The effect of chlorination on tensile strength and extractable protein content of surgical gloves from natural rubber latex

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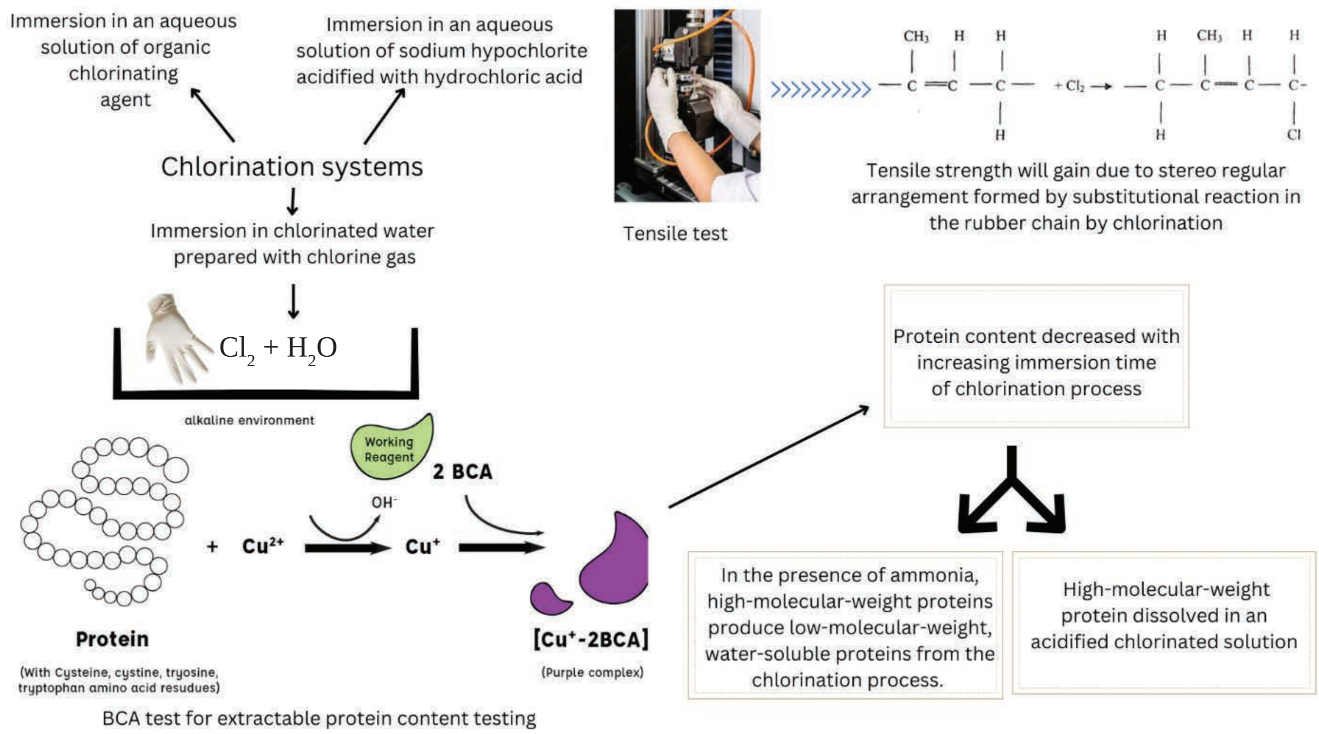


1. Introduction

Natural rubber is made from the latex sap found in the bark of rubber trees (*Heavea brasiliensis*). The rubber is composed of cis-1, 4-polyisoprene (with 4% trans structure in the polymer backbone). Latex is a stable polymeric substance dispersion in an aqueous medium. It is composed of negatively charged rubber particles dispersed in an aqueous medium. Sugars, lipids, proteins, fatty acid soaps, amino acids, and a variety of organic and inorganic salts, including soluble salts of calcium, magnesium, and alkali metals, make up the aqueous portion, or serum. Natural rubber latex has inherent characteristics such as high flexibility, strength, and tensile strength[1].

Glove manufacture accounts for the majority of latex usage[2]. Gloves are initially coated by dipping into a chemical coagulating agent; this process is called "coagulant dipping," which is the major method used in glove manufacture[3]. Different gloves are used for various purposes. Among these are industrial gloves[2], domestic gloves, examination gloves, and surgical gloves. It includes both disposable and non-disposable versions of gloves. Non-disposable surgical gloves are meant to be reused; disposable gloves are meant to be used just once. Examination and surgical gloves are in the disposable category. The usage of surgical gloves by healthcare professionals keeps their skin, free of viruses and body fluids contamination[3].

Natural rubber latex and synthetic rubber latex can both be used to make disposable surgical gloves[3]. Natural rubber latex has superior properties to synthetic rubber latex. Disposable natural rubber surgical gloves come in two types. They are powdered disposable surgical gloves and powder-free disposable surgical gloves. Some healthcare workers are unwilling to wear powdered gloves due to various allergic reactions to the powder[4]. As a result, the production of powder-free surgical gloves began.

Chlorination of gloves has become more common as a more long-lasting technique of lowering the inherent tackiness of natural rubber latex when contrasted to utilizing powder as a dusting lubricant. When natural rubber latex proteins from powdered gloves are discharged into the air, those who are allergic to them may experience major difficulties [1, 5]. Although these proteins in the finished glove pose little risk to the general public, certain groups, such as healthcare professionals, spinifida patients, and industrial workers, are at a higher risk of developing these allergies[6].

Surface halogenation in powder-free gloves is the most effective method for reducing surface friction and tackiness in NR latex films. It is a common process used in the manufacture of surgical gloves and offers a smooth feel, easy donning, and removal capabilities. Vulcanized rubber is softer than halogenated rubber. The three main methods of surface halogenation are chlorination, bromination, and iodination[3].

The best surface treatment is chlorination because it reduces surface tackiness and friction better than other halogens. It results in a microtextured film. The surface of micro-roughened gloves appears to have been lightly sanded, which adds a good amount of grip to these gloves. Chlorination was discovered to reduce proteins that can be extracted and excessive accelerators removed from the glove surface[1]. The chemical resistance of the glove film can also be enhanced by chlorination. Unless it is not excessively chlorinated, the qualities of the glove film increase without affecting the bulk properties.

In the manufacturing process of disposable surgical gloves made from natural rubber, chlorine is used for the surface halogenation of NRL. The interaction of the halogen with the olefinic double bonds of the natural rubber latex macromolecule results in the formation of a layer of halogenated rubber. Natural rubber that has been vulcanized is softer than rubber that has been halogenated. Hence, the coefficient of friction of halogenated natural rubber is lower. The surface obtained from chlorination is described as microtextured[2].

2. History of Chlorination

Reducing tackiness, and increasing lubrication are the main objectives of the chlorination process. Initial research related to chlorination treatment was done by G.F.Bloomfield in 1943-1944. To broaden knowledge and research of the chlorination process, great service was rendered by G.Kraus and W.B. Reynolds (1950), Gorton, Bratby, and Vanderbit.[3]

2.1 Chlorination Systems

There are three different ways of chlorination.

- Immersion of the glove in an aqueous solution of sodium hypochlorite acidified with hydrochloric acid[2].
- Immersion of the glove in an aqueous solution of an organic chlorinating agent[2].
- Immersion of the article in chlorine water prepared by dissolving chlorine gas (from cylinders) in water[2].

They show quick reactions and reaction mechanisms are assumed same.

2.1.1 Aqueous solution of an organic chlorinating agent

N-Chloro sodium dichloroisocyanurate is the commonly used organic chlorinating agent.

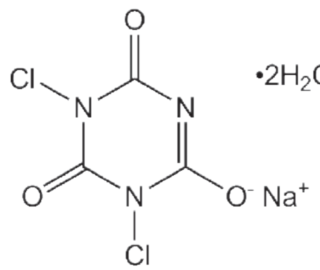
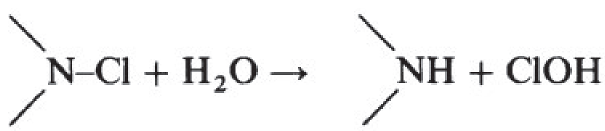


Figure 1: Structure of N-Chloro sodium dichloroisocyanurate[1]

This substance, also known as sodium 1,3-dichloro-5-triazine-2,4,6 (1H,3H,5H)-trione, is a disinfectant used to purify water (Figure 1). This can be applied both with and without acid. The ideal acid to use with this is hydrochloric. After the N-Cl is hydrolyzed, the process will produce hypochlorous acid (Figure 2).



Hypochlorous acid reacts with HCl and it will generate chlorine. The rate at which the N-Cl bond breaks down will determine how well chlorine may interact with rubber[2].

2.1.2 Chlorine water prepared with chlorine gas

The chlorine gas available in pressurized cylinders is passed into the water until it is saturated with chlorine. Stainless steel is used to construct the saturation tank.

The concentration of chlorine is 0.56% of the weight of water when it is completely dissolved. Water will be used to dilute chlorine to the necessary concentration level. The latex item is then dipped in the chlorine solution for a predetermined amount of time. According to Vanderbit, 4.5–7.5 min of immersion time is needed, and according to Bratby, 15–30 min are needed for a 0.08%–0.12% chlorine solution. However, different industries have their own chlorine systems, with proper concentrations suitable for their products.

It is somewhat difficult to handle and maintain this system. It needs expensive and high-quality machines. Since chlorine is a toxic gas, there should be extractions and proper ventilation when using gaseous chlorine.

2.1.3. The aqueous solution of sodium hypochlorite acidified with hydrochloric acid

This is the most basic method used in chlorination. According to Gorton and Pendle, 1% m/m of conc. hydrochloric acid is added to a 7.5% m/m solution of sodium hypochlorite.

$$NaOCl \longrightarrow Na^+ + OCl^-$$

$$H_2O + OCl^- \longrightarrow HOCl + OH^-$$

$$NaOCl + H_2O \longrightarrow HOCl + NaOH$$

In the presence of HCl,

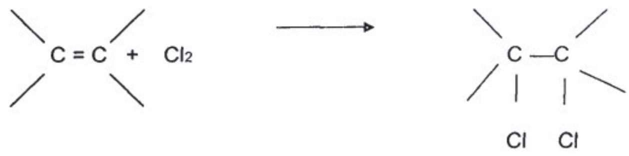
$$HCl \longrightarrow H^+ + Cl^-$$

$$HOCl + H^+ + Cl^- \longrightarrow Cl_2 + H_2O$$

Not only molecular chlorine solution it also consist of chloride anions, hydrogen ions, hypochlorus acid as well as hypochlorite anions. They are in an equilibrium[2] having 3×10^{-4} mol^2 dm^{-6} at 25 ^{0}C. 0.08 mo dm^{-3} will be chlorine concentration of saturated chlorine water under atmospheric pressure and normal temperature[2].

There are three potential mechanisms exist for chlorine to interact with rubber molecules.

1. Addition reaction



2. Substitution reaction

$$—CH_2— + Cl_2 \longrightarrow —CHCl— + HCl$$

Since hypochlorous acid is formed, an addition reaction will happen to give chlorohydrin[2].

$$CH_2=CH_2 + HOCl \longrightarrow ClCH_2\text{-}CH_2OH$$

Thermal stability is minimized due to chlorohydrin. According to Kraus et al. chlorination will happen in three steps at 30 ^{0}C.

- First step – Substitution occurs
- Second step – 1.2 molecules of Cl react by both substitution and addition reactions
- Third step – 2.2 molecules of chlorine per isoprene unit have reacted by the addition reaction

All subsequent reactions happen by substitution via UV catalyzed addition reactions and oxygen or peroxides catalyzed substitution. In this system, aging properties and thermal stability are less. Surface tackiness reduction and discoloration is not good as chlorine gas system.

Table 1 shows the advantages and disadvantages of chlorination.

Table 1: Advantages and disadvantages of chlorination

Advantages	Disadvantages
Powder free treatment	Inadequate thermal stability
Reduction in protein content	Poor anti-aging properties
Can be done in larger scale	Brittle surface
Less time consuming	Undergo discoloration
	Health hazards due to chlorine gas
	Environmental problems

3. Effects of chlorination on properties

The extractable protein content has been found to be lower after the chlorination treatment. More reduction will result from higher chlorine treatment. After chlorination, surface friction and tackiness decrease, increasing surface lubrication. The level of chlorination has an effect on tensile strength as well. Surface cracks have been discovered to appear at a specific chlorine concentration. Higher chlorine concentrations cause more surface cracks, which lead to leaks and damage the gloves' barrier properties. Depending on their needs, industrialists perform chlorination treatment at various levels. As a result, the glove's quality varies.

3.1 Effect on tensile strength

Tensile strength is the amount of force required to stretch a medical glove until it breaks. Amarasiri[1] tested 36 dumbbell-shaped latex films for tensile strength after immersing them in 6 different chlorine concentrations: 1700 ppm, 1500 ppm, 1400 ppm, 1300 ppm, 1150 ppm and 1000 ppm. The duration of the immersion varied as well: 0 minutes, 4 minutes, 8 minutes, 12 minutes, 16 minutes, 20 minutes, and 24 minutes. He has identified an increase in tensile strength in chlorinated samples compared to unchlorinated samples. According to Blackley[3], the tensile strength of post-vulcanized samples ranges from 22 MPa to 38 MPa. The maximum tensile strength was observed in the 1150 ppm chlorine concentration for 12 minutes[1], considering the immersion time in the chlorine bath and chlorine concentration. The relevant tensile strength was 31.746 MPa. As the leaching time increases, tensile strength of the latex film increases[7]. Leaching removes non-rubber substances from the film's rubber particles, improving inter-particle integration. In addition it was identified that the tensile strength values also vary according to the stereo regularity of the rubber hydrocarbon.

Figure 3 shows the reaction between one chlorine molecule and isoprene unit[3].

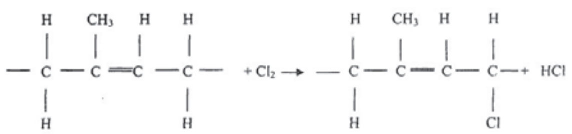


Figure 3: Reaction of rubber molecule with chlorine

The stereoregularity of the polyisoprene structure is distributed as a result of the introduction of chlorine groups into the main chain. This reduces strain-induced crystallinity, which in turn reduces tensile strength[1]. The tensile strength of the 12-minute sample increased dramatically[1]. As a result of the continuous substitution reaction, more chlorine groups are introduced into the polyisoprene main chain. This results in a stereoregular arrangement, which improves the strain-induced crystalline structure and other properties of the polyisoprene main chain. The tensile strength of chlorination begins to decrease at 16 minutes. The crystallization reaction has been discovered to occur during the initial substitution. The substitution reaction causes an increase in acidic behavior. Kraus at el. [7], and Gorden M.[8] proposed the following crystallization reaction (Figure 4). The distribution of stereo regularity in the cyclohexane ring reduces strain-induced crystallization and, consequently, tensile strength[1].

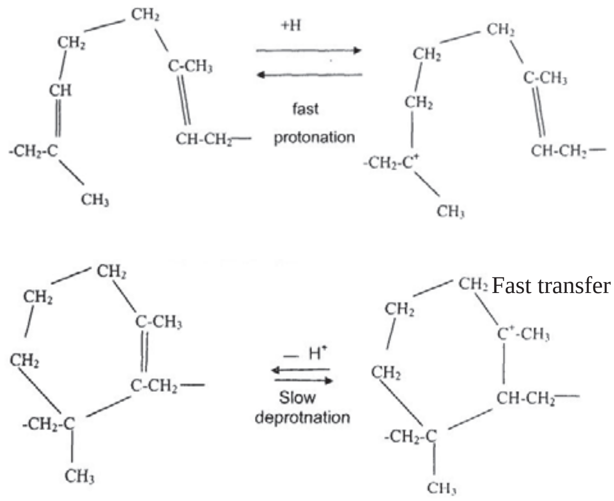


Figure 4: Proposed crystallization reaction[1]

3.2 Effect on extractable protein content

There are different methods to test extractable protein content in NR gloves. Because it is simpler and less complicated, the BCA-enhanced protocol method was used to determine the extractable protein content in the majority of previous research. Furthermore, this method is preferred by more manufacturers for measuring protein content, which can reach 50 ug/g. This method has identified the the number of peptides, nanomolecular structure of proteins, and the presence of four amino acids as being responsible for color formation.[9]

Ananda Amarasiri[1] has tested film immersed in an 1150ppm chlorine concentration bath for different immersion times (0 mins, 4 mins,8 mins,12 mins,16 mins,20 mins,24mins). He discovered that the protein content decreased with increasing immersion time. More water-soluble and insoluble proteins will be removed from the surface with a longer chlorination time[1]. Allergens, such as hevein, has a low molecular weight and dissolve easily in water at all pH levels[3]. Some proteins with high molecular weight, such as alpha globulin, do not dissolve in distilled water but they dissolve in acid, neutral salt, or alkaline solutions[3]. In ddition, these proteins dissolve more easily in the acidified chlorinated medium than in distilled water.

A successful double-leaching process can reduce proteins by up to 50 microgram/g. All of these proteins are water-soluble. Water-insoluble proteins dissolve in human sweat after being worn, because human sweat contains salt. An allergic reaction could result from the dissolved protein that surrounds the powder particle being absorbed[10]. The double-leaching system cannot remove these types of proteins. However, they can be removed with an acidic, alkaline, or neutral salt solution. Furthermore, when exposed to ammonia, a preservative, these high molecular weight proteins disintegrate to form water-soluble low molecular weight proteins[11]. To avoid protein allergy issues, it is critical to remove both water-soluble and water insoluble proteins. It is identified that the chlorination is the best solution for removing both of these proteins[1].

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