SCHOOL OF MATERIALS AND MINERAL RESOURCES ENGINEERING
UNIVERSITI SAINS MALAYSIA

# COMPARISON OF DIFFERENT TYPES OF DISPERSING AGENT ON MECHANICAL PROPERTIES OF NATURAL RUBBER LATEX FILMS

By

**NEO EN PEI**

**Supervisor: Assoc. Prof. Dr. Azura A. Rashid**

Dissertation submitted in partial fulfillment
of the requirements for the degree of Bachelor of Engineering with Honours
(Polymer Engineering)

Universiti Sains Malaysia

**JUNE 2017**

# CHAPTER 1

# INTRODUCTION

## 1.1 Research Background

The chemical structure of Natural Rubber (NR) latex is cis-1,4 polyisoprene which in the form of colloidal dispersion. The NR latex is obtained from the Hevea brasiliensis tree in the form of white milky sap. It is usually used to produce thin film products such as NR latex gloves. The production of NR latex gloves had increased extensively because of some diseases outbreak as well as the increasing demand and awareness of barrier protection against epidemic pathogens. Because of the NR latex gloves are as single use materials, the increase of gloves production also leads to solid waste disposal problems (Rose & Steinbuchel, 2005).

Rose & Steinbuchel (2005) stated that the solid waste problem arise due to the hardly degraded NR latex because the inorganic materials such as sulphur and antioxidants make the NR latex films to be resistant to microbial infections. NR latex films can be degraded in natural environment via oxidative cleavage of the double bond in the polyisoprene backbone chain. Therefore, the NR latex had been studied to be compounded with the other degradable materials to make the NR latex products being able to be decomposed by biological means through microorganism. In this study, sago starch is chosen as the degradable bio-filler because of its attractive characteristics of naturally abundant, low cost, renewable resources and highly susceptible to biodegradation (Afiq & Azura, 2013).

Starch is a polymer which can be found widely in plants. Biliaderis et al. (2009) reported that starch is polysaccharide material made up of random coiled amylose and a branched structure of amylopectin which linked by glucosidic linkages. Depending on the source, the starch has different ratio of amylose and amylopectin which has the range of 10-20% to 80-90% amylose and amylopectin respectively. However, there are some disadvantages of starch properties that would lead to the poor NR latex compound. Yahya et al. (2014) reported that the disadvantages of starch are large particle size, poor mechanical properties, poor dimensional stability, and hydrophilic in nature. Therefore, the starch as filler in NR latex was prepared in liquid medium during mixing process to improve the dispersion and compatibility in NR latex compounding process.

Junko et al. (2003) stated that when an aqueous suspension of starch is heated, the hydrogen bonds in starch molecules are weaken. Then the water is absorbed and the starch granules swell. This process is called gelatinization. Gelatinization is a process of breaking own the starch granules by subjecting mechanical shearing or heating in the presence of water. The mechanism of starch gelatinisation occurs when granules start to swell. During heating in water, starch granules become hydrated, swell, and are transformed into a paste. Thermal energy or shearing forces applied caused the crystalline region of starch (amylose and amylopectin structure) losing their configuration order as melting of crystallite, unwinding of double helices and breaking down of hydrogen bonds. Amylose begins to leach out from the granule including fragments of amylopectin, then starch stabilization occurred. Lastly, the starch granules which contain mostly amylopectin are collapsed and held in the matrix of amylose to form a gel network (Palav & Seetharaman, 2006). Consequently, penetration and adsorption of water or chemical reagents will result in starch granules swollen.

Moreover, the starch retrogradation happens upon cooling of gelatinized starch. Retrogradation refers to the re-association of the leached amylose from gelatinized granules into different ordered structure. The amylose and amylopectin chains realign themselves again to more crystalline structure after being cooled at lower temperature for long enough periods. Re-association and re-crystallization of amylose causes release of the water absorbed and bound during gelanization, leading to the phenomenon known as syneresis.

Re-association accompanied by syneresis also known as unacceptable water loss happen if the gels remain strong during undisturbed cooling. Further association of amylose and contraction of gel cause water loss and granule shrinkage (Rashid et al., 2010). The retrogradation causes the destabilisation of starch in the form of dispersion. This leads to making of poor NR latex compounds which the dispersion and distribution of starch filler in NR latex is unsatisfactory.

## 1.2 Problem Statement

For solving the solid waste disposal problem, landfill was always the most popular alternative. However, the problem still exits due to the time consuming degradation of rubber based products especially NR latex gloves as it is single use material. The degradation process of NR latex gloves takes long duration is because of the addition of several ingredients as protective agents and cross-linker which further prolong and increase the resistance towards degradation of materials.

Misman & Azura (2014) had proven that the incorporation of sago starch as biodegradable natural filler in NR latex film is able to promote the biodegradation process. The degradation of NR latex gloves occurred due to the breakdown of glucosidic linkages of amylose and amylopectin by means of enzymatic hydrolysis by microorganism.

Yahya et al. (2014) also reported that the hydrophilic nature of the starch due to the abundance of hydroxyl groups has poor compatibility with some hydrophobic polymers. Sago starch is prepared in liquid medium during mixing process to improve the dispersion and compatibility with NR latex. During pre-vulcanisation process, mixture is heated to improve the crosslinking of the rubber particles in NR latex, sago starch will undergo gelatinization. Starch gelatinization occurs when starch granules adsorb water and swell resulted in a disorder of crystalline region. Self-aggregation of starch in water was the source of poor mechanical properties of NR latex composite which it can be the stress concentration point where the starting point of failure of products.

In order to promote good sago starch dispersion, it is necessary to lower the surface energy of the particles to fit with that of the liquid (water). This can be achieved by coating the sago starch particle surface with a surfactant or replacing part of the surface hydroxyl groups by less polar groups (surface chemical modification). However, even if the dispersion of the particles in liquid medium is improved, hindered interactions between physically or chemically modified starch limit the formation of strong percolating particle network and then the reinforcing effect (Jin et al., 2015).

Well dispersion of sago starch can be indicated by highly separation of sago starch particles in aqueous by having surfactant coated on the starch granules surface. Surfactants lower the surface energy or interfacial tension between a liquid and a solid or between two liquids. Surfactants act as dispersing, wetting, emulsifying and foaming agents. Dispersants improve the separation of particles and prevent settling or clumping by adsorption at the interface created between liquid and solid or between liquid. The surface energy barrier at the interface can be due to steric or electrostatic repulsion (Hirsch, 2015).

According to Texter (1999), the most common physical property used in classifying the surfactants is ionicity: anionic, cationic, non-ionic and amphoteric or zwitterionic. Other physical properties include particles size or physical state under standard conditions. For electrostatic acting dispersing agents, they are containing cationic or anionic molecule groups. For steric acting dispersing agents, they are non-ionic or mainly non-ionic substances. The size of the dispersing agent is the important factor to determine the degree of well-dispersion. The smaller the powder dispersing agent, the greater the surface area can be absorbed to the filler surfaces, thus improved the dispersion of fillers (Hirsch, 2015).

## 1.3 Research Objectives

The objectives of this study are:

i. To study the effect of different types of dispersing agent (Sodium Naphthalene Sulphonate (Anchoid) and Nonyl Phenol) in preparation of sago starch filler dispersion.
ii. To investigate the effect of different dispersing agent loading on mechanical, biodegradable and post-processing properties of NR latex films.

## 1.4 Scope of Research Study

In this study, NR latex compounds with addition of sago starch were prepared to produce biodegradable films. Initial properties of NR latex follows ISO 2004:1979 standards where its total solid content (TSC) was 60.9%, dry rubber content (DRC) was 60.2%, mechanical stability time (MST) as 1225 seconds, alkalinity was 0.63 and KOH number was 0.62. Sago starch filler dispersion was prepared from sago starch powder by first mixing with distilled water, surfactants (Sodium Naphthalene Sulphonate or Nonyl Phenol), and potassium hydroxide. The surfactants and water ratio was varied with range of 4wt%-6wt% (surfactant) to 66wt%-68wt% (water) to obtain the optimum loading of surfactant for stable dispersion. Then, for the solid surfactant (Sodium Naphthalene Sulphonate powder) added sago starch dispersion was grinded in a ball mill for 18 hours to induce gelatinization process and improve homogeneity. The effect of ball milling time on the stability of sago dispersion was investigated. While for liquid surfactant (Nonyl Phenol) added sago starch dispersion, ball milling is not required. The stability of the sago starch dispersion was monitored by analysing particles size, zeta potential and viscosity.

Pre-vulcanisation was carried for the compound of NR latex and sago starch dispersion by subjecting to 75°C for 8 minutes. NR latex films were prepared by dry coagulant dipping process. Cleaned former were dipped into 10% calcium nitrate solution for 10 seconds and dried in oven at 100°C for 5 minutes. Then, the formers were dipped into pre-vulcanised biodegradable NR latex compound for 6 seconds and dried in oven at 100°C for 20 minutes. The dried biodegradable NR latex films were conditioned at room temperature until completely cooled. Leaching and ageing process were carried to study the mechanical properties of NR latex films. Soil burial test was performed to determine the biodegradation properties of NR latex films.

# CHAPTER 2

# LITERATURE REVIEW

## 2.1 Overview

Significantly of eco-friendly materials based on easily renewable natural resources, and the finite nature of petrochemical resources, have necessities for the development of polymers from agricultural processing by products such as soy protein, sago starch, tapioca starch etc. Two main reasons for the interest in natural based industrial products are environmental friendliness and legislation. Awareness about environmental issue has forced the industries to look for eco-friendly materials based on naturally occurring renewable resources.

The method for improving the sustainability of a polymeric material by introducing a biodegradable filler. Granular starch is an attractive option because it is one of the most abundant and inexpensive sustainable polymers. There are many types of starch each with a different combination of the linear polymer amylose and the branched polymer amylopectin. Some early research was premised on the hope that starch filler would increase the biodegradability of the synthetic polymer matrix, but it was demonstrated quantitatively that only the starch biodegrades when it is included in a matrix of non-biodegradable, synthetic polymer (Lu et al., 2009).

Stabilisation of filler particles with dispersants is generally due to charge or electrostatic stabilisation and steric stabilisation. Electrostatic stabilisation in an aqueous system involves adsorbed ionic polymers building up a charged layer around the filler, preventing aggregation. Ionic polymeric dispersants provide both electrostatic and steric stabilisation, while non-ionic polymeric dispersants stabilise the particles via a steric force. Ionic dispersants can be used in very small amount but they are sensitive to the presence of multivalent ions, pH and ionic strength. Non-ionic dispersants have the advantage of being pH insensitive, so they must be used in higher concentrations (Farrokhpay, 2009).

For electrostatic acting dispersing agents, they are containing cationic or anionic molecule groups. For steric acting dispersing agents, they are non-ionic or mainly non-ionic substances. The size of the dispersing agent is the important factor to determine the degree of well-dispersion. The smaller the powder dispersing agent, the higher the surface area where more dispersing agent can be absorbed to the filler surfaces, thus improved the dispersion of fillers (Hirsch, 2015).

## 2.2 Natural Rubber (NR) Latex

NR latex is derived from the Hevea brasiliensis rubber tree consists of cis-1,4-polyisoprene and other non-rubber substances. NR latex is a milky and white liquid which having a dry rubber content of 30% to 40% such as proteinous substance, resinous substances, carbohydrates, inorganic matter and others (Blackey, 1997). The structure of NR latex is shown as Figure 2.1.

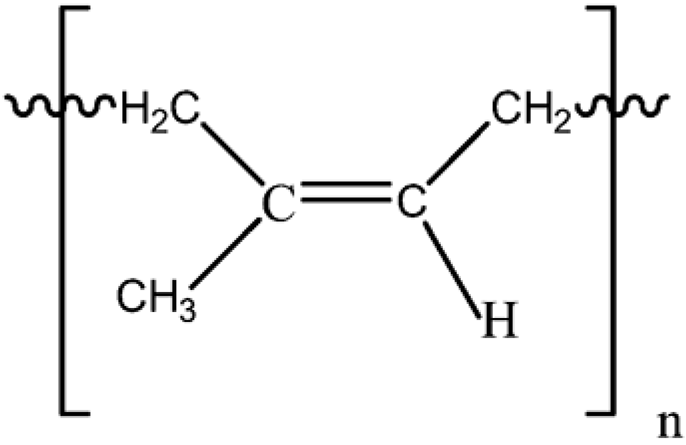

Figure 2.1: Molecular structure of NR latex (Braz, 2009).

Latex is simply defined as a stable dispersion of a polymer substance in an aqueous medium which is a two-phase system consisting of a dispersion phase and dispersion medium. Latex is an example of a colloidal dispersion. It consists of polymeric particles with diameter in nanometres, dispersed in water. The particles typically comprise about 50% by weight of the dispersion. The dispersion is colloidally stable if it can sit on a shelf for years and remain dispersed, without sedimentation of particles as a sludge at the bottom of the bottle (Keddie & Routh, 2010).

### 2.2.1 Field NR Latex

Field NR latex is an emulsion of rubber polymer in an aqueous dispersion. The NR latex system is comprised of 25% to 45% rubber hydrocarbon particles and only small percentage of non-rubber substances. NR latex can be separated into three main fractions when subjected to ultracentrifugation. According to Yip & Cacioli (2002), the three fractions include the rubber hydrocarbon particles phase at the top, ambient C-serum in which all NR latex particles are suspended, and non-rubber particles at the bottom. NR latex contains about 1 to 1.5% m/m proteins with about 27% found in rubber phase, 48% in C-serum and 25% in bottom non-rubber phase.

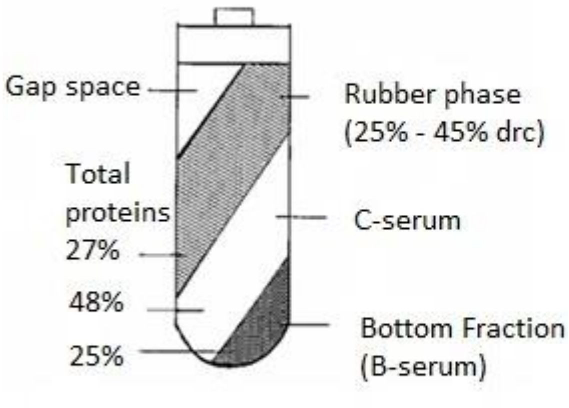

Figure 2.2: Freshly collected Hevea brasiliensis latex separated into its 3 main fractions on ultracentrifugation (Yip & Cacioli, 2002).

During rubber tapping, the barks of rubber tree were incised and white milky latex in liquid form is released. The latex is susceptible to instantaneous coagulation due to formation of acid compound because of the interaction with microbial or metal salts which leads to decreased of pH in latex, then contribute to poor colloidal stability of latex particles. In order to prevent the spontaneous coagulation reaction, high ammonia is necessary to be added into field NR latex for preservation purpose (Rivajan & Santipanusopon, 2009).

### 2.2.2 Concentrated NR Latex

Concentrated NR latex is derived from field latex which consists of 30% to 40% of dry rubber content (DRC) by weight and then concentrated into approximately 60%. The product is taken off at the top of the separator by means of difference in density of rubber particles and serum. Three common methods of concentration employed including centrifugation, evaporation and creaming; centrifugation is the preferred method and accounts for 95% of total production (Tillekaratne, 1990).

According to Eng & Ong (2001), in the centrifugation process, the NR latex is subjected to a centrifugal force via spinning at 6000 rpm, resulting in suspended rubber particles being separated into a concentrate at the centre of the bowl and the serum at the rim. Light rubber particles will rise up and forming a cream like layer, while the heavier rubber particles or non-rubber particles will be setting down, and converted as a skim rubber.

## 2.3 Colloidal Stability of NR Latex

The term “colloid” is derived from the Greek word “coll”, meaning “glue”. A major advance in colloid science was made by Robert Brown, who observed pollen particles "dancing" randomly when dispersed in a fluid. This phenomenon is now termed Brownian motion which defines the colloidal dispersion characteristic. The effect is the result of an imbalance of forces between the colloidal particles and the surrounding molecules of the solvent, and it provides evidence for the existence of molecules (Keddie & Routh, 2010).

Blackey (1997) stated that as applied to a lyophilic colloid, stability usually is defined as the tendency for the system to remain unchanged as a colloidal dispersion as time elapses. In the case of NR latex, there is a thermodynamic tendency for the particles to aggregate and coalesce through a mechanistic pathway. Stability of lyophilic solution due to the presence of barriers between the particles which discourage the closer approaches of those particles.

Stability of particles depends on the attractive and repulsive forces exerted, the potential energy barriers which characterise their stability contribute from the net energy forces. Moreover, the greater the barriers, the more stable the colloidal system. According to Keddie & Routh (2010), there are four types of interaction between particles such as electrostatic forces, steric forces, exclusion/depletion forces and solvation forces.

### 2.3.1 Electrostatic Forces

Liyanage (1999) reported that the electrostatic stabilisation of lyophilic colloids is a consequence of the counterion cloud which surrounds the latex particles in the dispersion medium. The counterion cloud is brought into the existence by the presence of electric charges of opposite polarity attached to the particle surfaces.

The origin of the surface charge can be either adsorption of ions from dispersion medium or ionization of bound macromolecules on the particle surface. The stabilisation with electrostatic repulsion is called electrostatic stabilisation. Electrostatic stabilisation of latex particles can be represented schematically as shown in Figure 2.3.

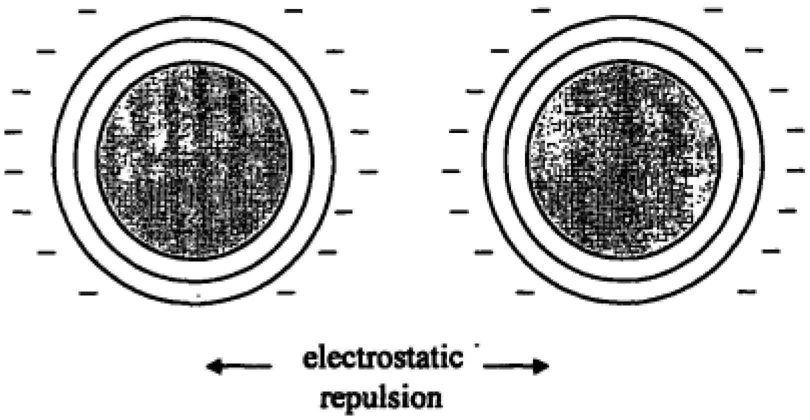

Figure 2.3: Schematic representation of electrostatic stabilisation of NR latex particles (Liyanage, 1999).

### 2.3.2 Steric Forces

Steric repulsion force is exerted when adsorbed lyophilic macromolecules are attached to the particle surface. The macromolecules adsorbed on the particle surface have affinity for both particle and dispersion medium (hydrophilic and hydrophobic end). When two particles approach each other, the adsorbed macromolecules on the surface will interfere with adsorbed macromolecules on the other particle. Strong repulsion developed due to the macromolecules hydrophobic ends cannot enter the particles. Stabilisation that conferred by the adsorbed macromolecules is called steric stabilisation (Liyanage, 1999). Steric stabilisation between latex particles is shown in Figure 2.4.

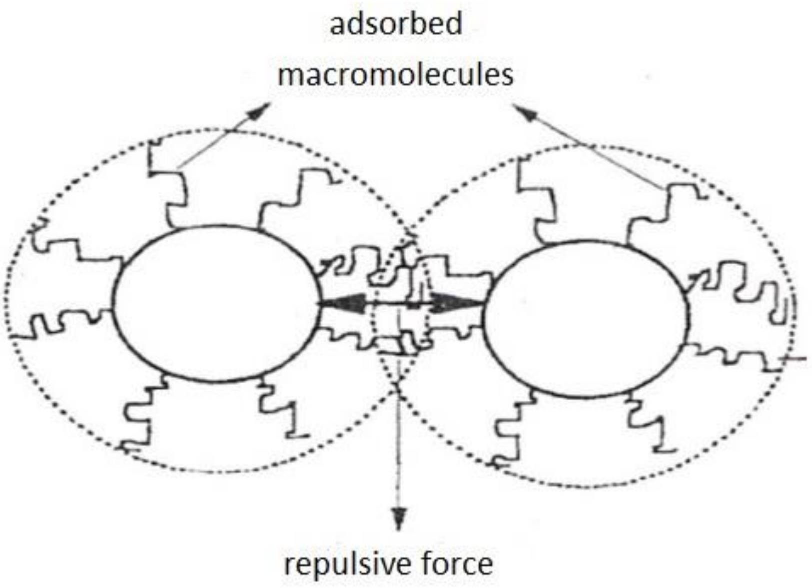

Figure 2.4: Schematic representation of steric stabilisation of NR latex particles (Liyanage, 1999).

### 2.3.3 Exclusion / Depletion Forces

Colloidal stability can also be imparted by the presence of free polymer dissolved in the dispersion medium which referred as “depletion” or “exclusion” stabilisation. Macromolecules dissolved in dispersion medium adopt spatial conformation and occupy the space between the particles. When two particles get closer, stability arises from the depletion of the concentration of free polymer between the surfaces of the particles. Closer approach of the particle can only be achieved by a further depletion of the segment concentration between the particles. At much closer approach between the particles, almost complete exclusion of polymer molecules occurs between the particles surface. Deformation and exclusion of macromolecules require energy discourages the two particles from coalescing (Liyanage, 1999). Depletion or exclusion of free polymer between latex particles can be represented schematically as shown in Figure 2.5.

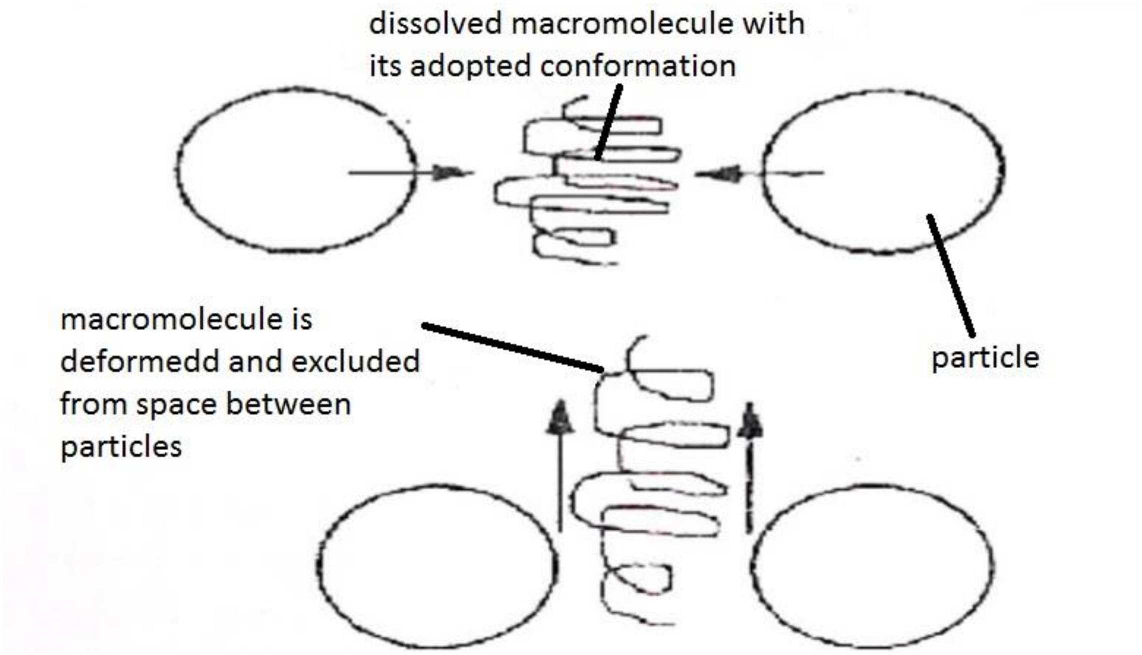

Figure 2.5: Schematic representation of depletion of macromolecules from NR latex particles (Liyanage, 1999).

### 2.3.4 Solvation Forces

Solvation layer arises from the presence of non-ionic hydrophilic materials adsorbed on the particle surface. The solvation layer that surrounds the latex particles enhances the colloidal stability. The interaction between the dispersion molecules (water) with the particles or with the bound macromolecules on the particle surface results in the formation of water-bound layer surrounding the particles.

According to Liyanage (1999), in NR latex based products industry, non-ionic hydrophilic polymeric materials are often used as secondary stabilisers. The water-bound layer enhances the NR latex stability and provides mechanical barrier to the close approach of the particles and prevents particles from coalescing. Figure 2.6 shown the schematic representation solvation force between NR latex particles.

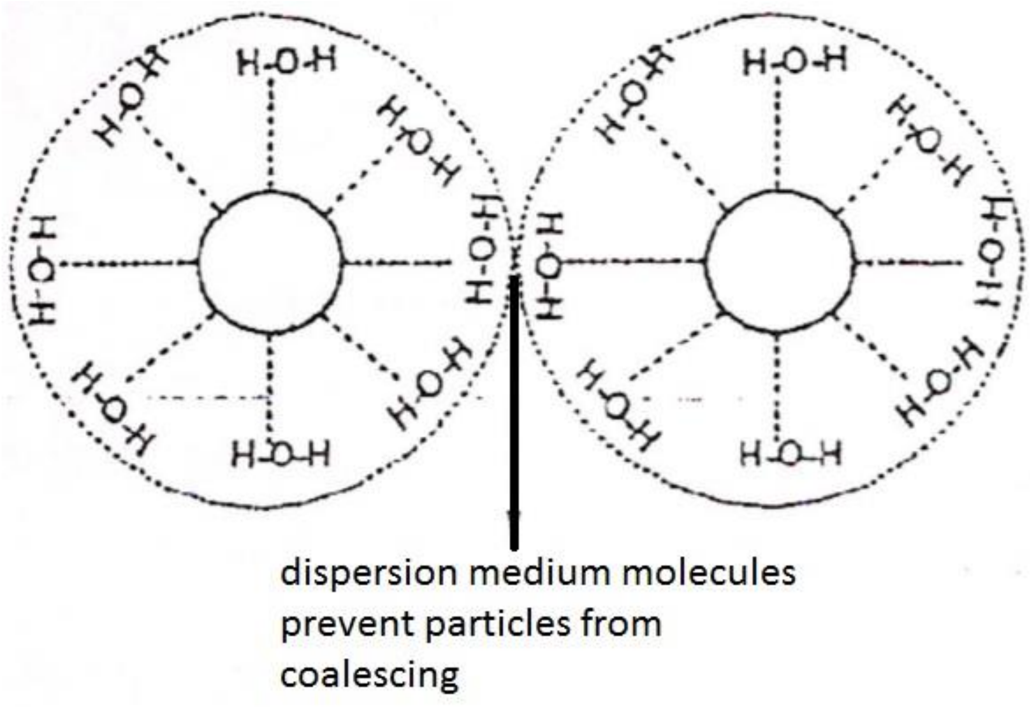

Figure 2.6: Schematic representation of solvation force between NR latex particles (Liyanage, 1999).

## 2.4 NR Latex Preservation

According to Booten et al. (2011), raw NR latex usually coagulates immediately after been collected. This phenomenon is undesirable because it renders further handling of latex. Chemically, this instantaneous coagulation is due to microbial infection. The time for this phenomenon to occur depending on the types of microbial infection, the temperature growth of microbial and colloidal stability of the latex. There are four key mechanisms for NR latex to coagulate in terms of instantaneous coagulation: infection of microbial growth, hydrolysis of various non-rubber substances, interaction of colloidal rubber particles with metal salts and manifestation of putrefaction.

Due to the instantaneous destabilisation of NR latex, it is often been preserved before used. The main purpose of preservation process is to eliminate microorganism growth in the NR latex which causes the destabilisation of fresh NR latex. The preservation process could also enhance the colloidal stability of the NR latex by increasing the density of bound electric in zeta potential barrier, increasing ability of surface bound hydrophilic macromolecules to confer steric stabilisation on NR latex and increase the degree on hydration on particle surface (Blackey, 1997).

Blackey (1997) reported that preservation of NR latex is normally achieved by adding 1.0% (w/w on aqueous phase) of ammonia. Ammonia is a good biocide that possesses several advantages. It can control the proliferation of bacteria, neutralise the free acid formed and help in neutralise undesirable effects of trace metal ions, particularly calcium and magnesium ions in NR latex. Moreover, ammonia also hydrolyses the interfacial protein and phospholipids, hence the NR latex can be more stable. Usually, the pH of NR latex is maintained at around 9 to 10.5. Preservation of NR latex by using ammonia is categorised into four systems which are best described in Table 2.1.

Table 2.1: Ammonia preservation system in NR latex (Blackey, 1997).

| Name | Preservation system |
|---|---|
| High Ammonia (HA) | 0.700% $NH_3$ |
| | 0.200% $NH_3$ |
| | 0.025% ZnO |
| Low Ammonia TZ (LA-TZ) | 0.025% TMTD |
| | 0.200% $NH_3$ |
| Low Ammonia Pentachlorophenate (LA-SPP) | 0.200% Sodium |
| | 0.200% $NH_3$ |
| | 0.200% $NH_3$ |
| Low Ammonia Boric Acid (LA-BA) | 0.240% $H_3BO_3$ |

## 2.5 Latex compounding

NR latex on its own is not sufficient and strong enough to make a film product. This is because the films made from NR latex have too much viscous components that promote the flow during deformation, thereby making the NR films very weak in tensile properties. So, crosslinking process is introduced. Besides tying up the rubber molecules, crosslinks also reduce the viscous components and improve the strength if films by reducing the flow during deformation.

According to Hossain et al. (2010), crosslinking process can be introduced by either using gamma-radiation or chemical alternative. The first method involved bombarding rubber molecules with gamma radiation in order to induce crosslinks between rubber molecules in latex. On the other hand, the second method involved introducing some chemical ingredients that could react with rubber main chain and tie the rubber molecules together. The reaction usually takes place at double bond which also known as unsaturated site in rubber main chain

However, chemical alternative is commonly used. Compounding is the process of addition the compounding ingredients into the latex. The first step of compounding is by preparing the solution (water soluble ingredients), dispersion, (solid ingredients), and emulsions (water insoluble ingredients). There are three general concerns to prepare these solutions, dispersions and emulsions which are:

i. Size of the particle must be compatible with latex particles.
ii. Colloidal stability of dispersions and emulsions should be compatible.
iii. pH of the solution must similar with pH of latex.

## 2.6 Compounding ingredients

According to Blackey (1997), the compounding ingredients comprises organic or non-organics materials that being introduced inside the latex during compounding process. The purpose is to alter the physical or chemical properties of raw latex due to rubber chain that may slide upon applied stress or during application. To avoid this problems, sulphur is introduced to create crosslinking between rubber particles. Moreover, other chemicals are added into the compound to meet certain purposes. There are three general classifications of chemical used in latex compounding which are surface active agent, liquid phase modifiers and elastomer phase modifiers.

### 2.6.1 Surface active agent

The purpose of adding surface active agent is to convert water insoluble solid and water immiscible compounding ingredients to water compatible system. There are three classification of surface active agent which is emulsifying agent, wetting agent and dispersing agent (Salager, 2002).

i. Emulsifying agent

   The function is to emulsify immiscible liquid in water, such as oil.

ii. Wetting agent

   Wetting agent is used to disperse the solid materials in water. It lowers the interfacial tension to permit wetting out of dry powder to ensure fast and even dispersion.

iii. Dispersing agent

   The function of dispersing agent is to disperse the substance which is in powder form. The dispersing agent is added to the mixture of water and solid to be dispersed before grinding.

Surfactants should be used carefully due to their retention in the finished products increases the hydrophilic properties thus giving it a tendency to swell in water. Moreover, surfactants also act as release agent which impairing the adhesion of rubber to treated substrate.

### 2.6.2 Liquid phase modifiers

The liquid phase modifiers can be classified into three which are stabilisers, thickeners and wetting agent, and coagulant or gelling agents.

i. Stabilisers

Stabilisers protect the latex particles by maintaining the colloidal properties and prevent premature coagulation and pre-flocculation formation during latex compounding and processing.

ii. Thickeners and wetting agents

Thickeners modify certain liquid latex properties by introducing desired flow characteristics to latex compounds while wetting agents improve the wetting ability and reduce interfacial tension.

iii. Coagulant or gelling agents

Coagulant or gelling agents convert liquid latex to solid form. Calcium nitrate is one of the example to promote destabilisation of latex particles, so that latex can be converted into products (https://www.google.com/patents/WO1998011157A1?c l=e) .

### 2.6.3 Elastomer phase modifiers

Elastomer phase modifiers are added to impart desired finished latex products properties. Most of the materials are in solid form. Thus, process of making dispersion in water in needed before adding into latex. Elastomer phase modifiers are classified into several types such as vulcanising agent, accelerators, activators, antioxidant, stabilizer and filler. Each type of material has their own functions in the latex compound.

Vulcanising agent such as sulphur is added to latex for introducing crosslinks between the rubber molecules in latex. Accelerators such as tetramethylthiuram disulphate (TMTD) and zinc diethyldithiocarbonate (ZDEC) have the function of speeding up the crosslinking process. Activators such as zinc oxide (ZnO) is used to activate crosslinking process. Antioxidants provide protection to the latex product against degradation. Stabilizers such as potassium oleate and potassium hydroxide (KOH) can be used to ensure adequate processing stability by maintaining the colloidal properties. Lastly, filler is used to modify physical properties and reduce cost of production (Blackey, 1997).

## 2.7 Dispersing agent

Dispersing agent is one type of surfactant which used to provide even distribution of the ingredients throughout the mixture. It makes the dispersion process easier and more stable. Texter (1999) classified the surfactants based on physical properties or functionality. The most common physical property used in classifying the surfactants is ionicity: charged or uncharged, ionic or non-ionic. Other physical properties include overall size (low molecular weight) or physical state (crystalline solid, amorphous paste, or liquid) under standard conditions.

According to Hirsch (2015), there are 4 types of surfactants that classified upon the composition of the head group polarity: anionic, cationic, non-ionic and amphoteric or zwitterionic, depending on the nature of hydrophilic domain. The first three classes refer to a head group with negatively charged, positively charged, and the absence of a formal charge, respectively (Rasheed, 1999). While for the amphoteric surfactants are characterized by a dipolar structure that is very sensitive to the pH of the system. The schematic illustration of the classification of surfactants as shown in Figure 2.7 (Sharma, 2014).

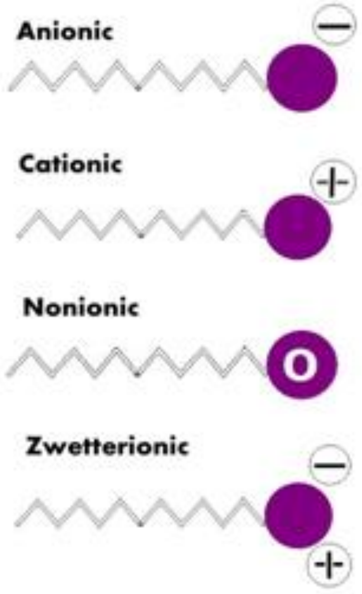

Figure 2.7: Schematic illustration of the classification of surfactants (Sharma, 2014).

In accordance with Rasheed (1999), anionic surfactants is the surfactants that possess negatively charged head group. Anionic surfactants contain anionic functional groups at their head, such as sulphonate, phosphate, carboxylates and sulphate . Many of these find utilization in emulsion polymerization. The most common surfactants made up the alkyl carboxylates (soaps), such as sodium stearate comprise >50% of the global usage of surfactants. In this study, alkylnaphthalenesulphonates type anionic surfactants, named sodium naphthalene sulfonate (trade named: Anchoid), is used.

Hirsch (2015) stated that cationic surfactants are comprised of a positively charged head which most of them are used as anti-microbials, anti-fungals. However, the cationic nature of the surfactants is not typically consistent with the world of non-ionic and anionic charges. The most prevalent cationic surfactants are based upon quaternary nitrogen, and most numerous one in this class are Alkylammonium halides and tetra-alkylammonium halides. Alkylammonium halides are excellent hydrogen bond donors while tetra-alkylammonium halides cannot form hydrogen bonds, but it behaves as strongly hydrophilic groups (Rasheed, 1999).

Many non-ionic surfactants are structurally analogous to anionic and cationic surfactants, but has no charge groups in its head. According to Texter (1999), in the absence of electrostatic charge, the steric and osmotic forces are dominated for interactions between non-ionic surfactant head group. The examples of non-ionic surfactants are alkanolamides, alkoxylates, fatty acid esters of sorbitol, sugar-based surfactants and alkyl glucamides (Rasheed, 1999).

The surfactant that contains a head group with two oppositely charged which both cationic and anionic centres are attached to the same molecule, it is called zwitterionic. They will behave as anionic or cationic suitably due to sensitivity to pH. The anionic part can be sulfonates while the cationic part is based on primary, secondary, or tertiary amines or quaternary ammonium cations (Hirsch, 2015).

According to Manroshan Singh et al. (2013), in general, among the four types of surfactants the most suitable surfactants that can be used in NR latex compounding are only non-ionic (Nonyl Phenol) and anionic (Sodium Naphthalene Sulphonate). Cationic surfactants is not recommended because the coagulation could be immediately happens due to the interaction of negative charged NR latex particles and positive charged surfactants. In this study, the effect of different types of dispersing agent (non-ionic Nonyl Phenol and anionic Sodium Naphthalene Sulphonate) on the filler dispersion was investigated. The mechanical and biodegradable properties of NR latex films were determined and compared.

## 2.8 Sago starch as biomaterial filler for NR latex films

Starch is added into NR latex films for biodegradation purpose. According to Afiq & Azura (2013), sago starch is polysaccharide material made up of random coiled amylose and a branched structure of amylopectin which linked by glucosidic linkages. The amylose and amylopectin content in starch are the key component for the biodegradability of NR latex films. Starch occurs naturally as discrete granules. Amylose is soluble in water while amylopectin is non-soluble in water. Amylose and amylopectin chains are able to form helical structures which crystallize. Starch granules possess hydrophilic properties and strong inter-molecular association via hydrogen bonding formed by the hydroxyl groups on the surface of granule (Lu et al, 2009). Thus, the starch is readily hydrolysed by enzymes.

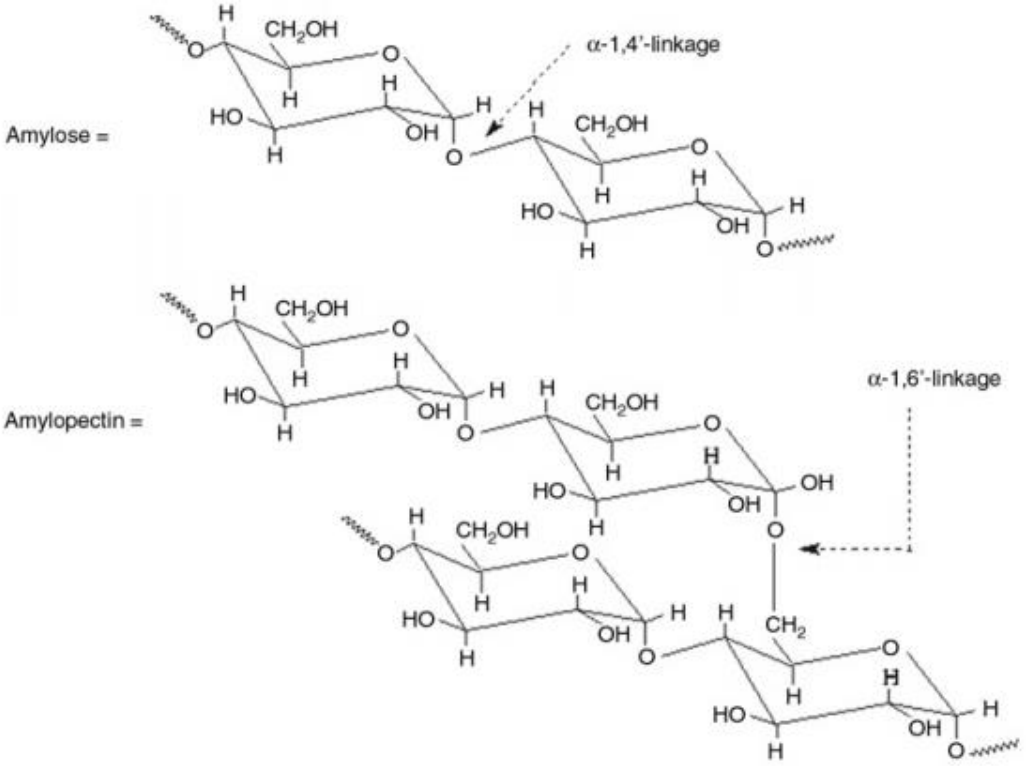

Figure 2.8: Molecular structure of starch (Lu et al., 2009).

Azahari et al. (2011) stated starch will rapidly degrade with the addition of enzymes because enzymes typically catalyse the hydrolysis of natural biodegradable polymers, and α-amylase catalyses the hydrolysis of starch. During decomposition of NR latex films, microorganisms consume these amylose and amylopectin to produce amylases and glucosidases enzymes. Enzymatic reaction takes place in both α-1,4-link in both amylose and amylopectin and α-1,6-link in amylopectin (Afiq & Azura, 2013).

Higher fraction of amylose components is expected to have more amylose-lipids complexes formed with NR latex colloidal particles, together with chain scission in glucosidic linkages of amylose during degradation process (Chandra & Rustgi, 1998).

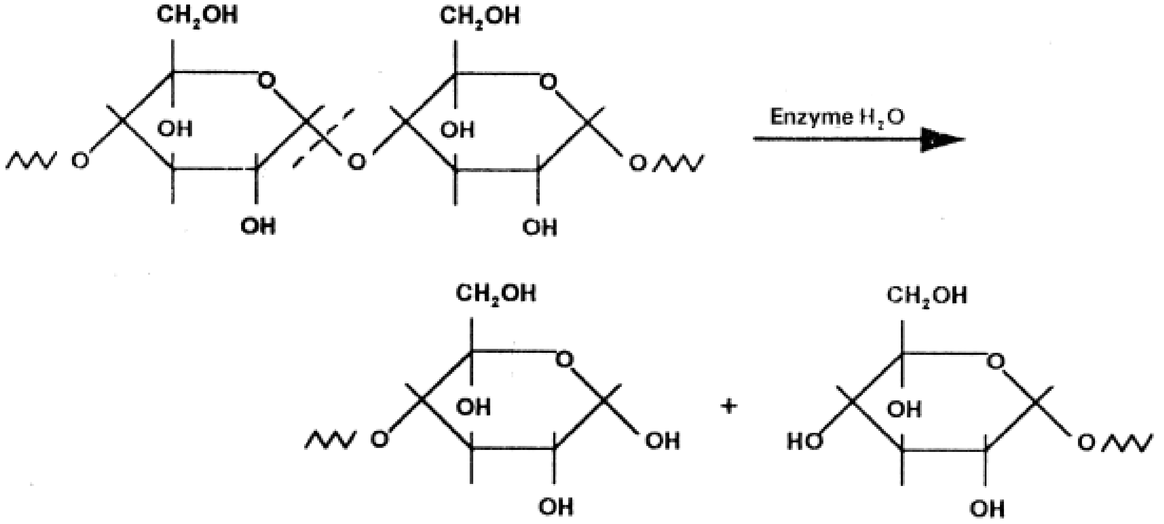

Figure 2.9: Enzymatic hydrolysis of starch (Chandra and Rustgi, 1998).

Figure 2.9 shows the mechanism of enzymatic reaction of starch. The α-1,4-link in both amylose and amylopectin is attacked by amylases while the α-1,6-link in amylopectin is attacked by glucosidases. In the starch molecules, there are two functional groups: -OH groups and C-O-C bonds which susceptible to substitution reaction and chain breakage reaction respectively. The crosslinking or bridging of the –OH groups changes the helical structure into network, thereby increasing the viscosity and resistance to thermomechanical shear and also reducing water retention (Chandra and Rustgi, 1998).

### 2.8.1 Starch Retrogradation

Aichayawanich et al. (2010) reported that the agglomeration mechanism of the starch is resulted from liquid bridge formation which the mechanism is related to phase