# DEVELOPMENT OF PRE-VULCANIZATION TESTING METHOD FOR NBR LATEX MATURATION AND STUDYING OF PROPERTIES OF NR LATEX AFFECTING GLOVE DEFECTS

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**หัวข้อสหกิจศึกษา** การพัฒนาวิธีการทดสอบระดับการเชื่อมโยงน้ำยางไนไตร์ลและการศึกษาสมบัติของน้ำยางธรรมชาติที่ส่งผลต่อจุดบกพร่องบนถุงมือ
Development of pre-vulcanization testing method for NBR latex maturation and studying of properties of NR latex affecting glove defects

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## บทคัดย่อ

งานวิจัยนี้เป็นส่วนหนึ่งของสหกิจศึกษา มี 2 หัวข้อวิจัยคือ การพัฒนาวิธีการทดสอบระดับการพรีวัลคาไนซ์ในการบ่มน้ำยางไนไตร์ล และการศึกษาสมบัติของน้ำยางธรรมชาติที่ส่งผลต่อตำหนิบนถุงมือ วิธีทดสอบแบบใหม่พัฒนาขึ้นโดยใช้การทดสอบสมบัติเชิงกลของก้อนยางที่ตกตะกอนด้วยตัวทำละลาย เพื่อหาเวลาที่เหมาะสมในการบ่มน้ำยางไนไตร์ลในกระบวนการผลิตถุงมือ วิธีนี้พัฒนาโดยอ้างอิงการทดสอบหมายเลขคลอโรฟอร์มในการบ่มน้ำยางธรรมชาติ จากผลการทดลองพบว่า อัตราส่วนไซโครเฮกซาโนนต่อคลอโรฟอร์มที่เหมาะสม คือ 90:10 โดยปริมาตร ทำให้เกิดก้อนยางตกตะกอนเป็นเนื้อเดียวกันและสามารถดึงยืดได้ อย่างไรก็ดีการดึงยืดก้อนยางที่เวลาบ่มน้ำยาง 24-42 ชั่วโมง ไม่สามารถแยกความแตกต่างได้ ก้อนยางมีลักษณะทางกายภาพไม่แตกต่างกัน พบว่าตัวทำละลายเมทิลเอทิลคีโตน (MEK) ตกตะกอนก้อนยางที่บ่มระยะเวลาต่างๆ ทำให้เกิดก้อนยางที่มีความแตกต่างกันอย่างชัดเจน ระยะเวลาการบ่มที่เหมาะสมอยู่ระหว่างระดับ 2-3 ในการทดสอบการบวมตัวด้วยตัวทำละลาย อุณหภูมิที่เหมาะสมในการทำให้ตัวอย่างแห้ง คือ 90-100 องศาเซลเซียส มีค่าการบวมตัวอยู่ระหว่าง 0.97-1.19 %TSI ซึ่งเป็นค่าที่เหมาะสมต่อการบ่มน้ำยาง จากการวิเคราะห์ปัจจัยที่มีผลต่อการเตรียมตัวอย่างก้อนยาง คือระยะเวลาการบ่มและอุณหภูมิอบตัวอย่าง โดยใช้โปรแกรมทางสถิติทำกราฟพาเรโต้พบว่า ระยะเวลาในการบ่มน้ำยางมีอิทธิพลมากกว่าอุณหภูมิอบตัวอย่าง ในการทดลองตอนที่ 2 พื่อศึกษาความสัมพันธ์ระหว่างสมบัติของน้ำยางธรรมชาติ (ได้แก่เปอร์เซ็นต์ของแข็ง ความเป็นกรดด่าง ความหนืด และเสถียรภาพของน้ำยาง) ที่

มีต่อตำหนิที่เกิดในตัวอย่างยางเพื่อใช้ในกระบวนการควบคุมคุณภาพการผลิตถุงมือยาง จากการทดลองพบความสัมพันธ์ในการทดสอบในห้องปฏิบัติการ อย่างไรก็ดีไม่พบความสัมพันธ์ในกระบวนการผลิตถุงมือจริง

**คำสำคัญ** : การทดสอบการบ่มน้ำยาง, ตำหนิบนถุงมือ, น้ำยางไตรล์, น้ำยางธรรมชาติ, เวลาการบ่มน้ำยาง

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## Abstract

In this cooperative study, two research topics were carried out, i.e., development of pre-vulcanization testing method for NBR latex maturation and studying properties of NR latex affecting glove defects. In order to find an optimum time for maturation of NBR latex compounds, a new test method was developed by using a solvent-coagulation test similar to chloroform number of NR latex. It was found that a suitable ratio of cyclohexanone and chloroform mixed solvent was 90:10 (by volume) since homogeneous and stretchable coagulum was found. However, appearances and %elongation of NBR coagulum at 24-72 hr were insignificantly different. It was found that methyl ethyl ketone (MEK) could be used to differentiate different solidification states of coagulum at different maturation times. Suitable level of NBR maturation could be level 2-3. In solvent swelling test, an appropriate drying temperature should be 90-100 °C resulting in 0.97-1.19 %TSI which is an optimum point for maturation. Two factors affecting to the swelling test were analyzed by using Pareto chart. It was found that latex maturation time had more effect compared to temperature for drying samples. In the second part, relationships between properties of NR latex, i.e., %TSC (total solid content), pH, viscosity, and latex stability, affecting glove defects were studied for quality control in glove manufacturing process. It was found that some trends were found in lab-scale experiments, however, there was no correlation between latex properties and glove defects in actual glove manufacturing production line.

**Keywords :** Test for latex maturation, Glove defects, NBR latex, NR latex, Maturation time

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Krittaphorn Longsiri
Panachai Srijuntaraviroj

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# Abbreviations

| Abbreviations | detail |
|---|---|
| AN | Acrylonitrile |
| BA | Butyraldehyde dianiline |
| BR | Butadiene rubber |
| °C | Degree Celsius |
| cal | Calorie |
| CBS | N-cyclohexyl-2-benzothiazolesulfenamide |
| $cm^3$ | cubic centimeter |
| CR | Chloroprene rubber |
| CSM | Chlorosulfonated polyethylene rubber |
| DBTU | N,N’-Dibutylthiourea |
| DCBS | N,N-Dicyclohexyl-2-benzothiazolsulfene amide |
| DOTG | N'-Diorthotolyl* Guanidine |
| DPG | Diphenyl Guanidine |
| DPTT | Dipentamethylenethiuram |
| DPTU | Diphenylthiourea |
| DRC | Dry rubber content |
| EPDM | Ethylene Propylene Diene Monomer rubber |
| EPM | Ethylene propylene rubber |
| ETU | Ethylene thiourea |
| EV | Efficient Vulcanization |
| FCC | Fluid catalytic cracking |
| HMT | Hexamethylene tetramine |
| IIR | Butyl rubber |
| IR | Isoprene rubber |
| µm | Micrometer |
| MBS | m-maleimidobenzoyl-N-hydroxysuccinimide ester |
| MBT | Mercaptobenzothiazole |
| MBTS | Benzothiazole disulfide |
| $MgCl_2$ | Magnesium chloride |

# Abbreviations (Continued)

| | |
|---|---|
| MgO | Magnesium oxide |
| MOR | N-Oxydienthylene-2-benzothiazole sulfenamide |
| MPa | Mega Pascal |
| NBR | Nitrile butadiene rubber |
| NDPA | N-Nitrosodi-n-propylamine |
| Nm | Nanometer |
| NR | Natural rubber |
| PA | Phthalic anhydride |
| Phr | Part per rubber |
| PVC | Poly vinyl chloride |
| PVI | N-(cyclhexyl thio) phthalimide |
| RH | Relative humidity |
| SR | Synthetic rubber |
| SBR | Styrene - butadiene rubber |
| TBBS | N-tert-butyl-2-benzothiazyl sulfenamide |
| TBzTD | Tetrabenzylthiuram disulfide |
| TETD | Tetraethyl thiuram disulfide |
| TMTD | Tetramethylthiuram disulfide |
| TMTM | Tetramethylthiuram monosulfide |
| TSC | Total solid content |
| TSI | Total swelling index |
| US | United states of America |
| ZBDP | Zinc-O,O-di-N-phosphorodithioate |
| ZBEC | Zinc dibenzyl dithiocarbamate |
| ZDBC | Zinc dibutyl dithiocarbamate |
| ZDEC | Zinc diethyl dithiocarbamate |
| ZDMC | Zinc Dimethyl dithiocarbamate |
| ZMBT | Zinc 2-mercaptobenzothiazole |
| ZIX | Zinc isopropylxanthate |
| Zn | Zinc |

# Abbreviations (Continued)

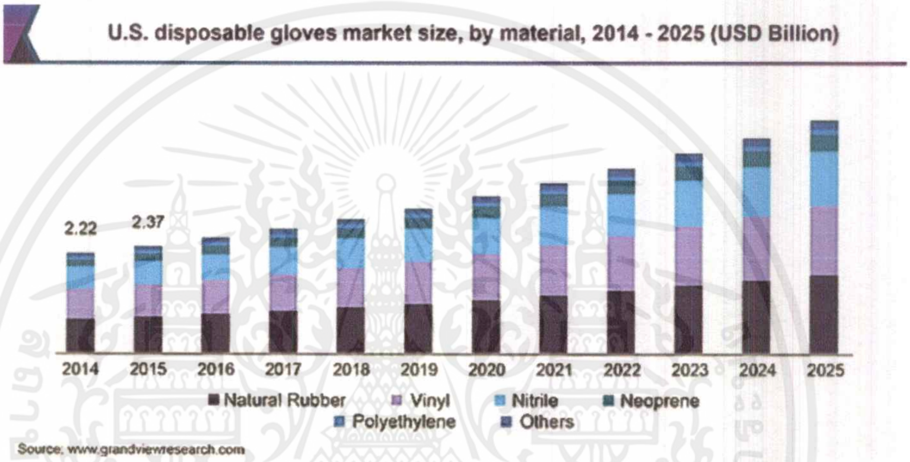
| | |
|---|---|
| $ZnCl_2$ | Zinc chloride |
| ZnO | Zinc oxide |

# Chapter 1

# Introduction

## 1.1 Research Motivation

Rubber glove industry has been generally considered recession-proof as demand for rubber gloves is for all times. The global demand in 2018 was estimated at 268 billion gloves with an expected annual growth of 15%. [1]



Source: www.grandviewresearch.com

**Figure 1.1** US disposable gloves market size in 2014-2025 [1]

This growth has been derived from the increasing awareness among people on the needs for better healthcare and safety and higher hygiene standards besides progressive healthcare reforms in emerging markets.

The market potential for gloves has been growing in the Latin American and African regions as well. In the United States, synthetic nitrile gloves are mainly used in healthcare sector and in many industrial establishments. Gloves of natural latex, vinyl polymers, chloroprene and polyisoprene are also used in the US; but they account for only a minor portion of the demand segment. The US Food and Drugs Administration (US-FDA) has laid down stringent regulations on gloves imported into the country to ensure better barrier protection. Europe is another major market for gloves, especially for the nitrile gloves. Most of the countries in the region have implemented regulations, setting quality standards for gloves imported from outside. Almost three-fourth of the gloves used in the region is made of nitrile latex.

**Figure 1.2** Nitrile gloves [2]

At present, nitrile glove usage is increasing demand because it has better chemical resistance than natural rubber. In addition, nitrile gloves have no protein which makes allergy for users.

Siri K. [3] studied effects of maturation and stabilizers on properties of nitrile latex gloves long maturation time affecting to percentage of swelling NBR latex film reduced while cyclohexanone number was increased but appearance of coagulum of NBR latex was negligy. The manufacturer would like to set standard for maturation time of NBR latex compound. It should be to control crosslink density and glove properties.

In natural rubber (NR) latex, glove manufacturer often has problems in dipping process. They usually find defects on gloves such as weakness and thin spots desire to improve latex properties for control quality of latex.

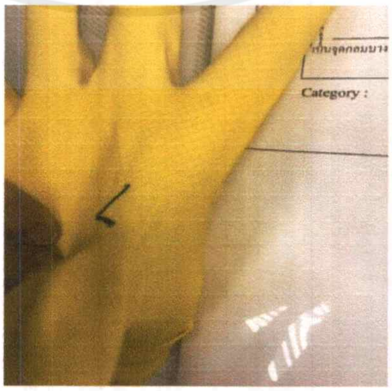


**Figure 1.3** Weakness on gloves

In this study, the work can be divided into 2 parts as shown belows;

Part 1 Nitrile latex: To find a standard method and conditions for solvent swelling test of maturation state in order to find optimum maturation time.

Part 2 Natural latex: To study relationship between NR latex properties (%TSC, viscosity and latex stability) and defects on gloves in order to control latex properties in dipping process.

## 1.2 Objectives of the Study

1. To study and set-up test methods for determining NBR compound latex maturation or degree of pre-vulcanization.
2. Solvent swelling test to determine the level of crosslink of NBR compound latex and study factors that can affect to this method.
3. To study relationship between properties of NR latex compound affecting defects on gloves.

## 1.3 Scopes of the Study

1. To develope methods of NBR compound latex maturation based on “chloroform number test for natural rubber”.
    a. Study suitable ratios of chloroform and cyclohexanone to determine maturation time of NBR compound.
    b. Find alternative solvent to reduce dangerous solvent and see obvious results by different maturation.
2. To vary temperature in oven to dry samples times in solvent swelling test.
3. To vary %TSC in NR compound latex to find relationship between latex properties, eg. pH, latex stability, viscosity and defects on gloves.

## 1.4 Benefits of the Study

Part 1 Nitrile latex : the expectation of this study was to define standard method of testing pre-vulcanized for NBR latex. To find optimum maturation time for keeping latex in holding tank.

Part 2 NR latex : relationship of NR latex properties and glove defects can be studied. NR latex properties (%TSC, viscosity and latex stability) can be set to standard limits for control quality of NR latex.

# Chapter 2

# Theory and Literature Reviews

This chapter discusses theory and academic information associated with the properties of synthetic rubber, especially acrylonitrile butadiene rubber (NBR) latex, chemicals used in rubber mixing, how to mix chemicals into the latex, rubber gloves processing, swelling of rubber, maturation time, crosslink density and sagging in polymers.

## 2.1 Synthetic rubber (SR)

Natural rubber (NR) in the form in which nature products has many useful product qualities. However, NR has property limitation, for example, oil and chemical resistance and also susceptibility to deteriorating effects of the usual atmospheric condition. For example, cracking or crazing of surfaces through the oxidation reaction exposed directly or indirectly to sunlight and loss of tensile strength can occur when NR is used for a long time. NR is not suitable for medical usage due to its protein allergic issues. Thus, synthetic rubbers (SR) has been developed. SR that could be vulcanized by using vulcanizing agent, activator and accelerator to improve rubber elasticity and strengths. [4]

Synthetic rubbers are complex chemical compounds built by means of polymerization of same monomers to produce homo-polymers while that of different monomers produces copolymers. Copolymers derived from three different monomers are called terpolymer. These are then treated by polymerization using catalyst and process steam to form chains of polymers which finally results in rubber substances. These substances are then processed to rubber products by vulcanization to produce three-dimensional cross-linking. Synthetic rubbers which contain olefinic bonds (unsaturated rubbers) or allylic hydrogen that could be vulcanized by using sulfur, in other way some synthetic rubbers did not have olefinic bonds (saturated rubbers) but can also be use a peroxide substance to produce free radicals attacking to rubber molecules and generated macro-radicals. When free radicals on two chains come together, they form carbon-carbon bonds crosslinking between the chains. [4]

### 2.1.1 Properties of synthetic rubbers

Synthetic rubbers have various chemical and physical properties resulting a variety of applications and the wide range of requirements obtained by using different monomers. The use of rubber is widespread, as the characteristics and properties of these elastomers make them useful in almost all economic sectors such as automobiles, civil construction, footwear or plastics so that they are of crucial importance in the daily life of society. Each application depends on the specific properties of each type of synthetic rubber. Properties of synthetic rubber are better than natural rubber as follows: [5]

- possibility of a product with an extremely constant quality
- better abrasion resistance
- high thermal stability
- high ageing properties
- oil and chemical resistance
- environment resistance
- better rebound resilience
- no protein that causes allergic reactions

### 2.1.2 Synthetic rubber production

Synthetic rubber production starts with the refining process of oil, coal or other hydrocarbons with naphtha as one of the resulting products. The naphtha is then combined with natural gas to produce monomers. As feed material, typically monomers such as butadiene, styrene, isoprene, chloroprene, acrylonitrile, ethylene or propylene are used. [6]

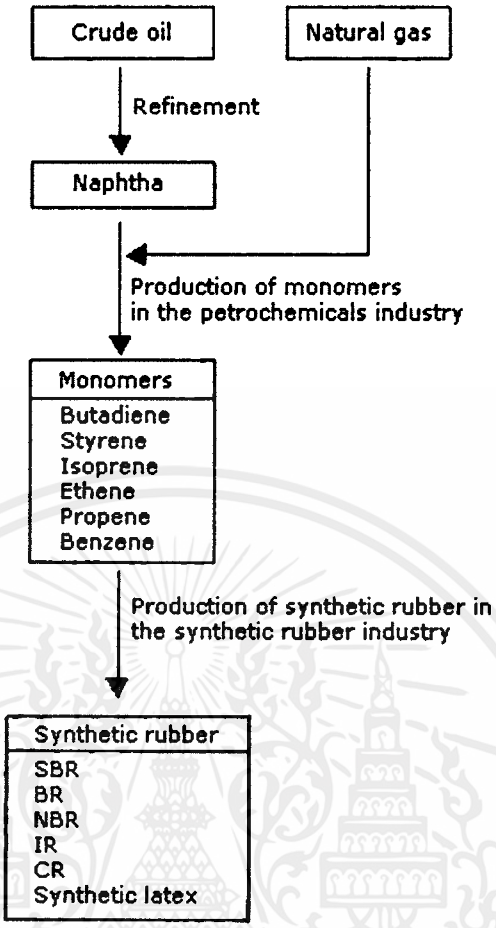
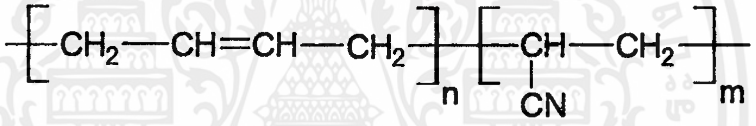


**Figure 2.1** Production process for synthetic rubber [6]

Synthetic rubbers are artificially produced materials with properties similar to natural rubber. Most are obtained by polymerization or polycondensation of unsaturated monomers. A wide range of different synthetic rubbers have emerged, reflecting the various different applications and the chemical and mechanical properties they require. Co-polymerization of different monomers allows the material properties to be varied across a wide range. Polymerization can take place under hot or cold conditions, which result in hot polymers (hot rubber) the polymer molecules are more branched or cold polymers (cold rubber) they are more linear and generally higher in molecular weight features that improve the rolling resistance and wear resistance. Synthetic rubbers are marketed as compressed bales and square blocks. They are also produced in the form of powder rubber, talcum-coated chips, granules and as latex concentrates in liquid form. The mechanical properties are improved by adding fillers such as carbon black during vulcanization with sulfur. Temperature resistance, abrasion resistance, aging resistance, resistance to oxygen and chemicals such as acids and petrol are properties which are improved in this way. [6]

## 2.2 Acrylonitrile butadiene rubber, Nitrile rubber (NBR)

Acrylonitrile butadiene rubber (NBR), also known as nitrile rubber, is a synthetic rubber produced from a copolymer of butadiene and acrylonitrile (ACN), which chemists combine using a process known as co-polymerization. It can be produced by free-radical emulsion polymerization of butadiene with 15 to 45 percent acrylonitrile either hot (hot rubber) or cold (cold rubber). It was invented by the chemists Eduard Tschunkur, Erich Konrad and Helmut Kleiner and a patent for this new oil-repellent rubber was awarded on April 26, 1930. The original name was Buna N and later changed to Perbunan in 1938. [6]



$$-\left[CH_2-CH=CH-CH_2\right]_n-\left[\underset{CN}{\underset{|}{CH}}-CH_2\right]_m-$$

**Figure 2.2** Structure of Acrylonitrile butadiene rubber [6]

NBR is one of the most commonly used elastomers in the rubber glove industry. This product provided specific advantages. Acrylonitrile enhances the highly oil and chemical resistance, while butadiene creates flexibility and tear resistance. The properties of these rubber compounds are determined by its acrylonitrile content, which is broken down into three classifications: [6]

- high nitrile >45% acrylonitrile content
- medium nitrile 30-45% acrylonitrile content
- low nitrile <30% acrylonitrile content

Physical and chemical properties of nitrile rubber vary depending on the composition of acrylonitrile. With increasing acrylonitrile content, the rubber shows higher strength, greater resistance to swelling by hydrocarbon oils, and lower permeability to gases. At the same time the glass transition temperatures and brittle temperatures are increasing. This causes elastic properties and flexibility falling-off at low temperatures but also improvement of NBR compounds processing caused by increase of their thermoplasticity. The lower the acrylonitrile content the better its flexibility in low temperature applications. Medium nitrile is, therefore, most widely specified due to its good overall balance in most applications. Typically, nitriles can be compounded to work over a temperature range of –35°C to +120°C and are superior to most elastomers in regard to compression set, tear and abrasion resistance. Nitrile rubber is considered to be the major oil, fuel, and heat resistant elastomer in the world. It is also resistant to aliphatic hydrocarbons. However, nitrile rubber contains double bonds and have limited resistance to aromatic hydrocarbon, ketones, ester and strong oxidizing chemicals. It has poor resistance to ozone, sunlight and weathering especially under strain condition. [6]

NBR does not crystallize under stress and they have low tensile strength. For the required properties of vulcanizes they have to be filled up with reinforcement fillers. Plasticizers and process aids added to NBR compounds must have polar character because of tolerance with rubber matrix. For this purpose, ester and ether based plasticizers or their oligomer derivatives are used. From the processing aids these are mainly different resinous materials of synthetic and natural character. NBR vulcanizes which are filled with reinforcement fillers have higher abrasion resistance than equivalent materials from NR and SBR. [6]

Nitrile rubber is widely used in automotive industry as automotive seals and gaskets, which subject to contact with hot oils. It is used as automotive water handling applications and in fuel and oil handling hose too. In healthcare industry, its resilience makes it a perfect material for non-latex gloves. Other applications of nitrile rubber include the rolls for spreading ink in printing and hoses for oil products, as an adhesive and pigment binder. [6]

### 2.2.1 Production of NBR

Nitrile rubber containing emulsion used in the process of this invention, can be synthesized by standard emulsion polymerization techniques. It is synthesized by the co-polymerization of acrylonitrile and 1,3-butadiene in an aqueous emulsion under free radical polymerization conditions. The emulsion polymerizations used in synthesizing such nitrile rubber emulsions used in the practice of this invention generally utilize a charge composition which is comprised of water, the monomers, an initiator and an emulsifier (soap). It is generally more preferred to be conducted at a temperature which is within the range of about 5° C. to about 30° C. [7]

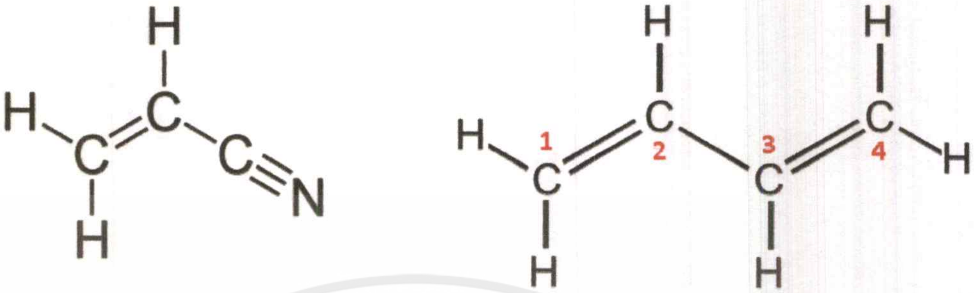


Figure 2.3 Structure of acrylonitrile and 1,3-butadiene [7]

#### 2.2.1.1 Emulsion polymerization of synthetic latex

Emulsion polymerization (EP) is a type of free-radical polymerization. The products of this type of reaction are usually called latexes. In a conventional recipe, its components are water, monomers, surfactant and a water-soluble initiator. Latexes are formed from monomer emulsions (monomer droplets immiscible dispersed in the medium) by polymerization and are liquids. Emulsion polymers are colloids, meaning that they consist of small (typically less than 1 μm), discrete particles dispersed in a continuous liquid media. [8]

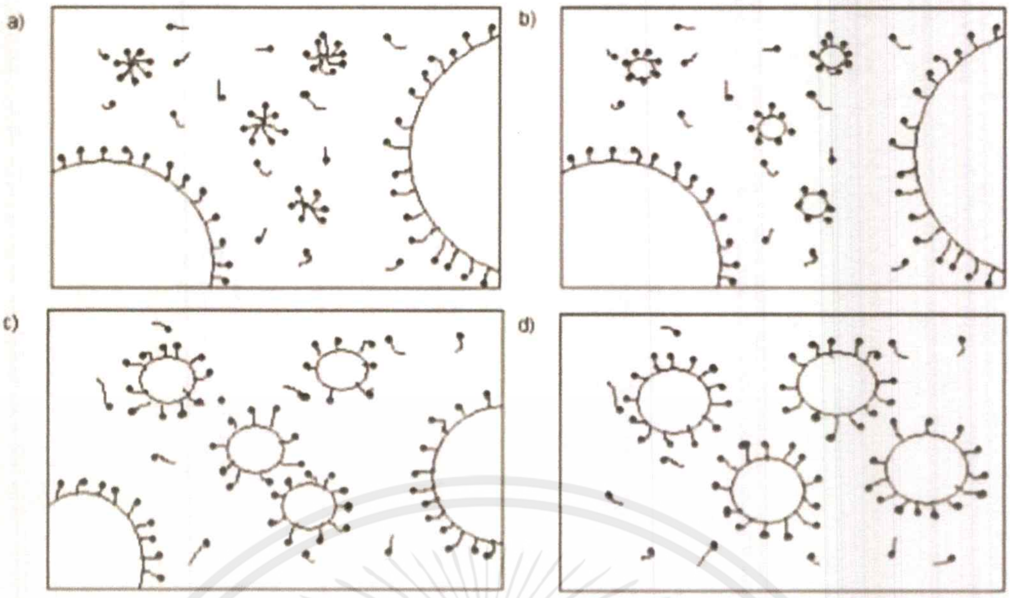


**Figure 2.4** Different intervals of the emulsion polymerization [8]

Figure 2.4 (a) the system of emulsion polymerization is initially composed by the monomer droplets which are stabilized by the surfactant on aqueous phase. In this phase, surfactant and monomer droplets are solubilized and also where the micelles of surfactant are present.

Figure 2.4 (b) the radicals start to be formed in the aqueous phase because a large percentage of the initiators are soluble in water these initial radicals are too hydrophilic to enter in the organic phases (monomer droplets), this causes them to react with the monomer dissolved in the aqueous phase (micelles of surfactant), allowing the formation of oligoradicals that grow slowly due to the low concentration of monomers in this phase.

Figure 2.4 (c) Inside the micelle the oligoradicals are feeded by the high concentration of monomers present in the droplets, promoting the fast growing of the polymer chain. When these oligoradicals enter into a micelle they start to be considered as a polymer particle. The transfer of the monomer from monomer droplets into polymer particle is carried out.

Figure 2.4 (d) the monomer droplets disappear since all monomer molecules were diffused into the polymer particles. A high percentage of monomer is consumed, depending on the solubility of the monomer in the water. A higher value of solubility means that there is still a lot of monomer in the water. This stage is also characterized by the decrease of the monomer concentration in the polymer particles.

## 2.3 Chemicals in rubber mixing

### 2.3.1 Fillers

Fillers not only reduce the cost of composites, but also frequently impart performance improvements that might not otherwise be achieved by the reinforcement and rubber ingredients alone. Fillers are often referred to as extenders. In comparison to rubber and reinforcements, fillers are the least expensive of the major ingredients. Fillers can improve mechanical properties including fire and smoke performance by reducing organic content in composite laminates. Also, filled resins shrink less than unfilled resins, thereby improving the dimensional control of molded parts. Important properties, including water resistance, weathering, surface-smoothness, stiffness, dimensional stability and temperature resistance, can all be improved through the proper use of fillers. [9-12]

### 2.3.2 Retarders

To avoid premature vulcanization during processing, retarders are often added to the cure system. These compounds increase the induction time by reacting with the active accelerator fragment which slows down or temporarily prevents zinc salt formation. [13]

Retarders, which are also called pre-vulcanization inhibitors (PVI), are often compounds that readily react with the accelerator (fragments) and only slowly release them. To function as a retarder, the associated polysulfides should also not readily react with the polydiene to produce sulfur bridges. A compound that meets both requirements is N-(cyclohexylthio) phthalimide (CTP). [13]

Despite its strong retardation effect, CTP has little effect on the actual cure rate once cure is initiated and all CTP is consumed. Furthermore, CTP does not (much) affect the degree of cure, the maximum cross-link density, and length of sulfur bridges. CTP has also the advantage that it does not cause staining and that it permits processing at higher temperatures which increases productivity. [13]

Other important (acidic) retarders/inhibitors include benzoic, salicylic, and phthalic anhydride when used with thiazoles. They not only delay the onset of cure but also slow down the cure rate of vulcanization. It is believed that the cure delay is caused by the formation of a PA-Zn-MBT complex during cure. An alternative explanation is "starvation" of zinc oxide by phthalic anhydride. However, this is not very probable because anhydrides are generally ineffective with sulfonamides. [13]

### 2.3.3 Processing Aids

#### 1) Peptizers

During mastication, while performing compromise liquidation and cutting the molecular chains of the molecular cohesion with mechanical shearing force on the raw rubber, this chemical is used to accelerate the cutting of the molecular chains. Also, it promotes plasticization and reduces the mastication operation time by lowering the viscosity of the rubber. [14]

#### 2) Plasticizer

Plasticizers have the function of plasticizing the rubber compound, improving its processing, reducing the energy required for processing and assisting in the incorporation of the ingredients, improving their dispersion. In vulcanizates they reduce hardness and stiffness, increase elongation at break and improve their flexibility at low temperature. These changes are accompanied by a reduction in mechanical properties and elastic properties. Plasticizers are often used in order to reduce the viscosity of the compound, thus allowing additional fillers to be added; when used for this purpose, are called ***extender.*** [15]

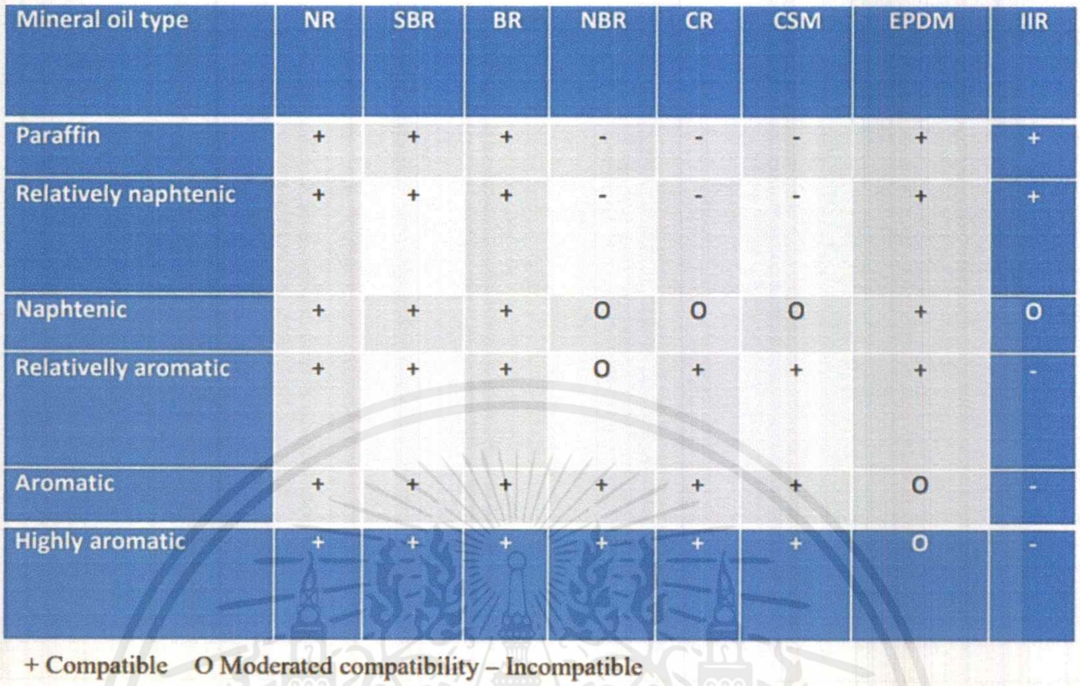
In addition to plasticizers and extenders there are other products which do not modify the viscosity of the compound nor the properties of the vulcanizates but facilitate the processing of the compounds and are called ***process aids,*** which are generally combinations of waxes, fatty acid salts and other products composition not disclosed; are used on the order of 1-3 phr. In some rubber devices where there is a need to increase the tackiness of the compounds, we employ the so-called ***tackifiers*** in the order of 2-5 phr. [15]

The plasticizing effect of a mineral oil increases with its aromaticity, which also contributes to the dispersion of the reinforcing fillers. A drawback of these oils is that they are staining and may partially interfere with peroxidic activity. [15]

Paraffinic oils function more as process aids than plasticizers and do not affect staining. Its use is limited to EPM and IIR rubbers and clear compounds.

Naphthenic oils occupy the intermediate position and are used as plasticizers and as extenders. [15]

**Table 2.1** Some oils and their compatibility with some rubbers [15]

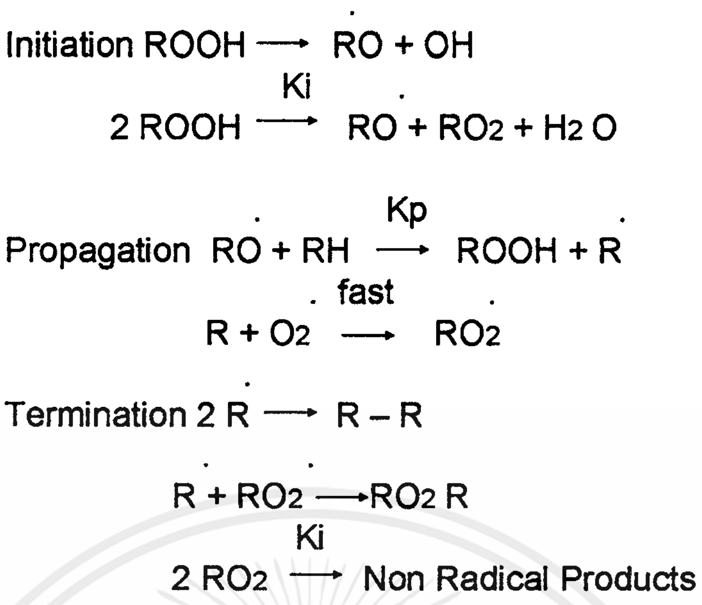


| Mineral oil type | NR | SBR | BR | NBR | CR | CSM | EPDM | IIR |
|---|---|---|---|---|---|---|---|---|
| Paraffin | + | + | + | - | - | - | + | + |
| Relatively naphtenic | + | + | + | - | - | - | + | + |
| Naphtenic | + | + | + | O | O | O | + | O |
| Relativelly aromatic | + | + | + | O | + | + | + | - |
| Aromatic | + | + | + | + | + | + | O | - |
| Highly aromatic | + | + | + | + | + | + | O | - |

+ Compatible O Moderated compatibility – Incompatible

### 2.3.4 Protective agents

Certain additives confer resistance to heat, sunlight, oxygen, and ozone. Amines, particularly para-phenylene diamines, are powerful retarders of oxidation, or antioxidants. Added to rubber compounds in small amounts (1–2 percent), they appear to disrupt the free-radical oxidation reactions that lead either to molecular rupture and softening or to increased interlinking and hardening as rubber ages. Hindered phenols, another antioxidant class, are less powerful than amines but have fewer tendencies to stain light-colored rubber compounds. Small amounts of certain metals, notably copper, manganese, and iron, act as powerful catalysts of oxidation; sequestering agents are therefore used to block the action of these elements if their presence is unavoidable. [16]



$$\text{Initiation}\quad ROOH \longrightarrow \dot{RO} + \dot{OH}$$

$$2\,ROOH \xrightarrow{Ki} \dot{RO} + \dot{RO_2} + H_2O$$

$$\text{Propagation}\quad \dot{RO} + RH \xrightarrow{Kp} ROOH + \dot{R}$$

$$\dot{R} + O_2 \xrightarrow{fast} \dot{RO_2}$$

$$\text{Termination}\quad 2\,\dot{R} \longrightarrow R - R$$

$$\dot{R} + \dot{RO_2} \longrightarrow RO_2R$$

$$2\,RO_2 \xrightarrow{Ki} \text{Non Radical Products}$$

**Figure 2.5** Reaction mechanism for the auto-oxidation of rubber [17]

Atmospheric ozone reacts readily with elastomers containing C=C double bonds, leading to breakage of molecules lying in the surface. As a result, small, deep fissures, termed ozone cracks, are formed if the rubber is stretched slightly (by more than about 10 percent). Cracks one millimeter long appear in unprotected rubber after only a few weeks of exposure to a typical outdoor concentration of ozone, about 5 parts per 100 million. However, certain diamines (e.g., alkyl-aryl paraphenylene diamines) prevent cracking, probably by competing with the C=C bonds in rubber for reaction with ozone. [17]

These antiozonants “bloom” to the surface and react there, protecting the rubber. A few percent of an antiozonant is therefore commonly included in the mix formulation of rubber compounds based on unsaturated elastomers. An alternative method of protection, often employed simultaneously, is to include a few percent of a microcrystalline paraffin wax in the mix formulation. Because it is incompatible with the elastomer, the wax blooms to the surface and forms a protective skin. [17]

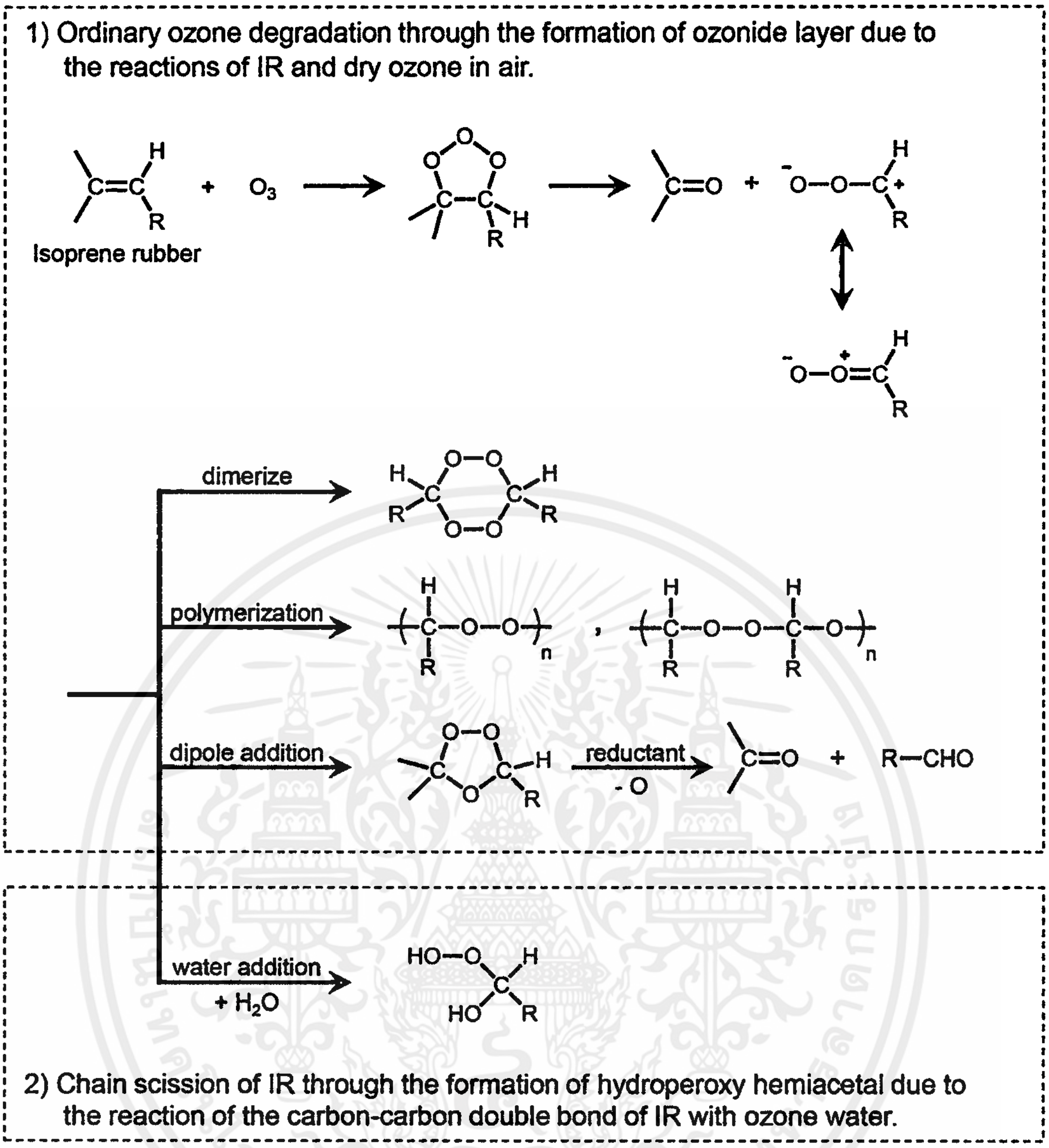


**Figure 2.6** Reactions of ozone with IR under high humidity condition [18]

## 2.4 Latex compounding process of rubber gloves

Compounding involves the addition of rubber chemicals like vulcanizing agents, rubber accelerators, antioxidants, stabilizers, pigments, and others to the concentrated latex. The chemicals are normally added in the form of solution if they are water soluble, but mainly chemicals they are solids and insoluble in water, it should be ground before adding to the latex. The chemicals are ground to dispersion in ball mills, pearl mills or attritors. The compounded latex is matured to get the required maturation before feeding on to the dipping line. [19]

### 2.4.1 Vulcanizing agents

Vulcanization is a crosslinking process in which individual molecules of rubber are converted into a three-dimensional network of interconnected chains through chemical crosslinks. The vulcanization process was discovered in 1839 and the individuals responsible for this discovery were Charles Goodyear in USA and Thomas Hancock in England. Both discovered the use of Sulfur and White Lead as a vulcanization system for Natural Rubber. [20]

This discovery was a major technological breakthrough for the advancement of the world economy. Vulcanization of rubbers by sulfur alone is an extremely slow and inefficient process. The chemical reaction between sulfur and the Rubber Hydrocarbon occurs mainly at the C=C (double bonds) and each crosslink requires 40 to 55 sulfur atoms (in the absence of accelerator). The process takes around 6 hours at 140°C for completion, which is uneconomical by any production standards. [20]

The vulcanizates thus produced are extremely prone to oxidative degradation and do not possess adequate mechanical properties for practical rubber applications. These limitations were overcome through inventions of accelerators which subsequently became a part of rubber compounding formulations as well as subjects of further R&D. [20]

#### 1) Sulfur vulcanization [22]

It is not possible to list all the chemicals used as accelerators, but some of the main groups used in association with natural rubber are: thiazoles; sulphenamides and guanidines. Vulcanization using sulfur alone is sluggish, but, when the sulfur level is increased to make the vulcanization faster, a problem of sulfur blooming arises. Organic accelerators were developed to overcome the sluggishness of sulfur vulcanization and to prevent blooming of unreacted sulfur.

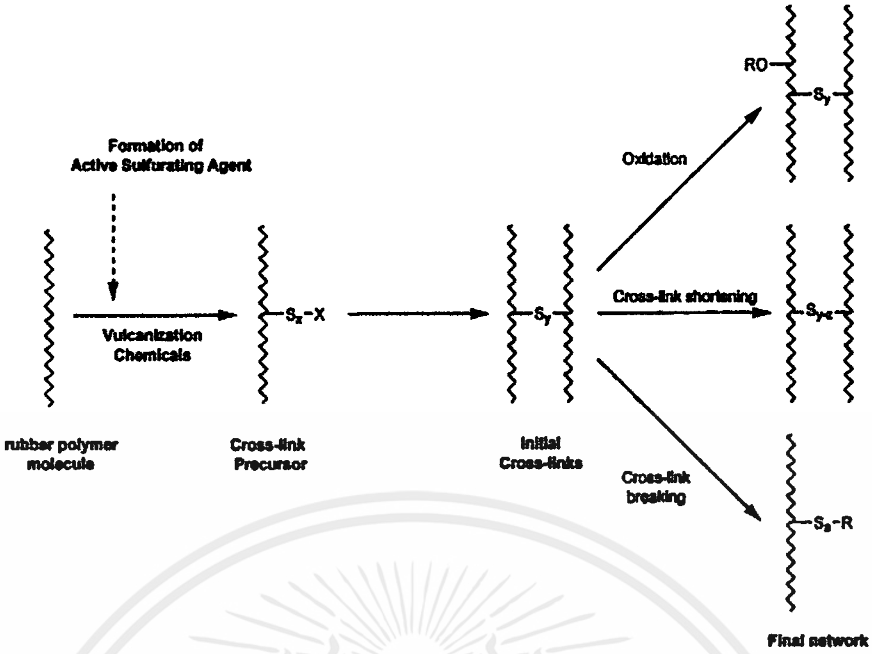


Figure 2.7 Reaction mechanism for sulfur vulcanization [22]

### 2) Peroxide vulcanization [23]

Elastomer crosslinking can be carried out by means of peroxides as well. The procedure can be applied in the case of both diene and saturated (silicone, urethane, ethylene-propylene, etc.) rubbers. Dicumyl peroxide performs crosslinking of NR, SBR, nitrile rubber, resulting in vulcanizates with good cold and aging resistance. Higher tensile strength of the vulcanizates obtained with peroxides as vulcanizing agents, can be obtained by the addition of small amounts of sulfur, amines or unsaturated compounds. By comparison with the vulcanization with sulfur and accelerators, peroxides produce a lower reaction rate and the resulting vulcanizates have a lower tensile strength, scorching tendency and unpleasant smell.

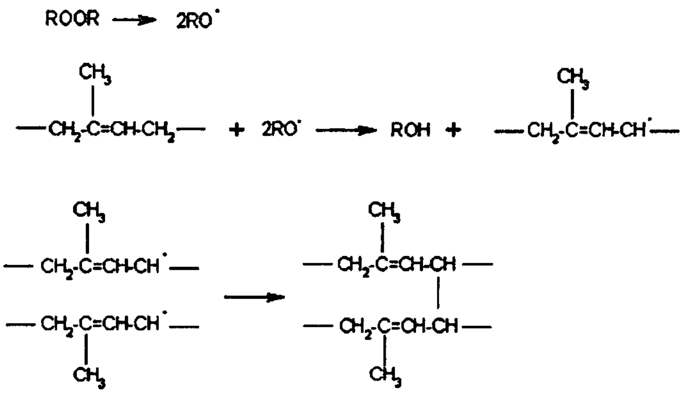


Figure 2.8 Reaction mechanism for peroxide vulcanization [23]

### 3) Metal oxide vulcanization [22]

Metal oxide cure is used for non-olefin rubbers like Polychloroprene, Chlorosulphonated polyethylene, etc. which contain some active group through which they can be cross linked. In case of Polychloroprene, the double bond is ‘hindered’ by the neighboring chlorine atom and hence vulcanization by sulfur is not possible. The allylic shift of chlorine atom in the presence of zinc oxide makes cross linking possible as shown below.

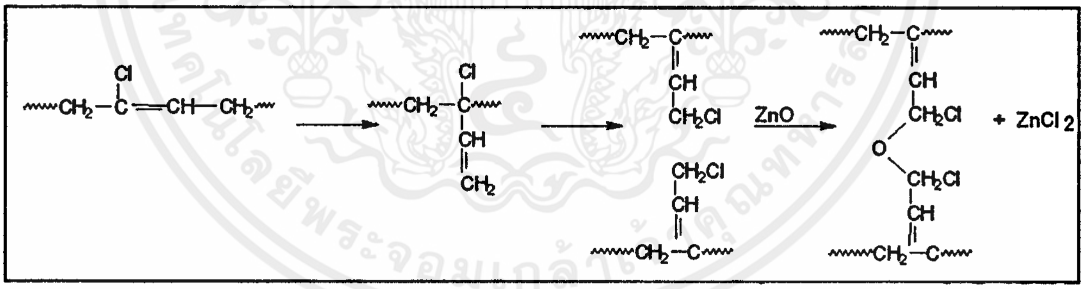
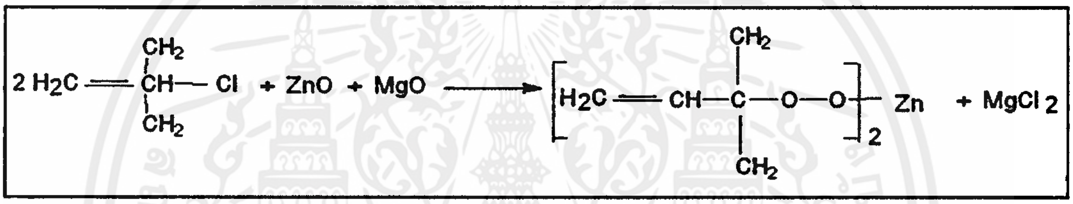


Figure 2.9 Reaction mechanism for ZnO vulcanization [22]

MgO is included in the vulcanization system to act as a scavenger of chlorine atoms (and acceptor). Use of ZnO alone gives a fast on-set of cure (scorch) and vulcanizates have poor mechanical properties. MgO when used alone is very safe but takes long time to vulcanize. Vulcanizates have moderate mechanical properties. When a combination of ZnO – 5 phr + MgO – 4 phr is used, the crosslinking effect is stronger and the scorch safety is within acceptable limits. Only Calcined and extra light MgO is used for high activity and is generally added first in the mixing cycle. Fine particle size ZnO is preferable and due to its scorch behavior, it is added at the end of the mixing cycle. Lead oxide and Red lead are used as vulcanizing agents for polychloroprene when lower absorption and higher acid resistance is desired. (The chlorides of lead are insoluble in water / acid). Lead oxide exhibits faster cure rates than Red Lead in case of Sulfur modified CR, however, the mercaptan modified CR responds in the similar manner to Lead Oxide as well as Red Lead. The crosslinking mechanism in the presence of ZnO + MgO combination may be represented as follows : Here, ZnO is main crosslinking agent and MgO is a chlorine acceptor. However, ZnO also serves as a chlorine acceptor (like MgO) and small amounts of MgO do take part in cross linking reaction.



$$2\,H_2C{=}\underset{CH_2}{\overset{CH_2}{CH}}{-}Cl + ZnO + MgO \longrightarrow \left[H_2C{=}CH{-}\underset{CH_2}{\overset{CH_2}{C}}{-}O{-}O\right]_2 Zn + MgCl_2$$

**Figure 2.10** Reaction mechanism for ZnO/MgO vulcanization [22]

### 2.4.2 Accelerators

An accelerator is defined as the chemical added into a rubber compound to increase the speed of vulcanization and to permit vulcanization to proceed at lower temperature and with greater efficiency. Accelerator also decreases the quantity of sulfur necessary for vulcanization and thus improving aging properties of the rubber vulcanizates. [22]

**Table 2.2** Classification of Accelerators [22]

| ***Accelerators*** | ***Chemical Group*** | ***Vulcanization Speed*** |
|---|---|---|
| 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 |

Accelerators are also classified as primary and secondary accelerators based on the role they play in a given compound. 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 cross link 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. [22]

The basic accelerators such as guanidines, thiurams, and dithiocarbamates 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. [22]

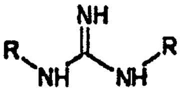
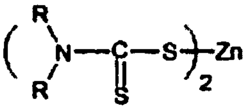
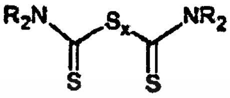
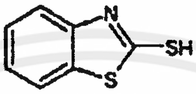
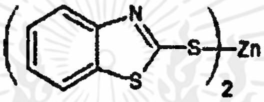
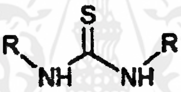
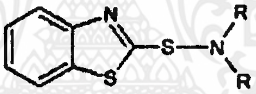
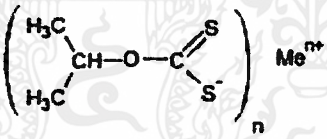
| Compound | Chemical Structure | Side Groups (R) |
|---|---|---|
| Guanidine (Moderate) |  | R = Phenyl, Toluoyl<br>R = Alkyl |
| Dithiocarbamate (Very fast) |  | R = Phenyl, Toluoyl<br>R = Alkyl |
| Thiuram (Very fast) |  | R = Alkyl |
| 2-Mercaptobenzothiazole (Moderate) |  | |
| Zinc-2-mercaptobenzothiazole (Very Fast) |  | |
| Thiourea (Very fast) |  | R = Alkyl, Phenyl |
| Benzothiazole Sulfenamide (Fast - Delayed Cure) |  | R = H, Alkyl<br>R = Phenyl |
| Isopropylxanthate (Ultra Fast) |  | $Me^{n+} = Zn^{2+}, Na^{+}$ |

**Figure 2.11** Commonly used accelerators [22]

Selection of accelerators for rubber compounds

Before selecting an accelerator system for the manufacture of a particular rubber product, following points have to be consider. [22]

- solubility in rubber (high solubility required to avoid bloom & improve dispersibility),
- processing operations & their temperatures the rubber compound is be required to undergo,

- adequate scorch time desired for 'scorch free' processing & storage stability,
- the cure rate requirements.
- reversion characteristics desired (delayed reversion on over cure),
- vulcanization method to be used (mode of heat transfer),
- maximum vulcanization temperature available,
- cure cycle desired at the available vulcanization method and temperature
- requirements of vulcanizates properties (to decide the type & state of cure) ,
- effectiveness over a wide range of cure temperatures & Suitability for use with different polymer blends,
- no adverse effects on other properties / materials (e.g. bonding, ageing, adhesion, non-rubber components in the rubber product),
- no known health hazards upon usage as chemical / its decomposition products and easy to handle dust suppressed physical form,
- no adverse effects during end-use of the rubber product (e.g. accelerators used in the manufacture of rubber articles intended for food contact / surgical use),
- stability of the accelerator as a chemical (e.g. problems with the use of decomposed sulphenamide accelerators).

### 1) Thiazoles class accelerators

This class of accelerators include commercially available and widely used accelerators such as MBT, MBTS and ZMBT (NaMBT the sodium salt of MBT also finds applications in few latex goods manufacture). [24]

Thiazoles are medium-fast primary accelerators with only moderate processing safety. Thiazoles are most widely used accelerators in the rubber industry for the production of wide variety of goods such as cycle tyres and tubes, footwear, beltings, hoses and other moulded and extruded goods. [24]

Thiazoles are activated by zinc oxide / stearic acid combination and produce flat cure with vulcanizates having very good reversion resistance. Activity of thiazole accelerators with respect to cure characteristics can be summarized as follows:

1. Scorch Safety (MBT < MBTS < ZMBT)
2. Cure Rate (ZMBT < MBTS < MBT)
3. Crosslink Density (ZMBT < MBT < MBTS)

Thiazoles act as retarders of cure in rubber compounds accelerated using thiurams (TMTD/TMTM)/Dithiocarbamates (ZDC, ZDBC) or ETU class accelerators as main accelerator and also reduce bloom of Thiurams and dithiocarbamates in EV cure systems. All thiazole accelerators can be further boosted to increase speed of vulcanization by using small quantities of basic accelerators such as DPG, DOTG, TMTM, TMTD, ZDC, etc. [24]

Thiazole accelerators can be retarded using small proportion of Pilgard PVI or other retarders like NDPA, pthalic anhydride, salicylic acid, etc. Addition of extra stearic acid or partial replacement by sulphenamide accelerator also control scorch to some extent. Thiazoles are particularly preferred for rubber to metal bonding applications as amine-accelerators affect the rubber-metal bond strength. [24]

### 2) Sulfenamide class accelerators

The sulfenamide class accelerators include CBS, TBBS, MBS, DCBS etc. and are most popular in the tire industry due to their delayed action as well as faster cure rate offered by them during vulcanization of rubber compounds containing furnace blacks. The sulfenamide accelerators are the reaction products of 2-Mercaptobenzothiazole with basic amines such as cyclohexylamine / tert-butylamine / morpholine / dicyclohexyl amine etc. [24]

These accelerators provide wide range of crosslink densities depending on type and dosage of accelerator used and exhibit flat & reversion resistant cure. Progressive increase in dosage of sulfenamide accelerator shows improvement in scorch delay, cure rate and state of cure. [24]

Sulfenamide accelerators can be boosted by using DPG, DOTG, TMTM, TMTD type basic accelerators for further increasing the cure rate (but at the expense of scorch safety). Sulfenamide accelerators can be effectively retarded using small proportion of Pilgard PVI (CTP) without affecting their rate of cure. [24]

Vulcanizates of sulfenamide accelerators have a typical 'aminic' odour and exhibit higher stress-strain properties along with better resilience and flex-fatigue resistance as compared to Thiazoles. Sulfenamide accelerators decompose rapidly in the presence of steam and hence are preferred for manufacture of open steam cured rubber products requiring faster onset of cure for better shape retention. However, this advantage is lost in the case of hot air cured products. [24]

Sulfenamide accelerators are usually incorporated in the rubber compound at the end of mixing cycle when temperature is above melting point of the accelerator to ensure proper dispersion. Generation of excess heat is avoided to prevent decomposition of sulfenamide accelerator. [24]

In case sulfenamide accelerator is to be added at a later stage; addition in the form of sulfenamide rubber master batch is recommended. Activity of sulfenamide accelerators can be summarized as follows:

1. scorch safety (CBS < TBBS < MOR < DCBS)
2. cure Rate (DCBS < MOR < CBS < TBBS)
3. crosslink density (DCBS < MOR < CBS < TBBS)

Sulfenamide accelerators have limited storage stability and the rate of degradation is greatly influenced by storage conditions such as humidity & heat and hence, is used on a strictly first in-first out basis. Sulfenamide accelerators should be stored in a cool & dry atmosphere (below 30°C & 60% RH) and away from acids / acidic substances / fumes to prevent rapid degradation. [24]

### 3) Thiuram Class Accelerators

Thiuram class includes accelerators such as TMTM, TMTD, TETD, TBzTD and DPTT. Thiurams are ultra-fast accelerators for NR, SBR, BR, NBR and other highly unsaturated rubbers and the most preferred primary accelerator for sulfur cured low-unsaturation content rubbers like butyl (IIR) and EPDM.

Thiurams are widely used as secondary accelerator generally at 0.05 - 0.4 phr with thiazole / sulfenamide class accelerators to achieve faster curing rate, higher crosslink density with a compromise on scorch safety and vulcanizate exhibit lower heat buildup compared to DPG/DOTG activated sulphenamide cures. [24]

Thiurams exhibit longer processing safety compared to dithiocarbamate accelerators. Thiurams, when used as vulcanizing agents (2.5 - 3.0 phr) in the absence of sulfur; the vulcanizates attain high degree of state of cure exhibiting high tensile strength, high modulus, lower elongation at break, higher rebound resilience at elevated temperatures and lower tear resistance. Thiurams are also used along with guanidine in polychloroprene compounds to achieve good processing safety. [24]

In combination with dithiocarbamates and xanthates, thiurams have retarding effect without changing the rate of vulcanization. Thiuram accelerators do not discolour the vulcanizates & the products are tasteless. Activity of various thiuram accelerators with respect to cure characteristics can be summarized as follows:

| | |
|---|---|
| 1. scorch safety | (TMTD < TETD << TMTM) |
| 2. cure rate | (TMTM = TETD = TMTD) |
| 3. crosslink density | (TMTM = TETD = TMTD) |

### 4) Dithiocarbamate Class Accelerators

Dithiocarbamate class includes accelerators such as ZDMC, ZDEC, ZDBC, ZBzDC etc. Dithiocarbamate accelerators are widely used as ultra-fast accelerator for NR latex based compounds and also find applications as primary or secondary accelerators in most dry rubber based sulfur cured compounds. [24]

Dithiocarbamate accelerators require Zinc oxide and Stearic acid for activation and produce rapid vulcanization. Dithiocarbamates exhibit very low scorch safety, faster cure rate and higher crosslink density and the rubber products can be vulcanized in a short time at low temperature (115 - 120°C). Compounds accelerated with dithiocarbamates have a very narrow plateau hence reversion due to over cure can take place very rapidly. Low unsaturation content rubbers such as EPDM and IIR can be cured using dithiocarbamate as a secondary accelerator (at relatively higher dosage) along with thiuram class accelerators as primary accelerators. [24]

Dithiocarbamate accelerators have limited solubility in rubber compounds and hence excess quantity tends to bloom on the surface of the vulcanizates. Dithiocarbamates are non-staining and non-discolouring even on exposure to light and are suitable for the manufacture of transparent goods. Activities of various dithiocarbamate accelerators with respect to cure characteristics in dry rubber compounds can be summarized as follows:

1. Scorch safety (ZDMC < ZDEC < ZDBC)
2. Cure rate (ZDBC = ZDEC = ZMDC)
3. Crosslink density (ZDBC = ZDEC = ZDMC)

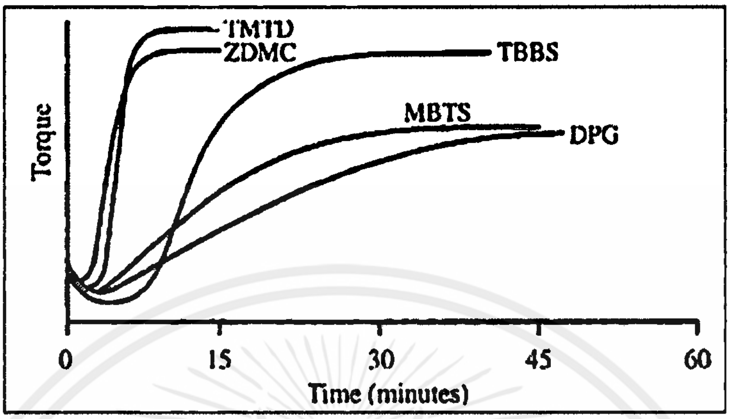


**Figure 2.12** Rheographs of accelerators 0.5 phr + sulfur 2.5 phr in NR at 145°C [22]

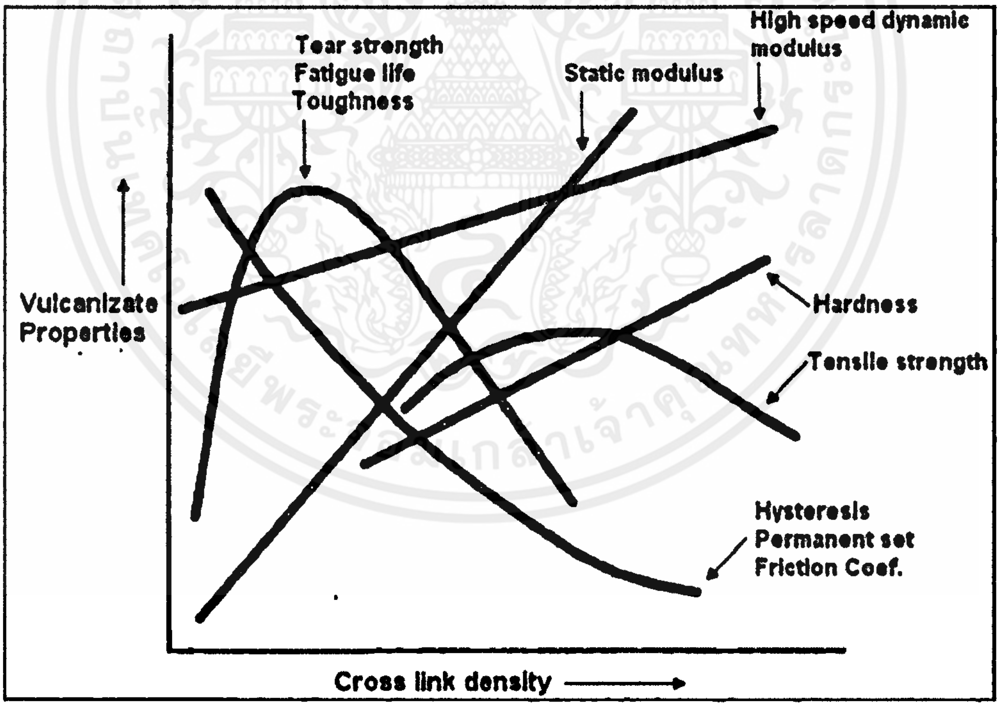


**Figure 2.13** Crosslink density & vulcanizate properties [22]

### 2.4.3 Activator

Typical rubber vulcanization systems consist of rubber, sulfur accelerator, metal oxide and fatty acid, where the last two ingredients represent the activator. They are important rubber processing additives that not only activate cure but also improve the efficiency of sulfur based cure systems. In fact, almost all organic accelerators require the addition of an organic activator to achieve the desired cure and end-use properties. [25]

The most common activator is zinc fatty acid ester which is often formed in-situ by reaction of fatty acid with zinc oxide. The most common fatty acids include stearic, lauric, palmitic, oleic and naphthenic acid. The fatty acid solubilizes the zinc and forms the actual catalyst. The zinc oxide can also act as a filler or white colorant in rubber products whereas the fatty acid improves filler incorporation and dispersion by wetting the oxide particles and reducing interfacial tension (wetting agent). The addition of activators in combination with secondary alkaline accelerators also allows for a more controlled onset of cure. [25]

The mechanism of zinc catalyzed sulfur vulcanization is very complex and is often not fully understood. The main catalyst is zinc whereas the fatty acid functions as a solubilizing agent for the zinc which forms a complex with sulfur in the accelerator-polysulfide or is covalently bonded to sulfur atoms in the accelerator molecules as shown below. Both the solubility and reactivity increase if the zinc coordinates with an amine or amide, for example with sulfenamide. The chelated amines increase the nucleophilicity of the sulfur in the polysulfide complex and thereby increase the reaction rate of precursor formation. The exact position where zinc complexes in the accelerator complex is often unknown. Three possible structures of a Zn-polythiobis(benzothiazole) complex are shown below. The position of the zinc in the accelerator complex affects both the reaction path and the product distribution. [25]

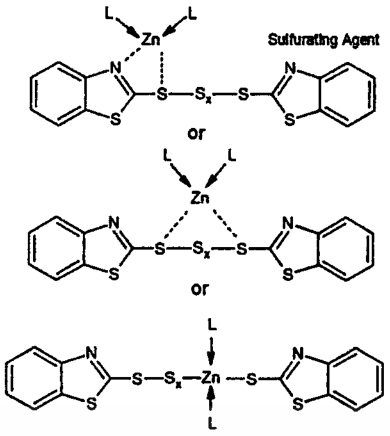


**Figure 2.14** Possible structures of a Zn-polythiobis(benzothiazole) complex [25]

The accelerator complex plays an important role in both the insertion of sulfur atoms into the complex and in the formation of initial polysulfidic crosslinks.2 As it is the case with other catalysts, remarkable small quantities of solubilized zinc are needed to initiate and speed up the vulcanization process. In the case 2-2'-dithiobis(benzothiazole) (MBTS), the zinc is assumed to complex with the nitrogen atom of a benzothiazole ring as shown below [25]

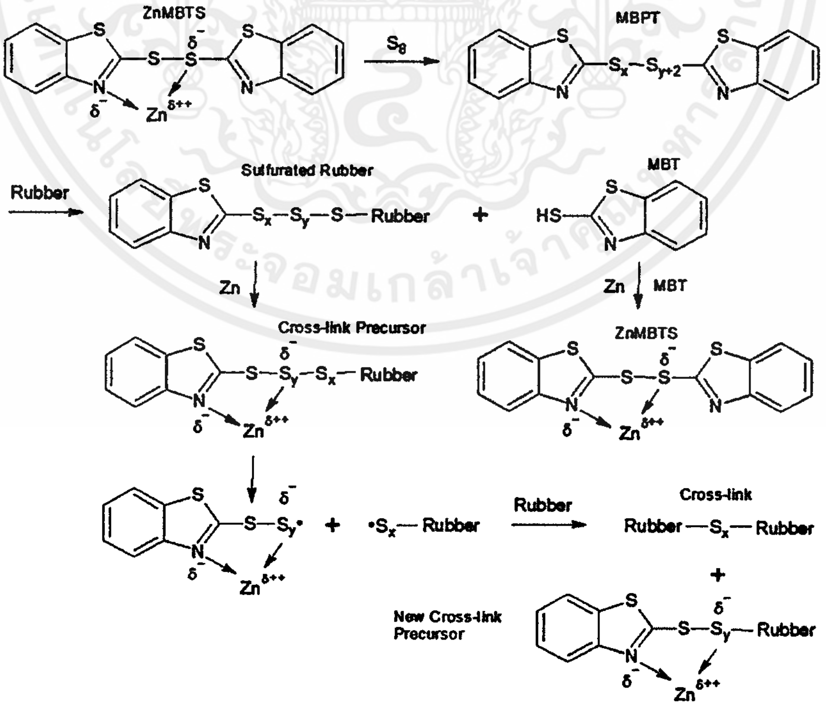


**Figure 2.15** Zinc complexes with the nitrogen atom of a benzothiazole ring [25]

The zinc catalyst lowers the energy of dissociation of the sulfur bonds and allows for faster insertion of sulfur molecules (cyclic $S_8$) into the polysulfide sulfurating agent which then reacts with rubber to form a crosslink precursor and 2-mercapto-benzothiazole (MBT). The later reacts with another MBT molecule in the presence of zinc to form another MBTS-zinc complex. Assuming a radical mechanism6, the cross-link precursor cleaves homolytically into a rubber-polysulfide and polysulfidic benzothiazole radical. The later reacts with rubber to form a new cross-link precursor whereas the polymeric persulfenyl radicals either combine or react with other rubber molecules to form sulfur bridges. [25]

The crosslinks that are formed initially are predominantly polysulfides. During post cure or service life, these polysulfidic crosslinks can degrade (desulfurate) to more stable mono or disulfidic crosslinks which changes the original rubber properties markedly, and/or the polysulfidic crosslinks degrade to elastically ineffective cyclic sulfides or pendant groups. The reaction rate of these post-vulcanization reactions is higher for longer sulfur bridges, since the S-S bonds are weaker when the crosslinks are longer. [25]

### 2.4.4 Preservatives

A preservative is a chemical or mixture of chemicals which when added to latex can prevent coagulation, bacterial action and at the same time stabilize in latex particle. Ammonia is the most popular latex preservative for natural rubber. Otherwise potassium hydroxide is the most popular for NBR latex. [12]

### 2.4.5 Pigments & Colorants

Pigment dispersions and color pastes can be added to resin or gel coat for cosmetic purposes or to enhance weatherability. In the case of gel coats, finely milled pigments are blended with resin using high shear mixers. Many pigments react differently in polyester resin than in paint, and various pigments may slow down or speed up resin gel time. Additives can be mixed in as part of the resin or applied as part of the molding process (as a gel coat). A wide range of coatings can be applied after molding. [12]

### 2.4.6 Release Agents

Release agents facilitate removal of parts from molds. These products can be added to the resin, applied to molds, or both. Zinc stearate is a popular mold release agent that is mixed into resin for compression molding. Waxes, silicones and other release agents may be applied directly to the surface of molds. [12]

## 2.5 Rubber gloves

The vast majority of rubber gloves used by health care professionals, emergency medical technicians, police officers, and fire personnel, are made from natural rubber latexes or synthetic rubber latexes. The gloves are manufactured by a rubber-dipping process whereby a form or mold (i.e., a model of a hand, sometimes with a forearm) is dipped into coagulant solution, such as calcium nitrate or calcium carbonate, partially dried, and then dipped into the latex bath and withdrawn, leaving a thin latex polymer coating on the form. The assembly is then dried at elevated temperatures to form the glove, which is finally removed from the form. [26]

The thickness of the latex film and resulting gloves can be controlled by modifying the immersion time of the form in the latex bath, the solids content of the latex, its viscosity, the concentration of the coagulant, and the presence of additives. [26]

### 2.5.1 Medical gloves

**Figure 2.16** Medical gloves [26]

Medical gloves are medical safety accessories that ensure sanitary hospital conditions by limiting patients' exposure to infectious matter. They also serve to protect health professionals from disease through contact with bodily fluids. Medical gloves are traditionally made of latex and powdered with cornstarch to lubricate the gloves, making them easier to don . Cornstarch replaced Lycopodium powder and/or talc but since cornstarch can also impede healing if it gets into tissues (as during surgery), non-powdered gloves are being used more often during surgery and other sensitive procedures. Special manufacturing processes are used to compensate for the lack of powder. [26]

### 1) Surgical gloves

Surgical gloves have more precise sizing (numbered sizing, generally from size 5.5 to size 9), and are made to higher specifications. They are hand specific. 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 non-latex materials such as vinyl or nitrile rubber. However, these gloves have not yet replaced latex gloves in surgical procedures, as gloves made of alternate materials generally do not fully match the fine control or greater sensitivity to touch available with latex surgical gloves. High-grade non-latex gloves (such as nitrile gloves) also cost two or more times the price of their latex counterparts, a fact that has often prevented switching to these alternate materials in cost sensitive environments, such as many hospitals. Powder-free medical gloves are also used in medical cleanroom environments, where the need for cleanliness is often similar to that in a sensitive medical environment. Similar but specially tested gloves are used in electronics cleanrooms. [26]

### 2) Examination gloves

Examination gloves glove is a disposable device intended for medical purposes that is worn on the examiner's hand or finger to prevent contamination between patient and examiner. They are ambidextrous (fitting both hands) and are generally thinner than surgical gloves. The performance characteristics of the exam gloves are lower than the surgical glove since they are used for less critical procedures. [26]

### 2.5.2 Industrial gloves

**Figure 2.17** Industrial Gloves [27]

Industrial gloves are Ideal hand protection for workers for multi-purpose industrial use. Industrial Gloves are used extensively in manufacturing and production facilities in the chemicals industry, electronics industry, paint and coatings industry, printing and dyeing industry, and various other industrial use and processes, which require additional protection for workers and their products. [27]

### 2.5.3 Household gloves

**Figure 2.18** Household glove [19]

Household gloves have been used for washing, cleaning at home, gardening food preparation. It is important to wear gloves with the right properties for each purpose as there are many gloves made of different materials, coatings, thicknesses and sizes. [19]

## 2.6 Production and manufacture of rubber gloves

General manufacturing process for rubber gloves are manufactured by dipping a former that mimics the shape of a hand in a liquid compounded latex, and then drying. The basic parameters (e.g. length, color, thickness, coating, power-free or powdered, high or low protein, textured or smooth, beaded or beadles, packaging) in glove manufacturing are closely monitored and controlled to adhere to the international standard such as American Standard Testing and Materials (ASTM), European Standard (EN) and International Organization for Standard (ISO). For instance, Standard D3577-09 and D3578-05 on ASTM states the minimum length for examination glove at 220 mm to 230 mm, while surgical glove length at 245 mm to 265 mm. The difference of tolerance length for each type of rubber gloves based on their functionality. In the production line, the former will have dipped deeper toward the marking line to obtain a longer length of the glove. Thickness parameter in accordance with ASTM standard for examination glove is 0.08 mm while minimum thickness for the surgical glove is 0.1 mm. [28]

### 2.6.1 Dipping Process

#### 2.6.1.1 Batch dipping process

Industrial gloves and household gloves are presently made on batch dipping process. Formers are mounted on pallets, often as 1.2 meters by 2.4 meters. The pallets are moved intermittently, normally on a consistent time cycle, to each machine station. For actual dipping stations, the pallets move over the tank, and the pallet is dipped into the tank, or alternatively, the tank is raised to the pallet of formers. After completing the dip cycle, the pallet indexes to the next station, with a fresh pallet indexed to the same dipping station. Generally, the formers are affixed to the pallet in rigid fashion. Batch dipping can be made consistent wall thickness and thickening more than continuous process. [28]

#### 2.6.1.2 Continuous dipping process

Surgical and examination gloves are presently made on high-speed continuous dipping lines with vary high output and thin wall thickness. Formers are mounted on multiple former racks, or individually and attached to a continuous moving conveyer chain. The line moves continuously at a constant speed, carrying formers through dip tanks, ovens, and associated process stations. Some continuous chain machines feature re-rotating forms, whereas for others, the forms are fixed. [28]

### 2.6.2 Process flow for rubber gloves

**Figure 2.19** Process flow for rubber gloves [28]

Raw latex is collected and sent for compounding with the addition of crosslinker, accelerator, initiator, antioxidants, stabilizers, pigments, and others require additive by each manufacturer private formula adding into the latex compound. To hold the film thickness uniform and obtain constant physical properties, it is important to control the compounded latex solid concentration, pH, viscosity, thermal stability and temperature, the surface roughness and temperature of the former, and the speed at which the former is lifted, all of which have an effect. [28]

Step 1: The formers are cleaned by using cleansing agent and physical wash then dried before.

Step 2: Dipped formers in a coagulant solution containing calcium nitrate, calcium carbonate, and suitable wetting agent. A gravimetric method was used.

Step 3: After drying the coagulant on the surface of the formers, they fed to compound latex tank for dipping in ambient temperature until the desired product thickness is obtained.

Step 4: Dried up the latex and beading in the cuff section by edge rollers to facilitate gripping of the gloves during the stripping section.

Step 5: Leaching in hot water for removing excess chemicals substances and particles in the latex film.

Step 6: Proceed to vulcanization for the latex in hot oven.

Step 7: Post-leaching for the glove film in the hot water again for removing soluble protein and chemicals.

Step 8: Formers with the gloves are dipped in the chlorine to decreases the surface friction of the glove thereby allowing for gloves to be easily donned without powder, then sent for leaching for removing excess chemical on the surface of the glove.

Step 9: Stripping process, gloves are stripped from formers.

Step 10: Segregated according to sizes. All the gloves will send to tumbling dried for removing excess moisture and powder.

Step 11: Subsequently, the gloves are allocated in lots, size, and quality inspection unit will randomly choose the glove in the production line for inspection.

Step 12: sterilization will conduct through ethylene oxide or gamma irradiation for removing microorganism which would not affect the properties of the rubber gloves.

The thickness of the latex film and resulting gloves can be controlled by modifying the immersion time of the form in the latex bath, the solids content of the latex, its viscosity, the concentration of the coagulant, and the presence of additives. [28]

## 2.7 Pre-vulcanization of latex

Pre-vulcanized latex is therefore a compounded latex in which molecules of rubber particles are partially cross-linked (i.e. vulcanized). However, there is no change in rubber particle size, shape and particle size distribution, the latex still retaining its original fluidity and colloidal property. [21]

Formulation could be designed to give different types and degree of cross-linking resulting in a varied range of pre-vulcanized latex for making products having different modulus with M700 (Modulus at 700% elongation) ranging from 9.0 MPa to 19.0 MPa, high heat resistance, low nitrosamine and nitrosatables, low copper-staining, sterilization resistance etc. All these could be made available both in high (0.6%) ammonia or low (0.3%) ammonia version. [21]

Modulus and hardness depend mainly on the degree of crosslinking and are more independent of the types of crosslink. Hence modulus is frequently used to measure the degree of crosslinking. The other factor affecting the film properties of prevulcanized latex is the nature of the crosslinking i.e. whether they are predominantly polysulphidic, disulphidic or monosulphidic. Increasing the percentage of polysulphidic crosslinking would increase resilience, tensile strength, tear strength and fatigue life. However, polysulphidic crosslinking are more thermally unstable, and prone to stress relaxation and permanent set compared to monosulphidic crosslinkings. Hence a compromise is normally made between strength and service life. [21]

Depending on what products are being made, the prevulcanized latex could be used as it is (as in the case of toy balloons after the addition of pigments) or after some dilution with water to achieve a final latex solid content of as low as 30% (as in the case of examination gloves). What one needs to do next is to mix for about 30 minutes and allow enough time, usually 16 to 24 hours for deaeration (i.e. for air bubbles to escape) before the latex is ready for dipping, casting, extrusion, spraying, painting, coating etc. No maturation period is required as in the case of post-vulcanizable latex compound where a "maturation" stage is almost always a prerequisite for making reasonably good quality latex products. [21]

"Maturation" is a stage when sufficient time must be allowed for both the naturally occurring and added surfactants and fatty acid soaps to reach an equilibrium.

Also, a controlled degree of vulcanization must take place during this stage before the latex compound is ready to be used. To use the latex compound too early or too late would result in under-curing and over-curing respectively. Generally speaking, unlike a pre-vulcanized latex, post-vulcanizable latex compound would have a marching curve immediately after compounding in terms of the degree of vulcanization. [21]

Hence, in the case of post-vulcanizable latex compound, it is more difficult to prevent situations of over-curing when cracking and tearing of, for instance, gloves and condoms are frequently encountered. This is attributed to the fact that the tensile strength reaches a peak before reclining as the crosslink density increases. In short, post-vulcanizable latex compound has short shelf-life of usually from 2 days to 2 to 3 weeks depending on the curative formulation. [21]

On the other hand, pre-vulcanized latex generally has a very much longer shelf-life of 6 to 9 months. Therefore, less stringent process controls are required for pre-vulcanized latex. Also, very often, one finds the viscosity of such compound increasing with time, unlike pre-vulcanized latex. This is basically a result of zinc ammine thickening. This involves the dissolution of zinc oxide by ammonia in the presence of ammonium salts releasing zinc ammine complex ions which in turn would react with the stabilizers on the latex particles namely the fatty acid soaps and proteins forming insoluble zinc soaps and proteinates. The end result is the loss of latex stability accompanied with increasing viscosity. [21]

Pre-vulcanized latex does not have all the aforementioned problems which very often give many a sleepless night to the latex products manufacturers. It goes without saying that the vulcanization stage is not required for pre-vulcanized latex although, in practice, an oven is still required to accelerate the drying. [21]

Another advantage is the low residual chemicals, particularly the accelerators. This results in a “cleaner” latex compound with low toxicity level which is of extreme importance for the manufacturing of medical devices such as gloves, baby teats, condoms, catheters and medical tubing. Testing of these articles have been carried out by medical device manufacturers considering their destination and service conditions. This includes chemical analysis of extracts, skin irritation, skin sensitization, muscle implantation, pyrogeneity, cell cytotoxicity etc. [21]

### 2.7.1 Level of pre-vulcanization

The chloroform coagulation test is a simple and rapid means for testing the degree of prevulcanization. It consists of mixing equal parts of prevulcanized latex and chloroform ($CHCl_3$) and stirring with a glass rod until coagulation is complete. The coagulum is allowed to stand 2 to 3 minutes and then numerically rated from 1 to 4. No 1 is judged as uncured and No 4 is precured to an advanced degree. The chloroform coagulation test is subjective and it does not allow for easy comparison of small differences between individual samples. [29]

Number 1: The coagulum is a tacky mass and break in a stringy manner when stretched. This represents an unvulcanized state.

Number 2: The coagulum is a weak lump which breaks short when stretched. This indicates a lightly vulcanized state.

Number 3: The coagulum is in the form of non tacky agglomerates. This indicates a moderately vulcanized state.

Number 4: The coagulum is in the form of small dry crumbs. This indicates a fully vulcanized state.

## 2.8 Crosslink density

Crosslink density of a vulcanized rubber can be measured by using the solvent swelling method. A three-dimensional network polymer such as vulcanized rubber may absorb large amounts of liquid when exposed to a compatible diluent or a good solvent. Under these conditions, swelling of the network will occur and an elastic retractive force develops. The driving force of the swelling process is mainly enthalpic in nature. As the volume of the network increases the chains are stretched which, in turn, causes a decrease in entropy because the extended configuration of the chains is less likely. Thus, an elastic retractive force develops. Equilibrium is eventually reached when the two opposing forces become equal. [30-31]

### 2.8.1 Solubility parameters

The solubility parameter concept is based on Hildebrand's solution theory and can be related to polymer solvent interaction coefficients and to cohesive energy density, which in turn yields information on intermolecular forces in polymers. This data will be useful in predicting a number of polymer properties, e.g. polymer solubility, compatibility with other polymers and solvent resistance. The solubility parameters of polymers are determined by studying their interactions with a series of solvents of known solubility parameters and assigning to the polymer the value of the liquid which appears to be the best solvent. This can be achieved by swelling the crosslinked polymer in a series of solvents or the intrinsic viscosity of the polymer can be determined in a series of solvents. In both cases, the solubility parameter of the polymer is assumed to be that of the solvent in which a maximum in the property measured, swelling or intrinsic viscosity occurs. The values of solubility parameter determined by the above methods can depend on the type of solvents used. This is particularly noticeable when strong hydrogen-bonding solvents are employed which can interact with functional groups in the polymer. A 'three dimensional' solubility parameter has been described to take account of dispersion forces, dipole forces and hydrogen bonding. [30-31]

### 2.8.2 Flory - Rehner equation

The Flory-Rehner equation is normally used to calculate the crosslink density of vulcanized rubber without filler. [30-31]

$$v = -\frac{\ln(1 - V_r) + V_r + \chi V_r^2}{V_s\left(V_r^{1/3} - 0{,}5V_r\right)}$$

V is crosslink density (mol/cm$^3$)

$V_r$ is volume fraction of rubber in equilibrium swolled vulcanizate sample

$V_s$ is mole volume of used solvent (cm$^3$/mol)

$\chi$ is Flory-Huggins polymer – solvent interaction parameter

## 2.9 Sagging in polymer

Technically, sag is the bowing of a plastic sheet during the heating phase of thermoforming. Practically, it is a major bugbear. Many processing problems, including the following are directly attributed to sag:

1. Nonuniform sheet thickness, even before the sheet contacts the mold
2. Nonuniform sheet temperature, since the top-center of the sheet moves away from the top heater while the bottom-center moves toward the bottom heater
3. Localized webbing owing to greater sheet surface area

Mathematically, the shape of the sagging sheet can be modeled in two dimensions as a plate flexing under its own weight, so long as the neutral axis remains within the thickness of the sheet. It has been shown that the extent of sag depends on the width of the sheet, the thickness of the sheet, and the instant elastic modulus of the polymer. When the sheet has sagged substantially, its shape can be modeled in two dimensions as a parabola or catenary. It has been proposed that the instant tensile strength be used instead of the instant elastic modulus. [32]

A recent review of the problem has yielded a new model, based on linear viscoelasticity. Consider the Maxwell parallel spring-and-dashpot mechanical model, Figure 2.23

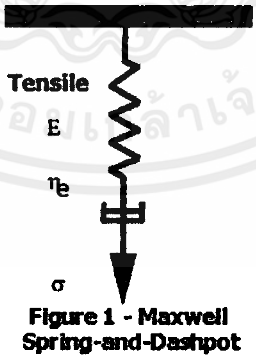


**Figure 2.20** Maxwell parallel spring-and-dashpot mechanical model [32]

In tension, the spring constant is related to the polymer elastic modulus, and the resistance of the dashpot is related to the polymer extensional viscosity. The equation that describes the Maxwell model is:

$$\frac{d\sigma}{d\theta} = \frac{E\sigma}{\eta_e} = E\frac{d\varepsilon}{d\theta}$$

The stress is $\alpha$, $\sigma$ is time, $\eta$e is extensional viscosity, E is elastic modulus, and $\varepsilon$ is elongation. The Maxwell model response to a constant stress, $\sigma_0$, is shown in Figure 2.20

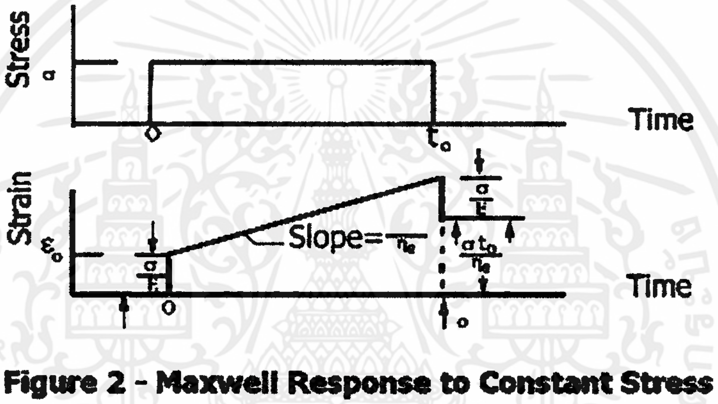


**Figure 2.21** Maxwell model response to a constant stress [32]

The solution to the Maxwell model for this loading configuration is:

$$\varepsilon = \frac{\sigma_o\theta}{\eta_e} + \frac{\sigma_o}{E}$$

Note that the elongation of the model is linear with time, $\sigma$, with the proportionality being the ratio of the stress and the extensional viscosity. The zero-time asymptotic sag is given as the ratio of the applied stress to the instant elastic modulus. For sag, the stress is just the weight of the sheet per unit area, the weight being a function of the density of the sheet and the sheet thickness. [32]

Can this model be verified? Figure 2.21 shows the time-dependent isothermal sag for unmodified and acrylic-modified polypropylenes. It is apparent that the extent of sag is linear with time. [32]

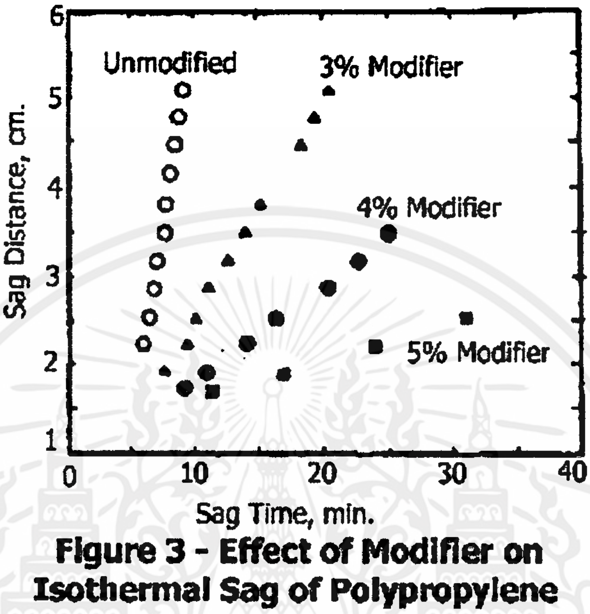


**Figure 2.22** Effect of Modifier on Isothermal Sag of Polypropylene [32]

Why is this important? Because in resin suppliers research laboratories, time-dependent module and elongational viscosities can be measured under very controlled conditions. It appears from here that the simple Maxwell linear viscoelastic model can be used to quickly screen materials to determine temperature-sensitive sag for polymers that are currently commercial, as well as those that are being proposed as lower sag polymers. [32]

## 2.10 Literature Reviews

Xiaoren, L. V., Wang, H. M., and Wang, S. J. [33] investigated the effect of cyclohexane on the swelling-induced ageing and tribological behaviors of NBR rubbers. The following conclusions were drawn as the main outcomes of this investigation. With increasing of swelling time, the swelling increment of NBR increased, the hardness decreased, and the surface damage became more serious due to the penetration of cyclohexane into rubber surface and the dissolution of dioctyl phthalate plasticizer with the cyclohexane. The wear volume of swelled NBR rubber under the cyclohexane lubrication condition was higher than that of original one due to its lower shearing strength. At the lower load, the wear loss of NBR samples in cyclohexane was low, and the wear process further promoted the swelling-induced ageing of NBR samples. At the higher load, the wear loss of NBR samples in cyclohexane was dramatically high due to the change of wear mechanism from mild abrasive wear to severe mild wear, and the swelling-induced ageing of NBR samples accelerated its wear process.

Sridharan, K. and Elangovan, K. [34] investigated on the swelling characteristics of NR/BR rubber blends. The paper analyzed the swelling and wear characteristics of NR/BR blended rubber blocks. The change in hardness values found to be negligible in the course of time variation for both the toluene and oil swelled samples. There found a rapid change in the hardness value initially and was almost negligible finally. The hardness values of the oil swelled samples even though with higher CB loading showed decrease in hardness values for longer duration. The wear rate of the swollen and un-swollen samples was more significant to understand their behavior under operating environments. The wear particles found to be very soft and almost even in size for toluene swelled. Comparatively the debris was of granular shape agglomerate with oil. Also, the oil swelled samples also showed resistance to wear which might be due to slip in the contact surfaces. The wear rate was extremely high for toluene swelled samples rather the oil swelled samples.

Sasidharan, K. and Kottayam, P. [35] studied novel compounding for room temperature prevulcanization of natural rubber latex. Room temperature prevulcanization of centrifuged natural rubber latex was done as per the combination of accelerators RT1, RT2, RT3 and also with a conventional prevulcanization under heating system. The results showed that the combination of accelerators can bring prevulcanization at room temperature. Products via., balloons, industrial gloves, rubber bands, etc were produced from room temperature prevulcanized latex and showed better clarity, color and technological properties.

Panu, D. Paitoon, L. and Rachatham, W. [36] studied correlation between dry rubber content in field latex and viscosity measured with efflux time method. The method of measuring the efflux time of diluted field rubber latex was proved to be beneficial in predicting the DRC of the latex sample. The dilution with water was done to eliminate the effect of dissolved solid in the rubber latex so it changed the correlation from non-linearity to linearity. However, there was an acceptable limit of dilution. Increasingly diluted suspension will yield more experimental errors. Therefore, dilution should be done with care. The recommended dilution is that the field latex could be diluted to the DRC of 9 wt% before checking the efflux time. However, more samples of rubber latex with various non-rubber contents should be experimented thoroughly in the future. It should also be noted that there are many factors influencing the viscosity of the latex. Those include the temperature during the measurement, the age of the latex, and seasonal and clonal variations.

Leblanc, J. and Staelraeve, A. [37] studied the storage maturation of freshly mixed rubber compounds and its effects on processing properties. The relationships between the variation upon storage of bound rubber (BR) and processing properties has been studied with polybutadiene and a natural rubber (NR) compound with various filler levels. It has been found that the two-stage model previously established for BR, i.e.,

$$\text{Property} = A + B \times Vi$$

$$\text{Property} = \text{constant}$$

$$\text{for } t < \text{tstabil.}$$

$$\text{for } t > \text{tstabil.}$$

Two-stage model of BR did apply to processing properties. High-strain rheological tests were, however, more sensitive to the maturation effect, which would indicate that similar effects were to be expected in factory processing. The differences between steady-shear and dynamic-shear variations upon storage could indicate that the tight BR rather than the loosely BR is modified during the early storage period after mixing.

Siri, K. [3] studied effect of maturation and stabilizers on properties of nitrile latex gloves. Solvent coagulation test is one of methods for predicting crosslink density in NBR latex during maturation. In general, NR latex used chloroform as solvent for coagulation. Thus, this study changed solvent to cyclohexanone to be appropriate for NBR latex compound. Figure 3.16 shows the coagulum of NBR latex compound each of the maturation time from 0 to 96 hours. shows cyclohexanone number of NBR latex compound. Level of prevulcanization was assessed by coagulation of NBR latex compound with cyclohexanone. 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 NBR latex.

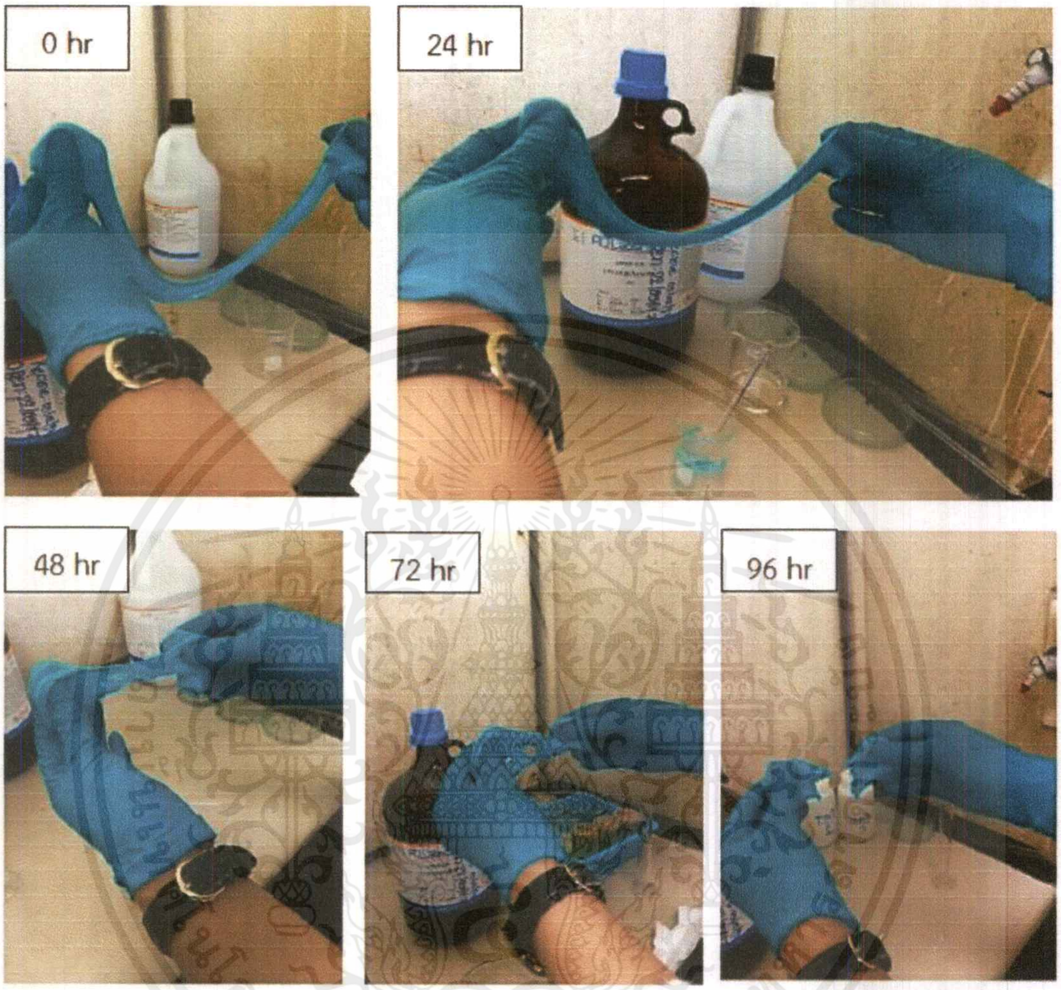


**Figure 2.23** Coagulums of NBR latex compound in different maturation times (0 to 96 hours) [3]

Mammadov, S. M. et.al [38] studied solubility of irradiate copolymer in mix acrylonitrile butadiene rubber with polyvinylchloride. The number of chains of crosslink in initial NBR is low; as a result, it must increase solubility and high value of thermal effect diffusion and solution as shown in Figure 2.23. NBR dissolves in Methyl Ethyl Ketene (MEK) with major positive thermal effect +7.2cal/hrs. Its copolymers also dissolute with heat, but in copolymers with increase content of PVC were observed decrease of thermal effects compared to initial BNR. BNR dissolves in toluene with the thermal effect of 4.5 cal /hrs.

| Irradiation dose, kGy | Contain in copolymer BNR and PVC, % | | $\overline{Q}$, cal/g | | d, $g/cm^3$ |
|---|---|---|---|---|---|
| | BNR | PVC | MEK | Toluene | |
| 0 | 0 | | 35,8 | 41,3 | 0,8452 |
| 10 | 90 | 10 | 32,3 | 38,2 | 1,1396 |
| | 80 | 20 | 27,4 | 36,5 | 1,1357 |
| | 70 | 30 | 25,3 | 35,9 | 1,1343 |
| | 60 | 10 | 23,0 | 35,3 | 1,1340 |
| 20 | 90 | 10 | 30 | 37,5 | 1,1426 |
| | 80 | 20 | 25 | 32,3 | 1,1278 |
| | 70 | 30 | 22,3 | 31,6 | 1,1224 |
| | 60 | 40 | 20,6 | 31,0 | 1,1201 |
| 30 | 90 | 10 | 27,4 | 36,3 | 1,1410 |
| | 80 | 20 | 23,8 | 31,2 | 1,1200 |
| | 70 | 30 | 19,4 | 28,5 | 1,1116 |
| | 60 | 40 | 16,3 | 26,2 | 1,1072 |
| 40 | 90 | 10 | 21,8 | 32,6 | 1,1278 |
| | 80 | 20 | 16,4 | 27,3 | 1,1224 |
| | 70 | 30 | 10,2 | 25,2 | 1,1116 |
| | 60 | 40 | 7,5 | 25,1 | 1,1115 |
| 50 | 90 | 10 | 15,1 | 29,3 | 1,1218 |
| | 80 | 20 | 10,3 | 24,6 | 1,1097 |
| | 70 | 30 | 7,1 | 20,5 | 1,0920 |
| | 60 | 40 | 4,3 | 17,8 | 1,0812 |

**Figure 2.24** Integral heat of solution and density irradiated copolymers BNR-PVC [38]

Tinker, A.J. et.al. [39] studied solubility parameter values for a series of epoxidised natural rubbers (ENR) by calculation and from equilibrium swelling data. Equilibrium swelling measurements on NR, ENR 26, ENR 48 and ENR 71 gum peroxide vulcanizates were carried out in a range of solvents of known solubility parameters. Solubility parameters can also be obtained from swelling data via the modified Flory-Rehner equation as shown in Figure 2.28

| Polymer | Solvent (δ)$^a$ | Vs | Vr | χ |
|---|---|---|---|---|
| NR | Pentane [14.4 (MPa)$^{1/2}$] | 0.623 | 0.377 | 0.618 |
| | Hexane [14.9 (MPa)$^{1/2}$] | 0.671 | 0.329 | 0.559 |
| | Octane [15.6 (MPa)$^{1/2}$] | 0.691 | 0.309 | 0.513 |
| | Decane [15.9 (MPa)$^{1/2}$] | 0.678 | 0.322 | 0.510 |
| | Cyclohexane [16.8 (MPa)$^{1/2}$] | 0.792 | 0.210 | 0.433 |
| | Butyl acetate [17.4 (MPa)$^{1/2}$] | 0.642 | 0.358 | 0.589 |
| | Methyl propyl ketone [17.8 (MPa)$^{1/2}$] | 0.505 | 0.495 | 0.736 |
| ENR 26 | Decane [15.8 (MPa)$^{1/2}$] | 0.444 | 0.556 | 0.782 |
| | Cyclohexane [16.8 (MPa)$^{1/2}$] | 0.717 | 0.283 | 0.526 |
| | Methyl isobutyl ketone [17.2 (MPa)$^{1/2}$] | 0.737 | 0.263 | 0.487 |
| | Butyl acetate [17.4 (MPa)$^{1/2}$] | 0.763 | 0.237 | 0.440 |
| | Methyl propyl ketone [17.8 (MPa)$^{1/2}$] | 0.667 | 0.333 | 0.581 |
| ENR 48 | Cyclohexane [16.8 (MPa)$^{1/2}$] | 0.525 | 0.475 | 0.715 |
| | Methyl isobutyl ketone [17.2 (MPa)$^{1/2}$] | 0.788 | 0.212 | 0.448 |
| | Butyl acetate [17.4 (MPa)$^{1/2}$] | 0.789 | 0.211 | 0.422 |
| | Toluene [18.2 (MPa)$^{1/2}$] | 0.830 | 0.170 | 0.376 |
| | Ethyl acetate [18.6 (MPa)$^{1/2}$] | 0.753 | 0.247 | 0.498 |
| | Methyl ethyl ketone [19.0 (MPa)$^{1/2}$] | 0.770 | 0.230 | 0.513 |
| ENR 71 | Butyl acetate [17.4 (MPa)$^{1/2}$] | 0.815 | 0.185 | 0.424 |
| | Methyl propyl ketone [17.8 (MPa)$^{1/2}$] | 0.824 | 0.176 | 0.435 |
| | Methyl proprionate [18.2 (MPa)$^{1/2}$] | 0.806 | 0.194 | 0.477 |
| | Methyl ethyl ketone [19.0 (MPa)$^{1/2}$] | 0.808 | 0.192 | 0.480 |
| | Acetone [20.3 (MPa)$^{1/2}$] | 0.746 | 0.254 | 0.560 |
| | Methyl formate [20.8 (MPa)$^{1/2}$] | 0.755 | 0.245 | 0.558 |

Vs = Volume fraction of solvent
Vr = Volume fraction of rubber
χ = Solvent polymer interaction parameter
$^a$Solubility parameter of solvent$^2$

**Figure 2.25** Equilibrium swelling of NR, ENR, 26, ENR 48 and ENR 71 gum peroxide vulcanizates at 23 °C [39]

All the results are collected together in Figure 2.28 which plots solubility parameter against the extent of epoxidation of the rubber. A linear relationship was observed with the solubility parameter increasing with the level of epoxidation.

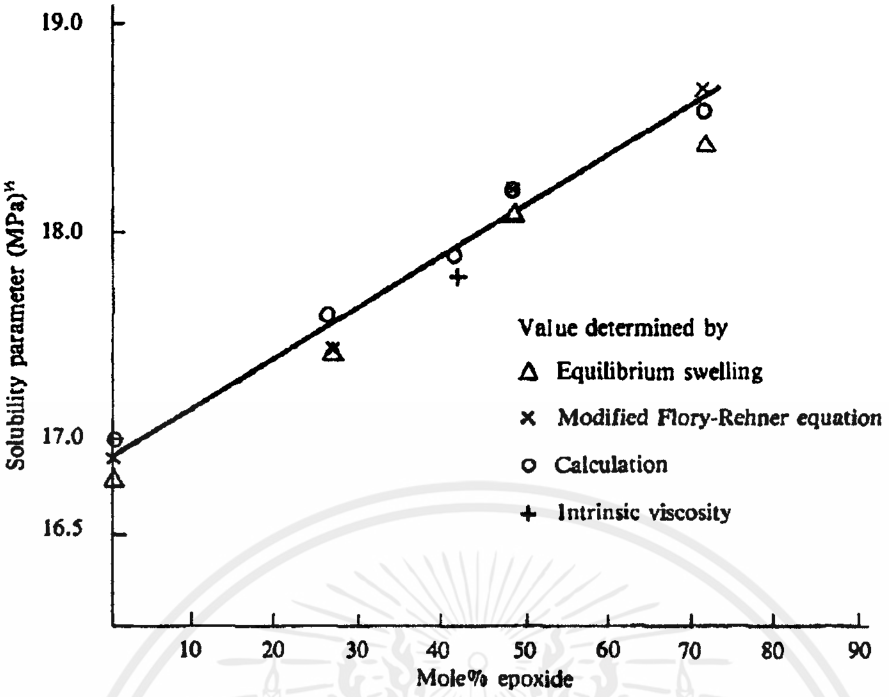


**Figure 2.26** Dependence of solubility parameters of ENR on epoxide content [39]

A number of ENR properties can be predicted from solubility parameter values, but this approach needs to be treated with care. For example, the adhesive strength between poly vinyl chloride (PVC) and ENR 50 is high and the two components have been shown to be completely compatible", only one glass transition temperature is observed intermediate between that of ENR 50 and PVC the solubility parameters of these materials are difference the adhesive strength between these two materials is only moderate and they are not compatible.

# Chapter 3

# Research methodology

Nowadays, there is no standard method to measure of pre-vulcanization of NBR latex compound in order to control maturation time of NBR latex compound. Premature or overmature can affect dramatically to production time and product quality. In this study, solvent coagulation and swelling test have been developed from previous work [3] and standard NR swelling method (chloroform number). After storing NBR latex compound at 0, 24 , 36, 48 and 72 hours, sample were prepared for solvent coagulation and solvent swelling test. Moreover, another study was carried out, i.e., properties of NR latex , correlation between NR latex properties and gloves defects in actual gloves production . This work can be divided into 2 parts :

- **Part 1 Developed method of testing pre-vulcanization for NBR latex**
- **Part 2 Studying of properties of NR latex affecting glove defects**

## 3.1 Chemicals and Materials

1. NBR latex compound, Ansell (Thailand) Co., Ltd.
2. NR latex compound, Ansell (Thailand) Co., Ltd.
3. Calcium nitrate pellet ($Ca(NO_3)_2$), Ansell (Thailand) Co., Ltd.
4. Chloroform, RCI Labscan Ltd.
5. Cyclohexanone, RCI Labscan Ltd.
6. Toluene, RCI Labscan Ltd.
7. Methyl Ethyl Ketone (MEK), RCI Labscan Ltd.
8. Coagulant solution, Ansell (Thailand) Co., Ltd.
9. Distillation water

## 3.2 Equipment

1. Glassware
2. Micro pipette
3. Desiccator
4. Gang stirrer
5. Oven; model Series FD, Binder Co., Ltd.
6. Distillation water bottle
7. Hot plate; Corning Co., Ltd.
8. Water bath
9. Ceramic plates 22×5 cm$^2$
10. Weight scales; Mettler Toledo: AB204
11. Brookfield viscometer; Model: LVDV2 AMETEK Brookfield
12. pH meter; Orian™ Star: A111
13. Mesh (200 mesh)
14. Stopwatch
15. Digital ; Sylvac Co., Ltd.
16. Thermogravimetric Analyzer; Perkin Elmer Co., Ltd.

## 3.3 Preparation

### 3.3.1 Developed method of solvent-coagulation test for NBR latex

#### 3.3.1.1 Solvent for testing pre-vulcanization for NBR latex

First, cyclohexanone was poured 100 mL into beaker 250 mL. chloroform was poured 50 mL into beaker 100 mL. Then, mixed solvent of cyclohexanone and chloroform were prepared in different ratios as shown in Table 3.1 Finally, mixed solvent was stired with glass rod until homogeneous.

**Table 3.1** Preparation of mixed solvents of cyclohexanone and chloroform (by volume)

| Cyclohexanone | Chloroform (mL) |
|---|---|
| 15.00 | 0.00 |
| 14.25 | 0.75 |
| 13.50 | 1.50 |
| 12.75 | 2.25 |
| 12.00 | 3.00 |
| 0.00 | 15.00 |

#### 3.3.1.2 Solvent for swelling test

First, cyclohexanone was poured 100 mL into beaker 250 mL. toluene was poured 100 mL into beaker 250 mL. Then, cyclohexanone was used 30 mL and toluene was used 40 mL. Finally, mixed solvent was stired with glass rod until homogeneous.

### 3.3.2 Studying of properties of NR latex affecting glove defects

#### 3.3.2.1 Solution for latex stability of compounded latex

First, calcium nitrate pellet was weighed 50 g. Then, calcium nitrate pellet was slowly added into distilled water 500 mL. Finally, solution was stired with glass rod until homogenous.

## 3.4 Experiment

### 3.4.1 Developed method of solvent-coagulation test for NBR latex

#### 3.4.1.1 pre-vulcanization of NBR latex compound with mixed solvent

First, NBR latex compound was poured 10 mL into beakers. Then, mixed solvent (cyclohexanone/chloroform) was poured 15 mL into NBR latex compound. It was stired with glass rod until change to coagulum completely. Start timer 2 minute then pick up coagulum on hand.  Finailly, coagulum was drawn out with constant speed and observe length.

### 3.4.1.2 Pre-vulcanization of NBR latex compound with optional solvent

First, NBR latex compound was poured 10 mL into beakers. Then, mixed solvent (cyclohexanone : chloroform) was poured 15 mL into NBR latex compound. It was stired with glass rod until change to coagulum completely. Start timer 2 minute then pick up coagulum on hand.Finally, coagulum drawn out with constant speed and observe length.

### 3.4.1.3 Solvent swelling test

Determination of swelling index involved the immersion of latex film in mixed solvent (toluene: chloroform, 3:2 by volume). First, 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 15 seconds. The wet films were allowed to dry in an oven as shown in Table 3.2.

**Table 3.2** Temperature and time for drying latex film

| Temperature (C°) | Time (minutes) |
|---|---|
| 80 | 10 |
| 90 | 10 |
| 100 | 10 |
| 110 | 10 |

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, placed the sample on graph paper to recording the swollen latex sample size. The swollen sample was calculated the percentage of swell index from equation below:

$$\text{\% Total swelling index (\%TSI)} = \frac{(W_s - W_d)}{W_d \times 100}$$

When $W_d$ = Weight of polymer

$W_s$ = weight of swollen polymer

#### 3.4.1.4 Thermogravimetric analysis (TGA)

Thermogravimetric analyzer is used to measure the amount of weight change of a material and decomposition reactions, which often allows quantitative composition analysis. in an atmosphere of nitrogen, helium, air, other gas, or in vacuum. The thermogravimetric analysis conditions are as follows:

| | |
|---|---|
| Temperature | 35 °C – 800 °C |
| Heating rate | 10 °C/min. |
| Atmosphere | Nitrogen ($N_2$) |

### 3.4.2 Studying of properties of NR latex affecting glove defects

#### 3.4.2.1 Determination of total solid content

Firstly, weight dish and record as $W_1$. Then, pour sample into dish 1.5-2.5 g and record as $W_2$. Gently swirl the contents of dish to ensure that sample covers the bottom. Place the dish in an oven at 110 °C for 1 hour and cool in a desiccator for 10 minutes. Weighing the dish and record as $W_3$. Finally, calculate %Total solid content from equation below:

$$\%\text{Total solid content (\%TSC)} = \frac{(W_3 - W_1) \times 100}{W_2}$$

When $W_1$ is the mass of dish (in grams)

$W_2$ is the mass of sample before oven in wet (in grams)

$W_3$ is the mass of the dried sample and dish (in grams)

#### 3.4.2.2 Determination of viscosity

First, compound latex was poured into beaker 500 mL. Then, Brookfield was set spindle number LV-02 and speed 60 RPM. Subsequently, sample was tested by place into Brookfield, after that setting spindle to prevent bubble effect. Finally, viscosity was taken reading at 1 minute and record viscosity value.

### 3.4.2.3 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.

### 3.4.2.4 Determination of latex stability of compound latex

Compound latex was weighted out 20 g of into a 100 ml beaker. Latex was slowly stired with a glass rod and add calcium nitrate drop-wise from a burette. Coagulums was appeared by using the glass rod, hold the coagulums onto the side of the beaker so as to allow excess latex to back into beaker. Coagulums was removed from beaker and was squeezed coagulums with the fingers. Calcium nitrate was repeated the subsequent steps until all the latex has been coagulated. Finally, volume was recorded.

### 3.4.2.5 Vary %TSC of NR latex

First, Latex 400 mL was prepared in 5 beakers. Distillation water was added as shown in Table 3.3. Then, it was stired with magnetic bar for 10 minutes. Finally, it was checked %TSC below 3.4.2.1

**Table 3.3** Volume of distillation water add in NR latex

| Beaker No. | Volume of distillation water (mL) |
|---|---|
| 1 | - |
| 2 | 20 |
| 3 | 40 |
| 4 | 80 |
| 5 | 160 |

### 3.4.2.6 Determination of defects

Each of production batch had gloves 3500 pieces and randomly 200 pieces is according to Acceptable Quality Level 1.0 (AQL 1.0). Finally, defect was recorded (repeat 30 batch).

### 3.4.2.7 Determination of thickness

Each of production batch had gloves 3500 pieces and randomly 200 pieces is according to Acceptable Quality Level 1.0 (AQL 1.0). Then, thickness was measured amount 3 positions and averaged. Finally, thickness was recorded (repeat 30 batch).

# Chapter 4

# Results and discussion

This research can be divided into two parts. In the first part: NBR latex compound has no method to control optimum point of maturation, so that needs to find a test method to determined ionic crosslink density. Therefore, solvent-coagulation test was used by adapted form chloroform number test in NR latex. In addition, the result of this method would be compared with solvent swelling method.

In second part: quality of gloves depends on properties of latex such as total solid content (%TSC), viscosity, latex stability and pH. It is necessary to control those factors in an appropriate range in order to control properties of gloves such as weakness and thickness. Therefore, relationships between %TSC, viscosity, pH and latex stability which inturn affecting glove defects were studied. This understanding can help glove manufacturers control their process and minimize NC poducts.

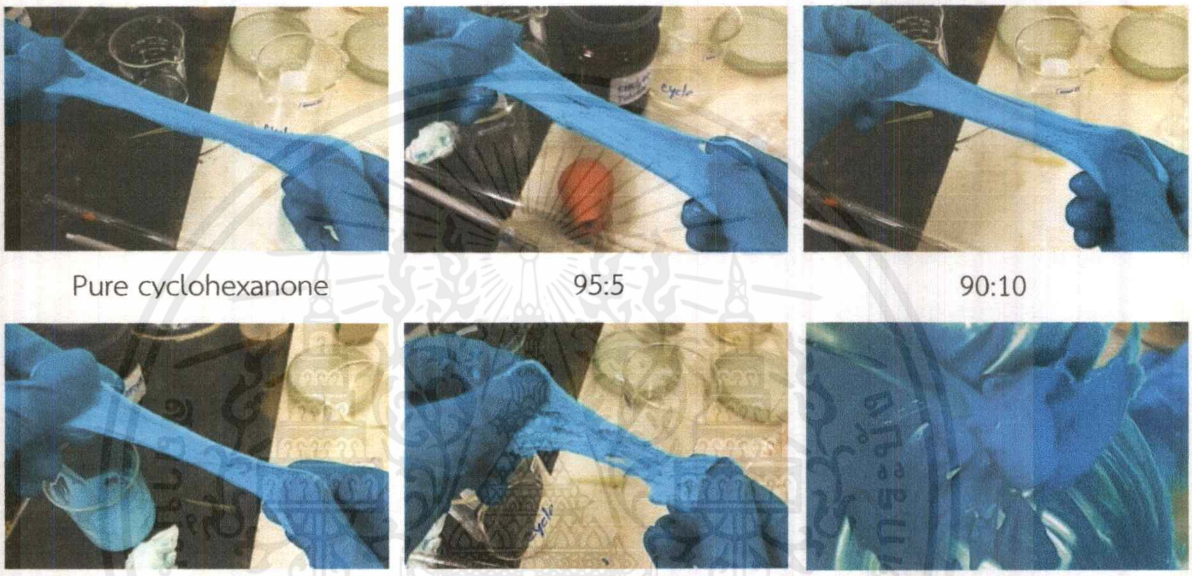
## 4.1 Developed method of solvent-coagulation test for NBR latex

In previous research of K. Siri, [3] maturation and stabilizers of NBR latex on properties of NBR gloves were studied. According to solvent-coagulation test in NR latex compounds, chloroform was used as solvent for coagulation. Since NBR rubber has different polarity compared to NR rubber solubility parameters of these rubbers are different. Therefore, cyclohexanone was used with NBR instead of chloroform. However, this solvent was not particularly adaptable for comparing with dis-similar compounds.

In this work, pure chloroform, pure cyclohexanone and mixed solvents were studied in order to find appropriate solvents to set up test method for determining maturation state of NBR latex.

### 4.1.1 Mixed solvent of chloroform and cyclohexanone

In order to develop the test, chloroform and cyclohexanone were mixed together in different ratios by volume. The ratios of the study included: pure cyclohexanone, cyclohexanone : chloroform (95:5, 90:10, 85:15, 80:20) and pure chloroform. These ratios are tested with NBR latex compound at 24 hr maturation time. The coagulation of latex as shown in Figure 4.1.



Pure cyclohexanone 95:5 90:10

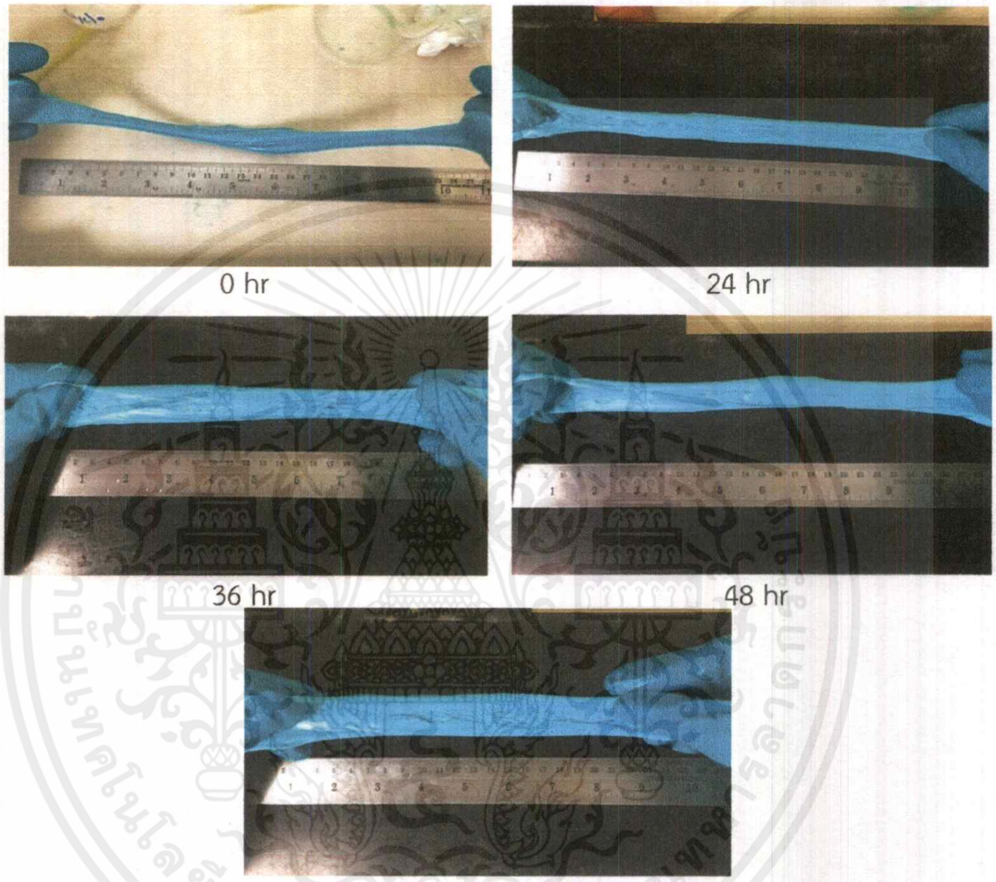
85:15 80:20 Pure Chloroform

**Figure 4.1** Coagulums of NBR latex compound by using different ratios of cyclohexanone and chloroform at 24 hr maturation time

As seen in Figure 4.1, the solidification state of coagulum at 24 hr maturation time was affected by using different ratios of the mixed solvent. It was found that when the pure cyclohexanone was used the coagulum became rigid and could not be stretched. On the other hand, the coagulum became creamy and did not form solid. This could be explained by solubility parameter of chloroform (18.7 $MPa^{1/2}$) and NBR (20.26 – 21.10 $MPa^{1/2}$) as shown in Appendix D. At the ratio 95:5 appearance of coagulum was not homogeneous and too brittle when it was stretched. As the chloroform ratios were increased, the coagulum became weak lump and difficult to stretch. A suitable ratio of cyclohexanone and chloroform mixed solvent was 90:10 since homogeneous and stretchable coagulum was found.

### 4.1.2 Suitable ratio of mixed solvent with different maturation times

Next, the suitable ratio (90:10) of the mixed solvent was used to test for NBR pre-vulcanization state at different maturation times. Solidified states of NBR coagulums at different maturation times were shown in Figure 4.2.



0 hr

24 hr

36 hr

48 hr

72 hr

**Figure 4.2** Coagulums of NBR latex compound by using mixed solvent of cyclohexanone and chloroform (90:10) at different maturation times

As seen in Figure 4.2, a ruler was used to measure stretch ability of the coagulums. Homogeneity of solidified coagulum was decreased when maturation time was increased. It was found that weak lump at 0 hr could not be measured by the ruler due to sagging. As the maturation time was increased, coagulum became less flexibility and %elongation decreased. However, appearances and %elongation of NBR coagulums at 24-72 hr were significantly different.

### 4.1.3 Alternative solvent with different maturation times

As shown previously the mixed solvent (chloroform and cyclohexanone) could not be used to differentiate between different maturation states of NBR latex . In this part, a new appropriate solvent was studied. The difference in solubility parameter between NBR latex and solvent shall be more than 1 MPa$^{1/2}$ and shall not be totally different. Many solvents have been tried e.g., isopropanol and propanone but the coagulum became creamy and did not form to solid. It was found that methyl ethyl ketone (MEK) could be to form a homogeneous and stretchable. In addition, toxicity of MEK is less than that of chloroform and cyclohexanone.

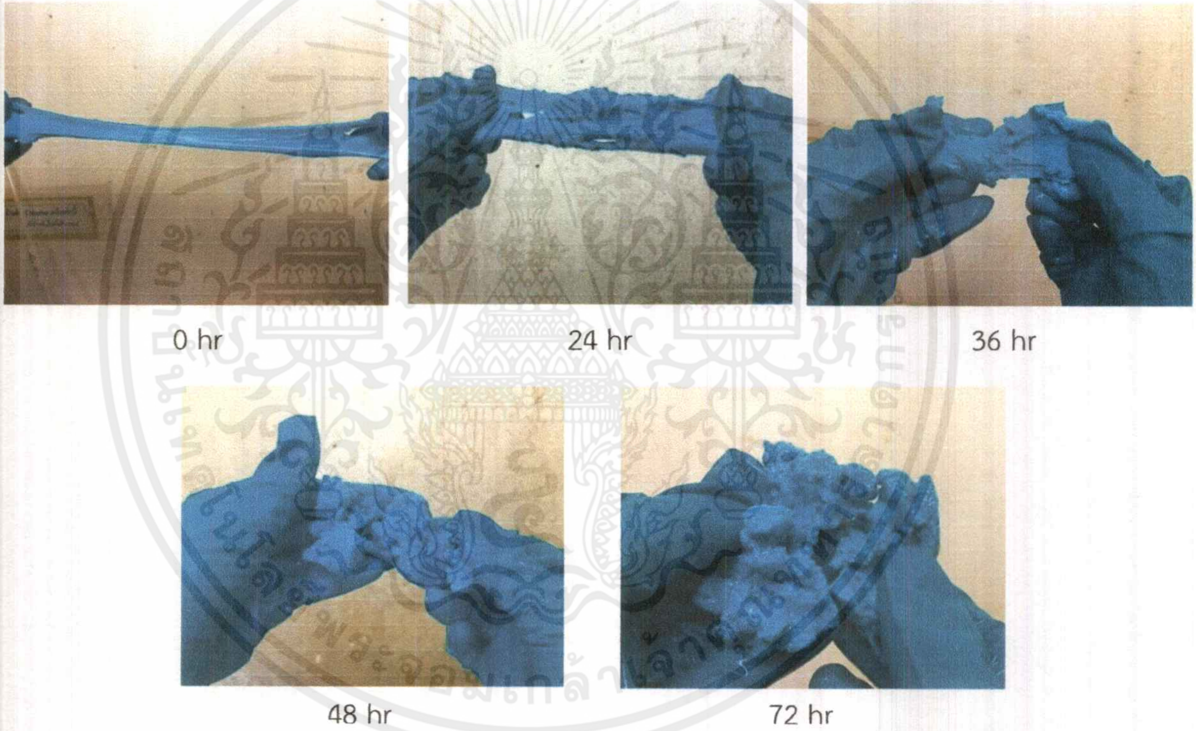

0 hr
24 hr
36 hr
48 hr
72 hr

**Figure 4.3** Coagulums of NBR latex compound at different maturation times (0 to 72 hr) when MEK was used as the solvent

As seen in Figure 4.3, different solidification states of coagulum at different maturation times can be seen. When maturation time was increased, coagulums became less homogeneous and more rigid. Moreover, after 36 hr the coagulum became crumbly and brittle. Rigidity of the coagulum might be derived from the increased degree of crosslinked rubber molecules when maturation time was increased. Similar to chloroform number for testing of maturation state of NR latex, MEK can be used to test for NBR latex as well. When MEK was used, the level of pre-vulcanized of NBR latex can be classified as:

At 0 hr maturation time comparable to level 1
At 24 hr maturation time comparable to level 2
At 36 to 48 hr maturation time comparable to level 3
At 72 hr maturation time comparable to level 4

In conclusion, suitable level of NBR maturation could be level 2-3. In the glove production line, more time (4-6 hr) is needed to fill up latex and additions in storage tank to dipping tank.

Nevertheless, solvent-coagulation method can be used to test the level of maturation however the method is a qualitative assessment. Another method could be used to confirm, e.g., solvent swelling method.

### 4.1.4 Solvent swelling method

Solvent swelling method can be used to test simultaneously with solvent coagulation method in order to confirm accuracy of measurement. The result of solvent swelling method can be analyzed by Minitab® software. Swelling in solvent is usually reported in form of percent of total swelling index (%TSI). %TSI can be used to indicate ionic crosslink density in pre-vulcanized NBR latex. Ionic crosslinks can occur between carboxyl groups in alkaline condition. Zinc oxide and zinc complex in accelerator can be ionized into zinc ions through ionization reaction. After that ionic bonds can be created between carbonyl groups in NBR moleculs as shown in Figure 4.4.

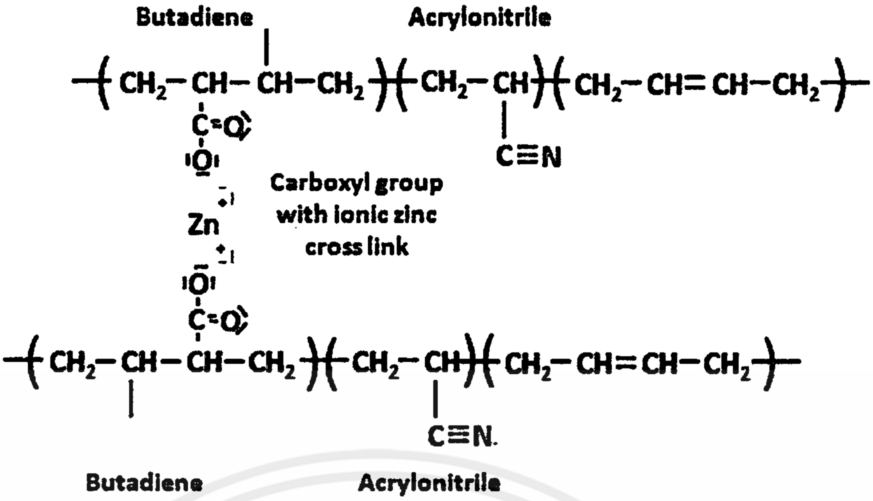


**Figure 4.4** Formation of ionic crosslink [40]

Pre-vulcanization can occur in 2 phenomena:

First phenomenon, is called "diffusion phenomenon". NBR latex created by emulsion polymerization has micelle molecules In sulfur vulcanization, 3 compositions, e.g., vulcanizing agent, activator and accelerator are needed. In maturation state activator (ZnO) and accelerator (ZDBC) can be easily ionized into ions by alkaline condition (KOH). In the form of ions, it can easily diffuse into rubber molecules pass through micelle particles. In general, sulfur cannot create at room temperature. But sulfur molecules can absorb on surface of micelles as shown in Figure 4.5. Crosslink density in rubber molecules increases after the sulfur and the $Zn^{2+}$ ions are slowly diffused into rubber molecules and reacted as shown in Figure 4.6.

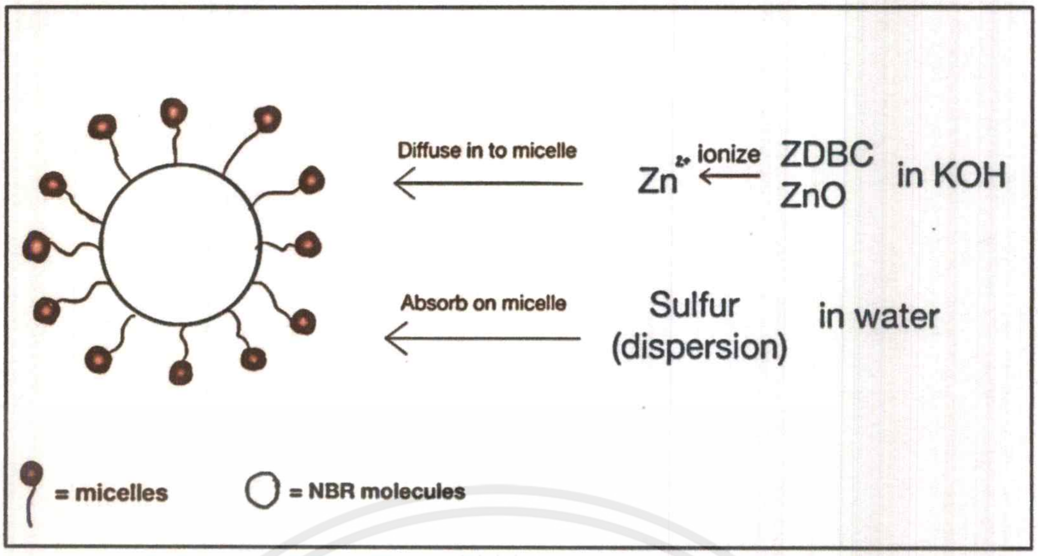


**Figure 4.5** Proposed model diffusion phenomena in prevulcanized latex

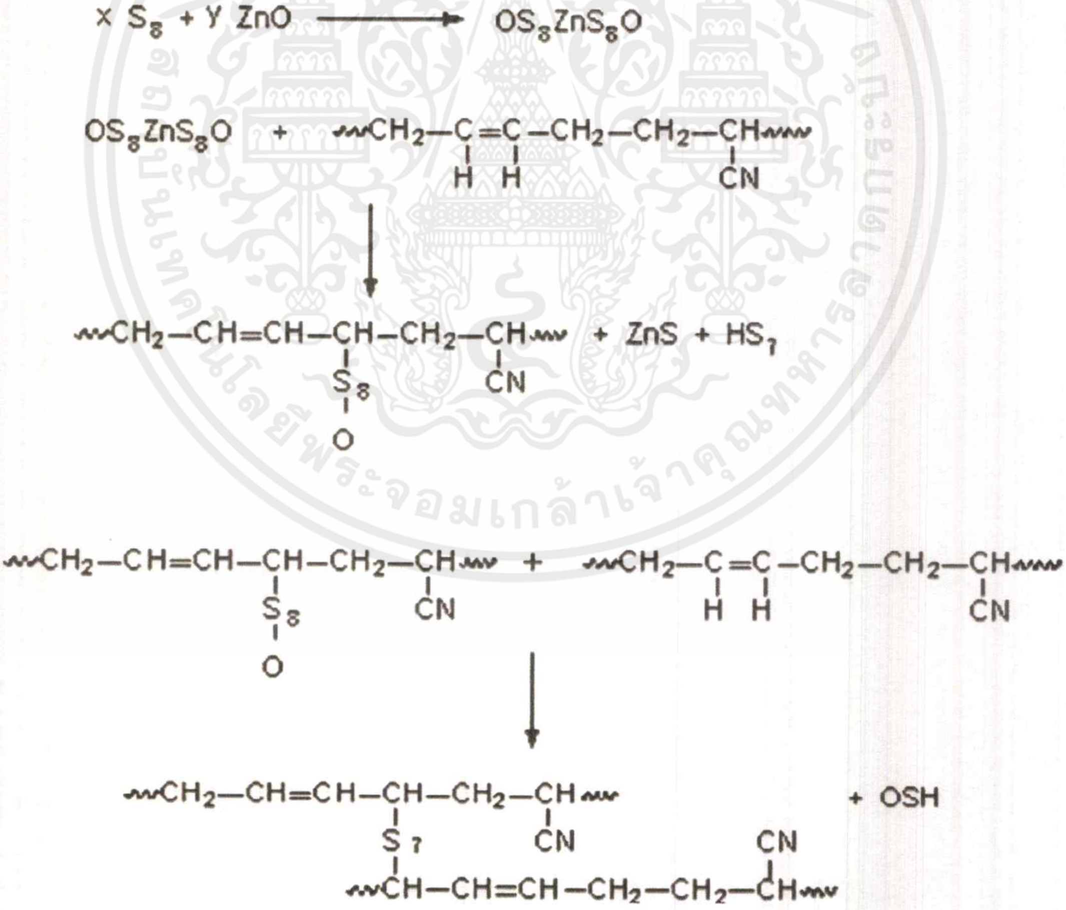


**Figure 4.6** Mechanism of zinc catalyzed in sulfur vulcanization [24]

Second phenomenon is called “swelling phenomenon”. NBR latex can be slowly vulcanized and three-dimension network is generated slowly according to diffusion rate of sulfur and zinc ions. Free volume of NBR and distances between crosslinking points in the network are decreased by increasing crosslink density. Therefore, solvent molecules cannot penetrate into free volume in rubber molecules as shown in Figure 4.7.

**Figure 4.7** Increased crosslink density when maturation time was increased

Some factors can affect solvent swelling method, e.g., latex maturation time and temperature to dry samples. Since solvent swelling method need solid rubber samples, drying of rubber latex to form the samples is required. However, drying state with different water content might result in errors of solvent swelling test. Samples should be prepared with minimum residual water.

The first factor, maturation time: compatibility of chemicals in latex was better when increase maturation time. Three-dimension network was slowly occurred as referred to Figures 4.6 and 4.7. That why solvent molecules cannot penetrate into gap between rubber molecules. Swelling in solvent was decreased when maturation time was increased as shown in Figure 4.8.

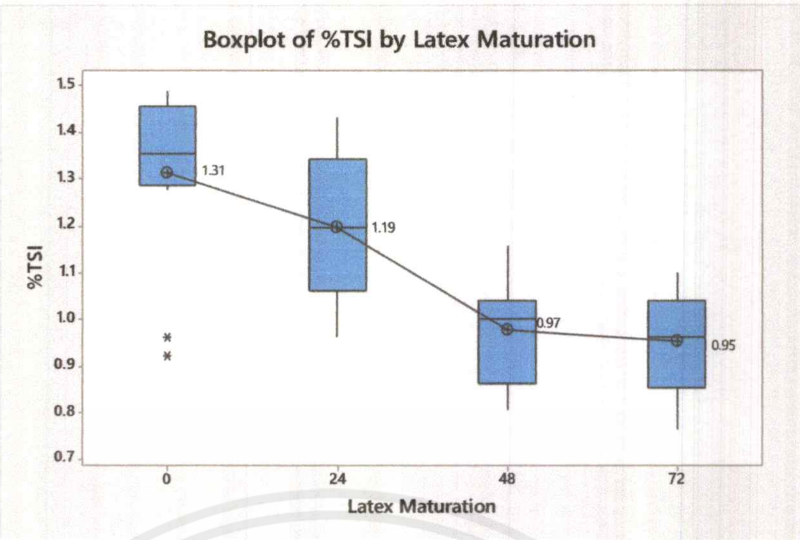


**Figure 4.8** Effect of latex maturation time to swell in solvent

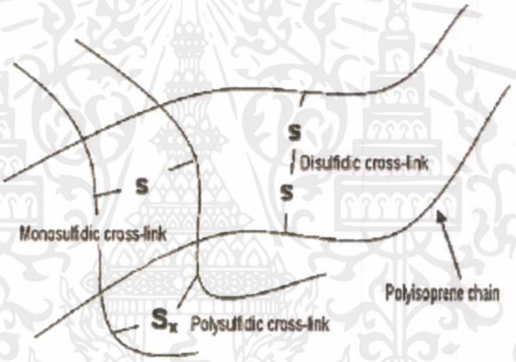


**Figure 4.9** Structure of vulcanized rubber [22]

The second factor, temperature for drying samples, can directly affect to vulcanization reaction. In Figure 4.10, %TSI was decreased by increasing temperature. When a high temperature was used, accelerators and activators can react with sulfur to form active sulfurating agents. The active sulfurating agents can react to rubber molecules and created monosulfidic or polysulfidic linkages referred to Figure 4.9. Therefore, vulcanization was accelerated and generated crosslinking network. As mentioned previously, solvent swelling test could be disturbed by water molecule 80-110 °C drying temperatures (for 10 min) were used to prepare the samples.

It was found that %TSI of NBR samples was decreased as the temperature was increased. At a high temperature, e.g., 110°C, extra crosslinking in sample drying process could be occurred yielding a sharp decrease in %TSI. However, at a lower temperature, e.g., 80°C, large amount of water might remain inside rubber samples resulting in high %TSI. Therefore, an appropriate drying temperature should be 90-100°C resulting in 0.97-1.19 %TSI which is an optimum point for maturation.

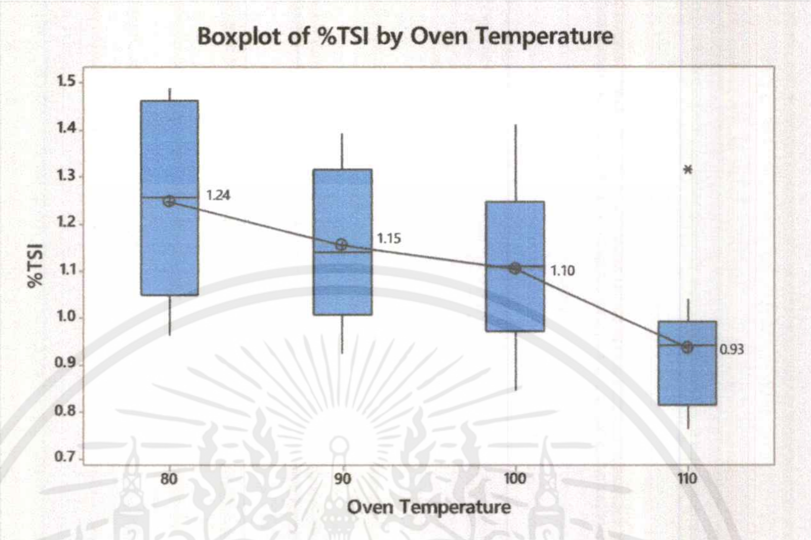


**Figure 4.10** Effect of oven temperature to swell in solvent

T-statistic is the ratio of the departure of the estimated value of a parameter from its hypothesized value to its standard error. It is used in hypothesis testing via Student's t-test. For example, it is used in estimating the population mean from a sampling distribution of sample means if the population standard deviation is unknown. [30]

The Pareto chart shows that the absolute values of the standardized effects from the largest effect to the smallest effect. The standardized effects are t-statistics that test the null hypothesis that the effect is 0. The chart also plots a reference line to indicate which effects are statistically significant. The reference line for statistical significance depends on the significance level (α or alpha). [31]

Analyzing of factor has affected to swelling in solvent by use Pareto chart found that in Figure 4.11, the effects to compare the relative magnitude and the statistical significance of both main and interaction effects. The largest effect is latex maturation time (B) because it extends the farthest. The smaller effect is oven temperature (A). However, both factors are significant effects to %TSI.

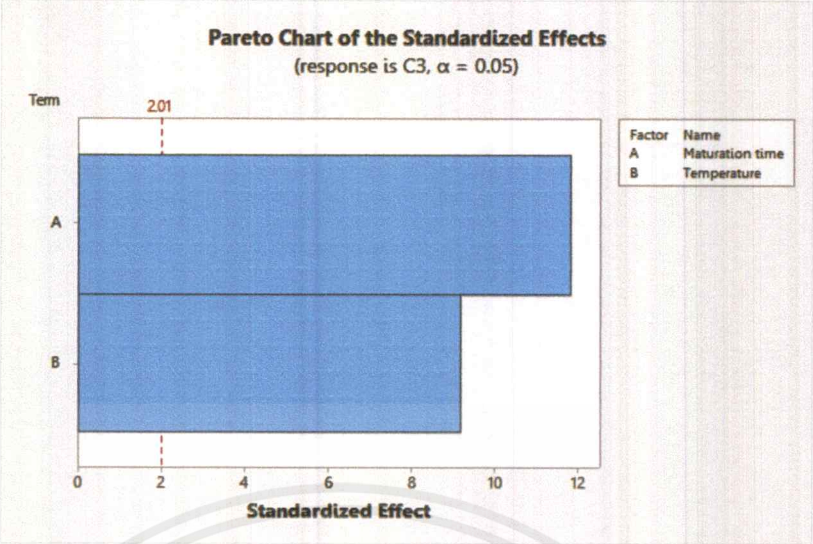


**Figure 4.11** Statistical result of standardized effect was analyzed by Minitab®

In conclusion, solvent swelling method can used with compound latex to find suitable pre – vulcanized and indicate crosslink density of ionic crosslink. Effect of maturation time and temperature for dry sample have a same trend. Appropriate maturation is 24-48 hour because after 48 hour %TSI is almost unchanged and base on solvent coagulation test. The temperature of 90 - 100 °C is suitable for dry samples with %TSI value of between 0.97% - 1.19%.

## 4.2 Studying of properties of NR latex affecting glove defects

Quality control (QC) of gloves has been concerned in glove manufacturing companies. In glove industries was used Acceptance Quality Limits (AQLs) are used defined as the "quality level that is the worst tolerable" in ISO 2859-1. They represent the maximum numbers of defective units, beyond which a batch is rejected. Importers usually set different AQLs for critical, major, and minor defects. Most Asian exporters are familiar with this type of setting. For example: "AQL is 1.5%" means "no more than 1.5% defective items in the whole order quantity, on average over several production runs with that supplier". [41]

In certain product categories, there will be defective products in virtually every production batch. It is often true even after manufacturers have checked each individual product and repaired the defective ones since the visual inspection is not 100% reliable. Therefore, in many supplier/buyer relationships (particularly when the application does not result in life or death outcomes), the supplier is not expected to deliver defect-free goods. The buyer needs to control the quality of purchased goods since he does not want too many defects. [41]

Before using the AQL tables, you should know three parameters:

1. Lot size

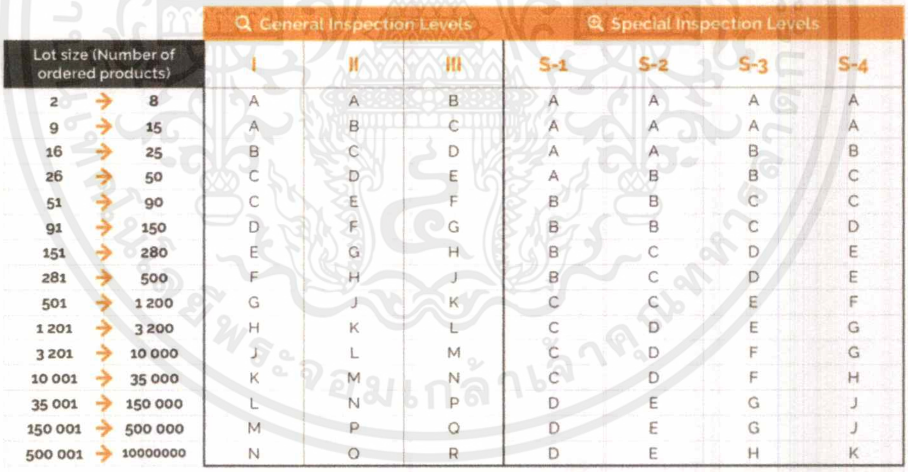
If supplier ordered different products, consider each product as a separate lot. (The quantity of each product is the lot size). If supplier ordered only one product, the lot size is the total batch quantity.

2. Inspection level

Different inspection levels will command different numbers of samples to inspect. In this article, so-called "level II" under "normal severity" and to single sampling plans.

3. AQL limits

The AQL limits appropriate for market. If customers accept very few defects, manufacturer might want to set a lower AQL for both major and minor defects.

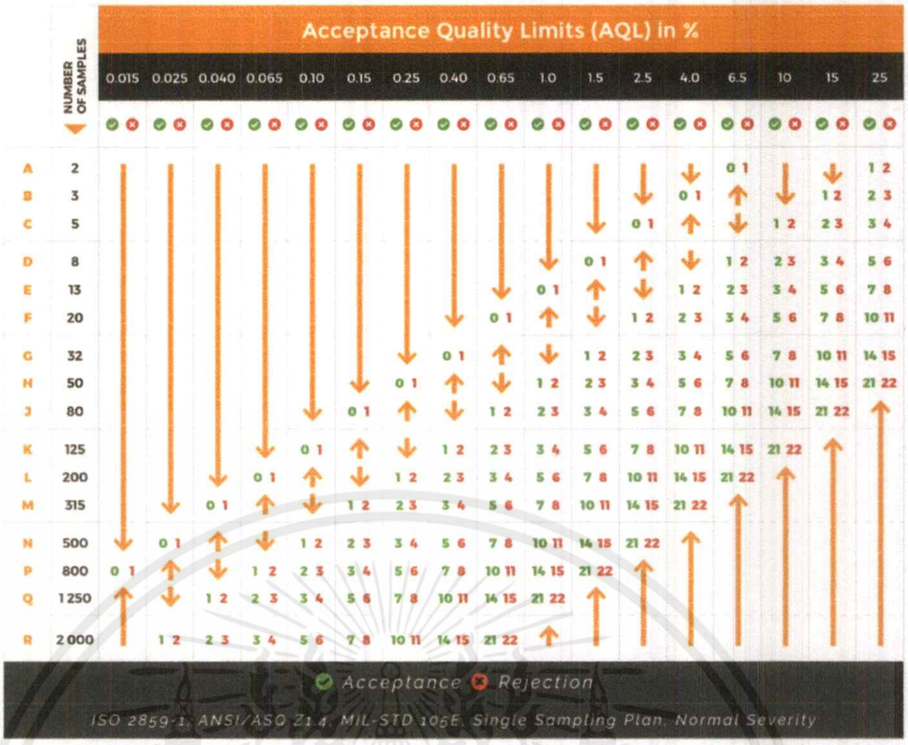


| | General Inspection Levels | | | Special Inspection Levels | | | |
|---|---|---|---|---|---|---|---|
| Lot size (Number of ordered products) | I | II | III | S-1 | S-2 | S-3 | S-4 |
| 2 → 8 | A | A | B | A | A | A | A |
| 9 → 15 | A | B | C | A | A | A | A |
| 16 → 25 | B | C | D | A | A | B | B |
| 26 → 50 | C | D | E | A | B | B | C |
| 51 → 90 | C | E | F | B | B | C | C |
| 91 → 150 | D | F | G | B | B | C | D |
| 151 → 280 | E | G | H | B | C | D | E |
| 281 → 500 | F | H | J | B | C | D | E |
| 501 → 1 200 | G | J | K | C | C | E | F |
| 1 201 → 3 200 | H | K | L | C | D | E | G |
| 3 201 → 10 000 | J | L | M | C | D | F | G |
| 10 001 → 35 000 | K | M | N | C | D | F | H |
| 35 001 → 150 000 | L | N | P | D | E | G | J |
| 150 001 → 500 000 | M | P | Q | D | E | G | J |
| 500 001 → 10000000 | N | O | R | D | E | H | K |

*ISO 2859-1. ANSI/ASQ Z1.4. MIL-STD 105E. Single Sampling Plan*

**Figure 4.12** Sample size code letters [42]

If manufacturers follow the example, it assumes that 'lot size' is comprised between 3,201 pcs and 10,000 pcs, and that inspection level is 'II'. Consequently, the code letter is "L".



Acceptance Quality Limits (AQL) in %

|  | NUMBER OF SAMPLES | 0.015 | 0.025 | 0.040 | 0.065 | 0.10 | 0.15 | 0.25 | 0.40 | 0.65 | 1.0 | 1.5 | 2.5 | 4.0 | 6.5 | 10 | 15 | 25 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
|  |  | ✓ ✗ | ✓ ✗ | ✓ ✗ | ✓ ✗ | ✓ ✗ | ✓ ✗ | ✓ ✗ | ✓ ✗ | ✓ ✗ | ✓ ✗ | ✓ ✗ | ✓ ✗ | ✓ ✗ | ✓ ✗ | ✓ ✗ | ✓ ✗ | ✓ ✗ |
| A | 2 | ↓ | ↓ | ↓ | ↓ | ↓ | ↓ | ↓ | ↓ | ↓ | ↓ | ↓ | ↓ | ↓ | 0 1 | ↓ | ↓ | 1 2 |
| B | 3 | ↓ | ↓ | ↓ | ↓ | ↓ | ↓ | ↓ | ↓ | ↓ | ↓ | ↓ | ↓ | 0 1 | ↑ | ↓ | 1 2 | 2 3 |
| C | 5 | ↓ | ↓ | ↓ | ↓ | ↓ | ↓ | ↓ | ↓ | ↓ | ↓ | ↓ | 0 1 | ↑ | ↓ | 1 2 | 2 3 | 3 4 |
| D | 8 | ↓ | ↓ | ↓ | ↓ | ↓ | ↓ | ↓ | ↓ | ↓ | ↓ | 0 1 | ↑ | ↓ | 1 2 | 2 3 | 3 4 | 5 6 |
| E | 13 | ↓ | ↓ | ↓ | ↓ | ↓ | ↓ | ↓ | ↓ | ↓ | 0 1 | ↑ | ↓ | 1 2 | 2 3 | 3 4 | 5 6 | 7 8 |
| F | 20 | ↓ | ↓ | ↓ | ↓ | ↓ | ↓ | ↓ | ↓ | 0 1 | ↑ | ↓ | 1 2 | 2 3 | 3 4 | 5 6 | 7 8 | 10 11 |
| G | 32 | ↓ | ↓ | ↓ | ↓ | ↓ | ↓ | ↓ | 0 1 | ↑ | ↓ | 1 2 | 2 3 | 3 4 | 5 6 | 7 8 | 10 11 | 14 15 |
| H | 50 | ↓ | ↓ | ↓ | ↓ | ↓ | ↓ | 0 1 | ↑ | ↓ | 1 2 | 2 3 | 3 4 | 5 6 | 7 8 | 10 11 | 14 15 | 21 22 |
| J | 80 | ↓ | ↓ | ↓ | ↓ | ↓ | 0 1 | ↑ | ↓ | 1 2 | 2 3 | 3 4 | 5 6 | 7 8 | 10 11 | 14 15 | 21 22 | ↑ |
| K | 125 | ↓ | ↓ | ↓ | ↓ | 0 1 | ↑ | ↓ | 1 2 | 2 3 | 3 4 | 5 6 | 7 8 | 10 11 | 14 15 | 21 22 | ↑ | ↑ |
| L | 200 | ↓ | ↓ | ↓ | 0 1 | ↑ | ↓ | 1 2 | 2 3 | 3 4 | 5 6 | 7 8 | 10 11 | 14 15 | 21 22 | ↑ | ↑ | ↑ |
| M | 315 | ↓ | ↓ | 0 1 | ↑ | ↓ | 1 2 | 2 3 | 3 4 | 5 6 | 7 8 | 10 11 | 14 15 | 21 22 | ↑ | ↑ | ↑ | ↑ |
| N | 500 | ↓ | 0 1 | ↑ | ↓ | 1 2 | 2 3 | 3 4 | 5 6 | 7 8 | 10 11 | 14 15 | 21 22 | ↑ | ↑ | ↑ | ↑ | ↑ |
| P | 800 | 0 1 | ↑ | ↓ | 1 2 | 2 3 | 3 4 | 5 6 | 7 8 | 10 11 | 14 15 | 21 22 | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ |
| Q | 1 250 | ↑ | ↓ | 1 2 | 2 3 | 3 4 | 5 6 | 7 8 | 10 11 | 14 15 | 21 22 | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ |
| R | 2 000 | ↑ | 1 2 | 2 3 | 3 4 | 5 6 | 7 8 | 10 11 | 14 15 | 21 22 | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ |

✓ Acceptance ✗ Rejection

ISO 2859-1, ANSI/ASQ Z1.4, MIL-STD 105E, Single Sampling Plan, Normal Severity

**Figure 4.13** Single sampling plans for level II inspection [42]

How to read this table?

Code letter is "L", so inspectors will have to draw 200 pcs randomly from the total lot size. Besides, it assumes inspectors have set AQL at 2.5% for major defects and 4.0% for minor defects. Therefore, here are the limits: the products are accepted if No more than 10 products with major defects and No more than 14 products with minor defects are found. For example, if inspectors find 15 products with major defects and 12 products with minor defects, the products are refused. If inspectors find 3 with major defects and 7 with minor defects, they are accepted. [41]

In this study, latex properties that effect to defects on gloves (AQLs) were studied for correlation. In Figure 4.14 when decrease %TSC that effect to viscosity and latex stability decrease but pH constant. Different %TSC (30 – 47%) of NR latex were studied for latex properties, i.e., viscosity, latex stability and pH as shown in Figure 4.14. It was found that viscosity and latex stability were decreased as %TSC were decreased. However, pH of latex was unchanged.

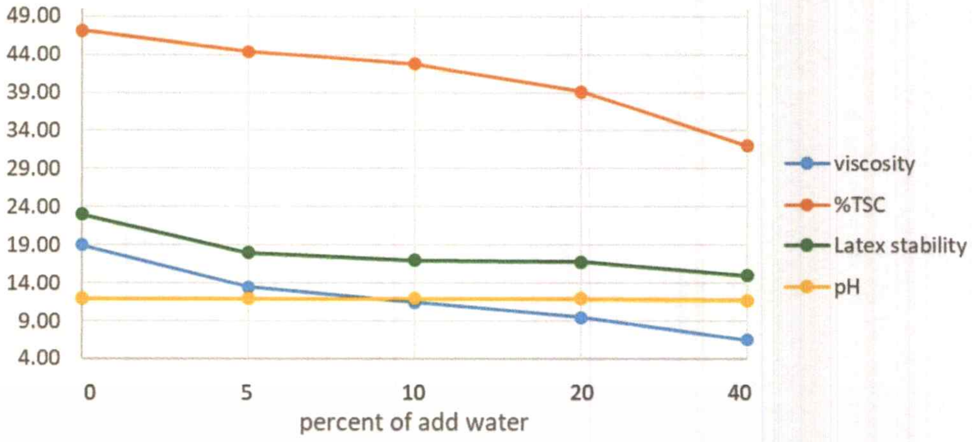


**Figure 4.14** Relationship of latex properties

This can be explained by dilution effect. The lower %TSC, the more the solvent (water). Distance between micelles were increased resulting in less interaction between solid particles. Constant pH of latex compound might derive from KOH stabilizer acting as pH buffer. Latex stability can be tasted by Ca(NO$_3$) titration. Since lower %TSC yielded less concentration latex, less negative charges of protein in NR latex were expected. Less amount of Ca$^{2+}$ ions were needed. Next, real data of latex stability vs. number of defects were collected for 30 batches in the glove manufacturing process. However, no correlation of the stability and numberof defected was seen as shown in Figure 4.15.

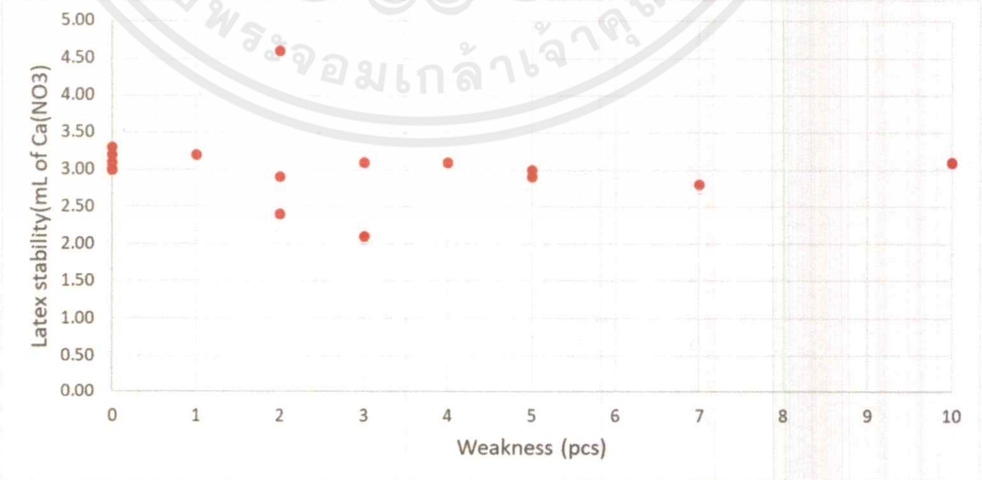


**Figure 4.15** Relationship between latex stability and weakness on glove

Sagging is a behavior of polymers. In Figure 4.16, it was found that glove thickness was increased when %TSC was increased. The more the %TSC, the higher the viscosity. This resulted in more solid rubber particles picked up in the dipping process

From Figure 4.16, more defects were found at the lower %TSC. Lower viscosity resulted from lower %TSC which in-turn causing more sagging defects.

**Figure 4.16** Relationship between %TSC and weakness on glove

In conclusion, some relationships between latex properties were found in lab scale. However, there was no correlation between latex properties and gloves defects in actual glove manufacturing production line.

# Chapter 5

# Conclusion and Suggestion

This study was divided in two parts ,i.e., 1) developed method of testing pre-vulcanization for NBR latex 2) studying of properties of NR latex affecting glove defects. The results can be concluded as follow:

## 5.1 Conclusion

Part 1 NBR latex: In solvent-coagulation test, a suitable ratio of cyclohexanone and chloroform mixed solvent was 90:10 since homogenenouse and stretchable coagulum was found. However, appearances and %elongation of NBR coagulums at 24-72 hr were insignificantly different. It was found that methyl ethyl ketone (MEK) could be used to form a homogeneous and significantly different coagulums. Suitable level of NBR maturation could be level 2-3. In solvent swelling test, it was found that %TSI of NBR sample was decreased as the temperature was increased. An appropriate drying temperature should be 90-100 °C resulting in 0.97-1.19 %TSI which is an optimum point for maturation. In analyzing two factors affecting to swelling test by using Pareto chart, it was found that latex maturation time had more effect compare to temperature for drying samples.

Part 2 NR latex: Relationships of latex properties were found in lab scale. However, there was no correlation between latex properties and glove defects in actual glove manufacturing production line.

## 5.2 Suggestion

1. Solvent coaulation test for NBR latex was tested in normal condition. However, temperature of storage latex can be studied to find if ther is any effect to the test.

2. Natural rubber latex should be stimulating decrease %TSC. More work should be carried out in actual glove production line, e.g. , vary %TSC of NR latex compound in actual dipping process to see glove defects.

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# Appendices

# Appendix A

## MSDS of Chemical

**Classification of the substance or mixture**
**Classification according to Regulation (EC) No 1272/2008**
Acute toxicity, Oral (Category 4), H302
Acute toxicity, Inhalation (Category 3), H331
Skin irritation, (Category 2), H315
Eye irritation, (Category 2), H319
Carcinogenicity, (Category 2), H351
Reproductive toxicity, (Category 2), H361d
Specific Target Organ Toxicity (single exposure), (Category 3), H336
Specific Target Organ Toxicity (repeated exposure), (Category 1), H372
For the full text of the H-Statements mentioned in this Section, see Section 16.

**Label elements**
**Labelling according Regulation (EC) No 1272/2008**

Pictogram

**Figure A-1** MSDS of chloroform [43]

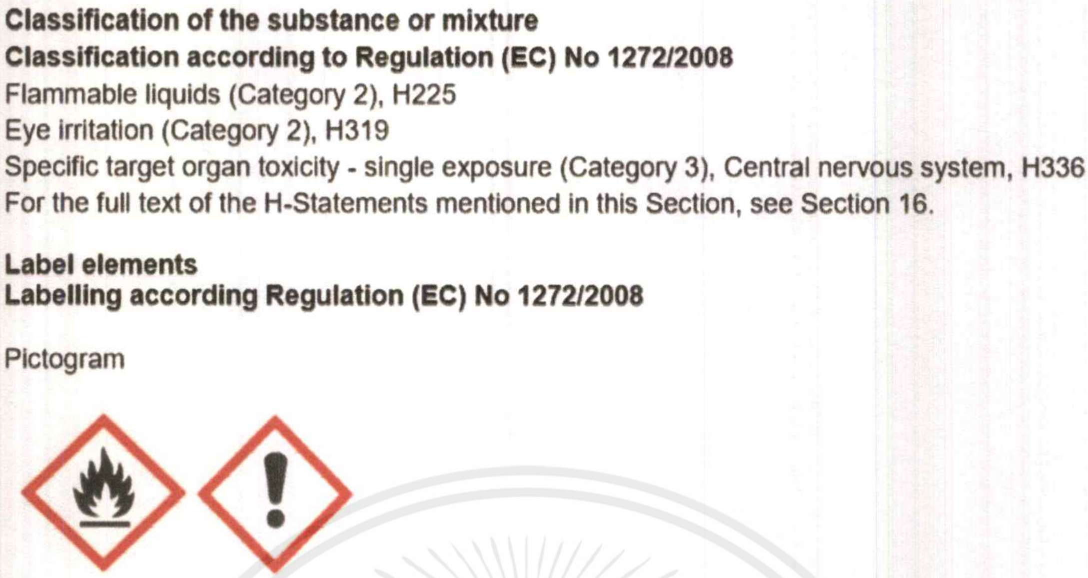
**Classification of the substance or mixture**
**Classification according to Regulation (EC) No 1272/2008**

Flammable liquids (Category 3), H226
Acute toxicity, Oral (Category 4), H302
Acute toxicity, Dermal (Category 4), H312
Acute toxicity, Inhalation (Category 4), H332
Skin irritation (Category 2), H315
Serious eye damage (Category 1), H318
For the full text of the H-Statements mentioned in this Section, see Section 16.

**Label elements**
**Labelling according Regulation (EC) No 1272/2008**

Pictogram

**Figure A-2** MSDS of cyclohexanone [44]



**Classification of the substance or mixture**
**Classification according to Regulation (EC) No 1272/2008**
Flammable liquids (Category 2), H225
Eye irritation (Category 2), H319
Specific target organ toxicity - single exposure (Category 3), Central nervous system, H336
For the full text of the H-Statements mentioned in this Section, see Section 16.

**Label elements**
**Labelling according Regulation (EC) No 1272/2008**

Pictogram

**Figure A-3** MSDS of methyl ethyl ketone [45]

# Appendix B

## Solvent swelling of nitrile latex

**Table B-1** Percent of total swelling index at maturation time 0 hour

| 0 hour | | | |
|---|---|---|---|
| Temperature (°C) | $D_0$ | $D_1$ | %TSI |
| 80 | 25.50 | 63.50 | 1.49 |
| 80 | 25.50 | 63.00 | 1.47 |
| 80 | 25.50 | 63.00 | 1.47 |
| 90 | 25.50 | 59.00 | 1.31 |
| 90 | 25.50 | 60.00 | 1.35 |
| 90 | 25.50 | 61.00 | 1.39 |
| 100 | 25.50 | 58.00 | 1.27 |
| 100 | 25.50 | 61.50 | 1.41 |
| 100 | 25.50 | 60.00 | 1.35 |
| 110 | 25.50 | 59.00 | 1.31 |
| 110 | 25.50 | 49.00 | 0.92 |
| 110 | 25.50 | 50.00 | 0.96 |

**Table B-2** Percent of total swelling index at maturation time 24 hour

| 24 hour | | | |
|---|---|---|---|
| Temperature (°C) | $D_0$ | $D_1$ | %TSI |
| 80 | 25.50 | 60.00 | 1.35 |
| 80 | 25.50 | 60.00 | 1.35 |
| 80 | 25.50 | 62.00 | 1.43 |
| 90 | 25.50 | 59.00 | 1.31 |
| 90 | 25.50 | 58.00 | 1.27 |
| 90 | 25.50 | 57.00 | 1.24 |
| 100 | 25.50 | 54.00 | 1.12 |
| 100 | 25.50 | 54.00 | 1.12 |
| 100 | 25.50 | 55.00 | 1.16 |
| 110 | 25.50 | 51.00 | 1.00 |
| 110 | 25.50 | 52.00 | 1.04 |
| 110 | 25.50 | 50.00 | 0.96 |

**Table B-3** Percent of total swelling index at maturation time 48 hour

| 48 hour | | | |
|---|---|---|---|
| Temperature (°C) | $D_0$ | $D_1$ | %TSI |
| 80 | 25.50 | 55.00 | 1.16 |
| 80 | 25.50 | 52.00 | 1.04 |
| 80 | 25.50 | 54.00 | 1.12 |
| 90 | 25.50 | 49.00 | 0.92 |
| 90 | 25.50 | 52.00 | 1.04 |
| 90 | 25.50 | 51.00 | 1.00 |
| 100 | 25.50 | 50.00 | 0.96 |
| 100 | 25.50 | 51.00 | 1.00 |
| 100 | 25.50 | 51.00 | 1.00 |
| 110 | 25.50 | 46.00 | 0.80 |
| 110 | 25.50 | 47.00 | 0.84 |
| 110 | 25.50 | 47.00 | 0.84 |

**Table B-4** Percent of total swelling index at maturation time 72 hour

| 72 hour | | | |
|---|---|---|---|
| Temperature (°C) | $D_0$ | $D_1$ | %TSI |
| 80 | 25.50 | 52.00 | 1.04 |
| 80 | 25.50 | 50.00 | 0.96 |
| 80 | 25.50 | 53.00 | 1.08 |
| 90 | 25.50 | 52.00 | 1.04 |
| 90 | 25.50 | 51.50 | 1.02 |
| 90 | 25.50 | 49.00 | 0.92 |
| 100 | 25.50 | 53.50 | 1.10 |
| 100 | 25.50 | 47.00 | 0.84 |
| 100 | 25.50 | 48.00 | 0.88 |
| 110 | 25.50 | 50.00 | 0.96 |
| 110 | 25.50 | 45.00 | 0.76 |
| 110 | 25.50 | 46.00 | 0.80 |

# Appendix C

## Relation of %TSC to properties of NR latex

**Table C-1** Relationship of %TSC to properties of NR latex

| | control | add water 5% | add water 10% | add water 20% | add water 40% |
|---|---|---|---|---|---|
| %TSC | 47.13 | 44.43 | 42.76 | 39.13 | 32.04 |
| Viscosity | 19.00 | 13.50 | 11.50 | 9.50 | 6.50 |
| Latex stability | 23.00 | 18.00 | 17.00 | 16.80 | 15.00 |
| pH | 12.01 | 11.97 | 11.97 | 11.96 | 11.79 |

# Appendix D

## Solubility Parameter

The most widely accepted three component system to date is the three parameter system developed by Charles M. Hansen in 1966. Hansen parameters divide the total Hildebrand value into three parts: a dispersion force component, a hydrogen bonding component, end a polar component. This approach differs from Crowley's in two major ways: first, by using a dispersion force component instead of the Hildebrand value as the third parameter, and second, by relating the values of all three components to the total Hildebrand value. This means that Hansen parameters are additive: [41]

$$\partial_t^2 = \partial_d^2 + \partial_p^2 + \partial_h^2$$

where

$\partial_t^2$ = Total Hildebrand parameter

$\partial_d^2$ = dispersion component

$\partial_p^2$ = polar component

$\partial_h^2$ = hydrogen bonding component

The numerical values for the component parameters are determined in the following way: First, the dispersion force for a particular liquid is calculated using what is called the homomorph method. The homomorph of a polar molecule is the nonpolar molecule most closely resembling it in size and structure (n-butane is the homomorph of n-butyl alcohol). The Hildebrand value for the nonpolar homomorph (being due entirely to dispersion forces) is assigned to the polar molecule as its dispersion component value. This dispersion value (squared) is then subtracted from the Hildebrand value (squared) of the liquid, the remainder designated as a value representing the total polar interaction of the molecule $\partial_a$ (not to be confused with the polar component $\partial_p$). Through trial and error experimentation on numerous solvents and polymers, Hansen separated the polar value into polar and hydrogen bonding component parameters best reflecting empirical evidence. [41]

**Table D-1** Hansen Parameters for Solvents at 25°C [41]

| Solvent | $\partial/\mathrm{MPa}^{1/2}$ |
|---|---|
| Chloroform | 19.00 |
| Methyl ethyl ketone | 19.00 |
| Cyclohexanone | 19.60 |

**Table D-2** Summary of Solubility Parameters for Selected Elastomers [41]

| Elastomers | $\partial$/MPa $^{½}$ |
|---|---|
| BR | 17.20 |
| IR | 16.40 |
| IIR | 16.06 |
| NR | 16.60 |
| NBR AN Content 16% | 19.40 |
| NBR AN Content 20% | 18.40 |
| NBR AN Content 30% | 20.26 |
| NBR AN Content 40% | 21.10 |

# Appendix E

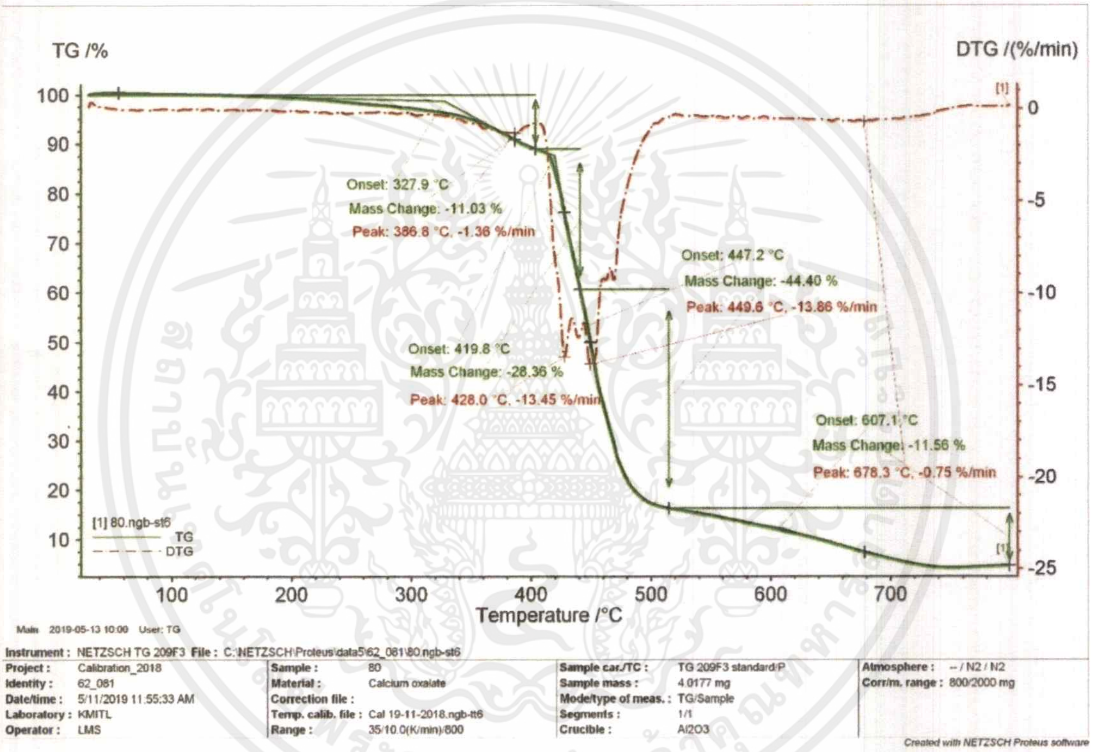
## Thermogravimetric analysis of NBR film

Form result of TGA show that step of decomposition has 3 steps:

Step 1 Volatile compounds peak at 386.8 °C

Step 2 Main step of the polymer pyrolysis peak at 428.0 and 449.6 °C

Step 3 Ash peak at 678.3 °C



Main 2019-05-13 10:00 User: TG

Instrument : NETZSCH TG 209F3 File : C:\NETZSCH\Proteus\data5\62_081\80.ngb-st6

Project : Calibration_2018
Identity : 62_081
Date/time : 5/11/2019 11:55:33 AM
Laboratory : KMITL
Operator : LMS

Sample : 80
Material : Calcium oxalate
Correction file :
Temp. calib. file : Cal 19-11-2018.ngb-tt6
Range : 35/10.0(K/min)/800

Sample car./TC : TG 209F3 standard/P
Sample mass : 4.0177 mg
Mode/type of meas. : TG/Sample
Segments : 1/1
Crucible : Al2O3

Atmosphere : -- / N2 / N2
Corr/m. range : 800/2000 mg

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**Figure E-1** Thermogravimetric analysis of NBR film at dried temperature is 80 °C