
12. Green pigment: grade TCD-9905, Sun Chemical Co., Ltd.
13. Talcum powder: Loxley Public Co., Ltd.
14. Toluene (analytical grade): RCL Labscan Co., Ltd.
15. 5% sodium lauryl sulphate: RCL Labscan Co., Ltd.
16. Chloroform (analytical grade): RCL Labscan Co., Ltd.
17. Distilled water: Ansell (Thailand) Co., Ltd.

3.2 Apparatus

1. Former (size m): Shinko Ceramics Co., Ltd.
2. Universal testing machine: model 2519-104, Instron Co., Ltd.
3. pH meter: model Orion Star™ A111, Thermo Fisher Scientific Inc.
4. Oven: model Series FD, Binder Co., Ltd.
5. Brookfield viscometer: model DV1 viscometer, Malvern Instruments Co., Ltd.
6. Gang stirrer: model Frenic-Multi, Fuji Electric FA Components & Systems Co., Ltd.
7. Analytical balance: model AB204, Marshall scientific Co., Ltd.
8. Micrometer: model Mitutoyo 7002, Willrich Precision Instrument Co., Inc
9. FTIR spectrometer: model Spectrum® 100, PerkinElmer Co., Ltd.
10. Latex mechanical stability test machines: model MST3, A&Y Separator Co., Ltd.
11. Desiccator: model Z317446-Duran®, Sigma-Aldrich Pte. Ltd.
12. Compounding mixing tank (size of 8,000 g)
13. Water bath
14. Nylon filter
15. Ceramic plate
16. Laboratory glassware

3.3 Preparation of NBR latex compounds

The NBR latex compounds were prepared using a mixing tank. Formulation of NBR latex compounds (batch size of 5,000 g) was listed in Table 3.4.

Table 3.4 Formulation of NBR latex compounds (batch size of 5,000 g)

Materials	phr	TSC (%)	Dry wt. (g)	Wet wt. (g)
1. NBR raw latex	100	43.00	1641.65	3,793.84
2. Stabilizer A	0.4	3.00	6.57	218.89
3. Zinc oxide dispersion	1.6	50.20	26.27	52.32
4. Sulfur dispersion	1.0	52.55	16.42	31.24
5. Accelerator 1	1.3	50.00	21..34	42.68
6. Accelerator 2	0.4	50.00	6.57	13.13

Table 3.4 Formulation of NBR latex compounds (batch size of 5,000 g) (continued)

Materials	phr	TSC (%)	Dry wt. (g)	Wet wt. (g)
7. Antioxidant A dispersion	0.5	49.93	8.21	16.42
8. Stabilizer B	0.4	12.33	6.57	53.26
9. Green pigment	1.0	60.25	16.42	27.25
10. Distilled water	-	-	-	750.97
Total	-	-	1750.00	5,000.00

Mixing procedure as follows:

1. Fill the NBR raw latex into the mixing tank as per amount required in formulation.
2. Turn on the stirrer and allow stirring for minimum 15 minutes at room temperature with a rotor speed of 5 rpm.
3. Slowly add the stabilizer A solution as per amount required in formulation into latex under agitation with minimum addition time of 30 minutes. Allow stirring for minimum 15 minutes.
4. All the dispersions and solutions adding in each step must be weighed and put into the mixing tank as per amount required in formulation and must be filtered through a nylon sieve (300 mesh).
5. Slowly add all the dispersion in each step as below:

Dispersion	Minimum addition time
Zinc oxide dispersion	15 minutes
Sulphur dispersion	15 minutes
Accelerator 1	15 minutes
Accelerator 2	15 minutes
Antioxidant dispersion	15 minutes

After complete addition of each step, wait for a homogeneous mixing at least 30 minutes.

6. Slowly add stabilizer B solution (minimum addition time 15 minutes) and continued stirring for minimum 15 minutes.
7. Then add the green pigment and the distilled water as per required in formulation. Finally allow latex to be stirred for 45 minutes.

8. Repeat all processes for studied effects of accelerators on maturation time of NBR latex gloves as shown in Table 3.5

Table 3.5 Formulation of NBR latex compounds for study effect of accelerator on maturation time of NBR latex gloves.

Materials	Formulation (phr)		
	Current	Ac1-free	Ac-free
1. NBR raw latex	100	100	100
2. Stabilizer A	0.4	0.4	0.4
3. Zinc oxide dispersion	1.6	1.6	1.6
4. Sulphur dispersion	1.0	1.0	1.0
5. Accelerator 1	1.3	-	-
6. Accelerator 2	0.4	1.0	-
7. Antioxidant A dispersion	0.5	0.5	0.5
8. Stabilizer B	0.4	0.4	0.4
9. Green pigment	1.0	1.0	1.0

9. Repeat all processes (Ac1-free) for other NBR raw latex as shown in Table 3.6 for studied effects of raw latex grades on properties of NBR latex gloves.

Table 3.6 Types of NBR raw latex

Grade	AN content	Stabilizer
HAN-NH_3	High (40%wt)	NH_3
HAN-KOH	High (40%wt)	KOH
MAN-NH_3 and KOH	Medium (26-30%wt)	NH_3 and KOH

<u>Note</u> All data are supported form Ansell (Thailand) Co., Ltd.

10. Studied effects of amount of stabilizer on NBR latex compound properties. The latex compounds were prepared as the Ac1-free formulation given in Table 3.7.

Table 3.7 Formulation of NBR latex compounds for study effect amount of stabilizer on NBR latex compound.

Materials	Ac1-free formulation (phr)					
1. NBR raw latex	100	100	100	100	100	100
2. Stabilizer A	0.0	0.4	0.8	1.2	1.6	2.0
3. Zinc oxide dispersion	1.6	1.6	1.6	1.6	1.6	1.6
4. Sulfur dispersion	1.0	1.0	1.0	1.0	1.0	1.0
5. Accelerator 2	1.0	1.0	1.0	1.0	1.0	1.0
6. Antioxidant A dispersion	0.5	0.5	0.5	0.5	0.5	0.5
7. Stabilizer B	0.4	0.4	0.4	0.4	0.4	0.4
8. Green pigment	1.0	1.0	1.0	1.0	1.0	1.0

3.4 Gloves preparation

After compounding, the NBR latex compounds were used for glove preparation via continuously dipping process. At first the formers were cleaned with water by dipping in hot water and then preheated before dipping in coagulant solution tank. After drying the coagulant, the formers were dipped in the NBR latex compound tank. Then the formers with the gelled latex film underwent pre-leaching, beading and curing in an oven before powdering. Finally, NBR latex gloves were stripped off the former. The dipping condition was listed below.

Preheating of former	50°C, 15 minutes
Leaching the former (hot water)	65-70°C, 20 seconds
Dipping in the coagulant tank	50°C, 12 seconds
Dipping in the latex compound tank	12 seconds
Pre-leaching (hot water)	65-70°C, 20 seconds
Curing	130°C, 15 minutes

For studying the effect of accelerator on maturation time, the dipping process was repeated in the same NBR latex compound tank every 24 hours until 96 hours. Moreover, in part of studying effect of NBR raw latex grade, the gloves were prepared at 24 hours maturation time.

3.5 Film preparation with ceramic plates

Firstly, ceramic plates were cleaned with water and then preheat in oven at 50°C for 15 minutes. The ceramic plates were immersed into coagulant solution. After drying the coagulant, the ceramic plates were dipped into NBR latex compound. The latex dwell time of 3 seconds was employed. Wet gel leaching of the dipped films was carried out by immersing the wet gel for 1 minute into water which was kept at 65-70°C for 20 seconds. Finally, the dipped films were curing in an oven at 130°C for 15 minutes.

3.6 Characterization

3.6.1 Determination of total solid content

Total solid content (TSC) of NBR latex compounds was determined by weighing a flat-bottomed lipless dish (90-100 mm) and pouring the 1.5-2.5 g sample into dish. Then, the sample was distributed until uniform in dish. With the dish uncover, dried the sample in an oven at 110 ± 5°C for one hour. The sample was cooled in desiccator for 15 minutes and then weighing the dish and calculated the TSC.

$$\%TSC = \frac{W_3 - W_1}{W_2} \times 100 \tag{3.1}$$

When

W_1 is the weight of dish

W_2 is the weight of sample in the dish

W_3 is the weight of the dried sample and dish

3.6.2 Determination of the viscosity

The viscosity of NBR latex compounds was determined using a Brookfield viscometer. The NBR latex compound must be conditioned at room temperature at least 3 hours before adding 500 ml in a breaker. The sample was placed into Brookfield viscometer, using number 2 spindle with the rotational speed of 60 rpm to prevent the bubble effect. Viscosity value was recorded after 1 minute on Brookfield viscometer.

3.6.3 Determination of pH

The pH value of NBR latex compounds was measured with pH meter, at room temperature. NBR latex compound was immersed with the electrode and then, the pH value to be stabilized before recording.

3.6.4 Determination of coagulum content

The NBR latex compounds was mixed with 5% sodium lauryl sulphate and then filtered that through a nylon filter (200 mesh). The residue on the nylon filter was dried and its weight was calculated in terms of percentage to total solid content of the latex sample.

$$\text{Coagulum content (\%)} = \frac{W_2\text{-}W_1}{W_0 \times \%\text{TSC}} \times 10{,}000 \qquad (3.2)$$

When
W_0: Weight of the latex sample
W_1: Weight of nylon sieve (200 mesh)
W_2: Weight of nylon sieve and dry coagulum

3.6.5 Determination of coagulum of mechanical stability time (%CMST)

Percentage of coagulum mechanical stability time (%CMST) was simulated from mechanical stability time (MST) test. This method was indicated stability of NBR latex concentrate to mechanical shear force in term coagulum content. Adding 40 ml of NBR latex in a breaker and then was stirred with latex mechanical stability machines at speed 8000 rpm for 30 minutes. After that, the NBR latex compound was filtered that through a nylon filter (200 mesh). The residue on the nylon filter was dried. Its weight was calculated similar coagulum content test (equation 3.2).

3.6.6 Cyclohexanone test

Cyclohexanone test was simulated from chloroform test of NR latex compound. Solvent was changed to be appropriate for NBR latex compound. The NBR latex compound 10 ml was mixed with cyclohexanone 15 ml and then stirring with a glass rod until coagulation was completed. The coagulum was examined and graded depending upon the form of coagulum. The following gradings were defined as:

No.1: The coagulum was a tacky mass and break in a stringy manner when stretched. This represents an unvulcanized state.

No.2: The coagulum was a weak lump which breaks short when stretched. This indicates a lightly vulcanized state.

No.3: The coagulum was in the form of non-tacky agglomerates. This indicates a moderately vulcanized state.

No.4: The coagulum was in the form of small dry crumbs. This indicates a fully vulcanized state.

3.6.7 Swelling test

Determination of swelling index involved the immersion of 25.4 diameter disks of NBR latex film in solvent mixtures (toluene: chloroform, 3:2 by volume). Firstly, ceramic plates were dipped into coagulant solution. Then, ceramic plates were allowed to dry at room temperature for 1 minute, before dipped into NBR latex compounds for 18 seconds. The wet films were allowed to dry in an oven at 100°C for 10 minutes and then, the NBR latex films was cut with a hole punch with the diameter of 25.4 mm. Samples were immersed in a Petri dish having solvent mixture and allowed to swell for 15 minutes. Finally, the samples carefully withdrew from dish and then, placed the sample on graph paper to recording the swollen latex sample size. The swollen sample was calculated the percentage of swell index, as equation 3.3.

$$\%\text{Swelling ratio}=\frac{(D_1-D_0)}{D_0}\times 100 \qquad (3.3)$$

When

D_0 is the diameter of hole punch (25.4 mm)

D_1 is the diameter of swollen latex

3.6.8 Thickness of NBR latex films

Thickness of NBR latex films was measured from the films prepared with ceramic plate. The thickness of NBR latex film was recorded using a micrometer, to median value of 3 points i.e. one at the center and two at each end of the section of the films.

3.6.9 Prevulcanizate relaxed-modulus (PRM)

PRM test can represent the degree of NBR latex prevulcanization by way of measurement of elastic tensile modulus at 100% extension of film dried down from NBR latex compound [29]. Firstly, the sample of the NBR latex film was prepared using a ceramic plate dipping process similar to that prepared for swelling test. However, it was allowed to dry at 70ºC for 5 minutes and cut to the rectangular testing specimens having a dimension of 15×100 mm^2. The PRM test was performed using universal testing machine (UTM model 2519-104, Instron Co., Ltd.). The specimen was stretched with a test speed of 500 mm/min to 100% extension and held for 1 minute and then the load in Newtons exerted by the film was recorded and then calculated for PRM.

3.6.10 Fourier-Transform Infrared (FTIR) spectroscopy

Fourier-transform infrared spectrometer was used to characterize the films of NBR raw latex including HAN-NH_3, HAN-KOH and MAN-NH_3 and KOH grades. The spectrum was scanned 32 numbers and the wavelength was controlled from 500 to 4000 cm^{-1}.

3.6.11 Tensile test

Tensile properties of gloves were examined using UTM. The tensile properties including tensile strength, % elongation at break, modulus at 100% and 300% elongation were measured according to ASTM D412-15a. The tensile testing conditions are as follows:

Load cell	500 N
Test speed	500 mm/min
Gauge length	25 mm

3.6.12 Chemical permeation

This test method was designed to determine resistance to permeation of organic chemicals using gas chromatography. The test specimens were cut out from palm area of the glove sample with a circular diameter of 48±0.5 mm and then were conditioned for at least 24 hours at 23 ± 1°C before testing. Nitrogen gas was introduced as a carrier gas and the testing conditions are listed below:

Injector temperature	270°C
Column temperature	250°C
Detector temperature	270°C
Make up flow	10 ml/min
H_2 flow	55 ml/min
Air flow	350 ml/min

Figure 3.1 The test specimen mounted in the permeation cell [46]

The result was recorded when cell reached the permeation rate of 1 $\mu g/cm^2 \cdot min$ or completed 8 hours testing duration if no breakthrough was detected (ASTM F739-85). The lowest breakthrough time was used for determination of the performance level. The resistance to permeation by chemical performance level shows in Table 3.7.

Table 3.8 Resistance to permeation with chemical performance level

Performance level	Breakthrough time
1	11-30 mins
2	31-60 mins
3	61-120 mins
4	121-240 mins
5	241-480 mins
6	>480 mins

Chapter 4

Results and Discussion

This research studied some effects of compounding and maturation of acrylonitrile butadiene rubber (NBR) latex on glove properties. NBR latex compounds using accelerator and accelerator-free systems are shown in Tables 3.4-3.7. There were investigated as a function of time. After compounding, NBR latex compounds were used for glove preparation via continuous dipping process. The results were divided in 3 parts i.e. effects of maturation time, effects of NBR latex properties (acrylonitrile content and type of stabilizer) and effects of stabilizers amount on NBR latex glove properties.

4.1 Effects of maturation on properties of NBR latex gloves

Effects of maturation on properties of NBR latex gloves were investigated by preparing the NBR latex compounds with control (thiazoles and dithiocarbamate compound), accelerator 1-free (dithiocarbamate compound) and accelerator-free systems. To study properties of NBR latex compounds and gloves, the samples were taken every 24 hours until 96 hours. The results were divided in 2 parts; effects of maturation on NBR latex compound and effects of accelerators on maturation of NBR latex gloves.

4.1.1 Effects of maturation on properties of NBR latex compound

4.1.1.1 pH of NBR latex compound

The pH of NBR latex compound was measured with a pH meter, at ambient temperature. Figure 4.1 shows pH of NBR latex compound with different maturation times. It was found that pH of compound slightly decreased as the maturation time was increased from 0 to 96 hours. This might be derived from the fact that ammonium hydroxide could be converted to ammonia having a low boiling point (24.7°C) [47]. Thus, ammonia could slowly evaporate during long maturation time. Also, the high shear force of stirrer during maturation could cause ammonia evaporation. Similar results was observed in previous work. Corruchaga, A. and Casal, J. [48] studied evaporation of ammonia from aqueous solution spills. It was found that ammonia showed high evaporation rate during the first period and then a low evaporation rate with time.

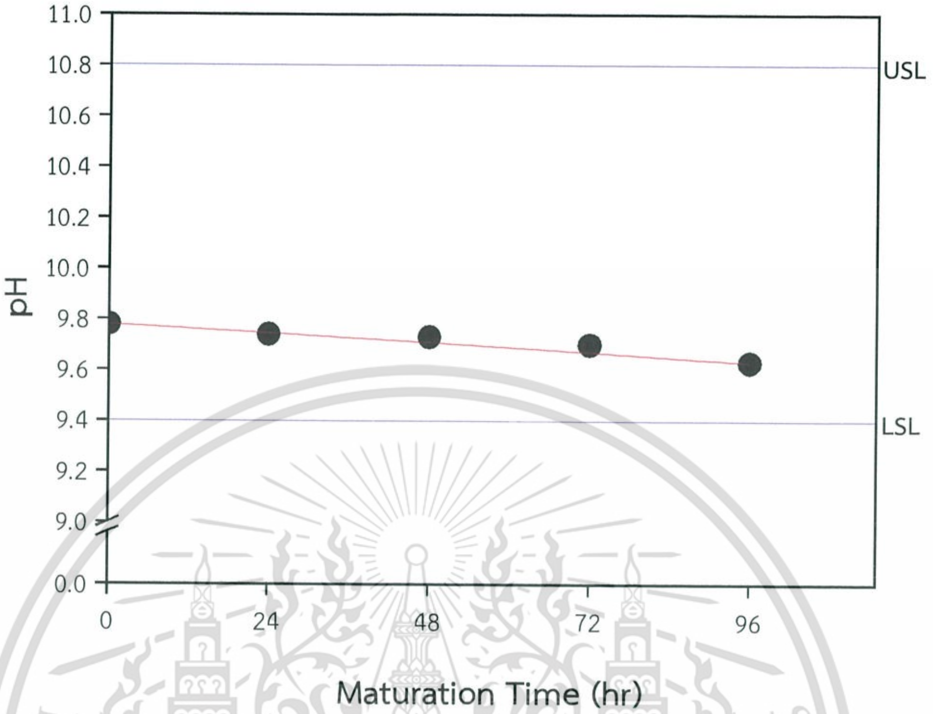


Figure 4.1 Effect of maturation time of NBR latex compound on pH

Moreover, a part of ammonium hydroxide could react with chemicals in compound (side reaction) causing loss of ammonium hydroxide in NBR latex compound tank. Loadman, M. J. R. and co-workers [49] found that some ammonium hydroxide was reacted with tetramethylthiuram disulfide (TMTD) and zinc oxide to form zinc dimethyldithiocarbamate (ZDMC) in the latex compound. Then ZDMC was decomposed during maturation with ammonium hydroxide to form dimethylamine, ammonium thiocyanate and thiourea. The accelerator used in this work has similar structure to ZDMC so that the reaction with ammonium hydroxide would be the same as shown in Figure 4.2. In addition, zinc oxide is the most common source of zinc ions. In the presence of water, it undergoes some hydrolysis to zinc hydroxide. Zinc ions released by the sparingly soluble hydroxide are complexed by free ammonia in the latex to form zinc ammine ions of various compositions [30]. Thus, this caused loss of some ammonia and reduction of pH in compound. The reaction shows in Figure 4.3. However, the pH in manufacturing process was controlled in lower specification limit (LSL) at 9.4 and upper specification limit (USL) at 10.8 respectively, thus the reduction of pH in this study would not significantly affect further steps.

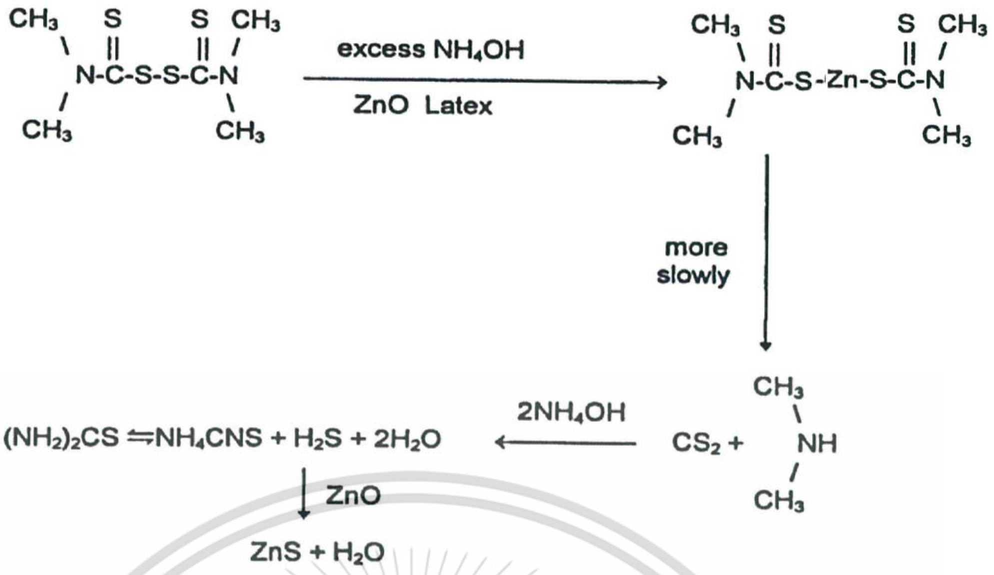


Figure 4.2 Proposed major routes for the decomposition of TMTD and ZDMC in latex [49]

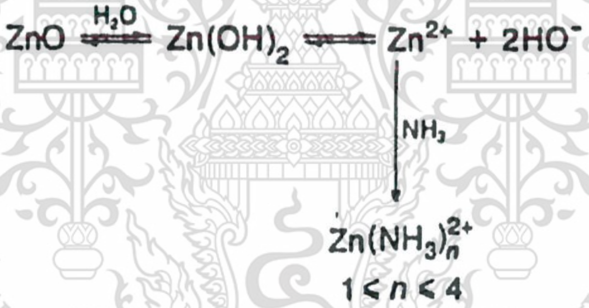


Figure 4.3 Formation of zinc ammines [30]

4.1.1.2 Coagulum of NBR latex compound

Figure 4.4 shows that percentage of coagulum increases from 0.0024 to 0.0066 with increasing maturation time from 0 to 96 hours, respectively. This might be becasue NBR latex particles were prevulcanized with vulcanizing agents. The enhanced solubility of sulfur and accelerator in the latex aqueous phase during maturation facilitated sulfur prevulcanization. As seen in SEM images (Figure 4.5), coagulum particles had spherical shape with diameters around 70 to 80 μm. Moreover, Figure 4.6 illustrates SEM/EDS elemental mapping images of coagulum particles. It was found that major elements including C, O, Zn and S, appeared at surface of coagulum particles.

These elements were component of vulcanizing agents. Thus, morphology confirmed that during maturation the NBR latex particles were swollen due to crosslinking with sulfur and sulfur-donor accelerator, inclusion of compounding ingredients and/or breakdown in colloidal stability of the latex.

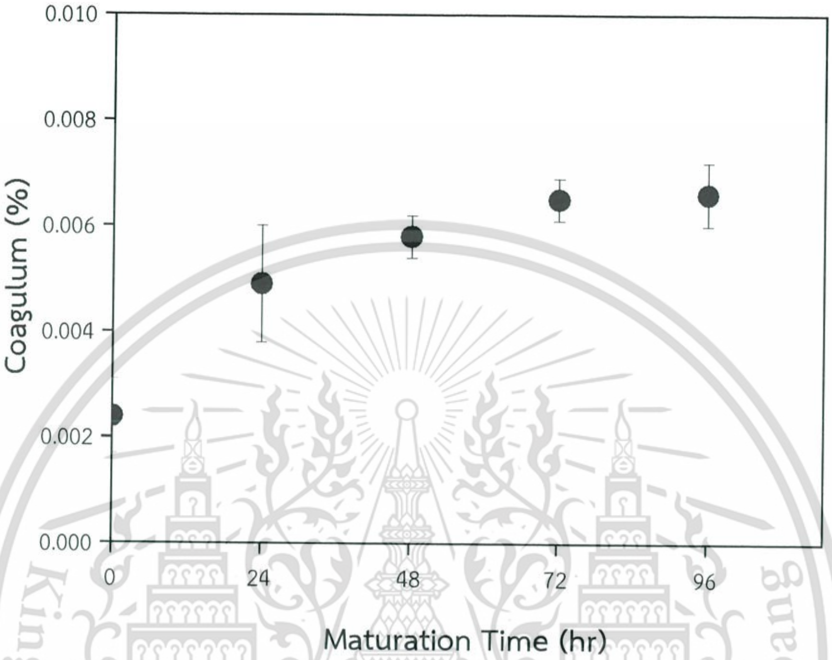


Figure 4.4 Effect of maturation time of NBR latex compound on percentage of coagulum

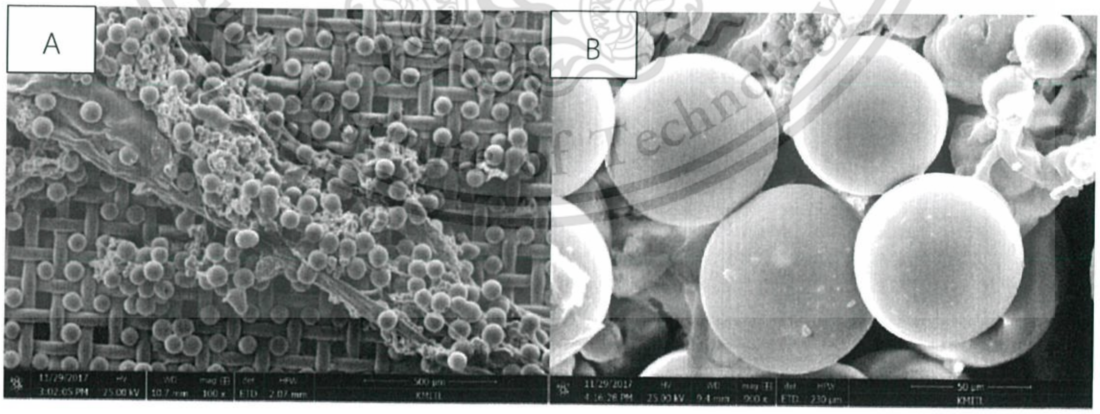


Figure 4.5 SEM images of coagulum particles of NBR compound; (A) 100X and (B) 900X

The important step of the reaction was the formation of sulfur-accelerator species in aqueous phase of the latex. These species transferred to rubber phase and crosslink the rubber molecules therein [50]. Moreover, NBR latex particle surface adsorbed some curative agents, causing loss of electric charges of NBR latex particles and agglomeration of latex particles.

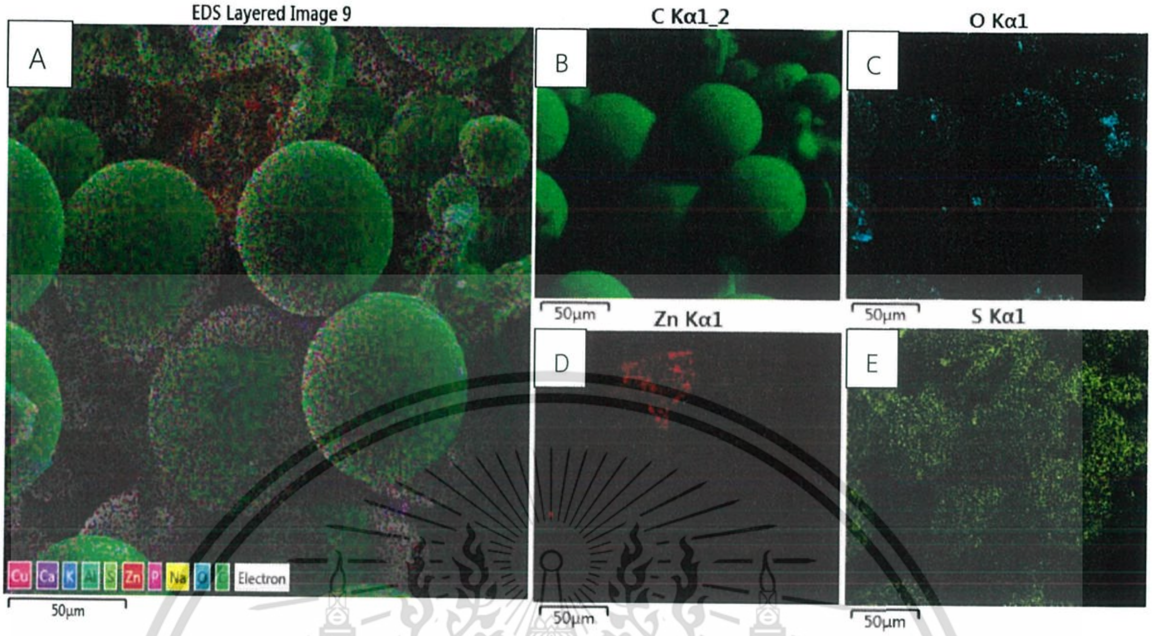


Figure 4.6 SEM/EDS elemental mapping images of coagulum particles of NBR compound; (A) SEM/EDS elemental mapping images, (B) – (E) the corresponding elemental mapping of C, O, Zn and S, respectively

The high shear force during maturation also could cause some ammonia evaporation leading to reduction in the colloid stability and coagulation of NBR compound. However, the percentage of coagulum in manufacturing process was controlled lower than 0.02% but requirement at lower than 0.005%, thus the high coagulum content caused defects of gloves.

4.1.1.3 Solvent swelling test of NBR latex compound

Prevulcanized NBR compound latex is allowed to mature for sufficient time before glove manufacturing process. During maturation, crosslinking of the rubber molecules takes place inside discrete rubber particles dispersed in the aqueous phase of NBR latex compound [50]. Thus, one of methods for assessing the degree of vulcanization during maturation is equilibrium solvent swelling test. In this method, the degree of vulcanization is judged via the extent of equilibrium swelling of films dried down from NBR compound latex. The swelling was carried out under controlled condition using a suitable solvent. Hasegawa, J. [51] used methyl ethyl ketone (MEK) in the swelling of NBR latex films. It was found that MEK was a stronger solvent compared to toluene. Ghazaly, H. M. et.al [9] used chloroform in the swelling in the swelling of XNBR films. It was found that chloroform was a very effective swelling agent. Thus, this method used solvent mixtures of toluene and chloroform (ratio 3:2 by volume). Figure 4.7 shows the percentage of swelling at ambient temperature with various maturation times. The NBR latex film without maturation (at 0 hour) was discarded as it had no prevulcanization. The swelling of latex films was slightly decreased with increasing maturation time. This result indicated that prevulcanization of NBR latex compound increased with increasing maturation times.

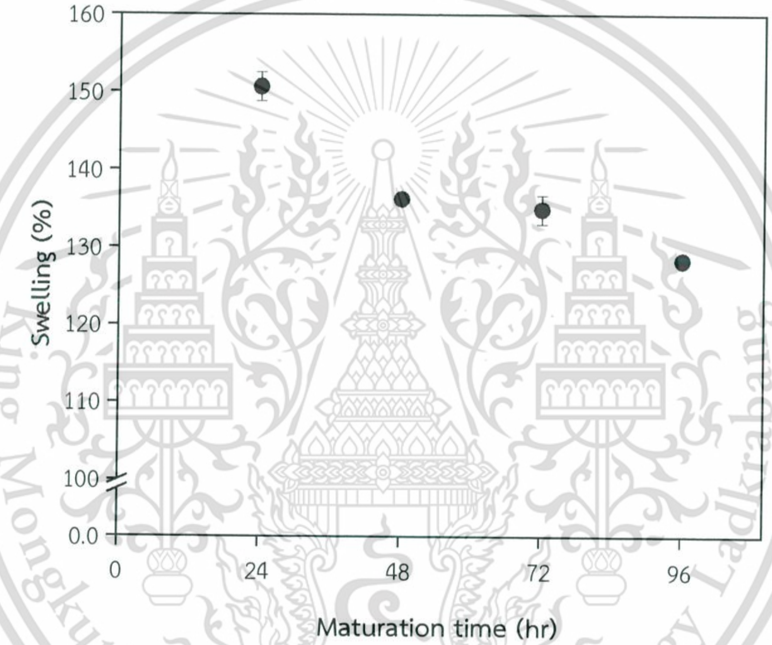


Figure 4.7 Effect of maturation time on mixed toluene/chloroform swelling of NBR latex films

The longer maturation times allowed vulcanizing agents to gradually react with rubber molecules, thus rubber chains were chemically crosslinked together and restricted the diffusion of solvent molecules [40]. Therefore, solvent swelling test can be used as an indicator for the formation and degree of vulcanization. The extent to which the sample swells is an inverse measure of the degree of vulcanization.

4.1.1.4 Cyclohexanone test for NBR latex compound

Solvent-coagulation test is one of method for especially valuable in predicting crosslink density in NBR latex compound during maturation. In general, NR latex compounds used chloroform as solvent for coagulation. Thus, this study changed solvent to cyclohexanone to be appropriate for NBR latex compound. Figure 4.7 shows the coagulum of NBR latex compound each of the maturation time from 0 to 96 hours. Table 4.1 shows cyclohexanone number of NBR latex compound.

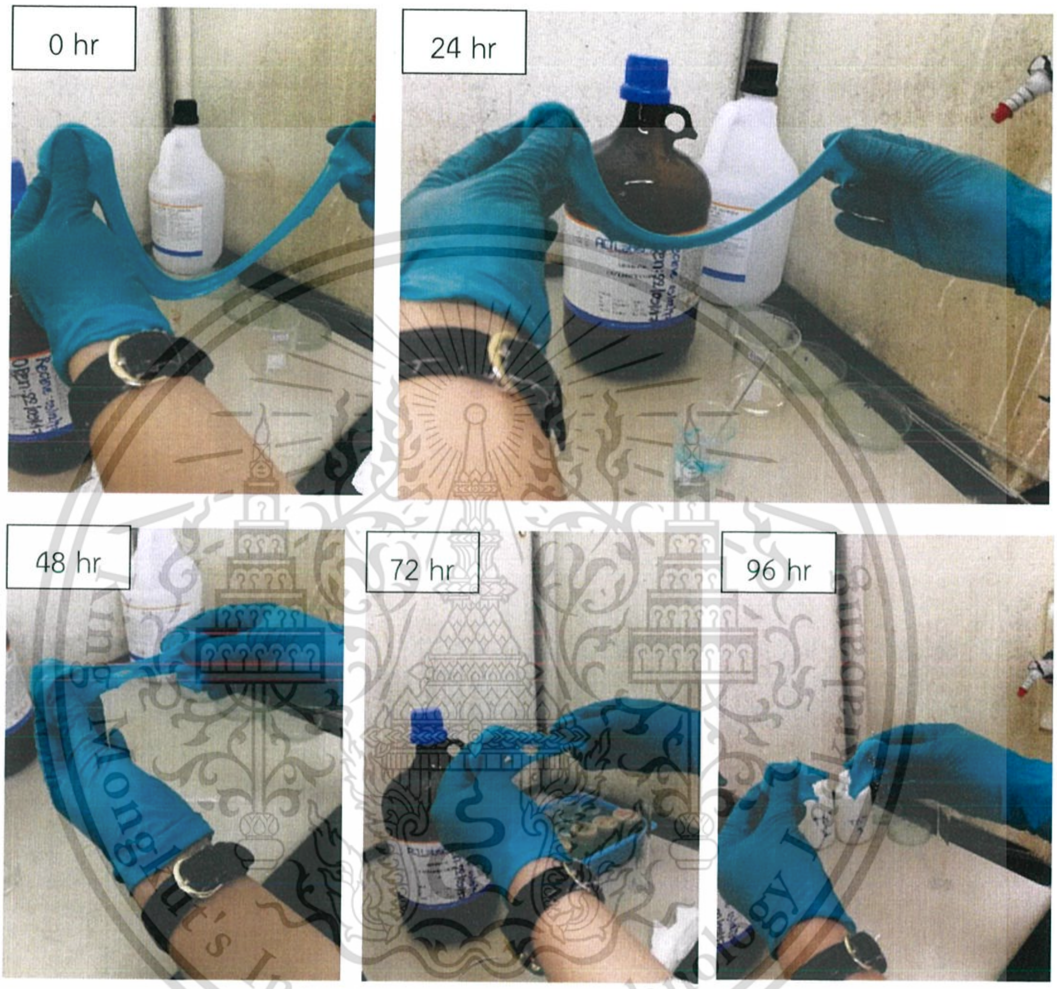


Figure 4.8 The coagulum of NBR latex compound each of the maturation time from 0 to 96 hours

Level of prevulcanization was assessed by coagulation of NBR latex compound with cyclohexanone. Figure 4.8 and Table 4.1 show that as maturation time was increased, the cyclohexanone number increased and reached a steady value of level 2 after 24 hours. Moreover, after 24 hours the coagulum was weak lump which breaks shot when stretched. This was due to increase in crosslinking of rubber molecules inside discrete rubber particles dispersed in the aqueous phase of the NBR latex compound. However, this method was not particularly adaptable for comparing with dis-similar compounds.

Table 4.1 Cyclohexanone number of NBR latex compound

Maturation time (hour)	Cyclohexanone number (level)
0	1
24	1
48	2
72	2
96	2

4.1.1.5 Prevulcanized relaxed-modulus (PRM) of NBR latex films

PRM of NBR latex films can represent the degree of NBR latex prevulcanization by way of measurement of elastic tensile modulus at 100% extension of film dried down from NBR latex compound.

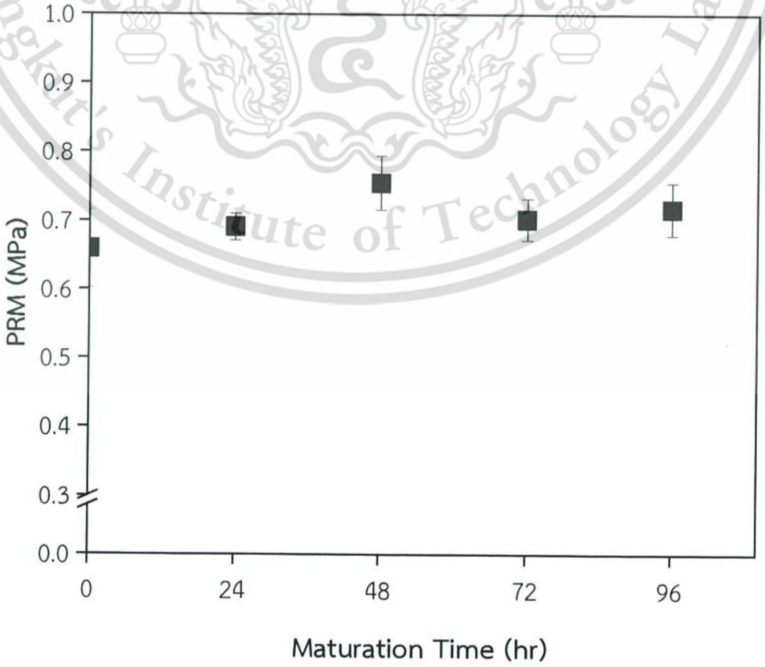


Figure 4.9 Effect of maturation time on PRM of NBR latex films

Figure 4.9 shows that the PRM of NBR latex film slightly increased with increasing maturation time and then, after 48 hours maturation time, the PRM slightly decreased until 96 hours maturation time. This result agreed with the percentage of coagulum, solvent swelling and cyclohexanone test results. The longer maturation time, the greater the stage of prevulcanized rubber. However, over-maturation time caused the poor film formation and thus resulted in slightly decreasing of PRM after 48 hours maturation time.

4.1.1.6 Tensile properties of NBR latex gloves

Tensile strength, rubber moduli at 300% and 500% extensions and percentage of elongation at break of NBR latex gloves with different maturation times were illustrated in Figures 4.10, 4.11 and 4.12 respectively.

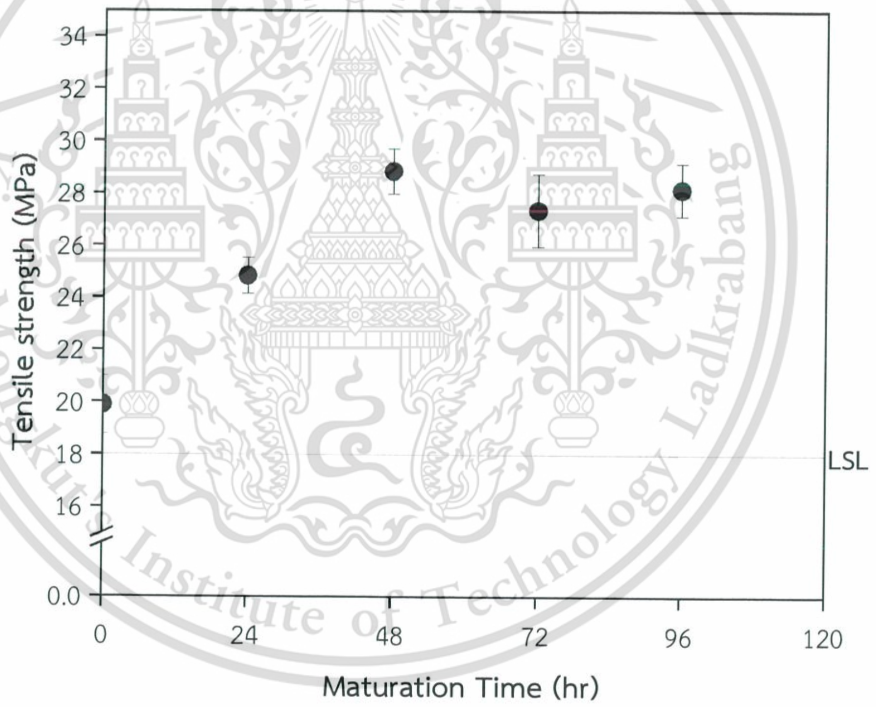


Figure 4.10 Tensile strength of NBR latex gloves with different maturation times

Similar trends were also observed for tensile strength and rubber moduli at 300% and 500% extensions. That was increased with increasing maturation time and then, after 48 hours maturation time, the tensile strength and rubber moduli slightly decreased.

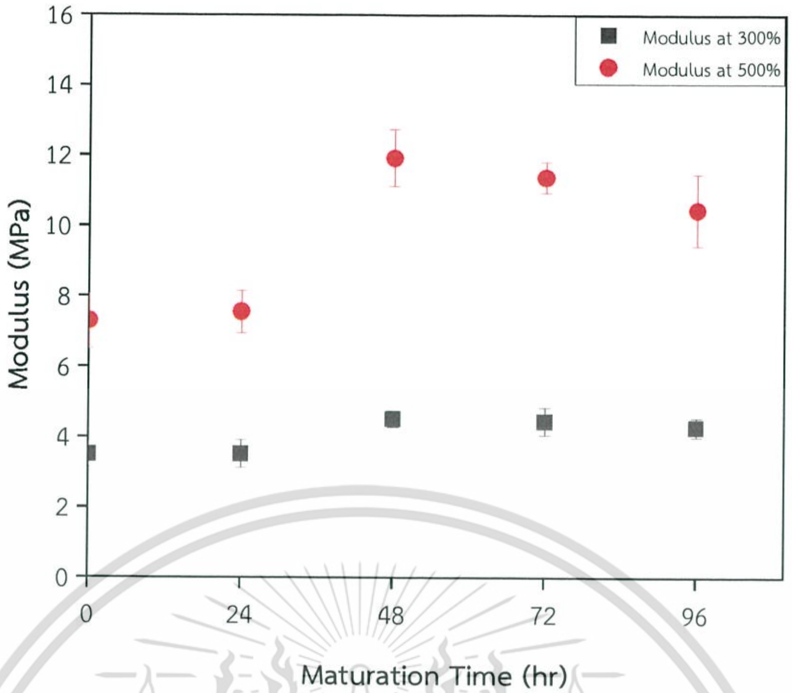


Figure 4.11 Rubber moduli at 300% and 500% extensions of NBR latex gloves with different maturation times

The results corresponded with PRM result (Figure 4.9). That indicated increasing prevulcanization of rubber with long maturation times. However, over-maturation times (after 48 hours) caused the ability of latex particles to coalesce was decreased. This can be explained by the partially vulcanized NBR latex particles retarding the diffusion of the rubber molecules, thus, hindering further gradual coalescence of the NBR latex particles in the films. This resulted in poor film formation [41]. The tensile strength in LSL was fixed at 18 MPa, however; the value grater than 25 MPa was the required target. Therefore, tensile strength of gloves at 0 hour maturation time was out of specification because it had no prevulcanization.

Figure 4.12 shows elongation at break of NBR latex gloves with different maturation times. It was found that elongation at break decreased with increasing maturation times and then, after 24 hours maturation times, the elongation at break was not significantly changed. This indicated the long maturation time leading to higher crosslink density. That caused stronger elastomer network but restrict chain motions, resulting in low elongation at break [52]. However, the manufacturing process was controlled elongation at break in LSL at 500%. Thus, the decreasing tend of elongation at break would not significantly affect on gloves properties.

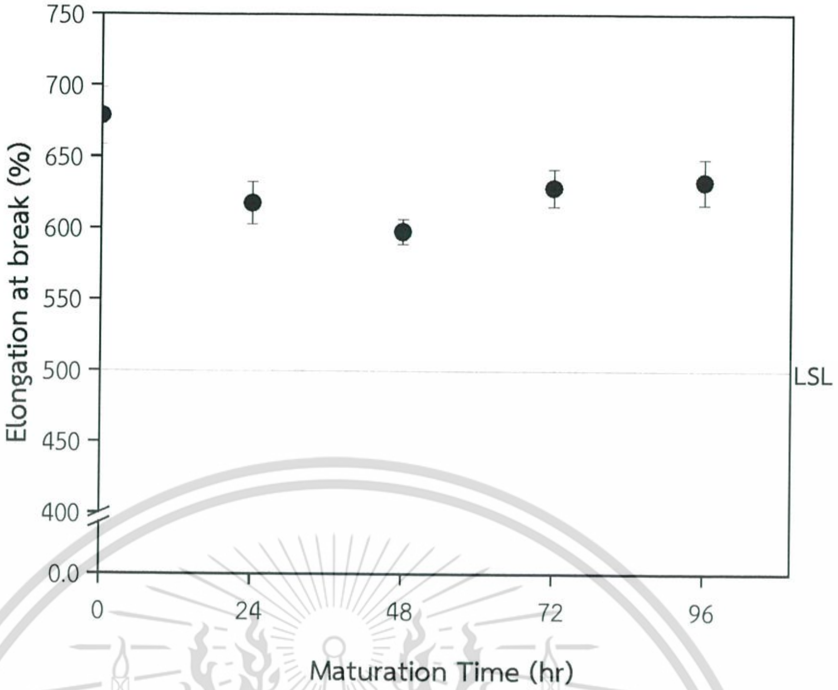


Figure 4.12 Percentage of elongation at break of NBR latex gloves with different maturation times

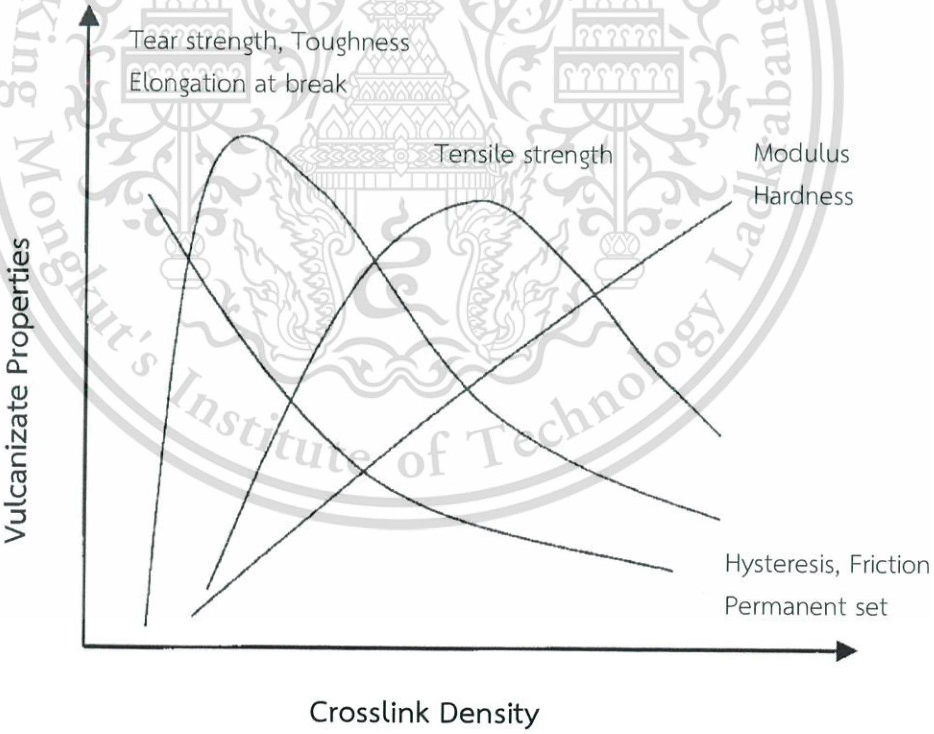


Figure 4.13 Effect of crosslink density on rubber physical properties [53]

Therefore, the long maturation times could cause higher crosslink density of NBR latex yielding higher tensile strength and rubber moduli but lower elongation at break. These tends corresponded effect of crosslink density on rubber physical properties shown in Figure 4.13.

4.1.2 Effects of accelerators on maturation time of NBR latex gloves

Rubber accelerators in manufacturing process constitute an important group of contact allergens, particularly in thiazole compounds [54]. That causes allergic reactions (type IV/chemical allergy). However, the accelerators increase the speed of vulcanization and permit vulcanization to proceed at lower temperatures with greater efficiency. Thus, this part studied accelerator systems for maturation of NBR latex compound. The NBR latex compound used Ac1 (thiazole compound) and Ac2 (dithiocarbamate compound) combination for controlled system and its comparison with Ac1-free and Ac-free systems. Some properties of accelerators were shown in Table 4.2.

Table 4.2 Accelerators system of NBR latex compound

Property	Accelerator-1 (Ac1)	Accelerator-2 (Ac2)
Chemical compound	Thiazole	Dithiocarbamate
Critical cure temperature (°C)	120-125 °C	104-106 °C
Speed	Semi-ultra fast	Ultrafast
Application	Primary accelerator	Primary and secondary accelerator

4.1.2.1 Solvent swelling of NBR latex films with different accelerator systems

Figure 4.14 shows the percentage of swelling of NBR latex films with different accelerator systems for maturation time. It can be seen, percentage of swelling of all accelerator systems slightly decreased with longer maturation time. This due to increase in crosslinking of rubber molecules and restricted the diffusion of solvent molecules. Thus, percentage of swelling was an inverse measure of the degree of vulcanization. The percentage of swelling for Ac1-free system was clearly lower than control and Ac-free system. This was because Ac1-free system using Ac2 alone (1.0 phr) as accelerator (Table 3.5). That had dithiocarbamate compound which faster curing at low temperature (104 - 106 °C) and higher crosslink density than thiazoles compound [35].

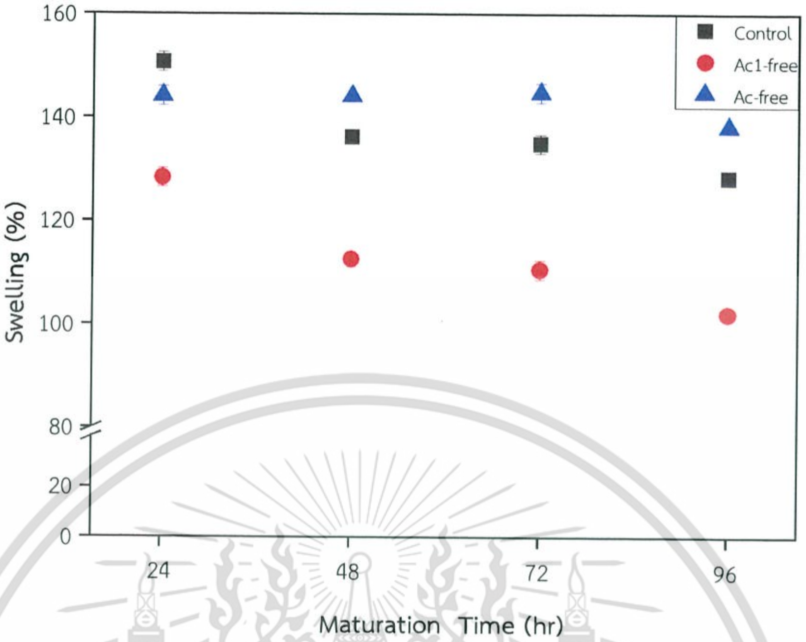


Figure 4.14 Percentage of swelling of NBR latex films with different accelerator system for maturation time

The NBR latex compound for control system prepared from mixed Ac1 and Ac2 contents of 1.3 and 0.4 phr respectively. The Ac1 has thiazoles chemical groups which contain abundant aromatic ring. This caused the bulky structures which hindrance to further diffusion accelerator into NBR latex particles. Moreover, the Ac1 used higher critical curing temperature than Ac2 in systems (Table 4.2). These caused the control system had lower prevucanization than Ac1-free system. The Ac-free system shows highest percentage swelling of NBR latex films. This result indicated the compounding without accelerator was lower crosslink density during maturation.

4.1.2.2 Tensile properties of NBR latex gloves with different accelerator systems

Tensile strength, rubber moduli at 300% and 500% extensions of NBR latex gloves with different accelerator systems shown in Figures 4.15, 4.16 and 4.17 respectively. Tensile strength and rubber moduli at 300% and 500% extensions of different accelerator systems showed slightly increasing with longer maturation time and then, after 48 hours, that slightly decreased (to be clearly observed in Ac1-free and Ac-free system).

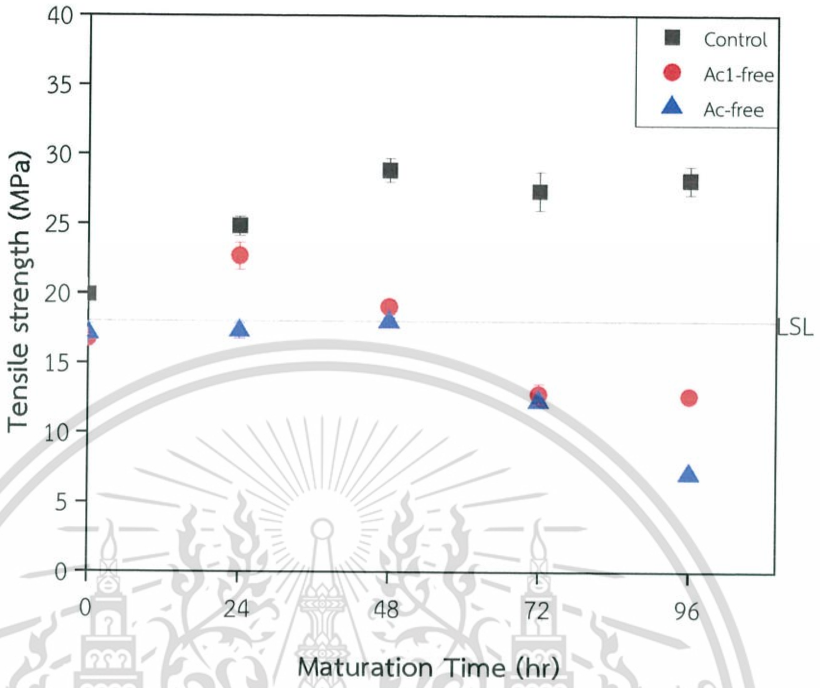


Figure 4.15 Tensile strength of NBR latex gloves with different accelerator systems for maturation time

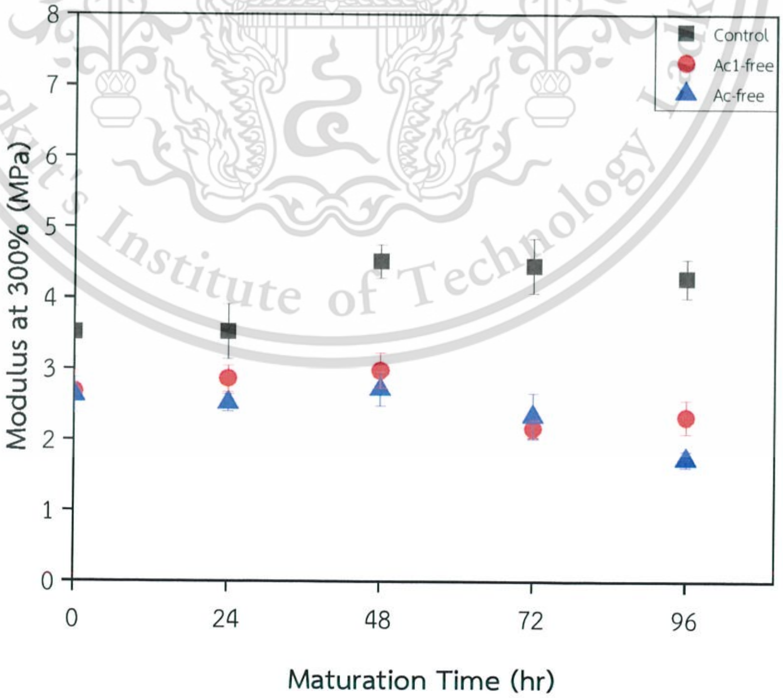


Figure 4.16 Rubber modulus at 300% extension of NBR latex gloves with different accelerator systems for maturation time

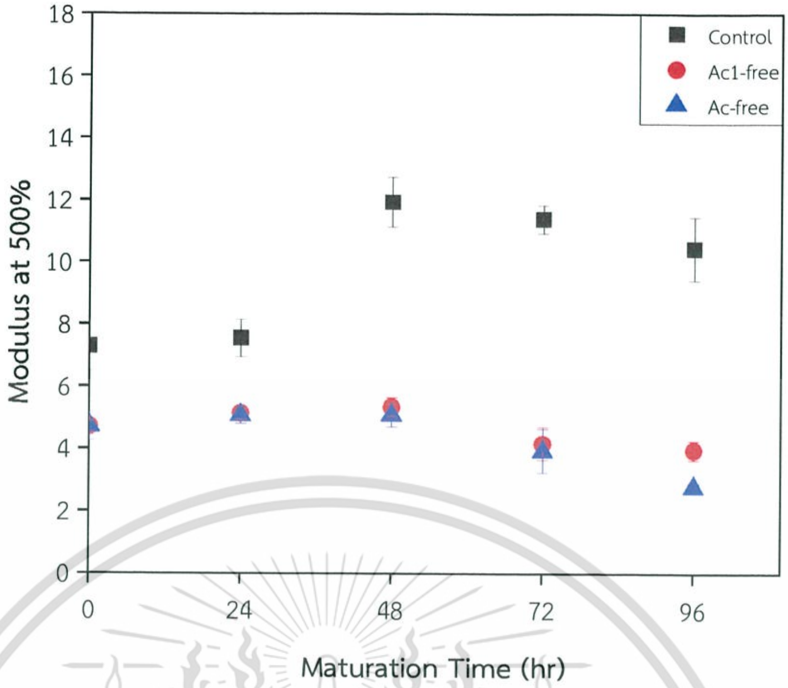


Figure 4.17 Rubber modulus at 500% extension of NBR latex gloves with different accelerator systems for maturation time

It was found that the control system clearly higher tensile strength and rubber moduli at 300% and 500% extensions than Ac1-free and Ac-free system. This might be because of positive synergistic effects between the thiazoles and dithiocarbomate compounds in control system. At high temperature (130°C) during dipping process caused more efficient of Ac1 (thiazoles compound) leading to a high degree of crosslinking. Furthermore, the control system had higher level of total accelerators (1.7 phr) than AC1-free (1.0 phr) and Ac-free (0 phr) system. Thus, the high level of accelerator caused on high efficiency of vulcanization in control system.

However, Ac1-free system demonstrated insignificantly different tensile strength and rubber moduli at 300% and 500% extensions when comparing with Ac-free system. Ac2 was used as the alone accelerator in Ac1-free system (1.0 phr), which presumably the Ac2 accelerator loss during maturation. This apparent loss of ZDBC accelerator from latex films had been studied by Loadman, M. J. R. and co-workers [49]. They investigated the tetramethylthiuram disulfide (TMTD) after addition, with zinc oxide, to field latex. Over a shot period time the TMTD reacted with zinc oxide to form zinc dimethyldithiocarbamate (ZDMC) in the latex. The ZDMC formed began to decompose during the time that the latex was stored. They were found that a number of decomposition products including, zinc sulfide (as a major product), dimethylamine, ammonium thiocyanate and thiourea. The proposed route for decomposition of TMTD and ZDMC is shown in Figure 4.2. Therefore, it seems reasonable to suggest that Ac2 also undergoed decomposition in the NBR latex compound. As mentioned earlier, the tensile strength was required to be greater than 25 MPa, thus NBR latex gloves with Ac1-free and Ac-free systems were lower than specification requirement.

Figure 4.18 shows the percentage of elongation at break of control system slightly decreased and then, after 24 hours maturation time elongation at break was insignificantly changed. Nevertheless, Ac1-free and Ac-free systems demonstrated elongation at break remained constant with increasing maturation time.

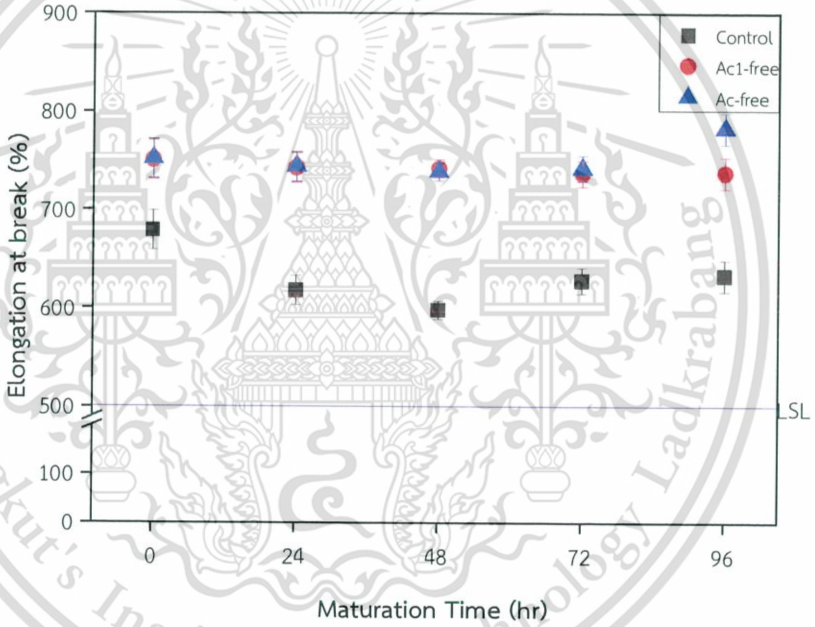


Figure 4.18 Percentage of elongation at break of NBR latex gloves with different accelerator systems for maturation time

Moreover, the control system showed lower percentage of elongation at break than Ac1-free and Ac-free systems. Since, the control system was higher crosslink density than Ac1-free and Ac-free systems, this result was confirmed by tensile strength and rubber moduli at 300% and 500% extensions. The longer maturation time leading to over cure, the both of reasons were restricted of the mobility of network chains [24]. The results here indicated that the accelerator type and dose play important roles on the tensile properties of the obtained vulcanizates.

4.2 Effects of NBR latex properties AN content and stabilizer on properties of NBR latex gloves

Alternative raw materials are one of the most important aspects in manufacturing latex gloves. This avoid disruptions to their supply chains due to the scarcity of resources. Thus, this part was focused properties of second source raw materials including effects of acrylonitrile (AN) contents and type of stabilizer on NBR latex gloves. The NBR latex compounding were prepared base on Ac-free system from raw latex with different AN contents (HAN-NH_3 and MAN-NH_3 and KOH grade) and types of stabilizers (HAN-NH_3 and HAN-KOH grades). The NBR latex gloves were prepared at 24 hours maturation time to characterization, including tensile properties, chemical permeation test and thickness. The results were divided in 3 parts, i.e. characterize of NBR raw latex, characterization of NBR latex compound and characterization of NBR latex gloves.

4.2.1 Characterization of NBR raw latex

Table 4.3 Properties of NBR raw latex including HAN-NH_3, HAN-KOH and MAN-NH_3 and KOH grades

Property	Type of NBR raw latex		
	HAN-NH_3	HAN-KOH	MAN-NH_3 and KOH
Stabilizer	NH_3	KOH	NH_3 and KOH
Acrylonitrile content (%wt)	High (40%wt)	High (40%wt)	Medium (26-30%wt)
pH	8.85	9.35	8.80
%TSC	43.67	43.36	44.63
Viscosity (cp)	29.7	98.48	57.1

Table 4.3 shows properties of NBR raw latex, the HAN-NH_3 and HAN-KOH grades were provided with the same supplier that having high acrylonitrile (AN) content but different types of stabilizer. While, the MAN-NH_3 and KOH grade has medium AN content and used NH_3 combination with KOH for stabilizer. The HAN-KOH grade (KOH stabilizer) had the highest pH and viscosity, compared with the other grades. Moreover, Figure 4.19 showed FTIR spectra of raw latex for analyzing AN and carboxylate groups. The result showed peaks at about 2920 and 2846 cm^{-1} ascribed to C-H stretching

groups on the rubber backbond. Another wavenumber at 2237 cm^{-1} was due to the CN-group in the acrylonitrile component.

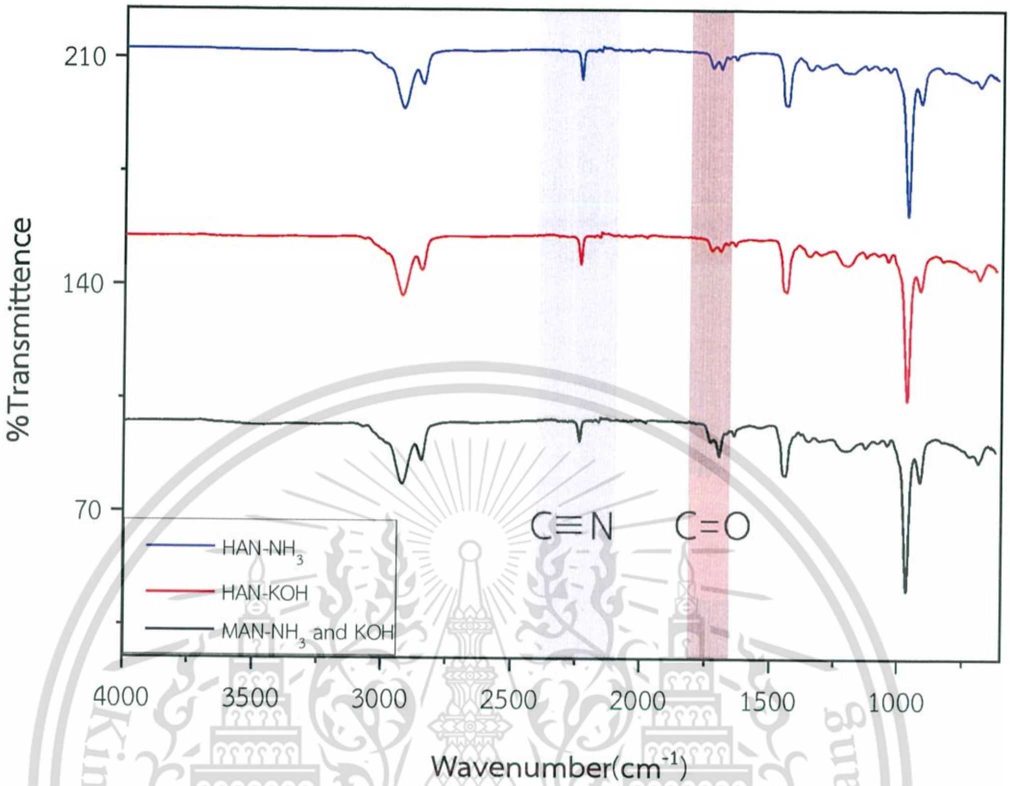


Figure 4.19 FTIR spectra of NBR raw latex with different grades

The peaks at 1699 and 1731cm^{-1} correspond to the C=O groups of the carboxylic component in the rubber. The first peak (1699 cm^{-1}) is attributed to carbonyl stretching of hydrogen-boned acid dimer, whereas the second one (1731 cm^{-1}) is due to carbonyl stretching of monocarboxylic acid [56-57]. In addition, the band peaks at 1436 and 969 cm^{-1} are attributed to the C-H bending, in-plane deformation of methylene group and C-H stretching vibrations of butadiene double bond, respectively.

4.2.2 Characterization of NBR latex compounds

Table 4.4 Properties of NBR latex compounding with different grades of raw latex

Properties	Types of NBR raw latex		
	HAN-NH_3	HAN-KOH	MAN-NH_3 and KOH
pH	9.79	10.49	9.39
Viscosity (cp)	8.5	22.5	10.0

Table 4.4 Properties of NBR latex compounding with different grades of raw latex (continued).

Properties	Types of NBR raw latex		
	HAN-NH_3	HAN-KOH	MAN-NH_3 and KOH
TSC (%wt)	35.38	35.43	35.39
Swelling (%)	121.78±2	140.16±0	109.97±2
Coagulum of mechanical stability time (%)	0.0246±0.006	0.0119±0.002	0.0109±0.003

After compounding, the NBR latex compounds were adjusted to TSC of 35.4%wt and then allowed to mature until 24 hours before testing. Table 4.4 shows the highest pH and viscosity of HAN-KOH compound, compared with other grades. This was because KOH is fully ionic which is 100% dissociated into potassium ions and hydroxide ions in compound so that it is stronger base than NH_3. Percentage of swelling of MAN-NH_3 and KOH compound was the lowest among other grades. This result indicated the highest degree of crosslinking of MAN-NH_3 and KOH compound during maturation. This may be attributed to higher butadiene and carboxylic acid groups in rubber molecules of the MAN-NH_3 and KOH compound as compared with other grades. These led to high performance for prevulcanization with sulfur (sulfur bridge) and zinc ion (ionic zinc crosslink) during maturation. Meanwhile, the compound with HAN-NH_3 was lower percentage of swelling than HAN-KOH compound. This was attributed to type of stabilizer and effect of viscosity of NBR latex compound. Ammonia, stabilizer of HAN-NH_3 raw latex, could evaporate during maturation. This caused on colloid destabilization of NBR latex compound and leading to higher prevulcanization in NBR latex particles than compound with HAN-KOH (KOH stabilizer). Moreover, Table 4.4 shows that HAN-NH_3 compound was lower viscosity than HAN-KOH compound. Thus, curative agents (sulfur, zinc ions and accelerator) in HAN-NH_3 compound diffused more easily into NBR latex particles and increasing prevulcanization during maturation.

Percentage of coagulum mechanical stability time (%CMST) was simulated from mechanical stability time (MST) test. This method indicated stability of NBR latex concentrate to mechanical shear force in term of coagulum content. Table 4.4 demonstrates that the highest %CMST was obtained from the HAN-NH_3 compound. Moreover, %CMST of HAN-KOH and MAN-NH_3 and KOH compounds were insignificantly different. The major reason was type of stabilizer in raw latex. The high shear force (8000 rpm) during test could cause some ammonia evaporation and destabilization of NBR latex particles in compound with HAN-NH_3. While, HAN-KOH and MAN-NH_3 and KOH compounds contained KOH stabilizer which maintains the uniformity of alkalinity for colloid stability throughout the life of a latex dipping compound [29]. Moreover, KOH was not volatile and its effects in the latex were permanent.

4.2.3 Characterization of NBR latex gloves

4.2.3.1 Thickness of NBR latex gloves

Figure 4.20 demonstrates thickness of gloves with different grades of raw latex at the same dwell time and condition during dipping process. The data was represented as the box plot graph of measurements from sixteen samples (n=16). Statistical analysis was carried out via one-way analysis of variance (ANOVA) test using Minitap® software. Thickness of MAN-NH_3 and KOH gloves was significantly different at $p<0.05$ when compared with HAN-NH_3 and HAN-KOH gloves. The highest thickness of HAN-NH_3 gloves corresponded the %CMST results. These indicated the ammonia stabilizer easy to evaporate during maturation and dipping former into NBR latex compound (50°C). This led to destabilization of NBR latex compound and to easily gel films on formers.

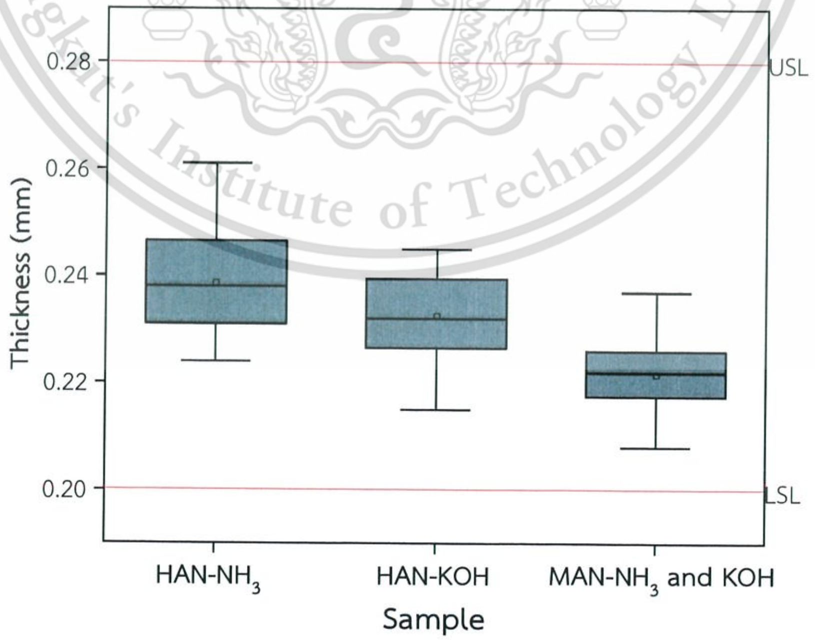


Figure 4.20 Thickness of gloves with different grades of raw latex

While, the HAN-KOH gloves and MAN-NH_3 and KOH gloves demonstrated lower thickness than HAN-NH_3 gloves. This was because KOH stabilizer was not volatile and maintained the uniformity of alkalinity for colloid stability of NBR latex compound. However, HAN-KOH gloves showed higher thickness than MAN-NH_3 and KOH ones. This was due to effect of the highest viscosity of HAN-KOH compound leading to high picking up of latex on formers. However, thickness of gloves with all raw latex grades showed in the range of specification (LSL at 0.20 and USL at 0.28 mm).

4.2.3.2 Tensile properties of NBR latex gloves

Figure 4.21 shows tensile strength of NBR latex gloves with different raw latex grades. It was found that tensile strength unaged of MAN-NH_3 and KOH gloves was the highest (29.52 MPa) and then drastically decreased (16.26 MPa) after ageing.

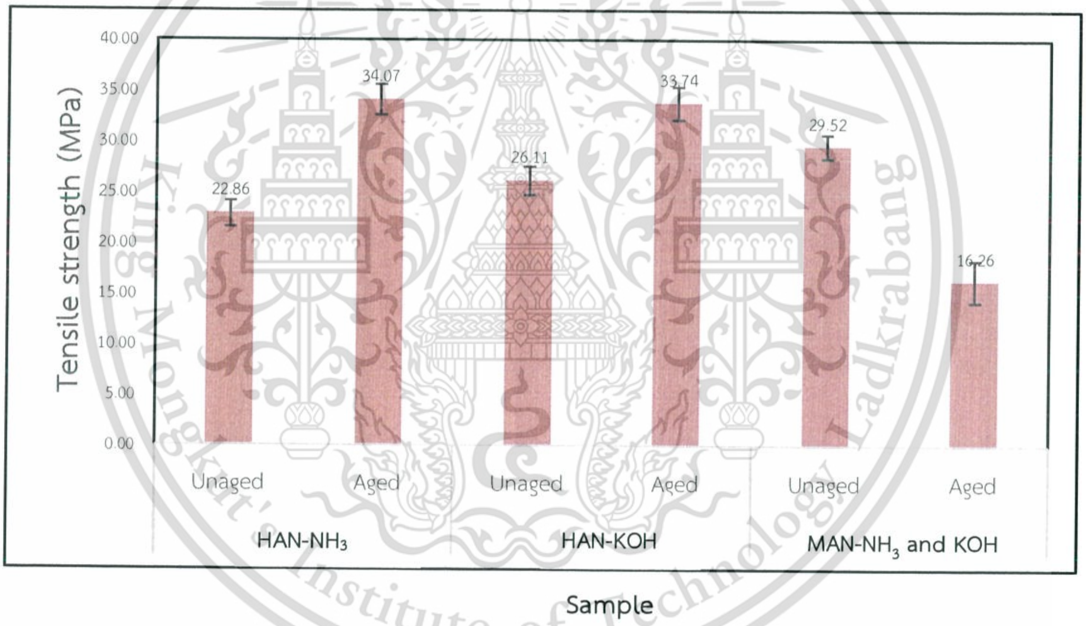


Figure 4.21 Tensile strength of NBR latex gloves with different grades of raw latex

This result indicated that MAN-NH_3 and KOH gloves were overcure at unaged condition. After that, ageing condition increased crosslink density of gloves led to tensile strength passing through a maximum value and reduction of tensile strength occured. The result corresponded to percentage of swelling of MAN-NH_3 and KOH latex films (Table 4.4) and rubber moduli at 300% extension (in Figure 4.22). On the other hand, tensile strength of HAN-NH_3 and HAN-KOH gloves were increased after ageing. These results indicated that undercure of these gloves and then their crosslink density increased after ageing. Similar trend was observed in rubber moduli at 300% and 500% extensions of HAN-NH_3 and HAN-KOH gloves. These increased after ageing condition which was clearly observed at 500% extension.

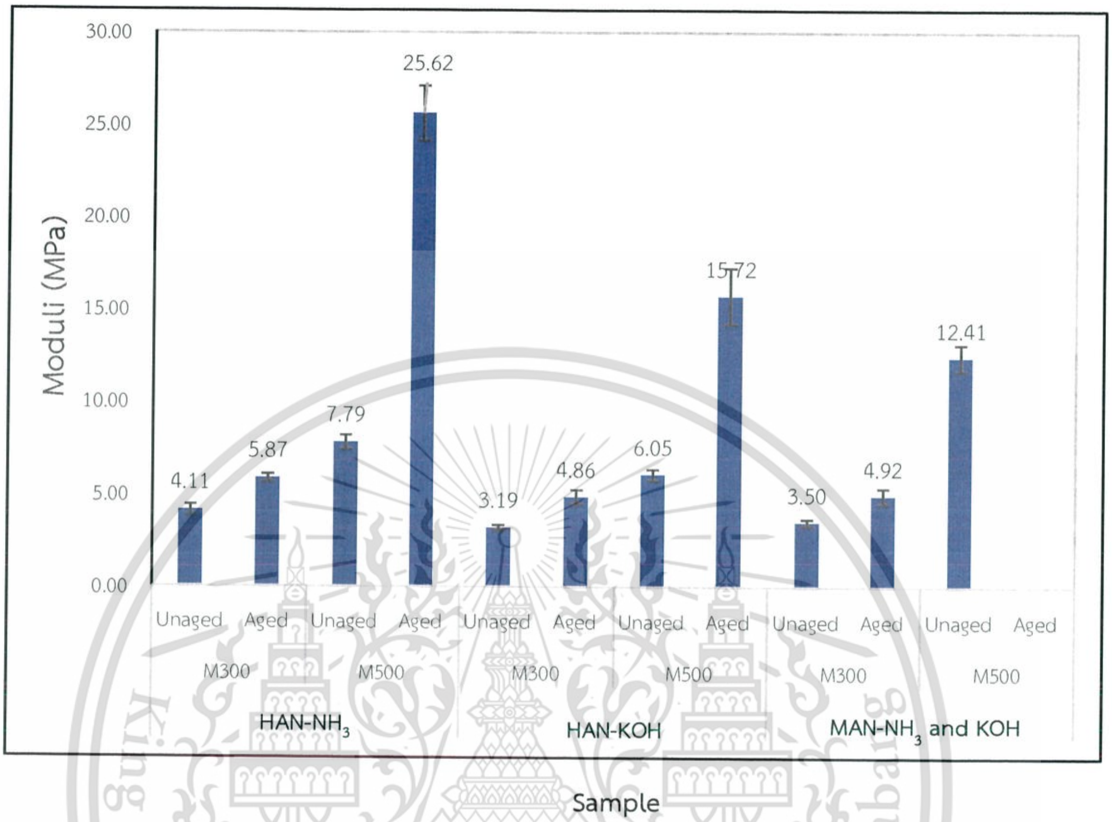


Figure 4.22 Rubber moduli at 300% and 500% extensions of NBR latex gloves with different grades of raw latex

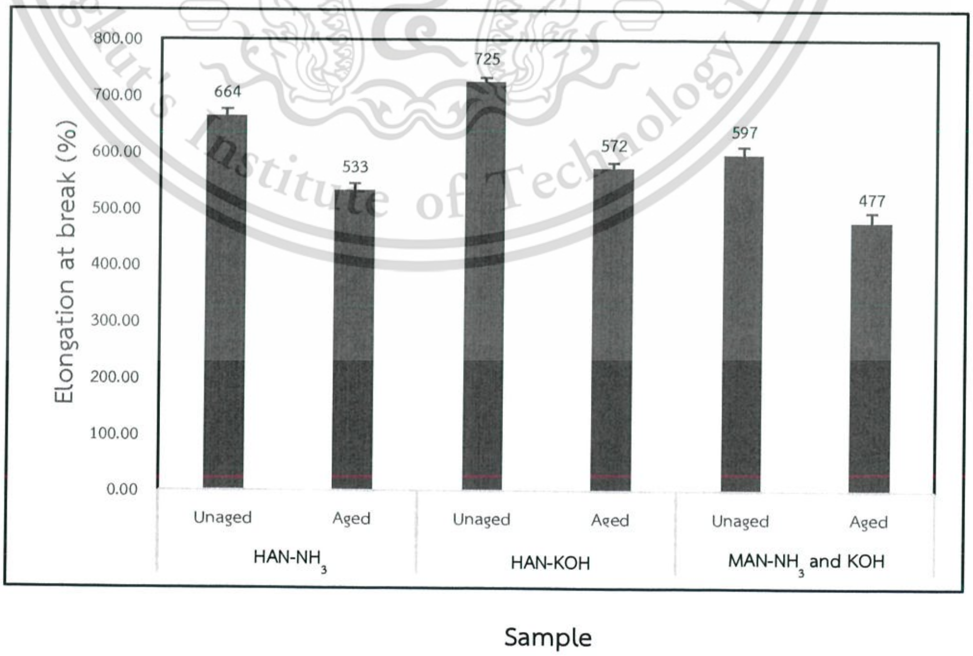


Figure 4.23 Elongation at break of NBR latex gloves with different grades of raw latex

Figure 4.23 demonstrates %elongation at break of all NBR latex gloves decreasing after ageing because at high crosslink level, chain motions become restricted and the tight network was not capable of dissipating much energy. In addition, MNA-NH$_3$ and KOH gloves showed the lowest %elongation at break at 476%.

4.2.3.3 Chemical permeation of NBR latex gloves

Chemical permeation was conducted according to American Society for Testing and Materials (ASTM) Method F739-85 with gas chromatography (GC) analysis of n-heptane organic solvent. Table 4.5 shows HAN-NH$_3$ and HAN-KOH gloves with high AN content having the highest breakthrough time (BT) at 480 minutes. In contrast, MAN-NH$_3$ and KOH gloves with medium AN content had the lowest BT at 260 minutes. These results indicated that chemical resistance of NBR latex gloves increased with increasing AN content. As the AN content was increased, the molecules became less hydrophilic and more polar leading to increasing chemical resistance [8]. Tariq, Y. and co-workers [8] studied effect of AN content of the NBR. It was found that AN content and nature of solvent were the two important factors in chemical resistance. In case non-polar solvent, it was found that chemical resistance increased with increasing AN content. But for polar solvent system, chemical resistance decreased with increasing AN content. In this study used non-polar solvent (n- heptane) for testing.

Table 4.5 Resistance to permeation with chemical of NBR latex gloves with different grades of raw latex

Grade	Chemical	No.	Breakthrough time (min)	Minimum value (Level)
HAN-NH$_3$	n-Heptane	1	>480	>480 min Level 6
		2	>480	
		3	>480	
HAN-KOH	n-Heptane	1	>480	>480 min Level 6
		2	>480	
		3	>480	
MAN-NH$_3$ and KOH	n-Heptane	1	>280	>260 min Level 5
		2	>260	
		3	>280	

Phalen, R. N. and co-workers [58] studied AN content as a predictor of the captan (N- trichloromethylthio-4-cyclohexene-1,2- dicarboximide) permeation resistance for disposable NBR latex gloves. It was found that the average, BT (hexane) of NBR latex gloves increased 120 minutes for every 5% increase in the AN content. The average steady-state permeation rate (SSPR) from 0.002 to 0.40 μg/cm^2/min, 200-fold difference. Thus, increasing the AN content resulted in decreased SSPR.

4.3 Effect of stabilizer amount on NBR latex films

This part studied effect of stabilizer (KOH) amount on NBR latex films. The NBR latex compound was prepared based on Ac1-free system (Table 3.7) with varying the amounts of KOH (0-2 phr). After that, the NBR latex compounds at 24 maturation time were used for film preparation with ceramic plates for characterization. The results were divided in 2 parts i.e., characterization of NBR latex compounds including pH and viscosity and characterization of NBR latex films including thickness and tensile property.

4.3.1 Characterization of NBR latex compound

4.3.1.1 pH of NBR latex compound

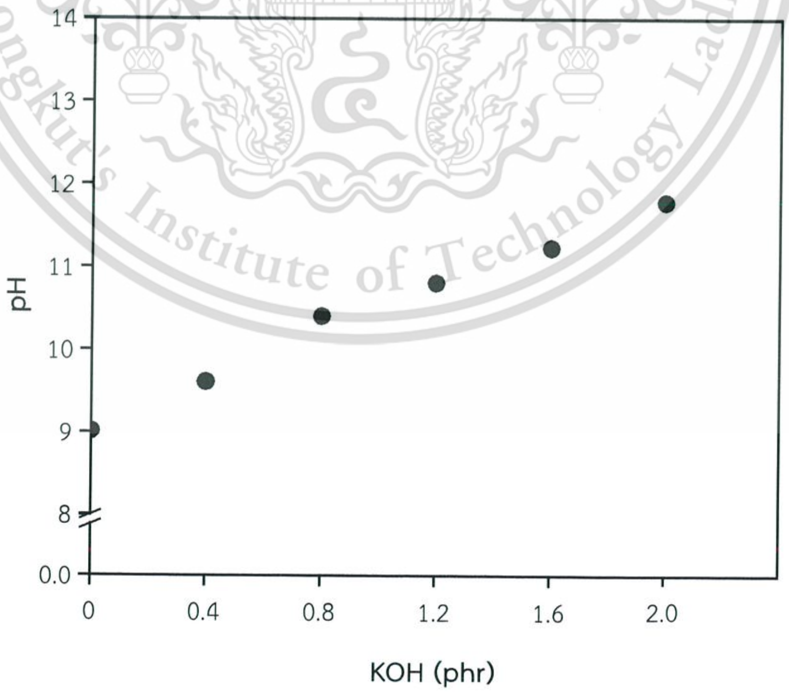


Figure 4.24 pH of NBR latex compound with varying amounts of KOH

Figure 4.24 shows that pH of NBR latex compound increases with increasing amount of KOH. KOH (strong alkali) is fully ionic which being 100% dissociated into K^+ and OH^- ions in compound [59]. The main function of KOH is to maintain the alkalinity (and therefore the colloid stability) if ammonia (stabilizer of raw latex) is lost by evaporation. Moreover, KOH was used for uniformity of colloid stability throughout the life of a latex-dipping compound [29].

4.3.1.2 Viscosity of NBR latex compound

Figure 4.25 demonstrates the effect of KOH amount on viscosity of NBR latex compound. The viscosity slightly increased with varying KOH from 0.0 to 0.8 phr, and then dramatically increased with adding KOH from 1.2-2.0 phr. This was because NBR latex particles, which have a high carboxyl content, might even dissolve under higher alkaline condition. The dissolved carboxylate chains may subsequently be absorbed onto the latex particles, thus conferring electrostatic and steric stability to the NBR latex [9].

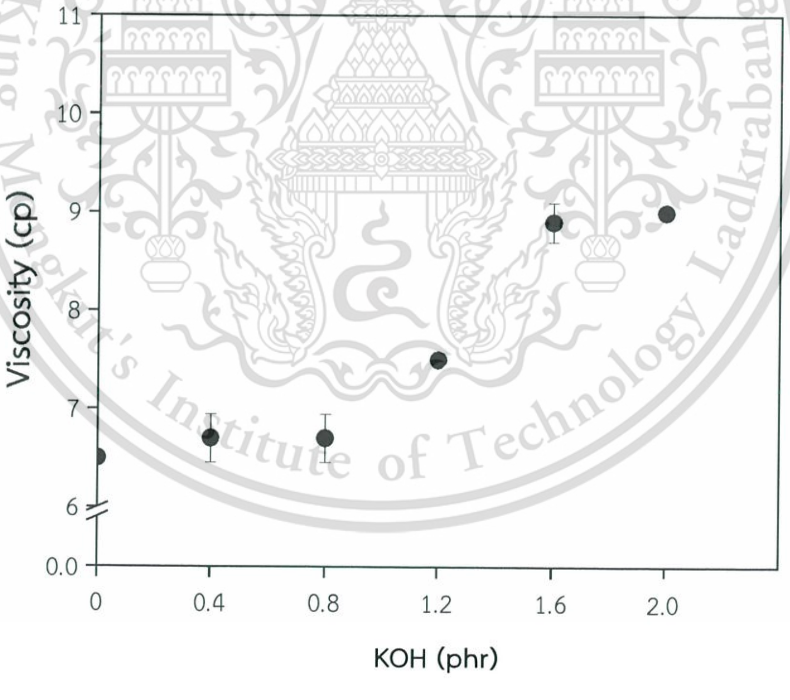


Figure 4.25 Viscosity of NBR latex compound with varying amounts of KOH

4.3.2 Characterization of NBR latex films

4.3.2.1 Thickness of NBR latex films

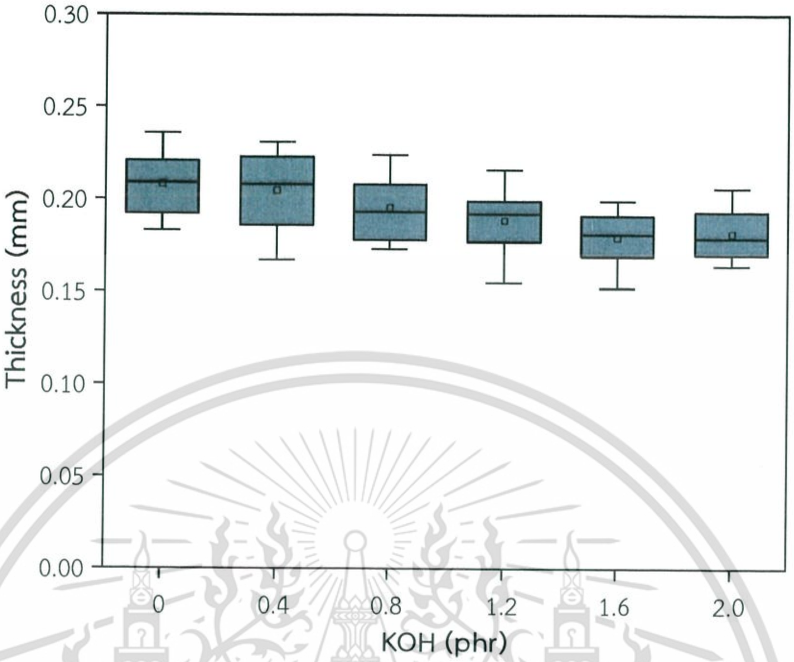


Figure 4.26 Thickness of NBR latex films with varying amounts of KOH

Thickness of NBR latex films was represented as the box plot graph of measurements of fifteen samples (n=15). It was found that thicknesses of NBR latex films decreased with increasing amounts of KOH from 0.0 to 2.0 phr. Thickness of films with adding KOH from 0.0-0.4 phr was significantly different at $p<0.05$ when compared with those films of adding KOH from 1.2-2.0 phr. As similar reason from thickness of NBR latex gloves results (4.2.3.1), the increasing amounts of KOH led to increased colloid stability of NBR latex compound and reduced picking up of latex on formers.

4.3.2.2 Tensile properties of NBR latex films

Figure 4.27 shows results of tensile strength of NBR latex films with varying amounts of KOH from 0.0 to 2.0 phr. It was found that tensile strength increased with increasing amount of KOH until 0.8 phr and then, tensile strength slightly decreased until 2.0 phr. Similar trend was also observed in rubber moduli at 300% and 500% extensions (Figure 4.28).

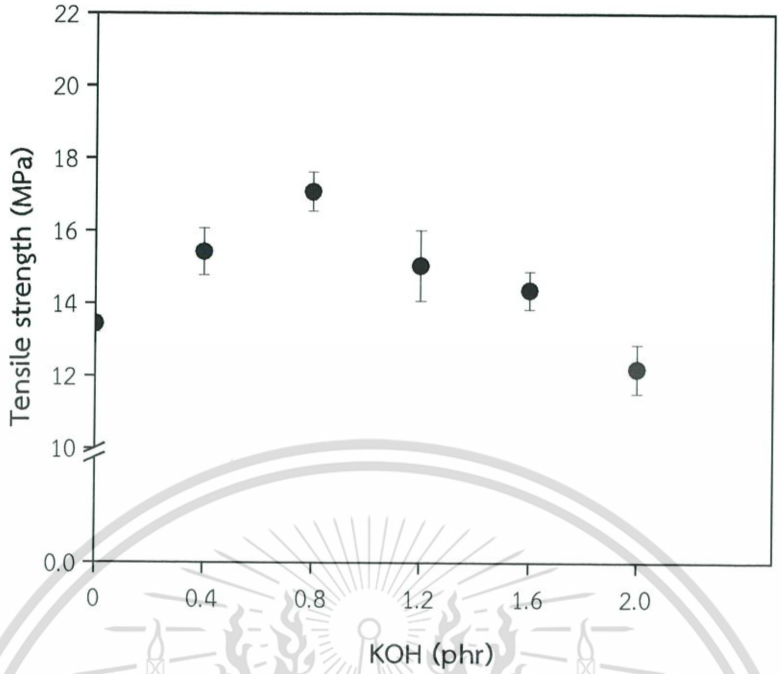


Figure 4.27 Tensile strength of NBR latex films with varying amounts of KOH

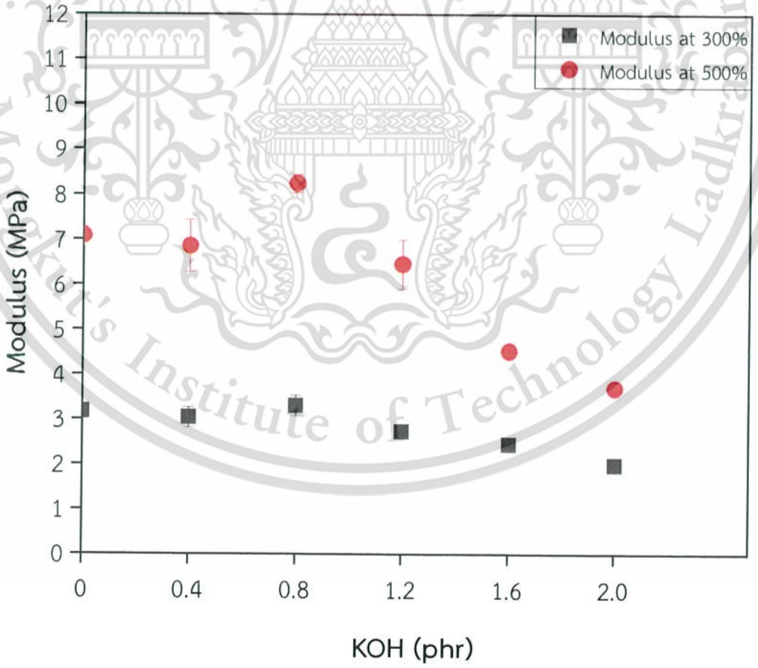


Figure 4.28 Rubber moduli at 300% and 500% extensions of NBR latex films with varying amounts of KOH

This could be because under higher pH conditions, curing agents employed might have high degrees of activation for complexes to form, favoring an increase in crosslinking efficiency [9].

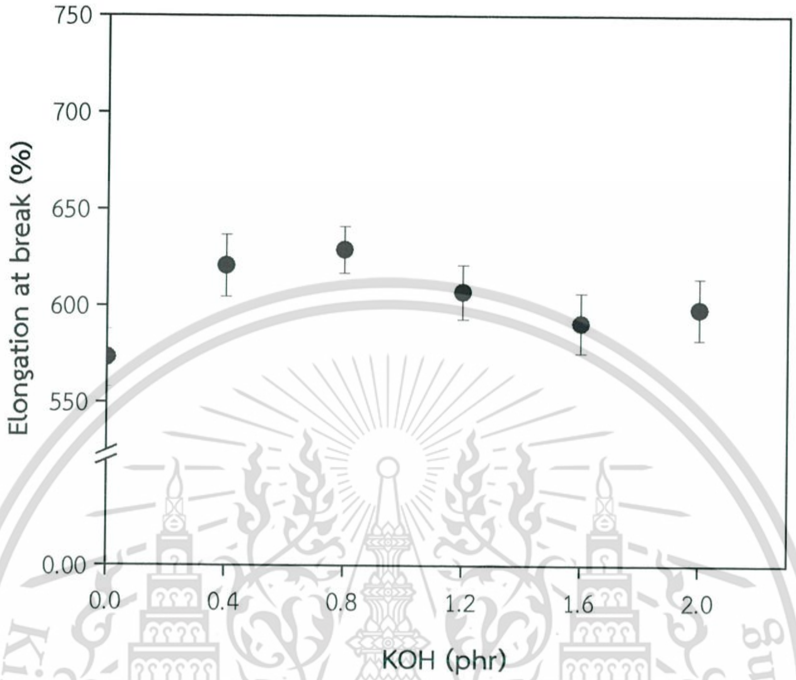


Figure 4.29 Percentage of elongation at break of NBR latex films with varying amounts of KOH

However, NBR latex compound with adding KOH from 1.2 to 2.0 phr led to reduction of tensile strength and rubber moduli at 300% and 500% extensions. This demonstrated that might pass a maximum value (overcure) and reduction of their properties. Figure 4.29 shows percentage of elongation at break of NBR latex film with varying amount of KOH. It was found that percentage of elongation at break slightly increased and then, after adding 0.8 phr of KOH the percentage of elongation at break slightly decreased. This indicated that under high pH conditions caused increasing in crosslink density of rubber chains which restrict chain motions, resulting in reduction of elongation at break.

Chapter 5

Conclusions and Suggestions

5.1 Conclusion

Effects of maturation on properties of NBR latex compounds showed that pH slightly decreased with time. This was because ammonia, the stabilizer of NBR latex, evaporated during too long maturation. Percentage of coagulum of NBR latex compound slightly increased with time. This could be because latex particles were prevulcanized with vulcanizing agent. Percentage of swelling of NBR latex films reduced while the cyclohexanone number results showed increment as maturation time was increased. These results indicated an increase crosslinking of rubber molecules during long maturation. Thus, rubber chains restricted the diffusion of solvent molecules. PRM, tensile strength and rubber moduli at 300% and 500% extensions results showed increment as maturation time was increased. However, after 48 hours maturation time, these properties slightly decreased. Over-matured NBR latex compound could cause poor film formation. Moreover, it was found that accelerator system affected on properties of NBR latex gloves. The control accelerator system demonstrated highest tensile strength and rubber moduli at 300% and 500% extensions. This could be due to the positive synergistic effect between thiazole and dithiocarbarmate compounds. On the other hand, Ac-free system demonstrated lowest tensile strength and rubber moduli at 300% and 500% extensions. These results indicated that accelerator type and dose play important roles on the tensile properties of the obtained vulcanizates.

In the study of NBR latex properties, it was found that percentage of swelling of MAN-NH_3 and KOH compounds were lower than those of other compounds. Moreover, MAN-NH_3 and KOH gloves showed the highest tensile strength and rubber moduli at 300% and 500% extensions. This should be because MAN-NH_3 and KOH compound having higher butadiene and carboxylic acid groups in rubber molecules as compared with other grades. HAN-NH_3 compound demonstrated the highest %CMST and thickness of gloves. The major reason could cause by ammonia evaporation leading to destabilization of NBR latex compound. However, HAN-NH_3 and HAN-KOH gloves showed highest breakthrough time (BT) at 480 minutes for chemical permeation test. This result indicated that chemical resistance of NBR latex gloves increased with increasing AN content.

In the study effects of stabilizer amount on NBR latex films, it was found that viscosity of NBR latex compound increased with varying KOH from 0.0 to 2.0 phr. This due to the dissolved carboxylate chains might subsequently be absorbed onto the latex particles. Thus, conferred electrostatic and steric stability to the NBR latex. Thickness of NBR latex films was decreased with increasing amounts of KOH. This was due to increased colloid stability of NBR latex compound and reducing picking up rate of latex on formers. In addition, tensile strength and rubber moduli at 300% and 500% extensions increased with increasing amount of KOH up to 0.8 phr and then, slightly decreased. This could be because under higher pH conditions, the curing agents employed may have a high degree of activation for complexes to form, favoring an increase in crosslinking efficiency.

Finally, it could be suggested that 24 to 48 hours maturation time in this work were adequate to achieve the effective crosslinking in nitrile latex gloves. The positive synergistic effect between thiazole and dithiocarbarmate compounds caused high performance tensile properties of NBR latex gloves. MAN-NH_3 and KOH compound demonstrated the highest tensile properties but lowest chemical resistance of NBR latex gloves. Thus, the AN content, stabilizer types affected on properties of NBR latex gloves. Moreover, KOH stabilizer of NBR compound latex was not volatile during maturation and maintain the alkalinity for uniformity of colloid stability throughout the life of a latex dipping compound.

5.2 Suggestions for future studies

1) Thiazole accelerator-free system of NBR latex compound should be investigated for higher physical properties.

2) Accelerator residual test of NBR latex gloves should be evaluated using the developed formulation gloves.

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Appendices

Appendix A

pH of NBR latex compound

Table A.1 pH of NBR latex compound with different maturation time

Repeat	pH				
	Maturation time (hr)				
	0	24	48	72	96
1	9.78	9.75	9.73	9.7	9.64
2	9.79	9.74	9.73	9.7	9.63
3	9.78	9.74	9.73	9.71	9.63
4	9.79	9.74	9.73	9.7	9.64
5	9.78	9.74	9.73	9.7	9.63
Average	9.78	9.74	9.73	9.70	9.63
SD	0.00	0.00	0.00	0.00	0.00

Table A.2 pH of NBR latex compound with varying amounts of KOH

Repeat	pH					
	Amount of KOH (phr)					
	0	0.4	0.8	1.2	1.6	2.0
1	9.02	9.62	10.41	10.82	11.22	11.77
2	9.02	9.61	10.41	10.79	11.22	11.78
3	9.01	9.61	10.4	10.8	11.23	11.78
4	9.01	9.6	10.4	10.81	11.23	11.8
5	9	9.61	10.39	10.82	11.25	11.79
Average	9.01	9.61	10.40	10.81	11.23	11.78
SD	0.01	0.01	0.01	0.01	0.01	0.01

Appendix B

Coagulum content of NBR latex compound

Table B.1 Coagulum content of NBR latex compound with different maturation time.

Repeat	Coagulum (%)				
	Maturation time (hr)				
	0	24	48	72	96
1	0.0031	0.0060	0.0062	0.0060	0.0060
2	0.0017	0.0038	0.0054	0.0069	0.0072
3	0.0023	0.0048	0.0056	0.0064	0.0066
Average	0.0024	0.0048	0.0057	0.0064	0.0066
SD	0.0007	0.0009	0.0003	0.0004	0.0005

Table B.2 Percentage of coagulum of mechanical stability time (%CMST) of NBR latex compound

Repeat	CMST (%)		
	Types of NBR raw latex		
	HAN-NH_3	HAN-KOH	MAN-NH_3 and KOH
1	0.0202	0.0140	0.0145
2	0.0327	0.0112	0.0091
3	0.0210	0.0105	0.0093
Average	0.0246	0.0119	0.0109
SD	0.0057	0.0015	0.0025

Appendix c

Percentage of swelling

Table C.1 Percentage of swelling of NBR latex films with different maturation time base on control system.

Repeat	Swelling (%)			
	Maturation time (hr)			
	24	48	72	96
1	148.0	136.2	132.3	128.3
2	152.0	136.2	136.2	128.3
3	152.0	136.2	136.2	128.3
Average	150.7	136.2	134.9	128.3
SD	1.9	0.0	1.9	0.0

Table C.2 Percentage of swelling of NBR latex films with different maturation time base on Ac1-free system.

Repeat	Swelling (%)			
	Maturation time (hr)			
	24	48	72	96
1	128.3	110.6	110.6	102.8
2	128.3	110.6	110.6	106.7
3	128.3	116.5	110.6	96.9
Average	128.3	112.6	110.6	102.1
SD	0.0	2.8	0.0	4.0

Table C.3 Percentage of swelling of NBR latex films with different maturation time base on Ac-free system.

Repeat	Swelling (%)			
	Maturation time (hr)			
	24	48	72	96
1	148.0	144.1	142.1	140.2
2	140.2	140.2	148.0	140.2
3	144.1	148.0	144.1	134.3
Average	144.1	144.1	144.8	138.2
SD	3.2	3.2	2.5	2.8

Table C.4 Percentage of swelling of NBR latex films at 24 hours maturation times with different NBR raw latex.

Repeat	Swelling (%)		
	Types of NBR raw latex		
	HAN-NH_3	HAN-KOH	MAN-NH_3 and KOH
1	108.7	124.4	140.2
2	112.6	120.5	140.2
3	108.7	120.5	140.2
Average	110.0	121.8	140.2
SD	1.9	1.9	0.0

Appendix D

Tensile properties

Table D.1 Tensile properties of NBR latex gloves with different maturation times.

Maturation time (hr)	Tensile strength at break (MPa)	Elongation at break (%)	Modulud at 300% (MPa)	Modulud at 500% (MPa)
0	19.9 ± 1.1	679 ± 20.0	3.5 ± 0.4	7.3 ± 0.8
24	24.8 ± 0.7	618 ± 14.7	3.5 ± 0.4	7.5 ± 0.6
48	28.8 ± 0.9	598 ± 8.6	4.5 ± 0.2	11.9 ± 0.8
72	27.4 ± 1.4	628 ± 13.0	4.5 ± 0.4	11.4 ± 0.4
96	28.2 ± 1.0	633 ± 16.0	4.3 ± 0.3	10.4 ± 1.0

Table D.2 Tensile strength of NBR latex gloves with different accelerator systems.

Maturation time (hr)	Tensile strength at break (MPa)		
	Control	Ac1-free	Ac-free
0	19.9 ± 1.1	16.8 ± 0.2	17.1 ± 0.7
24	24.8 ± 0.7	22.7 ± 1.0	17.3 ± 0.5
48	28.8 ± 0.9	19.1 ± 0.5	18.0 ± 0.3
72	27.4 ± 1.4	12.8 ± 0.7	12.3 ± 0.4
96	28.2 ± 1.0	12.7 ± 0.5	7.1 ± 0.3

Table D.3 Elongation at break of NBR latex gloves with different accelerator systems.

Maturation time (hr)	Elongation at break (MPa)		
	Control	Ac1-free	Ac-free
0	679 ± 20.0	751 ± 3.3	752 ± 18.0
24	618 ± 14.7	743 ± 17.8	744 ± 3.1
48	598 ± 8.6	742 ± 7.1	739 ± 7.9
72	628 ± 13.0	737 ± 17.3	742 ± 5.0
96	633 ± 16.0	738 ± 5.5	783 ± 5.2

Table D.4 Rubber modulus at 300% extensions of NBR latex gloves with different accelerator systems.

Maturation time (hr)	Modulus at 300% (MPa)		
	Control	Ac1-free	Ac-free
0	3.5 ± 0.4	2.7 ± 0.3	2.6 ± 0.3
24	3.5 ± 0.4	2.9 ± 0.2	2.5 ± 0.1
48	4.5 ± 0.2	3.0 ± 0.2	2.7 ± 0.2
72	4.5 ± 0.4	2.2 ± 0.1	2.3 ± 0.3
96	4.3 ± 0.3	2.3 ± 0.2	1.7 ± 0.1

Table D.5 Rubber modulus at 500% extensions of NBR latex gloves with different accelerator systems.

Maturation time (hr)	Modulus at 500% (MPa)		
	Control	Ac1-free	Ac-free
0	7.3 ± 0.8	4.7 ± 0.2	4.7 ± 0.4
24	7.5 ± 0.6	5.1 ± 0.2	5.1 ± 0.3
48	11.9 ± 0.8	5.3 ± 0.3	5.1 ± 0.4
72	11.4 ± 0.4	4.2 ± 0.5	3.9 ± 0.7
96	10.4 ± 1.0	4.0 ± 0.3	2.8 ± 0.1

Table D.6 Tensile properties at of NBR latex gloves with different grades of raw latex.

Property	HAN-NH_3		HAN-KOH		MAN-NH_3 and KOH	
	Unaged	Aged	Unaged	Aged	Unaged	Aged
Tensile strength (MPa)	22.9±1.3	34.1±1.5	26.1±1.4	33.7±1.6	29.5±1.1	16.3±2.1
Elongation at break (%)	664±12.2	533±11.7	725±7.6	572±10.0	597±13.7	477±17.7
Modulus at 300% (MPa)	4.1±0.3	5.9±0.2	3.2±0.1	4.9±0.4	3.5±0.2	4.9±0.4
Modulus at 500% (MPa)	7.8±0.4	25.6±1.5	6.0±0.3	15.7±1.5	12.4±0.7	0.00

Table D.7 Tensile properties of NBR latex gloves with different amount of KOH.

Amount of KOH (phr)	Tensile strength at break (MPa)	Elongation at break (%)	Modulud at 300% (MPa)	Modulud at 500% (MPa)
0	13.4 ± 0.2	573 ± 14.8	3.2 ± 0.2	7.1 ± 0.2
0.4	15.4 ± 0.6	621 ± 16	3.0 ± 0.2	6.8 ± 0.6
0.8	17.1 ± 0.5	629 ± 12.1	3.3 ± 0.2	8.2 ± 0.7
1.2	14.4 ± 0.5	607 ± 14.2	2.7 ± 0.1	6.4 ± 0.5
1.6	13.4 ± 1.4	591 ± 15.5	2.4 ± 0.1	4.4 ± 0.2
2.0	12.2 ± 0.7	598 ± 15.8	2.0 ± 0.1	3.7 ± 0.1

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