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Université de Montréal

Formulation of Emulsion Systems for the Preparation of Butyl Rubber Gloves

Par

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Mémoire présenté à la Faculté des études supérieures en vue de l'obtention
du grade de Maîtrise en chimie

June 2009

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Université de Montréal
Faculté des études supérieures

Ce mémoire intitulé

**Formulation of Emulsion Systems for the Preparation
of Butyl Rubber Gloves**

Présenté par
Sen Ge

à été évalué par un jury composé des personnes suivantes:

Président rapporteur

Directeur de recherche

Membre du jury

Résumé

Les gants résistants aux produits chimiques sont fabriqués industriellement à partir d'une grande variété de matériaux comme le nitrile, le néoprène, le PVC ou une combinaison de ces matériaux. Le défi posé pour fabriquer des gants avec le polybutyle est que celui-ci est déjà sous la forme d'un polymère, alors que les autres matériaux sont des émulsions aqueuses non polymérisées. En conséquence, lors de la fabrication traditionnelle de gants en caoutchouc butylique, une grande quantité de solvant organique, comme le toluène, est utilisée. Le toluène est un solvant toxique pour l'humain et l'environnement. Le choix d'un solvant non toxique, comme l'eau, est désiré. Mais l'eau ne peut pas dissoudre le caoutchouc butylique et une solution possible à ce problème reste la préparation d'une émulsion huile dans l'eau pour la solubilisation du polymère butyle.

Nous avons préparé des émulsions ternaires d'eau, de caoutchouc butylique et de solvant organique en optimisant la teneur en eau et en minimisant la quantité de solvant organique pour une concentration maximum de caoutchouc butylique. L'émulsion doit avoir une bonne stabilité et une viscosité appropriée. Le diagramme de phases ternaire montre le domaine de stabilité des différentes compositions en eau, caoutchouc butylique et solvant. Les solvants organiques étudiés sont le toluène, l'hexane et l'isooctane.

La rhéologie est utilisée industriellement pour suivre l'évolution de la concentration de l'émulsion lors de la fabrication de gants. Les effets du taux de cisaillement sur la viscosité ont été étudiés. La viscosité a servi à définir les domaines et types d'émulsions stables dans le diagramme de phases. Les deux types d'émulsions (huile-dans-eau et eau-dans-huile) ont des propriétés rhéologiques très différentes, domaines de valeurs d'environ 15 Pa.s comparés à environ 1500 Pa.s. Les propriétés mécaniques du caoutchouc butylique ont été étudiées par la méthode d'analyse mécanique dynamique.

Mots-clés: caoutchouc butylique; gants de protection; tensioactifs; émulsion.

Abstract

Chemically resistant gloves have been made by a variety of polymers such as nitrile rubber, neoprene, poly(vinyl chloride), or combinations of these materials in industry. Butyl rubber is the most commonly by utilized material to make rubber gloves. Unlike other kinds of rubber gloves which can be made by an emulsion polymerization process, a large amount of organic solvent such as toluene has to be used to solubilize the rubber in the traditional procedure of making butyl rubber gloves. Toluene is considered as a toxic solvent to human health and to the environment. A water-based system would be more desirable. Since butyl rubber cannot be dissolved in water, an emulsion system with a suitable organic solvent may be used.

We have prepared and optimized butyl rubber-organic solvent-water ternary emulsion systems with the help of suitable surfactant(s) for dissolving the maximum amount of butyl rubber in the emulsion. This type of emulsion maintains a good stability and a suitable viscosity. An optimized composition of the emulsion system was determined by ternary phase diagrams. The organic solvents studied include toluene, hexane, and isooctane.

Rheology is used to follow the evaluation of concentration of emulsion in the manufacturing of the glove. The effect of shear rate on the viscosity was studied, since the thickness of butyl rubber gloves is affected by the viscosity. The viscosity measurements were used to define the various zones in the phase diagram of the different types of emulsions. The viscosity of the oil-in-water emulsion is around 15 Pa.s, while that of the water-in-oil emulsion is around 1500 Pa.s. Dynamic mechanical analyses were used to evaluate the mechanical properties of butyl rubber gloves.

Keywords: butyl rubber; protection gloves; surfactant; emulsion.

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List of symbols and abbreviations

| | |
|---------------------------------|--|
| AOT | Sodium bis(2-ethylhexyl) sulfosuccinate |
| NPES-428 | Poly(oxy-1,2-ethanediyl), alpha-sulfo-omega-(nonylphenoxy)-, sodium salt |
| TMTD | Tetramethylthiuram disulfide |
| DMA | Dynamic mechanical analysis |
| FT-IR | Fourier transform infrared |
| NMR | Nuclear magnetic resonance |
| CMC | Critical micelle concentration |
| HLB | Hydrophile-lipophile balance |
| $\Delta G_m(l)$ | Free energy of micellization |
| $\Delta G_m(h)$ | Free energy of the hydrophilic moiety |
| NALP | Non-aqueous liquid phase |
| S | Shear stress |
| H | Viscosity |
| $\frac{\partial u}{\partial y}$ | Shear rate |
| N | Flow behaviour index |
| η_∞ | Limiting viscosity at high shear rates |
| η_0 | Zero-shear rate viscosity |
| $\dot{\gamma}$ | Shear rate |
| λ | Time constant |

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1. Introduction

1.1. General industrial rubbers

Rubber is an elastic polymer that exhibits unique physical and chemical properties; it is set apart from other solids due to its characteristic elastic or thermoelastic behavior.¹ In nature it exists as a milky colloid, known as latex, suspended in the sap of several varieties of plants.² The major commercial source of natural rubber is from Para rubber trees that grow in tropical areas. Nearly 22.7 million tons of rubber was produced in 2007, of which around 42% was natural rubber. Rubber products are forecast to increase by 4 percent annually. The aqueous synthetic latex process is not flammable and has little odor.³ Based on demand, up to fourteen types of rubber are commonly used in various industrial applications.⁴ Sometimes it is necessary to mix different kinds of rubber together, resulting in a material with special characteristics. The composition of rubber mixtures determines in large part their rheological and mechanical properties.⁵

1.2. Butyl rubber

1.2.1. Background

In 1942, butyl rubber was first produced as a commercial product. In 1944, Polysar, a Canadian company, began to produce butyl rubber in Sarnia, Ontario. In 1991, Bayer purchased all the Polysar installations.⁶ At the same time, ExxonMobil obtained the authorization for all production in France. Hence, the production of butyl rubber was monopolized by ExxonMobil and Bayer. In the 1950s and 1960s,

halogenated butyl rubber was developed in its chlorinated and brominated variants, providing significantly higher curing rates and allowing covulcanization with other rubbers such as natural rubber and styrene-butadiene rubber.⁷ Halobutyl rubber is today the most important material used for inner tubes.⁸

Butyl rubber is a generic name for a family of isobutylene-isoprene copolymers, that typically contains about 98% polyisobutylene with 2% isoprene distributed randomly on the polymer chain (Figure 1.1).⁹ It is a colourless, semi-solid elastomer.⁹ Problems associated with performing a detailed analysis of butyl rubber were largely due to the presence of this very small amount of the isoprene units in the polymer.¹⁰

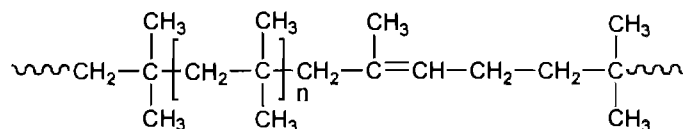


Figure 1.1. The structure of butyl rubber

The copolymerization of isobutylene with diolefins has been explored over the years.¹⁰ Isobutylene-based elastomers are valued for their excellent air retention, heat and steam resistance, ozone and weathering resistance, and outstanding dampening characteristics.¹¹ The long segments of polyisobutylene polymer chains provide good mechanical properties because of the flexibility of their chains. This type of rubber has many applications because of its special characteristics.⁹ As with all copolymers, their physical and chemical properties depend on how the diolefin units enter the polymer chain. Therefore, a study of the percentage of the isoprene units is important, as it can affect the physical and chemical properties of butyl rubber.¹² Butyl rubber is defined

both by the structure of the monomeric residues and the mode of their incorporation in the isobutylene-isoprene copolymers.¹³ In general, their incorporation can be defined by the following features:

- (a) Mode of incorporation of isobutylene units (head-to-tail or head-to-head),
- (b) Mode of incorporation of isoprene units (1,4, 1,2, or 3,4, and head-to-tail or head-to-head),
- (c) Distribution of isoprene units (random or block),
- (d) Configuration of incorporated isoprene units (Z or E).⁹

There are three possible structures that can represent the mode of isoprene addition (Figure 1.2):

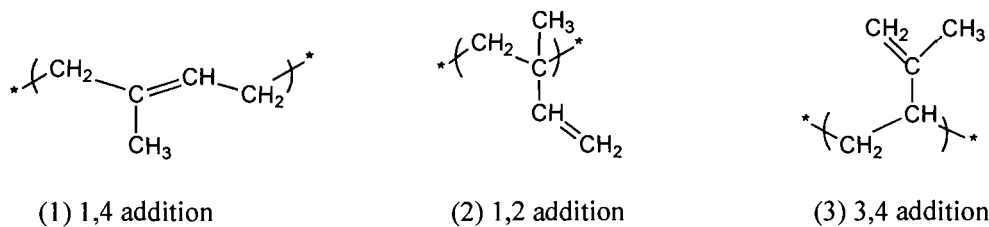


Figure 1.2. Three modes of isoprene addition.¹⁴

1.2.2. Properties and applications

The major advantages of butyl rubber are low gas permeability, thermal and oxidative stability, excellent moisture and chemical resistance. Butyl rubber has become widely used for inner tubes, tire inner liners, inner tubes for footballs, stoppers for medicine bottles, sealants and adhesives, o-rings, joint replacements, chewing gum, tank liners, speaker surrounds, and rubber tire-curing bladders.⁹ Despite these unique

properties, there are some deficiencies associated with this polymer, mainly its poor compatibility with other materials, including elastomers, plastics and carbon black.²

When butyl rubber is synthesized, high molecular weights can be obtained at a temperature of approximately -75°C . The detailed synthetic method of butyl rubber is given in the appendix. The isobutylene monomer should be cooled to -75°C in the first step of the synthesis; the initiator and co-initiator system is effective in non-aqueous solvents in a temperature range of -100°C to -20°C . Therefore, the making of butyl rubber products is controlled by temperature; this low temperature (-75°C) is easy to reach in the laboratory, but is difficult to obtain in a commercial setting.

Commercial halobutyl (chloro or bromo) rubbers are more easily vulcanized than butyl rubber.¹⁵ Chlorobutyl and bromobutyl derivatives of butyl elastomers are of greater commercial importance.⁸

1.3. Rubber Gloves

In industry, protective gloves play an important role in handling solvents because of their special properties and applications, there is demand for butyl rubber gloves.¹⁶ There are many ways to make rubber gloves, but industrial suppliers are looking for an environmentally friendly and easy method. In the most commonly used process for making gloves, butyl rubber is first dissolved in an organic solvent in order to prepare a solution, followed by a dipping step. In the dipping step, a metal hand-mold is immersed in the rubber solution. The polymer adheres to the mold's surface, and the viscous solution taking the form of a hand. This is followed by a vulcanization process that can crosslink the polymer chains. A large amount of organic solvent has to be used in this process. Driven by environmental and health concerns, industrial suppliers

intend to find new water-based methods to make protective gloves from butyl rubber. This is the major challenge of this research project.

1.3.1. Selection of rubber gloves

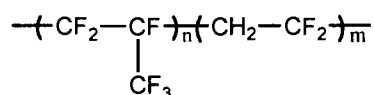
Chemically resistant gloves can be made from a variety of materials such as natural rubber or latex, butyl rubber, neoprene, nitrile rubber, poly(vinyl chloride) (PVC), and poly(vinyl alcohol) (PVA). Chemical resistant gloves are not totally “chemical-proof”. No rubber glove can resist even a single chemical agent forever. There is no one kind of “ideal” chemically resistant glove that can protect workers from all kind of chemicals. Chemicals will eventually penetrate the gloves over time by swelling, cracking or weakening of the glove material. Chemicals can pass through a protective glove even if the material does not contain pinholes or pores. The chemical can diffuse through the material at the molecular level without leaving any physical change observable to the human eye. Table 1.1 provides a general guideline for the selection of rubber materials required for handling particular solvents. The barrier effectiveness of synthetic rubber gloves is not as well established as for latex gloves.¹⁷ The correct glove can protect the skin from contact with damaging chemicals, while an improper choice may incur serious damage such as chemical burns, dermatitis, intoxication, or risk of cancer.

Table 1.1. Examples of glove recommendation¹⁸⁻²³

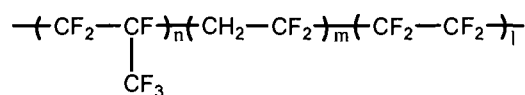
| Solvent | Recommended glove material |
|-------------------------|--|
| Acetone | Butyl rubber, Polythene rubber |
| Benzene | PVA, Viton®(fluoroelastomer) ^a , Polyurethane rubber, Neoprene rubber |
| Ethanol | Butyl rubber, Nitrile rubber, Neoprene, Natural rubber, Viton® |
| Gasoline | polyvinyl alcohol (PVA ^b), Nitrile rubber |
| Hexane | Viton®, Neoprene, PVA ^b , Nitrile rubber |
| Isopropanol | Natural rubber, Neoprene, Nitrile rubber, polyvinyl chloride (PVC) |
| Mesitylene | PVA, Viton® |
| Methyl cellosolve | Butyl rubber, PVA ^b |
| Methyl ethyl ketone | Butyl rubber, PVA ^b , Viton®, Polythene rubber |
| Methyl isobutyl ketone | PVA |
| Naphtha | Polyurethane rubber, Nitrile rubber |
| Toluene | PVA ^b , Viton®, |
| Toluene diisocyanate | PVA ^b |
| 1, 1, 1-Trichloroethane | Viton®, Natural rubber, Polythene rubber |
| Turpentine | PVA ^b , Nitrile rubber |
| Xylene | PVA ^b , Nitrile rubber |

^a Viton® is a fluoroelastomer. It has excellent heat resistance (200°C). Fluoroelastomers are used in a wide variety of high-performance applications. The main fluoroelastomers are shown below:

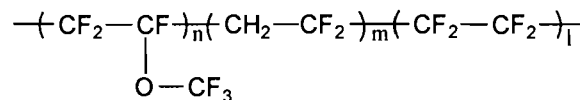
^b Polyvinyl acetate (PVA)



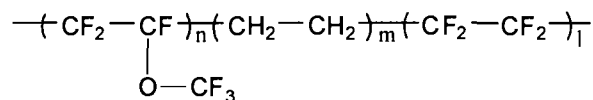
Copolymer fluoroelastomer



Terpolymer fluoroelastomer



Improved low temperature fluoroelastomer terpolymer



Non-VF₂ fluoroelastomer terpolymer

Four examples can be given to explain the importance of choosing the correct rubber glove. Natural latex rubber resists acids, alkalis, salts, and ketones. Latex is also blended with other polymers to make a combination glove which protects against several organic solvents. Neoprene gloves are suited for petrochemicals as they are resistant to acids, alcohols and oils. Nitrile rubber is a synthetic rubber that will not swell in aromatic solvents and petroleum solvents. Poly(vinyl chloride) (PVC) resists acids and alcohols, but will be weakened in petroleum solvents. To summarize, every kind of rubber glove has its specific purposes. Based on the chemicals to be used, users should select the correct rubber gloves for their application.

The synthesis of nitrile rubber is easy to control at room temperature.²⁴ Therefore, nitrile rubber gloves can be easily made by emulsion polymerization, since they can take their shape during the process of synthesis. However, butyl rubber must be synthesized at a very low temperature (-75°C) which creates a problem in commercial production. Another method than the emulsion polymerization process has to be found to make butyl rubber gloves.

Allergic reactions are another consideration in the selection of chemical protective gloves. There are three major types of reactions that affect the health of the worker:

immediate reaction, irritant dermatitis and delayed cutaneous hypersensitivity. It is important to consider the risk of allergic sensitization when selecting gloves, rather than just choosing the lowest cost item available. Even cornstarch powder, long used in rubber gloves to help conserve the rubber, can also cause allergies to some users.²⁴

The last consideration is price. In general, natural latex rubber gloves are cheaper than synthetic rubber gloves, but the price also depends on the technology of production.

1.3.2. Preparation of rubber gloves

The emulsion polymerization process used in making rubber is not suitable for butyl rubber because of the low temperatures requirement. It may be possible to develop a process for making rubber gloves by dipping into an emulsion containing butyl rubber. The first step is to prepare a polymer emulsion, which includes the polymer, water, an organic solvent if necessary, and some additives. Typically, the concentrated emulsion includes polymers (around 30~60 % of the emulsion) and water along with various stabilisers, dispersing agents, vulcanisation agents, accelerators, activators, antioxidants and other compounding ingredients. Approximately 5 % of the weight of the finished product consists of chemicals added during the preparation of the emulsion.²⁵

The prepared emulsion is then pumped into a dipping machine.²² Gloves are formed on glove-shaped porcelain molds (formers) mounted on a continuous chain that moves through the emulsion dipping tank. The formers are first cleaned, using either acidic or alkaline solutions, and then heated before pre-treatment with a coagulant such as calcium nitrate.¹⁸ The formers are then dipped into the bath, and a uniform film is

deposited. The coagulant converts the emulsion from a liquid to a solid. At the same time, a film is formed on the mold.²² The formers then pass through warm water baths (leaching tanks) to remove water and excess additives.¹⁹ Finally, the gloves are passed through vulcanisation ovens at approximately 80~90°C. Here, the polymers are crosslinked to improve the product's mechanical property.

In industry, butyl rubber gloves cannot be formed using the polymerization step, because butyl rubber must be synthesized at a temperature lower than -70°C. High temperatures cause the initiator and co-initiator system to take effect immediately, resulting in a reaction which is too fast to be controlled. The dipping procedure has been used for making butyl rubber gloves from a solution of butyl polymer in an organic solvent (toluene). When a mold is dipped into the polymer solution, the polymer adheres to the mold surface. The organic solvent is then vaporized at a high temperature, and the butyl rubber glove is formed on the mold. The whole process can be completed in a short time, but a large amount of organic solvent is needed.

The use of organic solvent has serious health and safety concerns, as well as environmental concerns. Therefore, an emulsion in a water-based solvent system would be an interesting alternative to address such concerns.

1.3.3. Stable emulsion for making butyl rubber gloves

1.3.3.1. Selection of surfactants

An emulsion is a mix of two or more immiscible substances dispersed in each other. In the emulsion, the phase interfaces scatter the light. For this reason, they have a cloudy appearance.²⁶⁻²⁸ In general, emulsions cannot form spontaneously and tend to

phase separate with time. An emulsifier (also called a surfactant) is a substance that stabilizes an emulsion. In general, there are water-in-oil emulsions (W/O emulsions) and oil-in-water emulsions (O/W emulsions) (see Figure 1.3). The type of emulsion depends on the relative volume of both phases and the surfactant. In a water-in-oil emulsion, the quantity of oil phase is more than the quantity of water phase. Inversely, an oil-in-water emulsion has the water phase larger than the oil phase. For this project, an oil-in-water emulsion should be prepared, because a water-based system is environmentally friendly. To obtain an oil-in-water emulsion of butyl rubber polymer, a water-surfactant mixture may be gradually added to a solution that includes butyl rubber and an organic solvent.

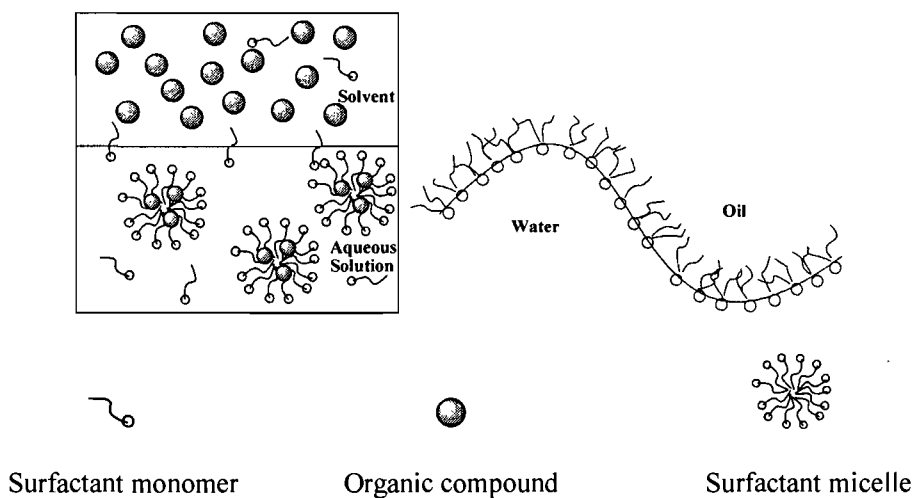


Figure 1.3. Oil-in-water emulsion.²⁹

Surfactants are amphiphilic compounds that can change the properties of fluid interfaces in an emulsion. Different types of surfactants are used for different organic solvents (oil phase). The hydrophile-lipophile balance (HLB) number is a measure of

the relative effect of the surfactant and can be used to characterize the relative affinity of surfactants for aqueous and organic phases.³⁰ The value of HLB is obtained by

$$HLB = C_1 + \frac{C_2 \Delta G_m(l)}{RT} + \frac{C_2 \Delta G_m(h)}{RT} \quad (1)$$

where $\Delta G_m(l)$ is the fraction of the free energy of micellization associated with the hydrophobic moiety,³¹ $\Delta G_m(h)$ the free energy of the hydrophilic moiety,³² C_1 and C_2 two scaling factors that can be found from literature,^{33, 34} R a gas constant, and T the temperature.

The HLB value can directly affect the type of emulsion obtained. Before the experiment, the range of HLB values of the surfactants should be examined. A high HLB number generally indicates that the surfactant can be well dissolved in water, while a low HLB number indicates a low aqueous solubility and high relative affinity for the organic phase. Water-in-oil emulsion needs a surfactant with a low HLB number, and oil-in-water emulsion needs a surfactant with intermediate to high HLB number. One of the objectives of this project is to maximize the water content in the emulsion system. Therefore, a surfactant with a high HLB value should be used for making oil-in-water emulsion. A HLB value of 10 is a turning point for emulsion preparation; when the HLB is higher than 10, oil-in-water emulsion can be prepared easily. Water-in-oil emulsion is relatively easy to make with a surfactant with a HLB value less than 10. The solubility of an emulsifier in water increases as its HLB value increases. As the HLB value increases, the dispensability of that compound in water increases along with the clarity of the solution that is formed (see Table 1.2).

Table 1.2. HLB values and properties, and applications of surfactants.^{35, 36}

| HLB | Properties applications |
|---------|---------------------------------|
| < 10 | Lipophilic (or water-insoluble) |
| > 10 | Water-soluble |
| 4 – 8 | Antifoaming |
| 7 – 11 | Water-in-oil emulsion |
| 12 – 16 | Oil-in-water emulsion |
| 11 – 14 | Wetting agent |
| 12 – 15 | Good detergency |
| 16 – 20 | A solubility or hydrotrope |

As shown in Table 1.2, oil-in-water emulsion is easy to prepare with a surfactant that has a high HLB value (more than 10).³⁷ Another criterion for choosing a surfactant is based on the type of organic solvent to be used. In this study, two kinds of surfactant were selected (AOT and NPES-428, ionic surfactants, see Figure 1.4).

AOT is a twin-tailed anionic surfactant with a very high HLB value (13.8). It has one hydrophilic head and two branches of hydrophobic tails, and it is often used to reduce the dispersion of interfacial tensions between two phases. AOT has been widely used in both research and technological applications since AOT is very soluble in water in the absence of any cosurfactant.³⁸ Poly(oxy-1,2-ethanediyl), alpha-sulfo-omega-(nonylphenoxy)-, sodium salt (NPES-428) is an oil-in-water emulsifier with a recommended usage level of 0.5-5 %. The HLB value of NPES-428 is 14.6.

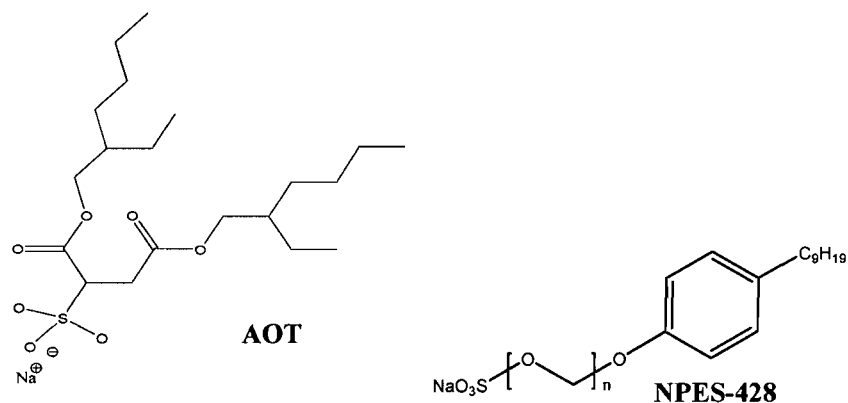


Figure 1.4. The structure of sodium bis(2-ethylhexyl) sulfosuccinate (AOT) and Poly(oxy-1,2-ethanediyl), alpha-sulfo-omega-(nonylphenoxy)-, sodium salt (NPES-428)

1.3.3.2. Selection of cosurfactants

A cosurfactant is often used to increase the effect of a surfactant. The cosurfactant induces changes in the interfacial film curvature between the organic solvent and the water.³⁹ Cosurfactant contributes to reduce the interfacial tension to very low values by increasing the lipophilicity of the surfactant system.

Alcohol is often used as a cosurfactant. Alcohol has the ability of both increasing the non-aqueous phase liquid solubility in water and decreasing the oil-water interfacial tension by increasing the flexibility of the interfacial film and by interacting with either the head-group or the tail-group region of the surfactant.⁴⁰ The critical micelle concentration (CMC) of the surfactant can be decreased effectively with a cosurfactant. The number of micelles may increase because of a lower CMC value. If the surfactant has a long tail (hydrophobic group), the solubility of the surfactant in water may be

lower than the CMC, so that neither micelles nor microemulsions can form.⁴¹ However, the alcohol additives can successfully stabilize micelles in water-surfactant-oil systems by decreasing the CMC, although it is not an essential compound for every emulsion system. The type of cosurfactant should be considered when the surfactant has been selected.

1.3.3.3. Calculation of viscosity

Viscosity may be used to define an emulsion system. The oil phase in this study contains butyl rubber and organic solvent. The viscosity of the emulsion depends on the content of butyl rubber. Butyl rubber gloves cannot be made by an emulsion with very high viscosity (water-in-oil emulsion), because the thickness of the glove would not be easy to control. The viscosity is one of the important criteria for choosing an appropriate emulsion. It helps define water-in-oil emulsion area and oil-in-water emulsion area in the ternary phase diagram.

Most concentrated emulsions show shear rate-dependent non-Newtonian type shear-thinning behavior at low and intermediate shear rates.⁴² On the contrary, the viscosity of the emulsion is stable (constant) at high shear rates. The viscosity of a Newtonian fluid is independent of shear rate, while that of a non-Newtonian fluid is not.⁴³ To measure the viscosity, a certain force may be applied to the fluid. This force is called yield stress and can correlate with other properties of a suspension. Newtonian fluids and non-Newtonian fluids can be distinguished by a power law (the Ostwald-de Waele power law). It is a useful and simple mathematical relationship (Equation 2) that describes the behavior of a fluid:⁴⁴

$$s = \eta \left(\frac{\partial u}{\partial y} \right)^n \quad (2)$$

where s is the shear stress, η viscosity of the material (Pa·sⁿ), $\frac{\partial u}{\partial y}$ the shear rate (s⁻¹), and n the flow behaviour index (dimensionless). The type of fluid can be defined by the behaviour index (n).⁴⁵ If $n < 1$, this fluid is pseudoplastic; if $n = 1$, the material is a Newtonian fluid; if $n > 1$, the sample is dilatant.⁴⁶

Power law is suitable for generalized Newtonian fluid (Equation 2), which is an idealized fluid that has a constant viscosity value at different shear rates.⁴⁷ The rheological properties of a fluid can be characterized in many ways. Numerical analysis such as curve-fitting may be used to obtain values of the parameters that characterize the fluid. There are many viscosity models to describe a shear-thinning fluid, such as the Cross model

$$\eta = \eta_{\infty} + \frac{\eta_0 - \eta_{\infty}}{1 + (C \dot{\gamma})^m} \quad (3)$$

where η_{∞} is the limiting viscosity at high shear rates, η_0 the zero-shear rate viscosity, $\dot{\gamma}$ the shear rate, and C a coefficient.⁴⁸ The Carreau model is expressed as

$$\eta = \frac{\eta_0}{\left[1 + (\lambda \dot{\gamma})^b \right]^c} \quad (4)$$

where λ is a time constant calculated from the reciprocal of the strain rate at which the zero strain rate component and the power-law component of the flow curve intersect.^{43,}

⁴⁴ The Carreau model suits shear-thinning fluid. The Carreau-Yasuda model^{49, 50} obtained from the Carreau model is expressed by

$$\eta = \eta_0 \left[1 + (\lambda \dot{\gamma})^a \right]^{\frac{n-1}{a}} \quad (5)$$

where λ is the calculated time constant, η_0 the viscosity at zero-shear rate, and n a constant with the same meaning in Equation 2. This model may be used for the rheological behaviour of grease that has high viscosities at low shear rates and low viscosities with high shear rates.⁴⁹

Zero-shear rate viscosity (η_0) is defined as the low shear rate limiting value of viscosity. In measuring the viscosity, a force is applied (shear rate $\neq 0$). Each sample's viscosity should be compared with its η_0 while it is impossible to measure this parameter, it is easy to estimate η_0 by a model (Carreau model or Carreau-Yasuda model), and other values and parameters can be obtained at the same time.⁵¹

1.3.4. Molding of rubber gloves

In manufacturing of rubber gloves, injection molding and dipping molding are two general processes used.

Injection molding is an important plastics manufacturing procedure. Molds are made from metals (steel or aluminum) that have much higher melting points than those of rubbers.⁵² Liquid plastic is injected into the mold with high pressure, but the injected material cannot easily reach all areas of the mold. In the dipping process, the mold is dipped into a mixture with rubber, and then dipped into a salt solution to coagulate the rubber.^{16, 53} This procedure can be repeated several times based on the desired thickness.

1.4. Objectives of the project

The objective of this project is to find a new procedure to reduce or eliminate the use of organic solvent (toluene) in the manufacturing of butyl rubber gloves. Toluene is an effective solvent to dissolve butyl rubber, but it is toxic to humans with potential damages internal organs and the central nervous system.⁵⁴ Toluene also affects women of reproductive age in occupational settings (such as long-term low-concentration exposures), or through wrong usage (e.g., episodic, binge exposures to high concentrations).⁵⁵ Toluene can break red blood cells and may also cause cancer.⁵⁴ When a large amount of organic solvent is used, safety and environment concerns may arise including health concern of workers, safety of the workplace, and pollution of the environment.

A water-based system is less toxic than organic solvent system and is more environmentally friendly. It is desirable to replace or at least to reduce the use of organic solvents. Since butyl rubber cannot dissolve in water, the use of some organic solvent is still necessary. Therefore, a ternary system of water-organic solvent-butyl rubber is proposed to reduce the amount of organic solvent used.

To prepare the emulsion, it is necessary to use some surfactants (including cosurfactant(s) according to the type of organic solvent used). The amount of surfactant in the emulsion has to be limited, since it may cause the formation of bubbles when the emulsion is heated during the glove molding steps. Some surfactants may also be toxic. The toxicity of surfactants to humans, micro-organisms, and various forms of aquatic life varies widely. Cationic surfactants are often more toxic than anionic or nonionic surfactants.⁵⁶ Therefore, the use of surfactants should be limited.

In this project, it is desirable to maximize the amount of water and to minimize the amount of organic solvent and surfactant in the emulsion. We also intend to optimize the viscosity of the emulsion mixture for a better adherence of the polymers onto the mold. Some methods have been used to control the viscosity and will be covered in Chapter 3 (Results and discussion). The major objectives to be achieved in this work include the following:

1. Selection of an organic solvent that is less toxic than toluene;
2. Replacement of a significant amount of organic solvent by water;
3. Selection of an appropriate surfactant for the W/O emulsion;
4. Development of procedures of mixing all the compounds;
5. Formation of the film (the molding of butyl rubber gloves);
6. Study of the mechanical properties of the film and the rheology of emulsion.

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2. Experimental procedures

2.1. Materials

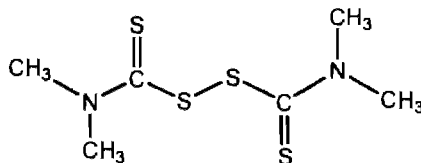
The butyl rubber used in this study, ExxonMobil Butyl 065, was kindly supplied by ExxonMobil Chemical, and had an unsaturation level at 1.05-0.20 mol %.¹ The Mooney viscosity (ML 1+8, see Appendix B) at 125 °C was 32 ± 3 . The halobutyl rubber, ExxonMobil chlorobutyl rubber 1066, had a Mooney viscosity (ML 1+8) of 38 ± 5 at 125°C and a chlorine content of 1.26 ± 0.08 wt%. The characteristics of butyl rubber were supplied by ExxonMobil laboratory. The commercial samples were used without further purification.

The organic solvents used, including toluene (ca. 98%), hexane (ca. 98%), isooctane (ca. 98%), and heptane (ca. 98%), were obtained from Sigma-Aldrich.

The surfactants Aerosol OT (AOT, 96%, sodium bis(2-ethylhexyl) sulfosuccinate) and NPES-428 (Poly(oxy-1,2-ethanediyl), alpha-sulfo-omega-(nonylphenoxy)-, sodium salt) were purchased from Sigma-Aldrich. AOT is very hygroscopic and absorbs moisture from air. It was thus recrystallized three times from hot methanol and dried under vacuum.

Cosurfactant can reduce the critical micelle concentration (CMC) in the emulsion.^{2, 3} Therefore, the emulsion will be more stable with a cosurfactant.⁴ The reduction of CMC is more significant with a longer hydrocarbon chain and a higher cosurfactant concentration.^{1, 5} Short chain alcohols are directly influencing properties of the emulsion. Considering the price, the toxicity, and the impact on the stability of emulsion, isopropanol (ca. 98%) was selected as cosurfactant.

Vulcanizing agents, sulfur and zinc oxide (ZnO, 99.9%), were used as received from Sigma-Aldrich. ZnO was used as an activator in the curing process. The accelerator, tetramethylthiuram disulfide (TMTD, 97%), has the following structure.⁶



2.2. Preparation of samples

2.2.1. Emulsion preparation

The emulsions were prepared at room temperature. The butyl rubber was first dissolved in the organic solvent for about 24 hours to make sure that the butyl rubber was dissolved. The surfactant was dissolved in water and the mixture was added into the oil phase containing butyl rubber. The emulsification was made with a high-speed dispersing and emulsifying apparatus (PowerMax AHS 200 homogenizer) at an agitation speed of 35,000 rpm for 2 minutes.

Many commercial surfactants are sold with different water contents. For example, Poly(oxy-1,2-ethanediyl), alpha-sulfo-omega-(nonylphenoxy)-, sodium salt (NPES-428) is a surfactant used in hexane but it contains 72 % of water. Before adding the surfactant to butyl rubber solution (butyl rubber with organic solvent), it should be dissolved in water to help mix with the butyl rubber solution. Based on the water contained in the commercial surfactant and quantity of water added in the solution, the amounts of NPES-428 and water were calculated.

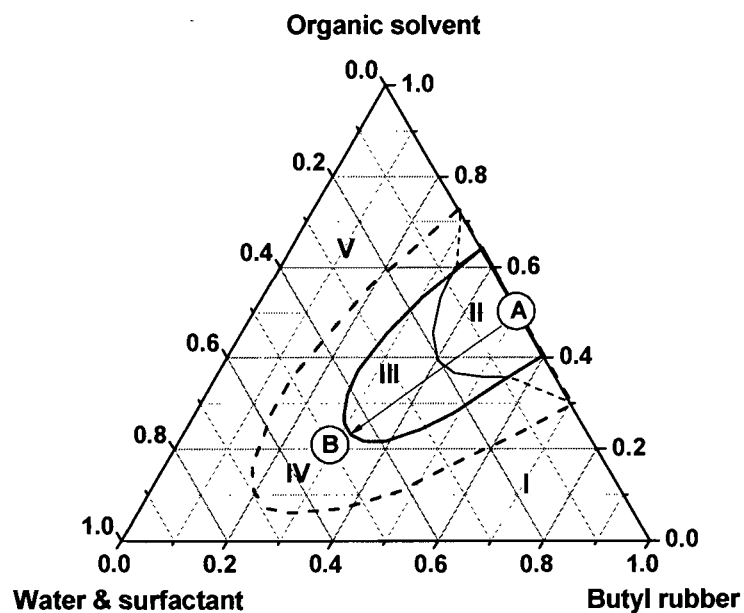
2.2.2. Phase diagrams

To find the best proportion of ingredients, a ternary phase diagram was determined from the three-component systems. It may be represented as a three-dimensional diagram, more commonly, or as a triangular phase diagram, with each axis representing the content of butyl rubber, the organic solvent, and the water-surfactant mixture (see Figure 2.1).

To obtain a phase diagram for the ternary systems, butyl rubber was first dissolved into organic solvent (point A), followed by the addition of the water-surfactant mixture. To move from point A to point B, a measured amount of the water-surfactant mixture was added gradually to the solution and the viscosity of the mixture was closely examined after each addition. Along the AB line, the sample may exist as a gel (area II), a stable emulsion (area III), or an unstable emulsion (area IV). The phase diagram contains both a stable emulsion area (oil-in-water emulsion) and a gel area (water-in-oil emulsion). The gel area was defined by its high viscosity and the experimental definition of this area is discussed in Section 3.2.6. In a typical experiment, butyl rubber with organic solvent (point A) was placed in a 10-ml test tube, and then the water-surfactant mixture was added gradually (AB line). The solution was mixed for 2 minutes by the use of a homogenizer. After 24 hours, if the sample is still stable (the emulsion is uniform, and there is no phase separation), more water-surfactant may be added (along the AB line in Figure 2.1). Normally, around 0.2 ml of the water-surfactant mixture was added each time in the stable emulsion until an unstable emulsion (area IV) was obtained (with phase separation in 24 hours). In this way, the stable area can be defined in the phase diagram.

Upon the completion of the experiment along the AB line, another starting point with a new composition of the butyl rubber in organic solvent mixture was selected and the same procedure was repeated for the verification of the state of the ternary mixture. This was repeated until the entire phase diagram was mapped to define the boundaries of each of the areas as indicated in Figure 2.1.

A large amount of organic solvent in the sample should be avoided, since the major objective of this project is to replace or reduce the amount of organic solvent used. In area I, the samples cannot be used, because butyl rubber swelled in a small quantity of the organic solvent. In area V, the sample phase is separated when the water-surfactant mixture is added to it. Therefore, the sample in areas I and V cannot be considered for this project. In a large portion of the ternary phase diagram, gels were obtained at a low content of the water-surfactant mixture. The stability of the sample decreases with an increase in the content of the water-surfactant mixture. The viscosity of the samples in gel area (area II) is too high to make butyl rubber gloves. A stable emulsion is required to make butyl rubber gloves, and the appropriate composition can be found in area III.



- I : butyl rubber swelling
- II : gel
- III: stable emulsion
- IV: unstable emulsion
- V : emulsion with a large amount of organic solvent

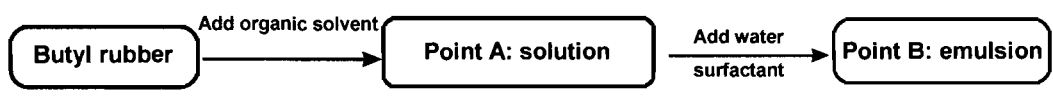


Figure 2.1. Scheme of construction for a ternary diagram. The composition of each component is defined by its weight fraction.

2.2.3. Procedure of vulcanization

Vulcanization is the basic process for establishing crosslinks between unsaturated hydrocarbon chains.⁷ The mixture containing ZnO, sulfur, and TMTD (in a ratio of butyl rubber : ZnO : sulphur : TMTD = 100 : 10 : 2 : 2 (w/w)), was agitated with the

homogenizer. The mixture was heated at 55~60°C on the mold. During the process, all the vulcanizing agent mixture should not be added in one shot because it is not easy to make the solution homogenous with a large amount of vulcanizing agents. Therefore, it should be added gradually. In the ternary phase diagram, a stable emulsion zone needs to be identified. ZnO was added into the emulsion and mixed for 1 minute. After the addition of the vulcanizing agents (sulfur and TMTD), the mixture was mixed for an additional 3 minutes by the use of the homogenizer. The temperature of the mixture increased because of the high mixing speed (35,000 rpm). Therefore, the sample should be cooled down to room temperature after mixing to prevent the evaporation of the organic solvent. The suspension, which includes butyl rubber, organic solvent, and water, was crosslinked in the last step. The mixture was poured onto an aluminum plate to make the film, heated at 55~60°C for 5 to 10 minutes for crosslinking. All the organic solvents and water were evaporated during the vulcanization process.

2.3. Instruments and measurements

2.3.1. Viscosity

In these experiments, the cone-and-plate geometry was used. The cone-and-plate and parallel plate measurements are most often used for highly viscous paste gels and concentrated suspensions.⁸ The parallel plate geometry can be considered as a simplified version of the cone-and-plate having an angle of 0°.⁹ If the sample has a very high viscosity, the parallel plate geometry is preferred, because it is easy to measure if the sample is constrained in the narrow space between the two surfaces. For our study, the viscosity of the samples (ca. 10 Pa.s) was not very high. Therefore, the cone-and-plate geometry was a good choice.

The viscosity was measured with an AR2000 rheometer from TA Instruments equipped with a cone-and-plate geometry. The cone-and-plate geometry is used frequently for measuring the viscosity of emulsions.⁹ The cone-and-plate geometry consists of an inverted cone in near contact with a lower plate. The cone used has an angle of $1^{\circ}59'18''$ (Figure 2.2). The upper part rotates while the bottom is fixed stator and allows proper control of heating or cooling of the sample on the plate.

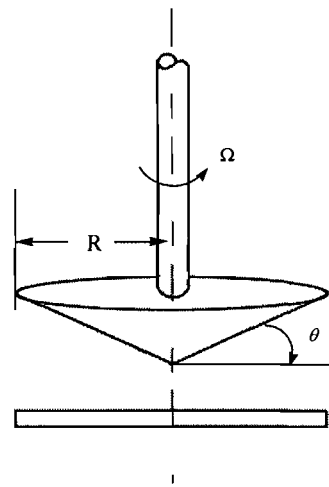


Figure 2.2. Schematic diagram of the cone-and-plate geometry for the rotational rheometer

The range of the shear rate is from 0.01 to 100 s^{-1} . The shear rate is fixed during making butyl rubber gloves, because the dipping speed of the mold is not changing. A rational dipping speed can be selected from this range. Steady state flow data was recorded with an increase of the applied torque followed by a decrease (the viscosity was measured with a decreasing shear rate). The torque was imposed using a logarithmic ramp in order to decrease the initial acceleration and the effect due to

instrument inertia. Experiments close to the boundary zone between the “gel area” and the “emulsion area” were repeated 3-4 times under the same conditions. The distance between the cone and the plate was 600 μm , which determined the amount of sample to be used. A batch of 0.75 ml of sample for each set of measurements was placed on the plate. During all experiments, the cone-and-plate part was always covered with a solvent trap to prevent the evaporation of the solvent.

2.3.2. Dynamic mechanical analysis (DMA)

DMA measurements were done with a DMA 2980 instrument from TA Instruments. The test sample was fixed on a tension film clamp. The samples were measured at an operating frequency of 1 Hz and a heating rate of 2°C/min from -80 to 40°C. The sample was prepared by placing the mixture of stable emulsion and vulcanizing agents on the aluminium plate and heating at 60°C. The polymer was vulcanized in the form of film (thickness 0.2 mm) after 8-10 minutes.

2.3.3. Fourier transform infrared (FTIR) spectroscopy

FTIR spectra were recorded before and after vulcanization on a Varian 3100 FTIR spectrometer from Varian equipped with a mercury cadmium telluride (MCT) photodiode detector. A resolution of 4 cm^{-1} was chosen and 128 scans were accumulated.¹⁰ The spectra were recorded at room temperature and at 90°C. For FTIR analysis, the membrane samples were prepared by drying the stable emulsion on a aluminum plate at room temperature.

2.3.4. Nuclear magnetic resonance (NMR) spectroscopy

The ^1H NMR spectra of butyl rubber and chlorobutyl rubber were recorded on a Bruker AMX-400 spectrometer operating at 400.13 MHz at room temperature. Butyl rubber was dissolved in deuterated chloroform (from Sigma-Aldrich) and at a concentration of 1-2 %wt.

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3. Results and discussion

3.1. Raw material of butyl rubber

The butyl rubber was provided by ExxonMobil. Butyl rubbers are available with different degrees of unsaturation, which is an important factor for the vulcanization process. Their characteristics of some of the products supplied by ExxonMobil are listed in Table 3.1.

Table 3.1. Specifications of butyl rubbers from ExxonMobil.^{1,2}

| Grades | Unsaturation (mol%) | Mooney viscosity ^a (mooney) |
|-------------|------------------------|---|
| 065 | 1.05 ± 0.20 | 32 ± 3 |
| 068 | 1.15 ± 0.20 | 51 ± 5 |
| 165 | 1.50 ± 0.20 | 32 ± 3 |
| 268 | 1.70 ± 0.20 | 51 ± 5 |
| 269 | 1.70 ± 0.20 | 57 ± 5 |
| 365 | 2.30 ± 0.30 | 33 ± 3 |
| Chlorobutyl | 1.05 ± 0.20 | 63 ± 1 |

^a Mooney viscosity is defined as the shearing torque resisting rotation of a cylindrical metal disk (or rotor) embedded in rubber within a cylindrical cavity. The mooney viscosity is tested at 125°C. (ML 1+8: Minimum mooney viscosity (M) has been measured by a large rotor (L) with a diameter of 38.1 mm, at preheating time of 1 minute and test time of 8 minutes.)

A high concentration of C=C double bonds may be needed for making butyl rubber gloves.³ C=C double bonds are needed for crosslinking during the vulcanization step. In the vulcanization step, polymers are linked to other polymers composed of carbon bonds. A butyl rubber with a high concentration of C=C double bonds is needed for the vulcanization step. In industry, butyl 268 is widely used because of its relative high concentration of C=C double bonds. In order to check the feasibility of the new procedure, butyl 065, which has a lower concentration of C=C double bonds, has been selected. If butyl 065 can be used in the new procedure, a butyl rubber with a higher concentration of C=C double bonds (for example butyl 268) should be more efficient with the same procedure.

The concentration of C=C double bonds in the butyl rubber was characterized by FTIR spectroscopy (Figure 3.1) and ¹H NMR spectra (Figure 3.2). The molar fraction of isoprene unsaturation in the butyl rubber can be determined from the testing results.

In Figure 3.1, the two peaks at around 1630 and 3450 cm⁻¹ are due to the presence of water in the sample. The C=C double bonds should be present at around 3200 and 1660 cm⁻¹. Therefore, one band of the C=C double bonds (around 1660 cm⁻¹) overlaps with the peak of water (at around 1630 cm⁻¹). Water has to be removed from the sample in order to show the characteristic peaks of C=C double bonds in the spectra. A second FTIR measurement was carried out at 90°C. One of the characteristic peaks of C=C double bonds (3200 cm⁻¹) is still present, while the peak at around 1680 cm⁻¹ is not as high as the peak at room temperature. The peaks from 1640 to 1660 cm⁻¹ are due to the presence of water in the sample. The peaks at around 3200 and 1660 cm⁻¹ are evidences of presence of the C=C double bonds in the butyl rubber, but those peaks are not clearly

shown in the spectra. The concentration of C=C double bonds in the butyl rubber is lower than the measurement limit of FTIR.

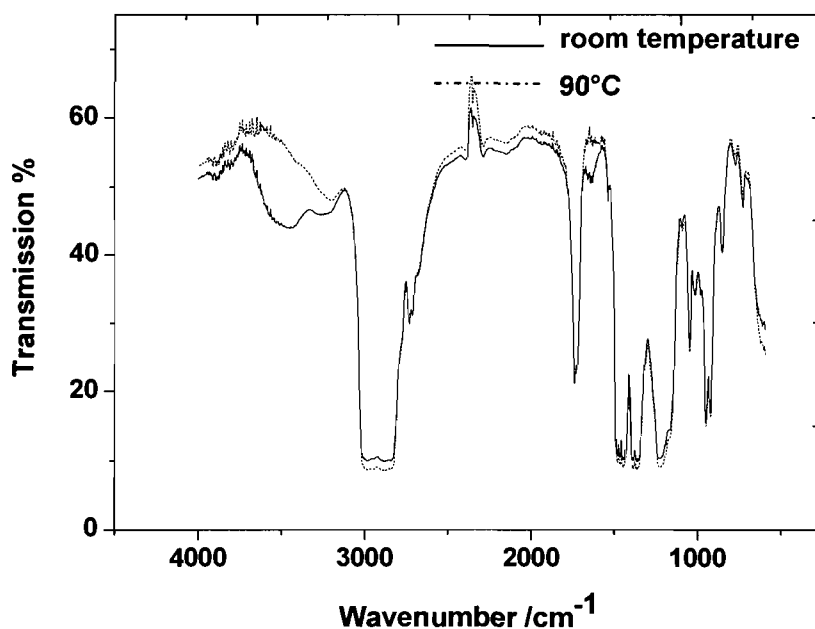


Figure 3.1. FTIR spectra of butyl rubber at room temperature and at 90°C.

¹H NMR spectroscopy has also been used to estimate the concentration of C=C double bonds. Figure 3.2 shows ¹H NMR spectra of butyl 065 and chlorobutyl rubber. From Figure 3.2-A, the ¹H NMR signals at around 1.2 and 5.1 ppm are assigned to the methyl protons of the polyisobutylene units and the olefinic methane proton of isoprenyl units of butyl rubber.⁴ Chlorobutyl rubber was synthesized from butyl 065. In Figure 3.2-B, ¹H NMR spectra of chlorobutyl rubber can also help to estimate the number of C=C double bonds in the butyl rubber.

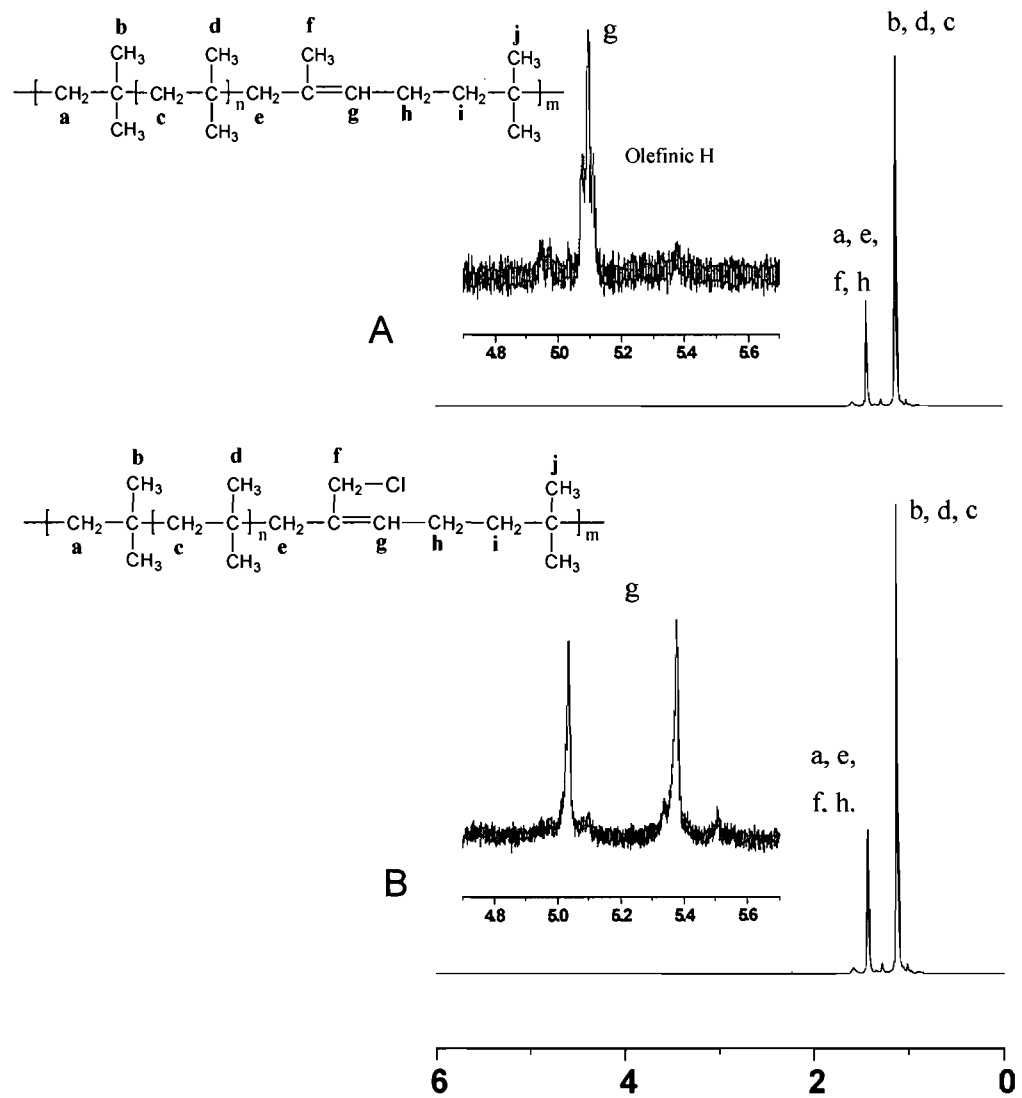
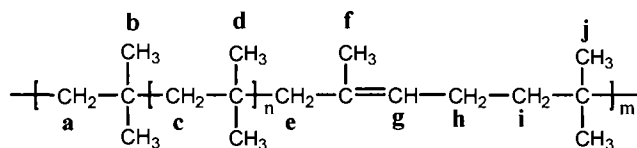


Figure 3.2. ¹H NMR spectra of butyl 065 (Figure 3.2-A) and of chlorobutyl rubber (Figure 3.2-B) in CDCl₃ at room temperature (Both materials were obtained from ExxonMobil.).

In the case of chlorobutyl rubber, because there are two kinds of isomers (E isomer and Z isomer), the chemical shifts of the isoprenyl group protons were different from those of butyl rubber 065. In Figure 3.2-B, there are two weak individual triplets at 5.04 (E isomer) and 5.37 ppm (Z isomer), which are due to the olefinic protons, providing important information about the isomeric composition of the hydrocarbon mixture.

Table 3.2. Assignment of ^1H NMR signals of the butyl rubber sample.⁵



| Chemical shift (ppm) | Multiplicity ^a | Assignment |
|----------------------|---------------------------|------------------------------|
| 1.11 | s | 6H-b & 6H-d, t-Bu |
| 1.13 | s | 2H-c, CH ₂ |
| 1.25 | t | 2H-a & 2H-h, CH ₂ |
| 1.71 | s | 3H-f, CH ₃ |
| 1.88 | s | 2H-e, CH ₂ |
| 1.96 | m | 2H-h, CH ₂ |
| 5.04 | t | olefinic H, E isomer |
| 5.09 | t | olefinic H |
| 5.37 | t | olefinic H, Z isomer |

^a s = singlet, m = multiplet, and t = triplet

The molar fraction of isoprene unsaturation for the butyl rubber (or chlorobutyl rubber) can be calculated from the following formula:^{2,4}

$$\text{Isoprene unsaturation (mol \%)} = \frac{8A}{A+B} \times 100 \quad (1)$$

where A and B are the integral signal intensities of the peaks at 5.0-5.4 and 0.8-2.2 ppm in Figure 3.2.

A strong signal in the 1.06 to 1.11 ppm region (the methyl protons of the polyisobutylene groups) of the ¹H NMR spectrum of butyl rubber can be compared to the signal at 5.09 ppm (from the isopropyl groups). The ratio between isopropyl groups and methyl groups was around 1:658 indicating a low concentration of isoprene in the butyl rubber. The molar fraction of isoprene unsaturation for the butyl 065 is 1.21 mol%. Therefore, butyl 065 has a low level of unsaturation for the vulcanization. The molar fraction of isoprene unsaturation for the chlorobutyl rubber can be calculated similarly, which is 1.20 mol%. Based on the ¹H NMR spectra, the same molar fraction of isoprene unsaturation was obtained as the analysis results from ExxonMobil.

3.2. Emulsion preparation

3.2.1. Process development

In the experiment, the emulsion system contains butyl rubber, organic solvent, water, and surfactant. Water and surfactant were considered as one component (aqueous phase). A ternary phase diagram is defined by three components (butyl rubber, organic solvent and aqueous phase). In order to find the best proportion of the ingredients, a procedure for the emulsification is shown as an example on a ternary

phase diagram (Figure 2.1). Based on the stability of the sample and the viscosity value of the stable emulsion, different areas have been defined in the ternary phase diagram. In the ternary phase diagram, stable emulsion composition could be found along the AB line. In industry, butyl rubber gloves should be made within 24 hours. If the emulsion remains stable (without phases separation) for duration of 24 hours, the emulsion can be classified as a stable emulsion, and the concentration of the ingredients of the stable emulsion shows in the stable emulsion area (area II or III in Figure 2.1) in the ternary phase diagram. The stable oil-in-water emulsion is represented in area III from the ternary phase diagram (Figure 2.1). In the stable emulsion area, two parts (the water-in-oil emulsion part and the oil-in-water emulsion part) have been defined by the viscosity value and the stability time. A water-in-oil emulsion (area II) has a high viscosity while an oil-in-water emulsion (area III) has a low viscosity.

To prepare an emulsion, the surfactant was first dissolved in water to obtain a homogeneous mixture, and then this mixture (aqueous phase) was added in butyl rubber solution (butyl rubber dissolved in the organic solvent). The concentration of surfactant in water remained constant for all samples in the same ternary phase diagram.

Several factors can influence the stability of the emulsion. For example, the stability of the dispersing-phase may be affected by the average droplet size. The duration of a stable emulsion can be prolonged with a high mixing speed, because the emulsion can have small droplet size with a high mixing speed.

Furthermore, the stability of the emulsion depends on the type of organic solvents and surfactant, the concentration of the surfactant, the type of cosurfactant used, and the viscosity of the emulsion, as discussed in the following sections.

3.2.2. Effect of the type of organic solvent

The selection of a suitable organic solvent was based on a high solubility of butyl rubber and the toxicity of the solvent. The study of the solubility of butyl rubber in different organic solvents has been carried out in our research group. To characterize the polymer solubility, a butyl rubber sample was immersed into an organic solvent, weighed at different intervals of time until no more butyl rubber can be dissolved. The results are presented in Table 3.3, and the solubility is calculated from Equation 2.⁶

$$\text{The solubility of butyl rubber} = \frac{\text{weight of butyl rubber}}{\text{volume of organic solvent}} \quad (2)$$

Table 3.3. Solubility of butyl rubber (g/ml) in organic solvents

| | Acetone | Benzene | Hexane | Toluene | Isooctane | Heptane |
|--------------|---------|---------|--------|---------|-----------|---------|
| Butyl rubber | 0.06 | 1.13 | 1.88 | 2.04 | 1.94 | 2.33 |

The solubility of butyl rubber is a critical factor for choosing an organic solvent. In the butyl rubber glove manufacturing industry, toluene is the most often used organic solvent. From Table 3.3, the solubility of butyl rubber in toluene is high, so butyl rubber is easy to dissolve into toluene. Butyl rubber can be dissolved easily in hexane and isooctane as well. At the same time, the price and the toxicity of the organic solvent should be considered. Toluene, hexane and isooctane have been selected to make the stable emulsion in this project. An ideal system will be selected from these three kinds of systems based on the stability and the viscosity of the emulsion.

3.2.3. Effect of the type of surfactant

Surfactant can be used to reduce the oil-water interfacial tension to diminish the related positive free energy change of dispersion associated with surface formation.⁷ Surfactants are often classified into four primary groups: anionic, cationic, non-ionic, and zwitterionic. They can solubilize both oil-in-water emulsion (O/W emulsion) and water-in-oil emulsion (W/O emulsion).⁸ The hydrophilic group of the surfactant remains in water, whereas its hydrophobic group prefers to reside in a hydrophobic phase such as organic solvent (oil phase). When the concentration of surfactant is high enough, the emulsion forms oil-in-water micelles (O/W emulsion).⁹ Surfactants can also assemble in oil to form reverse micelles or water-in-oil emulsion (W/O emulsion). The type of emulsion is determined by the amount of organic solvent and of water. Whereas oil-in-water emulsion has a large amount of water in the emulsion, on the contrary water-in-oil emulsion is usually obtained with a large amount of organic solvent (oil phase). For the project, an oil-in-water emulsion seems more appropriate. The emulsion can also be more complex (e.g. O/W/O emulsion or W/O/W emulsion).¹⁰

¹¹ Surfactants are important in many applications and products (e.g. the petroleum industry, fabric softener, emulsifiers, biocides, agrochemicals, and so on.), as they reduce surface tension to make the emulsion stable. The critical micelle concentration (CMC) is defined as the concentration of surfactants reaching the point where micelles are spontaneously formed.^{12, 13} At this concentration, the surface area between two liquids is fully loaded with surfactant molecules and there is no room for additional ones.¹⁴ After reaching the CMC, the number of micelles will increase with adding extra surfactants. The air bubbles can be found from the bottom of the solution.

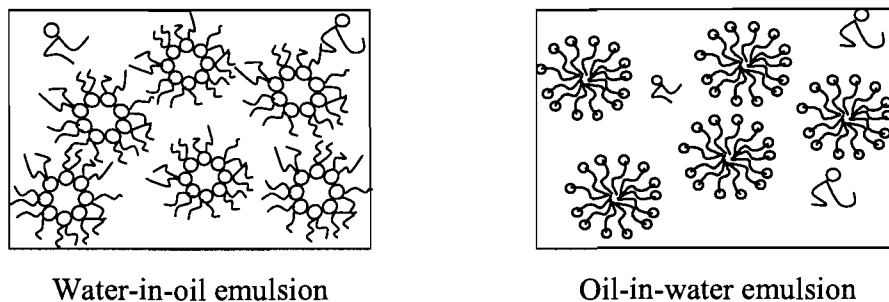


Figure 3.3. Water-in-oil emulsion and oil-in-water emulsion

Based on the ideal emulsion (oil-in-water emulsion) for this project, a surfactant with a high HLB value should be selected, because the oil-in-water emulsion is easier to prepare with a surfactant which has a high HLB value. The HLB values of both surfactants used (AOT and NPES-428) are high. However, they behave differently when used with different organic solvents. We intend to reduce the amount of organic solvent used with the help of a minimum amount of surfactant. In the ternary phase diagram (Figure 3.4-A), AOT was used as the surfactant in the toluene system. A large stable emulsion area, which includes water-in-oil emulsion (in the gel area) and oil-in-water emulsion (in the emulsion area), can be obtained. In Figure 3.4-B, the condition was the same as in the first ternary phase diagram except for the use of hexane as the organic solvent. However, the stable emulsion area in Figure 3.4-B is smaller than the stable emulsion area in Figure 3.4-A. In Figure 3.4-C, another surfactant (NPES-428) was used in hexane system. The stable emulsion area in Figure 3.4-C is larger than in Figure 3.4-B. The large stable emulsion area can be obtained with a correct surfactant selection. Based on the size of stable area in the ternary phase diagram, an appropriate surfactant can be chosen. NPES-428 is a good choice for the hexane system, while AOT works better in the toluene system.

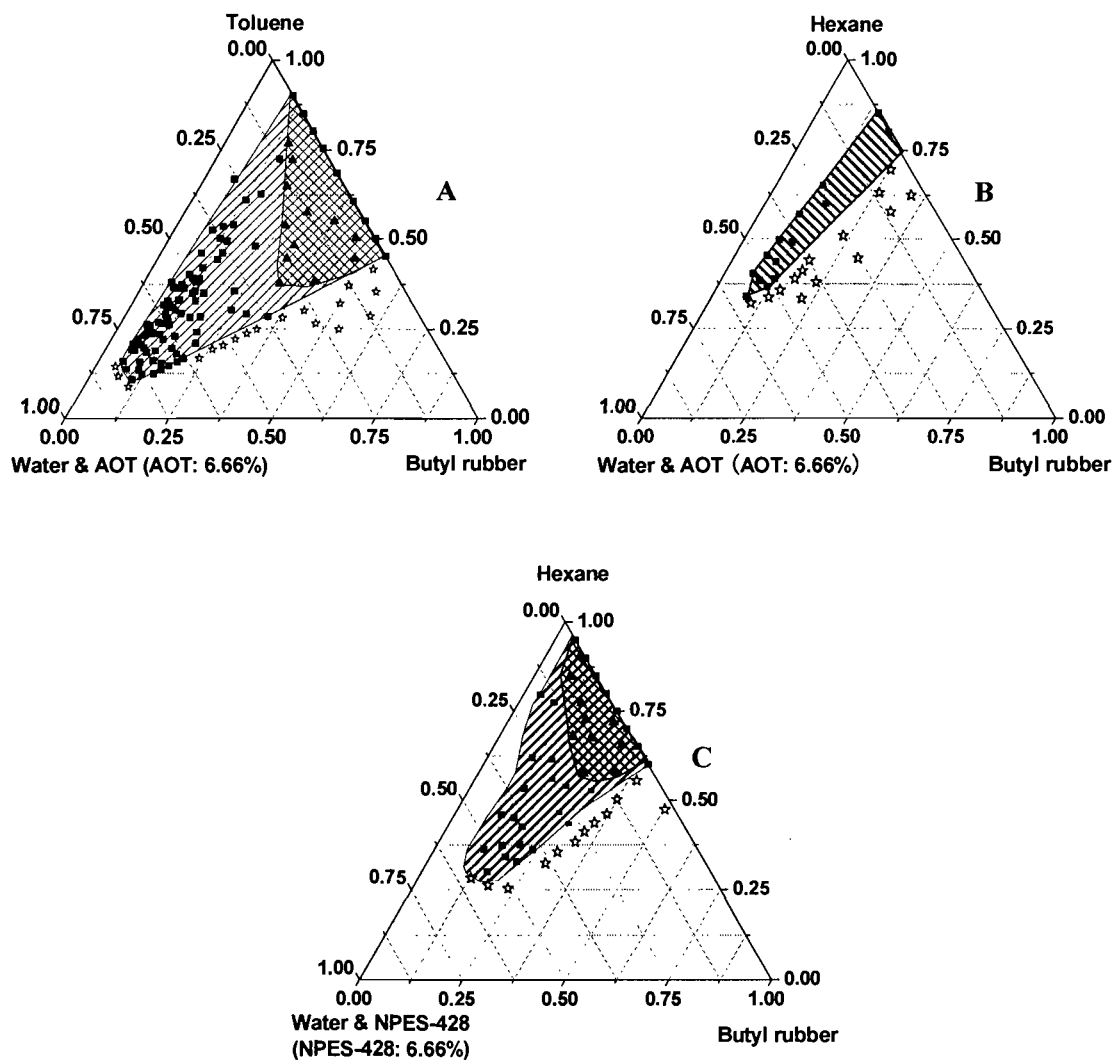
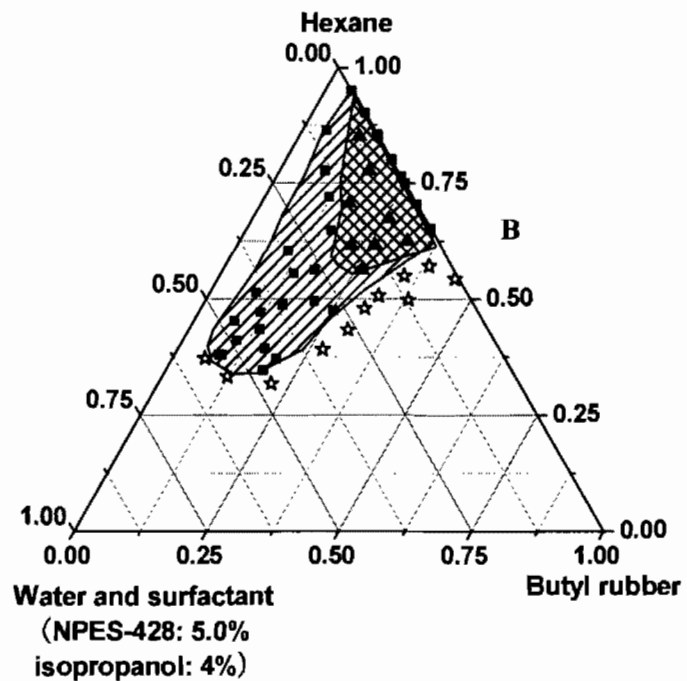
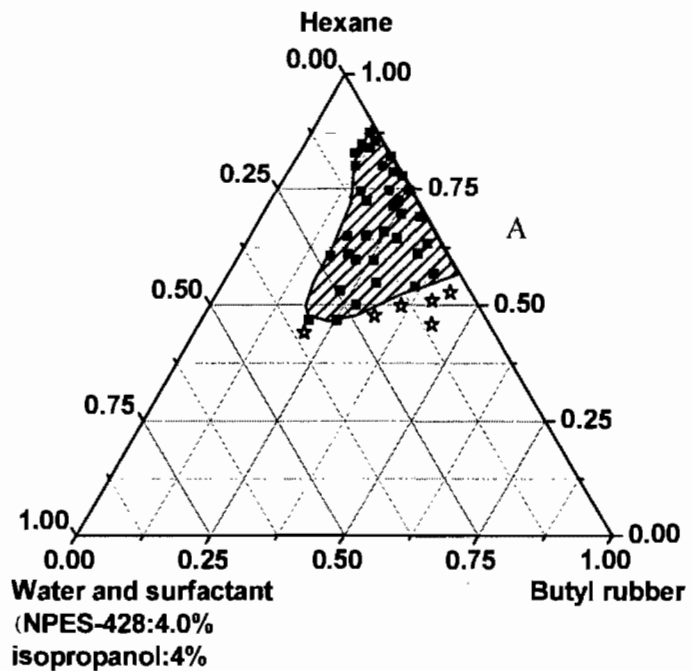


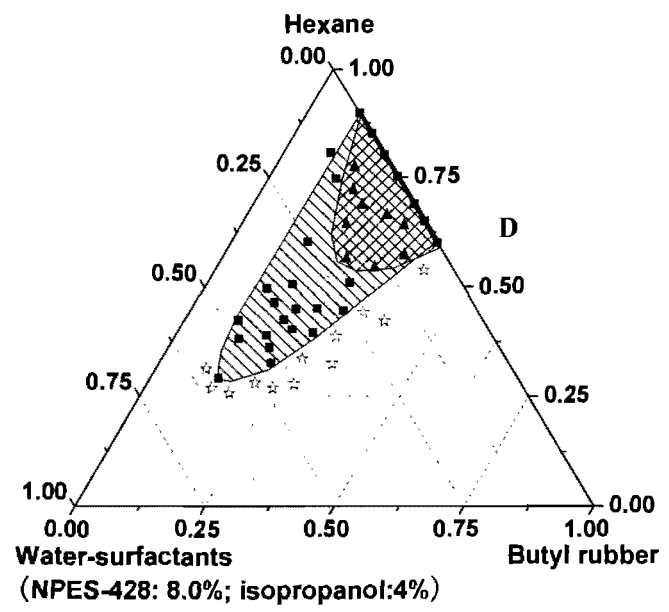
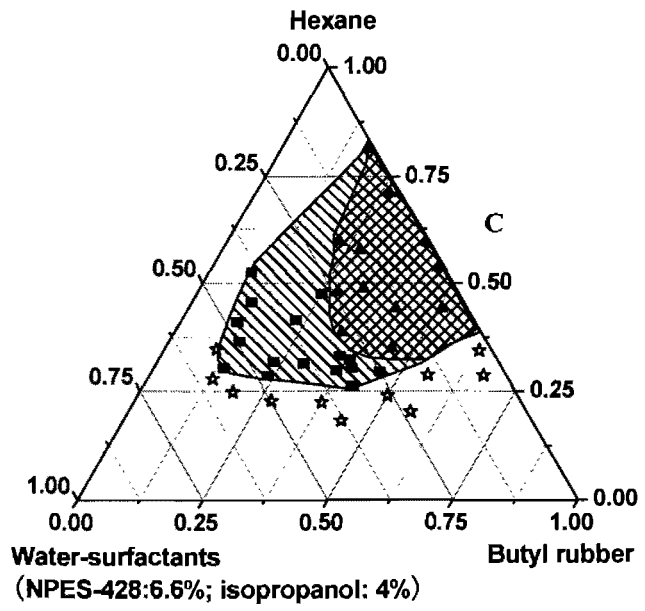
Figure 3.4. Phase diagrams of butyl rubber-organic solvent-aqueous systems under different conditions. A: Toluene system with AOT as the surfactant; B: Hexane system with AOT as the surfactant; C: Hexane system with NPES-428 as the surfactant. ■: oil-in-water emulsion (emulsion area); ▲: water-in-oil emulsion (gel area); ☆: unstable emulsion.

3.2.4. Effect of the surfactant concentration

To prepare the emulsion, surfactant is first dissolved into water (the two are regarded as one component) in the phase diagram. A series of experiments were performed with different concentrations of the surfactant in water (Figure 3.5). The emulsions contain hexane, butyl rubber, water, NPES-428, and isopropanol (as a cosurfactant to stabilize the emulsion). The concentration of the surfactant indicated is that of the surfactant in water before the addition of organic solvent.

In Figure 3.5, it can be observed that the size of the stable emulsion area varies greatly with the different of amount of surfactant in the aqueous phase. The optimal concentration of surfactant in the water was found to be 6.6 %. At this concentration, the largest stable emulsion area can be obtained in the ternary phase diagram. When the concentration of the surfactant was lower than 4 %, there was no emulsion obtained at all. Adding around 2 % more surfactant (Figure 3.5-A, B, and C), the stable area was enlarged. The size of stable emulsion area enlarges with increasing concentration of surfactant in the aqueous phase (water and surfactant). However, there was no improvement, when the concentration of surfactant in the aqueous phase was more than 6.6%. Consequently, 6.6 % surfactant (NPES-428) in the aqueous phase is an optimal concentration in the hexane system.





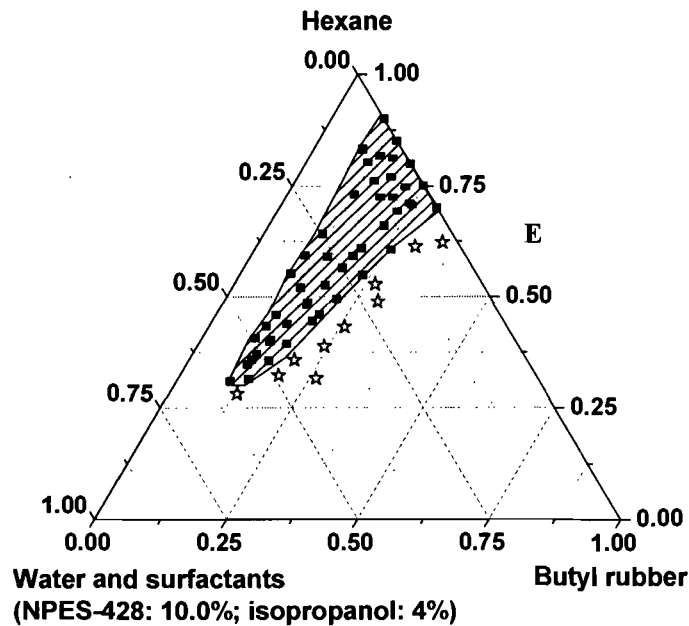


Figure 3.5. A series of ternary phase diagrams of the hexane system, prepared with different concentrations of the surfactant (NPES-428) in the aqueous phase. (A. 4.0 wt%; B. 5.0 wt%; C. 6.6 wt%; D. 8.0 wt%; and E. 10.0 wt%.)
 ■: oil-in-water emulsion; ▲: water-in-oil emulsion; ☆: unstable emulsion

3.2.5. Effect of agitation

An important characteristic of emulsion from a formation point of view is their stability, which can be adequately improved by reducing the droplet size. The choice of a homogenizer and the speed of agitation have a direct effect on the preparation of a stable emulsion.

Emulsions cannot remain stable forever. Energy input through shaking and stirring is needed to form an emulsion. Many devices have been designed to produce

emulsions. In our experiments, Ultra Turrax was selected (from VWR, Figure 3.6 shows the cross section of the homogenizer, the dimensions of the saw tooth generator being 10 mm × 150 mm (diameter × length)). The size of the rotor-stator probe can be different from the diameter of a rotor shaft for different sample volumes. In general, rotor-stator machines exist in great variety, often under the name homogenizer.

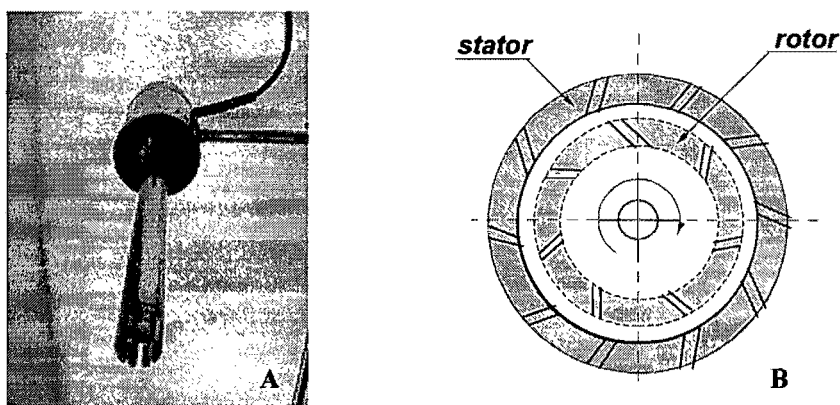


Figure 3.6. A. Ultra Turrax homogenizer. B. Cross section of an emulsifying machine (Ultra Turrax homogenizer).

The minimum agitation speed for the emulsion preparation was determined by the concentration of butyl rubber and the type of organic solvent. The solution can be quite viscous at a high concentration of butyl rubber. Consequentially, a high speed of agitation should be used. A high quality of the stable emulsion was obtained with a vigorous agitation. Normally, the quality of the emulsion can be determined by visual observation. During the process, a lot of air was mixed into the suspension, resulting in the formation of foam. As shown in Figure 3.7, the stable emulsion can be made easily

with a homogenizer. Figure 3.7-A shows that emulsion prepared with a homogenizer is quite uniform, while a phase separation is shown in Figure 3.7-B, when the sample was mixed by magnetic stirring.

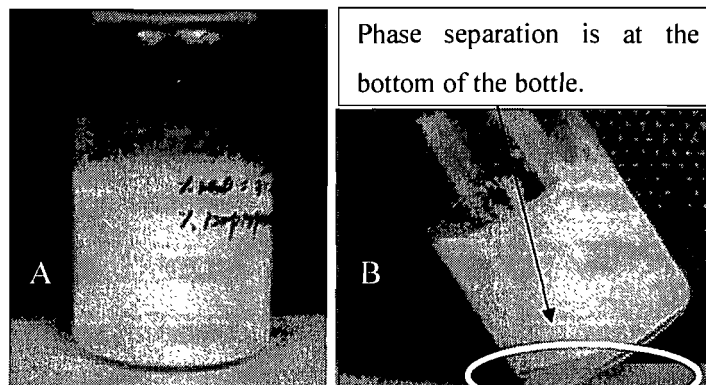


Figure 3.7. A. Emulsion mixed by the homogenizer; B. Sample mixed by the magnetic stirring with phase separation at the bottom.

An unstable emulsion separates into two layers rapidly. A homogeneous emulsion can remain stable for a long time. Emulsions were produced with agitation speeds from 17,500 to 35,000 rpm. Based on the solubility of butyl rubber, an agitation speed was selected (if the solubility is low, a high agitation speed should be used). For toluene, the best results were achieved at around 20,000 rpm. For other organic solvents (hexane and isooctane), a higher agitation speed should be used (35,000 rpm is the recommended speed, because the solubility of butyl rubber is low.). Unfortunately, the size of the homogenizer restricts the amount of sample used, normally in the range of 1.5 to 100 ml. For a different volume of emulsion, a different agitation device is

needed. The present homogenizer is only suitable for liquid samples in the low to medium viscosity range (less than 10,000 Pa.s).

3.2.6. The viscosity of the emulsion

Zero-shear rate viscosity is an important value for comparing the shear-thinning emulsions. Zero-shear rate viscosity cannot be measured by instruments, but it may be estimated by the use of viscosity models. The viscosity data has been analyzed by different theoretical models. We have used three viscosity models to fit all the viscosity measurement data, including the Cross model, the Carreau model, and the Carreau-Yasuda model. Based on the fitting results and the viscosity measurement data, a suitable model will be selected. The three models and their fitting parameters are listed in Table 3.4, and the fitting curves for the viscosity data are shown in Figure 3.8. The viscosity becomes stable at high shear rate. However, the difference of the viscosity is significant when the shear rate is close to zero. The Carreau model is widely used for fitting the shear-thinning viscosity data.¹⁵ The Carreau-Yasuda model is a modification from the Carreau model with a parameter “ a ” describing the transition region, which is between zero-shear rate viscosity and the power-law region. Parameter “ a ” dictates the curvature at the top of the curve. A higher “ a ” means a sharper transition of viscosity into the power-law region.¹⁵

Table 3.4. Viscosity models and fitting parameters calculated from the viscosity data for selected sample tested (T203, the chemical composition shown in Table 3.5).

| Viscosity model | Equation | η_0 (Pa.s) | Parameters | R^2 * |
|----------------------|--|-----------------|---|---------|
| Cross model | $\eta = \eta_{\infty} + \frac{\eta_0 - \eta_{\infty}}{1 + (C \dot{\gamma})^m}$ | 100 ± 5 | $\eta_{\infty} = 2 \pm 1$ $c = 2 \pm 1$ $m = 2 \pm 1$ | 0.87 |
| Carreau model | $\eta = \frac{\eta_0}{\left[1 + (\lambda \dot{\gamma})^b\right]^c}$ | 60 ± 1 | $\lambda = 3 \pm 1$ $b = 9 \pm 1$ $c = 2 \pm 1$ | 0.96 |
| Carreau-Yasuda Model | $\eta = \eta_0 \left[1 + (\lambda \dot{\gamma})^a\right]^{\frac{n-1}{a}}$ | 60 ± 1 | $\lambda = 3 \pm 1$ $a = 9 \pm 1$ $n = 2 \pm 1$ | 0.93 |

* R^2 is the coefficient of determination. When the regression line perfectly fits the data, R^2 is close to 1

As shown in Figure 3.8, the Carreau model and the Carreau-Yasuda model provide similar results with good fitting to the viscosity data, while the Cross model deviates obviously from the experimental data in the low shear rate region. The R^2 values obtained for the Carreau model (0.96) and the Carreau-Yasuda model (0.93) are higher than that of the Cross model (0.87), indicating better fittings with the Carreau and the Carreau-Yasuda models. Other samples were fitted by these three equations as well with fitting results in Table 3.5, and additional parameters listed in Tables C1-C3 (Appendix C).

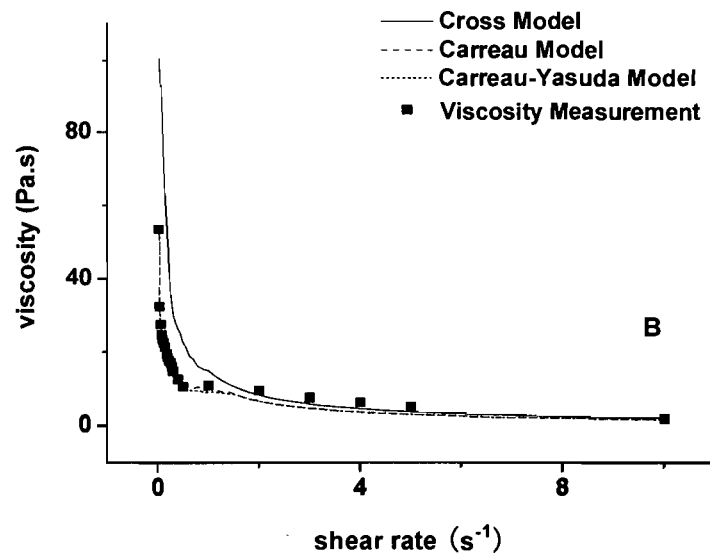
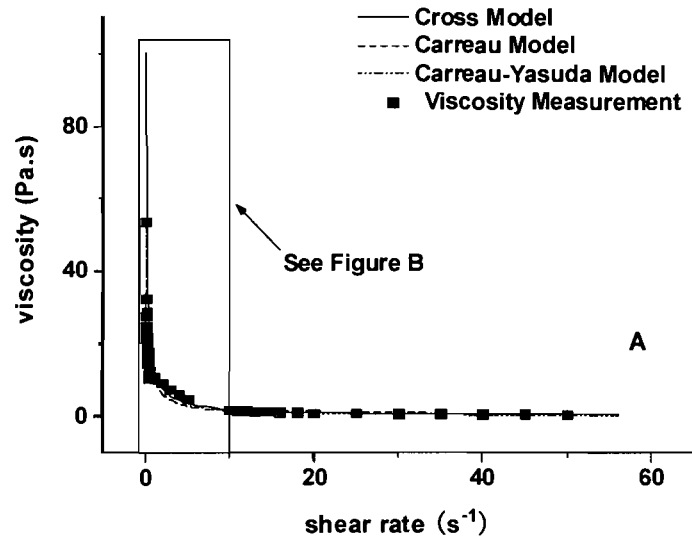


Figure 3.8. Variation of viscosity as a function of the shear rate for an example of a stable emulsion (T204). A. Fitting of the viscosity data with three viscosity models; B. Figure enlarged.

Table 3.5. Chemical composition of selected samples used for viscosity measurements.

| Sample | Butyl rubber (%) | Toluene (%) | Water (%) | AOT (%) | η_0^a (Pa.s) | η_0^b (Pa.s) | η_0^c (Pa.s) |
|--------|------------------|-------------|-----------|---------|-------------------|-------------------|-------------------|
| T201 | 40 | 31 | 27 | 2 | 140 ± 6 | 100 ± 2 | 100 ± 1 |
| T202 | 37 | 30 | 31 | 2 | 115 ± 4 | 74 ± 3 | 73 ± 3 |
| T203 | 36 | 28 | 34 | 2 | 100 ± 5 | 60 ± 1 | 60 ± 1 |
| T204 | 35 | 27 | 36 | 2 | 99 ± 4 | 56 ± 1 | 57 ± 1 |
| T205 | 34 | 27 | 36 | 3 | 96 ± 3 | 54 ± 1 | 54 ± 1 |
| T207 | 23 | 20 | 53 | 4 | 89 ± 8 | 37 ± 3 | 37 ± 3 |
| T208 | 20 | 16 | 60 | 4 | 84 ± 2 | 36 ± 3 | 34 ± 3 |
| T209 | 16 | 13 | 66 | 5 | 80 ± 6 | 36 ± 7 | 35 ± 7 |
| T210 | 13 | 11 | 71 | 5 | 57 ± 1 | 34 ± 2 | 33 ± 2 |

η_0^a : zero-shear rate viscosity calculated from Cross model; η_0^b : zero-shear rate viscosity calculated from Carreau model; η_0^c : zero-shear rate viscosity calculated from the Carreau-Yasuda model (more information see appendix C).

The zero-shear rate viscosity values can be plotted as a function of the weight percentage of aqueous phase containing the surfactant. The weight percentage of aqueous phase is the percentage of water and surfactant to the total weight of the sample (listed in Table 3.5). As shown in Figure 3.9, the viscosity decreases when approaching the aqueous phase (water and surfactant).

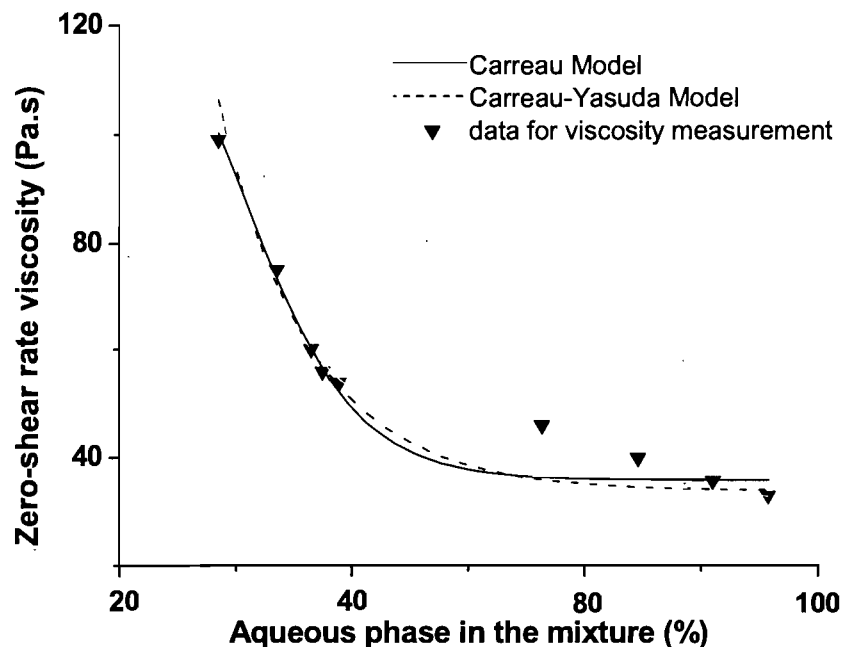


Figure 3.9. Zero-shear rate viscosity as a function of percentage of the aqueous phase containing water and surfactant (AOT). Solid line: the Carreau Model; dotted line: the Carreau-Yasuda Model.

In the ternary phase diagram, the stable area is separated into two parts (Figure 3.10). One is the oil-in-water emulsion area (emulsion area), and another is the water-in-oil emulsion area (gel area). The area boundary in the ternary phase diagram can be defined by the viscosity values. Figure 3.11 shows that the viscosity of the emulsion decreases very fast when the weight percentage of aqueous phase lies between 30% and 40%. The water-in-oil emulsion behaves as a gel that is very viscous. In Figure 3.11, the concentration of butyl rubber in organic solvent is kept constant. The viscosity of the mixture is very high (around 1600 Pa.s) below around 36 % of aqueous phase in the emulsion. The sample from this area can be defined as a viscous gel (water-in-oil

emulsion). A crossing the border of gel area, the viscosity decreases immediately, and this is area defined as the emulsion area (oil-in-water emulsion).

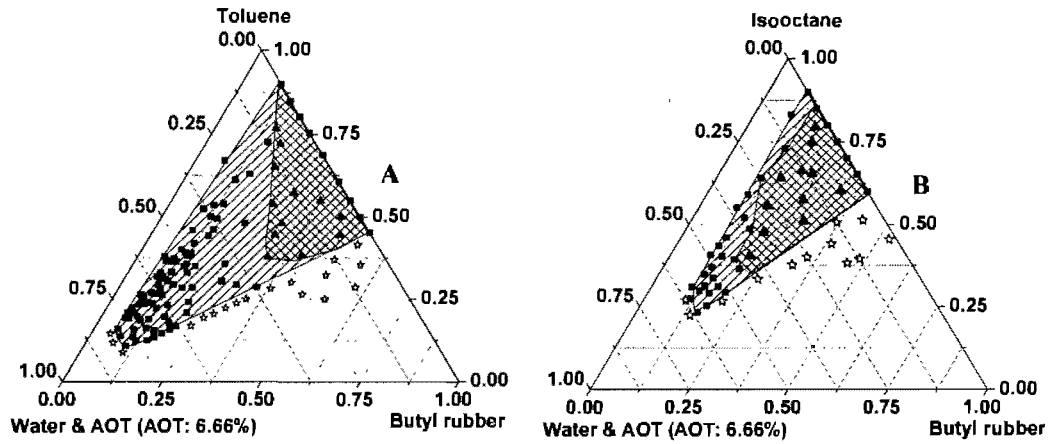


Figure 3.10. The water-in-oil emulsion area and the oil-in-water emulsion area shown in the ternary phase diagram.■: the oil-in-water emulsion (emulsion area); ▲: the water-in-oil emulsion (gel area); ☆: unstable emulsion.

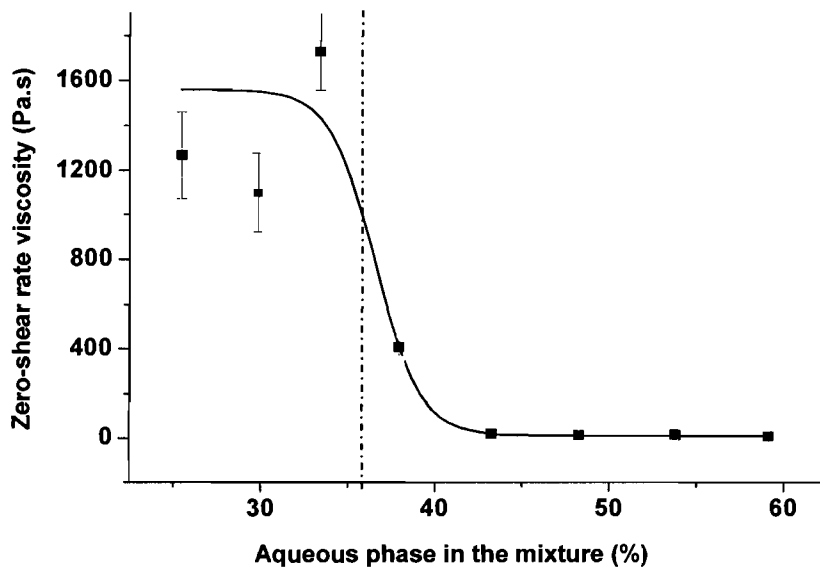


Figure 3.11. The variation of the zero-shear rate viscosity of a ternary system containing butyl 065 as a function of the percentage of the aqueous phase. A sharp change in zero-shear rate viscosity is shown from a water-in-oil emulsion to an oil-in-water emulsion at about 36% of aqueous phase in the mixture. On the right side of the dashed line, the viscosity of the emulsion is low, and the viscosities measured have less error.

The samples have a high viscosity in the water-in-oil emulsion area (the gel area), and cannot be used for dipping process since it is very difficult to control the thickness of the membrane in the preparation of butyl rubber gloves. Therefore, only the water-in-oil emulsion may be used in a molding process.

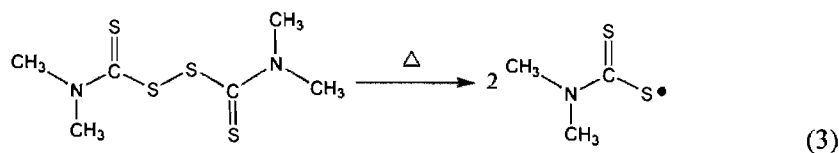
The viscosity of the emulsion can obviously affect the quality of rubber gloves. In the vulcanization step, the viscosity of the mixture increases (from around 7 to 50 Pa.s) with the addition of the vulcanizing agents. Even so, the viscosity is still much lower

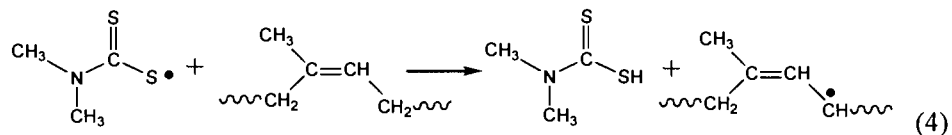
than the viscosity of the water-in-oil emulsion (gel). To control the viscosity of the final emulsion, the amount of added vulcanizing agents has to be controlled also.

3.3. Preparation of butyl rubber films

3.3.1. Vulcanization

The vulcanization process is important for the preparation of butyl rubber gloves. During the vulcanization step, the rubber molecules are crosslinked to form a three-dimensional structure with a better mechanical property. The crosslinked materials are insoluble in solvents and become more resistant to heat, light, and air. Based on the concentration of the C=C double bonds, the rubber may have different degrees of unsaturation in its structure. Sulfur vulcanization is the most widely used curing technique for rubbers, preferably for unsaturated ones.¹⁶ TMTD (Tetramethylthiuram disulfide) can accelerate sulfur crosslinking in the butyl rubber. When a rubber is vulcanized by sulfur without any accelerators, it may take several hours. However, the time of vulcanization can be reduced to 2-5 minutes with an accelerator. The isoprene provides the polymer with a certain degree of unsaturation. As shown in Equations 3 and 4, free radicals can be formed upon the degradation of TMTD, which initiates the crosslinking of the double bonds in the rubber.





The monosulphenyl radical can abstract an allylic hydrogen atom from the rubber chain. The vulcanization can be done at room temperature with an accelerator. TMTD is usually used together with zinc oxide since zinc oxide can lead to an increase in the crosslinking density.¹⁷

3.3.2. Effect of dipping speed

Normally, most emulsions show non-Newtonian behavior and shear thinning.^{18,19} For the systems studied here, the viscosity is constant over time at each shear rate (Figure 3.12-A), and the stable emulsions in this study show shear thinning behavior (Figure 3.12-B). The viscosity of the emulsion may vary with the shear rate change caused by the dipping speed of the mold used for making butyl rubber gloves. The dipping speed may thus affect the thickness of the butyl rubber glove, because the emulsion is a shear thinning fluid whose viscosity decreases with increasing dipping speed.

In industry, the dipping speed of the butyl rubber glove mold is around 10 cm.s⁻¹. Since the emulsion of butyl rubber has a shear thinning effect, its viscosity changes with different dipping speeds (the viscosity decreases when the dipping speed increases). To ensure the adhesion of enough emulsion on the glove mold, the viscosity of the stable emulsion should be around 15 Pa.s when the dipping speed is around 10 cm.s⁻¹.

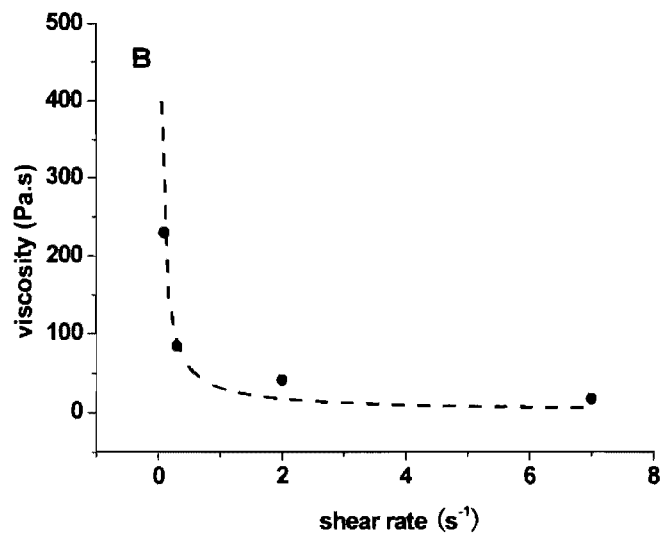
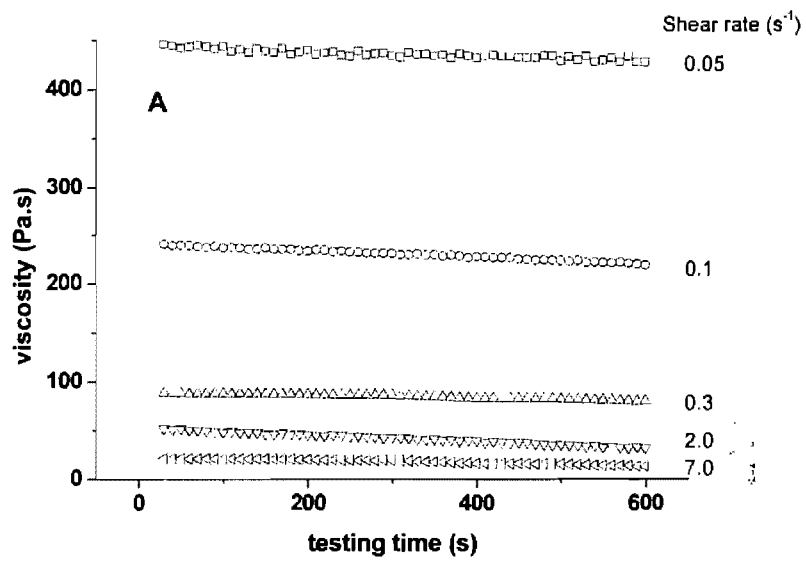


Figure 3.12. A. The viscosity as a function of the testing time. B. The viscosity as a function of the shear rate.

3.3.3. Mechanical property test

Dynamic mechanical analyses (DMA) were performed for the butyl rubber films.²⁰ The dynamic storage modulus is one of the parameters that can be measured by DMA. Dynamic modulus is the ratio of stress to strain under vibratory conditions.²¹ Dynamic storage modulus can be calculated from the following formula:

$$E' = \frac{\sigma_0}{\epsilon_0} \cos\delta \quad (5)$$

where σ_0 and ϵ_0 are the stress and strain, δ the phase angle between stress and strain.

The variation of the storage modulus as a function of the temperature is shown in Figure 3.13-B. Three samples have been tested. The first sample was obtained from company Best Gloves. Other two samples were made from the toluene system and isooctane system, whose compositions of the samples are listed in Table 3.6.

Table 3.6. Compositions (wt%) of butyl rubber-water-solvent ternary systems used for the preparation of the samples for the DMA tested.

| | Organic solvent | Butyl rubber | Water | AOT | ZnO ^a | TMTD | Sulfur |
|------------------|-----------------|--------------|-------|-----|------------------|------|--------|
| Toluene system | 34 | 24 | 39 | 3 | 2 | 1 | 1 |
| Isooctane system | 40 | 27 | 31 | 2 | 3 | 1 | 1 |

^aThe percentage of the vulcanization agents ZnO, TMTD, and sulphur was calculated as the weight percentage of the agent in comparison to the weight of the butyl rubber (e.g.

$$\%Agent = \frac{Agent}{Butyl\ rubber} \times 100).$$

At the low temperature, all the samples in the glassy state have a storage modulus in the range of 2.7 to 3.1 MPa. In the glassy state, the storage modulus values are almost equal. The storage modulus decreases rapidly in glass transition temperature

range, and the drop in storage modulus is about the same for three samples. Figure 3.13- A shows that the glass transition occurs over a relatively large range of temperatures, showing the heterogeneity of the crosslinked rubber samples. The mechanical properties of the samples made from the toluene and isooctane systems are in an acceptable range for use as gloves.

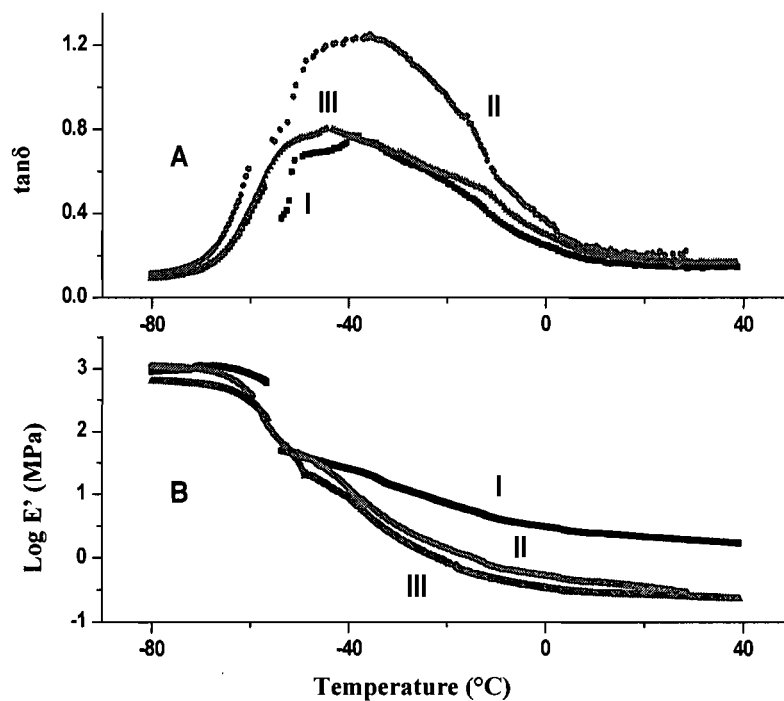


Figure 3.13. Dynamic mechanical analysis (DMA) of rubbers as a function of temperature. A. $\tan\delta$ (storage modulus E' divided by loss modulus E''), B. Log storage modulus. I: Gloves provided by Best Gloves; II: Films made from the toluene system; III: Films made from the isooctane system.

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4. Conclusions

We have studied the use of water-based systems for the preparation of a protocol in the industrial fabrication of butyl rubber gloves. To avoid the use of large amounts of organic solvents such as toluene in the procedure, water-based emulsion systems have been examined in an effort to reduce or replace the amount of organic solvent used. Even though the results may be preliminary in certain aspects, we can draw the following conclusions from this study, which should provide useful guidelines in this area of research.

(1) Generally, a stable emulsion can be formed by a ternary mixture containing butyl rubber, an organic solvent, and an aqueous phase. In the ternary phase diagrams, an area of usable emulsion can be defined close to the following composition: organic solvent at 30-40%, butyl rubber at 20-30%, and aqueous phase at 30-40%. Two organic solvents, isooctane and toluene, can be used for such emulsion systems. The oil-in-water emulsions prepared are stable and can be stored for 24 hours at room temperature (the procedure of making butyl rubber gloves can be finished in 24 hours in industry).

(2) A surfactant is essential for the preparation of the emulsion. AOT was selected for the two kinds of oil-in-water emulsions (both toluene and isooctane systems). For the oil-in-water emulsion prepared in this study, a surfactant with a HLB value higher than 10 should be selected. The selection of a surfactant depends on the choice of the organic solvent. The effect of the surfactant concentration can be optimized by verifying the size of the stable emulsion zone in the ternary phase diagrams.

(3) In the stable homogeneous area of the ternary phase diagram, a “gel area” and an “emulsion area” exist as characterized by their marked difference in viscosity. An

optimal area in a phase diagram can be defined by a viscosity that is not too high but high enough for the polymer to adhere onto the mold used for glove-making (ca. 10 Pa.s). The emulsion is a shear thinning fluid that can be described by the Carreau and the Carreau-Yasuda models. An efficient agitation system is needed to obtain stable emulsions, since adequate agitation was found to be essential in the preparation of the emulsion. Vulcanization of the rubber membrane has to be carried out to enhance the mechanical properties of butyl rubber materials.

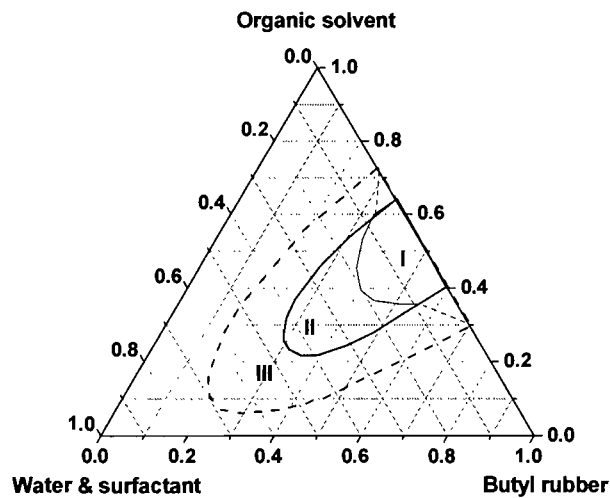


Figure 4.1. The ternary phase diagram shows the different areas. I. Stable gel area with high viscosity; II. Emulsion area that can remain stable for at least 24 hours; III. Emulsion area that can remain stable for a certain time shorter than 24 hours.

(4) The oil-in-water emulsions cannot remain stable indefinitely. We defined stable emulsions as those which could remain stable for 24 hours. This time can be considered as sufficient for the industrial production of butyl rubber gloves. Such a definition of stability can be modified depending on the need of the production process.

This means that, if the emulsions are to be used within a shorter time, a larger area of the mixture compositions can be redefined as a stable area, as shown in Figure 4.1.

Based on the results obtained, recommendation of usable emulsion systems with suitable chemical compositions can be made for the preparation of butyl rubber gloves. Our study offers a better understanding of the emulsion systems for the butyl rubber materials. Technological details may still be needed for the development of a practical industrial procedure. The choice of surfactants and the possible use of mixed solvents and mixed surfactants may be further explored.

Although we cannot replace the organic solvent completely, the reduction of the amount of organic solvents used in the water-based emulsion system can help to improve the safety of the workplace and to reduce the pollution to the environment.

Appendix

A. Synthetic method of butyl rubber

In the synthesis of butyl rubber, methyl chloride was used as a diluent and aluminum chloride as a coinitiator. Due to health risks of methyl chloride, alternative reaction media are needed to manufacture butyl rubber. Presently, a new method to make butyl rubber without methyl chloride is widely used.¹ The initiating system is composed of a mixture of ethylaluminum sesquichloride $[(C_2H_5)_2AlCl \cdot Cl_2AlC_2H_5]$ and water or hydrogen sulphide.² The reaction occurs in hexane. High molecular weights of butyl rubber can be obtained at a temperature around $-75^\circ C$, because isobutylene should be cooled to $-75^\circ C$ in the first step of the synthesis. Other materials such as hexane and isoprene do not need cool down. The reactions are carried out with an overhead stirrer. The stringent temperature control during the synthesis is achieved by the use of a thermocouple. At end of the reaction, the polymerization is terminated by adding some ethanol. There are some impurities and unreacted monomers in the polymer solution. The polymer solution is poured into an aluminum tare lined with Teflon, and organic solvents and unreacted monomers are allowed to evaporate at room temperature. The polymer is dried in vacuum oven at about $70^\circ C$. In the homopolymerization of isobutylene to make polyisobutylene, chain transfer to monomer is the important chain breaking step (Figure A.1)

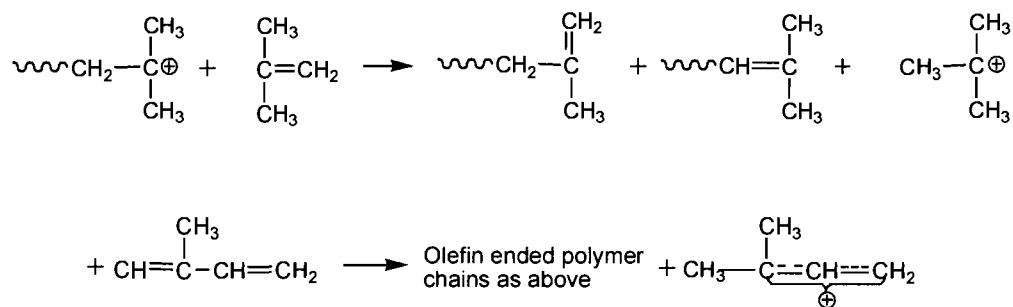


Figure A.1. Chain transfer to monomer during the synthesis of butyl rubber³

Compared to the first step, the termination reaction is a minor process (Figure A.2). It involves the propagating reaction of the macromolecular carbonation with the counter-ion where AB is BF₃ or Cl₃CCOO-ester groups.

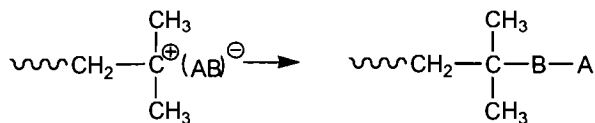


Figure A.2. Termination with counter-ion in the preparation of butyl rubber³

Another possible reaction of the carbonium ion is with a hydride donor (Figure A.3).

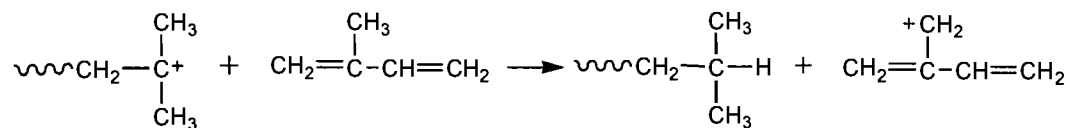
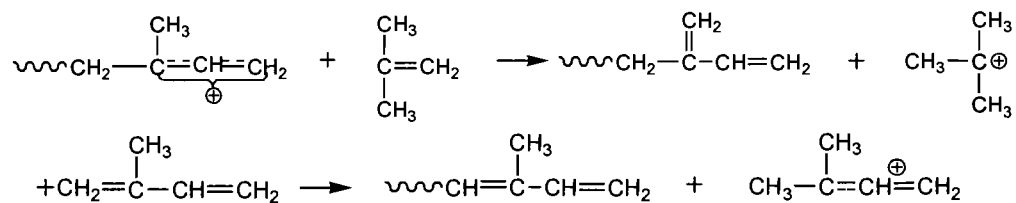
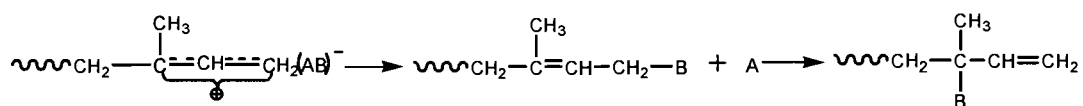


Figure A.3. Termination by hydride donor during the synthesis of butyl rubber³

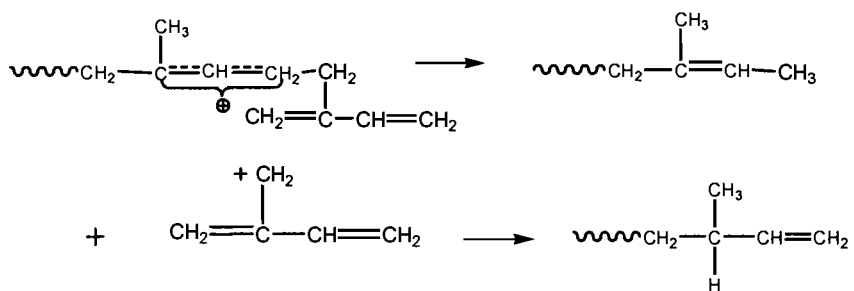
The isoprene chain end can also be terminated by chain transfers to monomer with counter-ion, or by hydride donor, as shown in Figure A.4.



A. Chain transfer to monomer:



B. Termination with counter-ion:



C. Termination by hydride donor:

Figure A.4. Involvement of isoprene derived chain-ends in the synthesis of butyl rubber

In this project, halobutyl rubber is chosen as the raw material to make an emulsion. The commercial halobutyl rubbers are more easily vulcanized than butyl rubber.⁴ Commercially, chlorobutyl and bromobutyl derivatives of butyl elastomers are of greater importance.⁵ Figure A.5 and A.6 show the isoprenyl units in the bromobutyl rubber and chlorobutyl rubber.

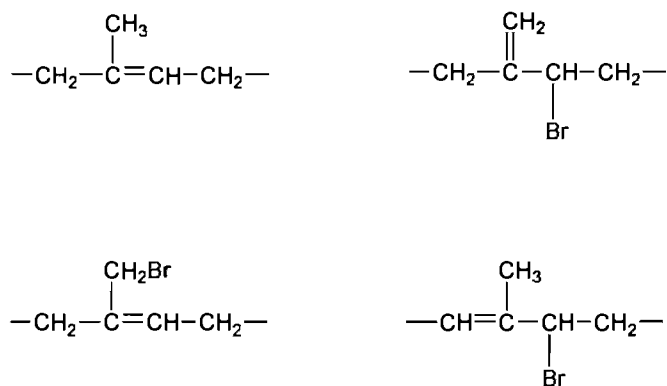


Figure A.5. Structures of isoprenyl units in bromobutyl rubber⁶

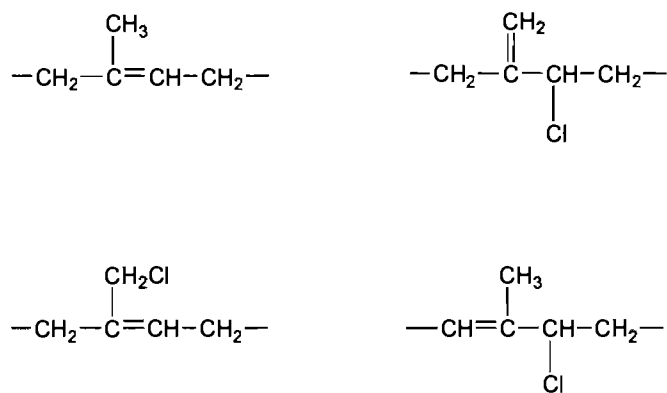


Figure A.6. Structure of isoprenyl units in chlorobutyl rubber⁶

B. Mooney viscosity

Mooney viscosity is defined as the shearing torque resisting rotation of a cylindrical metal disk (or rotor) embedded in rubber within a cylindrical cavity. The mooney viscosity is testing at 125°C. minimum mooney viscosity (M) has been measured by a large rotor (L), which it has a diameter of 38.1 mm, at preheating time of 1 minute and test time of 8 minutes (e.g. 45 ML 1+8 100°C, this means that the mooney viscosity (M) is 45 when the large rotor (L) was used. The warm-up time is 1 minute, at the test temperature of 100°C. The large rotor is rotated for 8 minutes before reading the value.

C. Viscosity measurements

Table C.1. Viscosity data and fitted parameters calculated by the Cross model for selected emulsion samples.

| Sample | η_0 (Pa.s) | η_∞ (Pa.s) | C | m | R ² |
|--------|-----------------|----------------------|--------|-------|----------------|
| T201 | 140 ± 6 | 2 ± 1 | 3 ± 1 | 2 ± 1 | 0.79 |
| T202 | 115 ± 4 | 2 ± 1 | 2 ± 1 | 2 ± 1 | 0.81 |
| T203 | 100 ± 5 | 2 ± 1 | 2 ± 1 | 2 ± 1 | 0.87 |
| T204 | 99 ± 4 | 1 ± 1 | 5 ± 1 | 1 ± 1 | 0.83 |
| T205 | 96 ± 3 | 1 ± 1 | 6 ± 1 | 1 ± 1 | 0.73 |
| T207 | 89 ± 8 | 1 ± 1 | 45 ± 3 | 1 ± 1 | 0.86 |
| T208 | 84 ± 2 | 1 ± 1 | 22 ± 1 | 1 ± 1 | 0.79 |
| T209 | 80 ± 6 | 1 ± 1 | 49 ± 4 | 1 ± 1 | 0.82 |
| T210 | 57 ± 1 | 1 ± 1 | 19 ± 1 | 1 ± 1 | 0.91 |

Table C.2. Viscosity data and fitted parameters calculated by the Carreau model for selected emulsion samples.

| Sample | η_0 (Pa.s) | λ | b | c | R ² |
|--------|-----------------|-----------|------|-----|----------------|
| T201 | 100±2 | 4±1 | 12±2 | 1±1 | 0.95 |
| T202 | 74±3 | 3±1 | 10±2 | 1±1 | 0.95 |
| T203 | 60±1 | 3±1 | 9±1 | 1±1 | 0.96 |
| T204 | 56±1 | 4±1 | 4±1 | 1±1 | 0.97 |
| T205 | 54±1 | 4±1 | 3±1 | 1±1 | 0.99 |
| T207 | 37±3 | 10±3 | 2±1 | 1±1 | 0.96 |
| T208 | 36±3 | 10±1 | 2±1 | 1±1 | 0.94 |
| T209 | 36±7 | 14±4 | 2±1 | 1±1 | 0.99 |
| T210 | 34±2 | 12±1 | 1±1 | 1±1 | 0.96 |

Table C.3. Viscosity data and fitted parameters calculated by the Carreau-Yasuda model for selected emulsion samples.

| Sample | η_0 (Pa.s) | λ | A | N | R ² |
|--------|-----------------|-----------|------|-----|----------------|
| T201 | 100±1 | 4±2 | 14±3 | 1±1 | 0.95 |
| T202 | 73±3 | 4±1 | 11±1 | 1±1 | 0.97 |
| T203 | 60±1 | 3±1 | 9±1 | 1±1 | 0.93 |
| T204 | 57±1 | 4±1 | 4±1 | 1±1 | 0.99 |
| T205 | 54±1 | 4±1 | 3±1 | 1±1 | 0.97 |
| T207 | 37±3 | 10±3 | 2±1 | 1±1 | 0.98 |
| T208 | 35±3 | 10±1 | 2±1 | 1±1 | 0.99 |
| T209 | 35±7 | 14±3 | 2±1 | 1±1 | 0.96 |
| T210 | 33±2 | 12±1 | 1±1 | 1±1 | 0.96 |

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