

**ANTI-FREEZE STABILIZER SYSTEM BASED ON
AZIDATED GLYCEROL FOR NATURAL
RUBBER LATEX**

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**ANTI-FREEZE STABILIZER SYSTEM BASED ON
AZIDATED GLYCEROL FOR NATURAL
RUBBER LATEX**

by

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I was raised in a family of rubber tapper. Growing up as the daughter of a rubber tapper has given me a deep interest in studying and playing with rubber latex. Many experts have said that these latex are complicated and it is true, but it did not drop my interest in becoming a modern rubber tapper/researcher in this field.

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“Thank you for always being there during the hardships”

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LIST OF SYMBOLS

w_0	Initial weight of latex films before water absorption test
w_1	Final weight of latex films after water absorption test
$\%W$	Water absorption
W_1	Initial weight of latex films before swelling test
W_2	Swollen weight of latex films after swelling test

LIST OF ABBREVIATIONS

AG	Azidated glycerol
CaNO ₃	Calcium nitrate
DRC	Dry rubber content
DSC	Differential scanning calorimetric
FDA	Food and Drug Administration
FTIR	Fourier transform infrared
HA	High ammonia
HCl	Hydrogen chloride
IPS	Institut Pengajian Siswazah
KOH	Potassium hydroxide
M ₁₀₀	Modulus at 100 of elongation
M ₃₀₀	Modulus at 300 of elongation
MST	Mechanical stability time
N	Nitrogen
NaN ₃	Sodium azide
NRL	Natural rubber latex
OH	Hydroxyl
phr	Part hundred rubber
PO	Potassium oleate
SEM	Scanning electron microscopy
TEA	Triethylamine
TEM	Transmission electron microscopy
TSC	Total solid content
VFA	Volatile fatty acid
ZDEC	zinc diethyldithiocarbamate
ZnO	Zinc oxide

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AFTER LEACHING TREATMENT

SISTEM PENSTABIL ANTI-PEMBEKUAN BERASASKAN GLISEROL TERAZIDA BAGI LATEKS GETAH ASLI

ABSTRAK

Lateks getah asli (LGA) dihantar ke destinasi dalam bentuk koloid/cecair. Ia memerlukan bekas penyimpanan yang besar seperti dram dan kebarangkalian tumpahan lateks semasa pengangkutan berlaku adalah lebih tinggi. Bagi mengelakkan tumpahan susu getah, bentuk cecair LGA diubah menjadi pepejal/beku dengan kaedah penyejukbekuan. Walau bagaimanapun, lapisan protein yang bercas negatif yang menstabilkan zarah LGA akan dipecahkan oleh hablur ais semasa penyejukbekuan dan zarah LGA yang tidak stabil ini akan membentuk gumpalan selepas dinyahbeku. Oleh itu, kajian ini mencadangkan penstabil suhu rendah baru yang dinamakan gliserol terazida (GT) yang akan dimasukkan ke dalam cecair LGA sebelum proses penyejukbekuan. Dijangkakan GT mampu bertindak sebagai penstabil koloid lalu menghalang ketidakstabilan getah daripada berlaku selepas dinyahbeku. GT dihasilkan melalui tindak balas kimia antara gliserol dan natrium azida. GT yang terhasil kemudiannya dimasukkan ke dalam koloid LGA sebagai penstabil anti-pembekuan untuk mengelakkan zarah-zarah getah daripada bergumpal pada suhu yang lebih rendah. LGA yang mengandungi GT kemudiannya disejukbekuan pada suhu $-4\text{ }^{\circ}\text{C}$. Selepas 24 jam penyejukbekuan, lateks beku dinyahbeku pada suhu bilik selama 1 jam diikuti dengan pemanasan dalam air pada suhu $40\text{ }^{\circ}\text{C}$ selama 1 jam. Cecair lateks yang diterhasil semula kemudiannya dibiarkan pada suhu bilik sebelum penghasilan filem lateks. Fokus utama kajian ini adalah untuk menghasilkan GT melalui tindak balas kimia gliserol dan natrium azida, untuk mengkaji kesan GT terhadap prestasi koloid dan filem LGA sebelum dan selepas penyejukbekuan. GT

yang dihasilkan telah dibuktikan oleh spektrum Fourier Transform Infrared (FTIR) dengan kehadiran gelombang pada nombor $2160 - 2120 \text{ cm}^{-1}$ yang sepadan dengan regangan $\text{N}=\text{N}=\text{N}$ dengan itu mengesahkan pengenalan kumpulan azida dalam molekul gliserol. Bahagian kedua dan ketiga kajian mendapati bebanan 0.2 phr GT menunjukkan sifat koloid dan filem yang optimum sebelum dan selepas proses penyejukan. Kestabilan koloid LGA yang bagus pada 0.2 phr GT ditunjukkan oleh nilai potensi zeta yang lebih tinggi iaitu -59.63 mV dan -56.27 mV sebelum dan selepas proses penyejukan. Disimpulkan, GT yang dihasilkan dalam kajian ini dapat digunakan sebagai penstabil anti-pembekuan untuk LGA.

ANTI-FREEZE STABILIZER SYSTEM BASED ON AZIDATED GLYCEROL FOR NATURAL RUBBER LATEX

ABSTRACT

Natural rubber latex (NRL) normally transported to any destination in colloid / liquid form. It requires large storage containers such as drums and the probability of latex leakage during transportation to happen is higher. To prevent the latex spillage, the liquid form of NRL was transform into solid / frozen latex by freezing method. However, negatively charged protein layer that stabilized NRL particles may be broken by ice crystals during freezing and these destabilized NRL particles will form big lump after thawing. So, this study proposed a new low temperature of stabilizer named azidated glycerol (AG) that will be incorporated in NRL liquid before freezing process. It is expected that AG able to act as colloid stabilizer thus preventing the coalescence of rubber particples from occurring after thawing. AG was prepared by a chemical reaction of pure glycerol with sodium azide. The resulting AG was then added into NRL colloid as an anti-freeze stabilizer to prevent the rubber latex particles from coalesces at a lower temperature. NRL containing AG was then freeze at a temperature of -4 °C. After 24 hours of freezing, the frozen latex was thaw at ambient temperature for 1 hour followed by heating in a water bath at 40 °C for another 1 hour. The regenerated latex was then allowed to stand at room temperature before the production of latex film. The main focus of this study are to produce AG by chemical reaction of glycerol with sodium azide, to study the effect o f AG on the performance of NRL colloid and films before and after freezing processes. After modification of tosylated glycerol with sodium azide, the appearance peak at the range of 2160 - 2120 cm^{-1} was corresponds to the N=N=N stretching thus confirmed the

introduction azide group in the glycerol molecule. The second and third part of the study found that 0.2 phr loading of AG gave optimum properties of NRL colloid and films before and after freezing processes. Good stability of NRL colloid at 0.2 phr AG shown by higher zeta potential value of -59.63 mV and -56.27 mV before and after freezing processes, respectively. It is concluded, the AG produced in this study can be use as anti-freeze stabilizer for NRL.

CHAPTER 1

INTRODUCTION

1.1 Research background

Natural rubber latex (NRL) is a colloidal dispersion of rubber hydrocarbon in an aqueous medium. The chemical composition of rubber hydrocarbon has been identified as a linear cis 1,4-polyisoprene of high molecular weight, and it is present in latex as molecular aggregates in the form of discrete particles which are usually spherical with diameters ranging from 15 nm to 3 μm (Lim & Misni, 2016). NRL also consists of non-rubber constituents that are dissolved in an aqueous medium. Some of these non-rubber constituents are adsorbed on the surface of the rubber particles. The others are suspended in the latex medium. The non-rubber constituents, which are adsorbed on the rubber particles, are mainly proteins and lipid materials, possibly in the form of a complex. The protein-phospholipid layers covering the rubber particle surface are especially interesting due to their ability to enhance the colloid stability of freshly tapped latex (Chaveewan Kongkaew et al., 2017). However, this layer is partially removed during the processing of NRL, especially during the centrifugation process. To further enhance the stability during processing, additional stabilizers are added. Figure 1.1 shows the morphology of the rubber particle with the non-rubber components surrounding it.

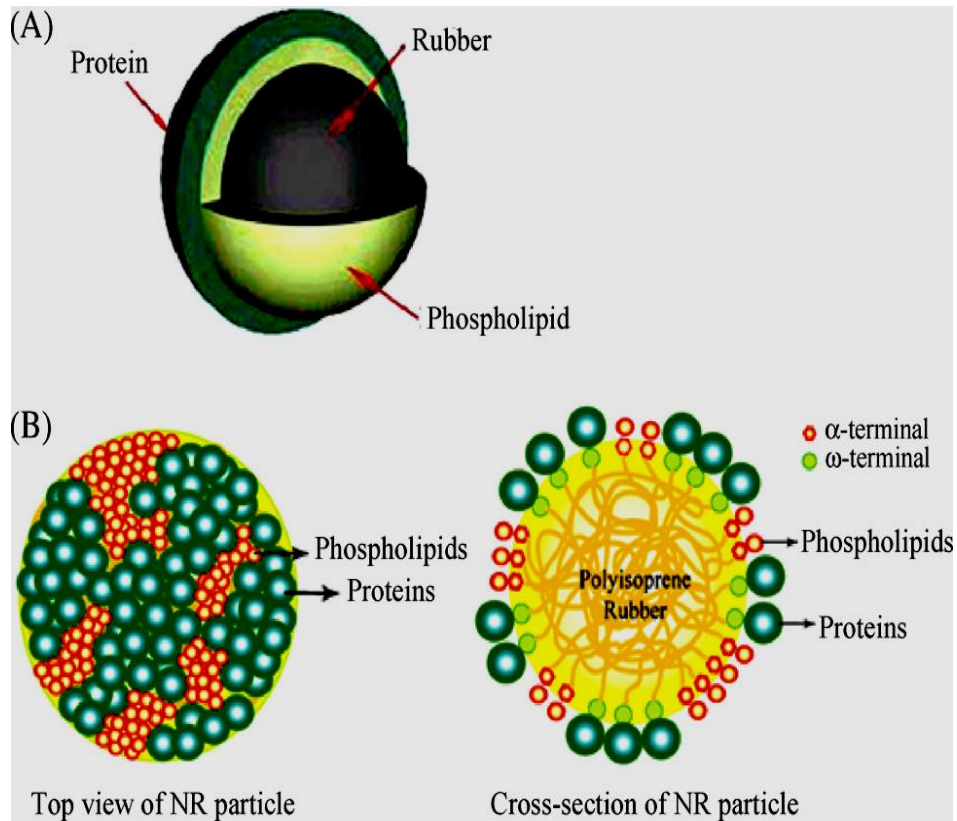


Figure 1.1 Two possible models for the structure of the rubber latex particle surface (A) A 3D current model of an NR latex particle surrounded by a double-layer of proteins and Phospholipids and (B) the proposed new model consisting of a mixed layer of proteins and phospholipids around the latex particle (Kanjaneer Nawamawat et al., 2011).

Dipping process is the favourite process of dipped latex products like glove, ballon, condom and toys (Rattanapan et al., 2012). The dipping process involved the process of coagulant and latex dipped. The chemicals used in dipping process are found to have great influence on the product's quality. However, its also influence the colloidal stability of the latex compound. In addition, the mechanical action such as high stirring of latex compound also affects the colloid stability hence influence the quality of the final products (Ng et al., 2013).

In latex technology, the addition of stabilizer is mainly for stabilization of rubber particles. As well known, the fresh latex contains a protective layer of proteins and lipids which act as a natural stabilizer. However, this layer is partially removed

during the processing of NRL. Thus, additional stabilizers are added in order to enhance the colloid stability of NRL during processing. In general, an ionic type stabilizer mainly confer mechanical stability, meanwhile the use of nonionics is more extensive as they can be used to confer both mechanical and chemical stability to the rubber particles (Manroshan Sigh & Evelyn Lim Hui Mei, 2013)

The typical stabilizers used in rubber latex can only enhance the colloid stability of NRL during processing and transportation/exportation to temperate countries. However, this stabilizers cannot prevent particles from coalescing at low temperature. Prevention of particle coalescence after freezing and thawing processes is important not only to export latex to temperate countries, where the temperature could drop below zero during winter, but freezing could be used as a method of storing the latex. Storage of latex by freezing could prevent bacteria from attacking the latex, and thus the latex is free from preservatives. In this study, the new stabilizer (AG) was added in latex liquid in order to form solid rubber (frozen latex) for storage and transportation. Thus, the storage and transportation were done in solid form of NRL. No active studies have been done on the freezing stabilizer recently in NRL and the latest study on freezing NRL was in the Year 1969, by Cockbain and co-workers.

In general, preservatives used in latex are toxic, and some are carcinogenic. The most popular preservative is ammonia, which is toxic, and ammonia could affect the gelation process of latex especially in making foam (Dinesha Thavaseelan et al., 2022). Meanwhile, glycerol is known as an anti-freeze. When glycerol is added to latex and if glycerol molecules could form a layer around the latex particles, glycerol can prevent particle coalescence by inhibiting the formation of ice crystal of latex serum when the latex is frozen (Britannica, 2022). Since glycerol is miscible with

water, its molecules will be dispersed in the latex serum, not around the latex particles. Modification of glycerol to AG will make the molecules occupy the space around the latex particles.

In this study, a new stabilizer was generated by the modification of pure glycerol with an azide group of sodium azide. Sodium azide was selected in this study due to its high solubility in water than other polar solvents. In addition, more recently, azides group have become popular in click reactions. Click chemistry is the use of biocompatible compounds that can help researchers trace metabolic pathways in living organisms. This is accomplished by attaching the chemical tag to the biomolecule of interest (<https://study.com/academy/lesson/organic-inorganic-azides-definition-reactions-uses.html>, July 2022). Thus by using azide group in this study, the chemical tag of AG molecules between NRL particle is guaranteed between the negatively charged N_3 of azide with positively charged stern layer of NRL particles.

Meanwhile, glycerol is a simple polyol compound that is colorless, odorless, viscous liquid, and non-toxic. Due to having microbial and antiviral properties, it is widely used in the Food and Drug Administration (FDA) approved wound and burn treatments. Owing to the presence of three hydroxyl groups (OH), glycerol is miscible with water and is hygroscopic (Adi et al., 2006).

Glycerol is a non-ionic kosmotrope that forms strong hydrogen bonds with water molecules, competing with water-water hydrogen bonds, which also stabilize intra-molecular interactions in macromolecules. This interaction disrupts the formation of ice. Generally, glycerol has been used as an anti-freeze agent/emulsifier in ice-cream technology to maintain the smoother texture, increase the resistance to rapid meltdown during consumption, and to increase the resistance to shrinkage

during storage (Adiel et al., 2019). Based on that, glycerol will be used in stabilizing the latex particles upon the freezing and thawing process as an anti-freeze stabilizer.

Pure glycerol is highly polar (containing 3 hydroxyl groups) and non-charged solvent because all the electrons in all the chemical bonds of glycerol are shared equally between atoms. Modification of glycerol with azide group is done by replacing one of the hydroxyls (OH) group with the azide group and transform glycerol into azidated glycerol (AG). The azide group induces dipole moment by partial displacement of the nitrogen (N) atom, which is the most electronegative in the AG molecule. AG that produced from the azidation process is neutral in pH due to the balance of nitrogen atoms charges (+ve and -ve charges), but it is a polar solvent. The chemical structure of AG is shown as in Figure 1.2. No research work was done on the AG, especially in the NRL field.

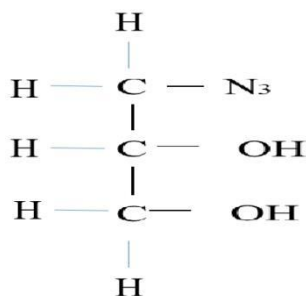


Figure 1.2 Chemical structure of azidated glycerol (AG)

However, the presence of negative (-ve) charge on one of N atom in the AG is highly attractive to the +ve charge in the stern layer of latex particle, thus forming a dipole moment interaction. The dipole moment interaction is a reversible interaction, which is contrary to covalent bonding (not reversible). The dipole moment interaction is crucial because it ensures that the modified glycerol molecules form a layer around the latex particles. This layer increases the colloidal stability of the latex. During freezing, the whole latex will be frozen because the water in the latex serum is frozen.

On the other hand, the water entrapped by the AG around the latex particles will not be frozen due to the anti-freezing properties of glycerol. When the temperature is increased, the frozen latex serum will thaw, and the latex particles will be released into the latex without undergoing coalescence. Thus, the frozen latex is said to be regenerated again on thawing. The AG functions not only as a stabilizer but also as an anti-freeze agent.

1.2 Problem statement

Field latex after tapping is sieved into a large reception tank and the sample is extracted from the tank for dry rubber content (DRC), ammonia content, and volatile fatty acid (VFA) test. If all the testing results are suitable, the ammonia gas is added as a preservative against the spontaneous coagulation and to prolong the storage time. The level of ammonia maybe needs to be adjusted according to the time of the processing. Since the middle of the 19th century, ammonia has been considered as the common preservative for NRL. Ammonia is an efficient bactericide, impart alkalinity to the aqueous phase of NRL, and able to deactivate some multivalent ions. However, this chemical has certain drawbacks as well. To be effective for longer periods, a higher dosage must be used. Higher levels of ammonia in latex also lead to environmental pollution. Because of that, preservation systems comprising of the low level of ammonia, in combination with other chemicals were introduced such as a low ammonia system containing sodium pentachlorophenate (SPP), zinc diethyldithiocarbamate (ZDC) or boric acid along with 0.2% by weight of ammonia. The main drawback of these systems is high toxicity, lower mechanical and storage stability, poor chemical stability, slow rate of cure, respectively for the SPP, ZDC and boric acid preserved latex (Cheong and Ong, 1974, John et al., 1986). Since then, the

mixture of 1:1 of zinc oxide (ZnO) and tetramethylene thiuram disulfide (TMTD) has been used for a long time to represent promising alternative latex preservative, typically in an amount of 0.1% to 0.5% w/w on total latex. However, World Intellectual Property, 2015, found that the addition of a small amount of a particular mixture of ZnO modified with urea and isothiazole, significantly prolong the fresh latex storage.

The major drawback of ammonia as a preservative for NRL is that it obstructs some established latex processes. Thus ammonia-preserved NRL undergoes a marked and progressive thickening when compounded with sparingly-soluble zinc compounds, notably ZnO. After a sufficient time has elapsed, the compounded latex may gel. The rate of this thickening, and the subsequent gelation, increases markedly with increasing temperature (Blackley, 1997).

Due to that problem, the only practical important substitute to ammonia as a sole preservative is to change the method of preserving by the freezing method as reported in this study. However, to make sure the latex is colloidally stable at a lower temperature (freezing), a small amount of azidated glycerol (AG) was added to the latex before the freezing process. The amount of AG should be sufficient to impart the necessary degree of colloid stability during freezing but not to enhance the colloid stability of the latex as well it will interfere with subsequent processing such as during the dipping process for film formation.

AG is a non-toxic solvent thus there are no environmental pollution and goods issues to the consumers. Besides, addition of AG in latex colloid (basis condition) will produce movement of electron within its molecule and thus will result in a slightly negatively charged molecules due to the deprotonation of hydrogen atom of AG (Yuki

et al., 2014). This negative charged AG occupies the space around the latex particles by formation of a layer thus contributed to the development of repulsive forces between particles. This layer plays a role as a protecting colloid of the latex especially under the regular storage and processing temperatures and also during freezing. By changing the liquid NRL to solid NRL (frozen latex) form, it can ease the storage and transportation to the manufacturing factories. There is no latex leakage during transportation and no large storage containers such as drums that required large areas for storage. Frozen latex can be easily re-pack in a small container and well organize in the storage area like an ice cream.

In addition, the transportation of NRL in liquid state can easily contaminant when exposed with galvanized materials, brass, copper and yellow metals. Proper precaution must taken during transportation of liquid latex. NRL is carried in bulk or in drums. In vessels with deep tanks that coated with candle wax or similar substances to allow the tanks to be sliced of residue on discharge. In Malaysia (don't have problem with low temperature weather), the rubber latex should be protected by prolong exposed to high temperature that may harmful. The transportation cost of frozen latex may be higher compared to general transportation due to the maintenance of the ice truck, but the latex leakage and destabilization of liquid can be prevented by transforming the liquid form of NRL into the solid form of frozen NRL. However, the common truck that has been used in transferring the latex liquid also needs special maintenance especially to maintain the pressure and the temperature inside the tank. On the other view, if the latex liquid is destabilized during transportation, it will make a lot of loss because flocculated latex cannot be used in making dipping products and extra expense in discharge may arise owing to coagulation. The exact shipping/transportation costs could not be included in this thesis due to lack of

information on shipping costs but the advantages of frozen latex and transport using ice trucks were explained before.

The usage of PO as a stabilizer in NRL dipping products is a common practice to maintain the colloidal properties of the NRL compound. However, higher content of PO in latex formulation to retain the colloidal properties after freezing and thawing processes will be associated with skin reactions such as irritation, itching, and debilitating. This is because PO is soap based stabilizer, that mainly uses in detergents that can cause contact allergies. By replacing the soap-based stabilizer with AG, skin allergies could be prevented.

Thus, this thesis will focus on using AG as anti-freeze stabilizer in NRL to maintain the colloidal properties during freezing and after thawing processes also to produce good mechanical properties of NRL films.

1.3 Objectives of research

The main objectives of this research work are as follow:

1. To produce azidated glycerol (AG) as stabilizer in NRL by chemical reaction of pure glycerol with sodium azide.
2. To study the effect of azidated glycerol (AG) as stabilizer on the performance of NRL before freezing, in comparison with commercial stabilizer potassium oleate (PO).
3. To study the effect of azidated glycerol (AG) as anti-freeze stabilizer on the performance of NRL after freezing, in comparison with commercial stabilizer potassium oleate (PO).

1.4 Scope of research study

The main idea of this research is to modify glycerol to make it more compatible with NRL colloid and able to protect the latex particles at a low temperature (freezing). The idea was to come out of the effectiveness of anti-freeze in protecting frozen food at a lower temperature. Antifreeze agents can be directly added to food and interact with ice, therefore influencing ice crystal size and crystal structure within the food, which are two functionally distinct and opposite classes of proteins (Hew & Yang, 1992). Antifreeze agents can lower the freezing temperature and retard recrystallization on frozen storage, while ice-nucleation proteins raise the temperatures of ice nucleation and reduce the degree of supercooling (Fenney & Yeh, 1993, Li & Lee, 1998).

This thesis will only focus on the (a) use of molecular stabilizer as a new low temperature stabilizer system, (b) total solid content (TSC) of NRL must be diluted and maintained at 50% TSC before mixing with stabilizer, (c) temperature of freezing is at -4 °C, freeze for 24 hours, (d) amount of stabilized NRL to be freeze must be maintained about 300 g for each plastic container and tightly closed the container during freezing, and finally (e) rapid thawing condition will be used by thawing the frozen latex at ambient temperature for 1 hour followed by heating at 40 °C for another 1 hour.

Meanwhile, this thesis will not cover issues such as (a) no polymeric or particulate stabilizer will be used, (b) no variable freezing conditions/parameters will be studied, and (c) no changeable amount of NRL to be frozen. However, those issues were recommended for future study to discover the utmost condition of AG to produce good NRL colloidal and film properties.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Chapter 2 provides an overview of NRL, followed by stabilizer in NRL, latex film formation and colloidal destabilization of NRL by freezing. Glycerol as anti-freeze stabilizer system and azidation reaction that later will be used to modify the glycerol are also discussed.

2.2 Natural rubber latex (NRL)

Natural rubber latex (NRL) is a colloidal dispersion of *cis*-1,4-polyisoprene rubber hydrocarbon in an aqueous medium. It is present in latex as molecular aggregates in the form of discrete particles which are usually spherical with diameters ranging from 15 nm to 3 μ m. NRL also contains non-rubber constituents such as proteins, lipids, sugars, carotenoids, mineral salts, enzymes, and numerous other nitrogenous substances (Lim & Misni, 2016). Most of these non-rubber constituents are dissolved in the aqueous phase of the latex, some are adsorbed at the surface of the rubber particles, and the others are suspended in the latex. Latex particles are negatively charged on their surface (Sansatsadeekul et al., 2011). This confers a colloidal stability of a latex at basic pH, whereas latex coagulates at low pH. The NRL particle has been described as a hydrophobic core of polyisoprene surrounded by a complex lipo-protein layer, and the particle membrane was shown to be a fluid monolayer. Rubber particles contain in total about 1.6-3.7% of lipids, which are classified into neutral lipids, glycolipids, and phospholipids (Liengprayon, 2008). Not only lipids, but also proteins may contribute to the global negative charge of the particle surface. The proposed structure of the NRL particle is shown in Figure 2.1.

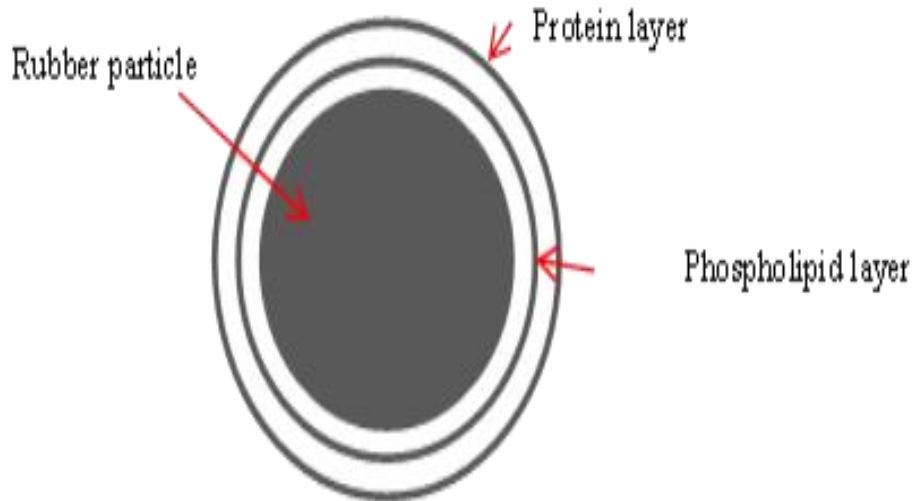


Figure 2.1 2D of outline structure of NRL particle (Kalyani, 1999)

2.2.1 Spontaneous coagulation of fresh natural rubber latex (NRL)

NRL is a very good source for microbial growth since it contains various nutritious substances such as proteins, sugars, and amino acids. As a result, NRL gets contaminated by microorganisms on tapping as well as during collection. The organisms feed on the nutritious substances and produce a volatile fatty acid that coagulates NRL within few hours. This process is known as spontaneous coagulation. The time required for coagulation depends on the ambient temperature and upon the colloid stability of the latex. Still, always the result is that the latex separates into clots of rubber and a clear aqueous phase. Thus, it is necessary to add a preservative to keep the latex as a fluid until it is ready for processing.

Two theories have been proposed to explain the phenomenon of spontaneous coagulation. The first postulates that the process is primarily a consequence of the development of acidity through the interaction of microorganisms with the various non-rubber constituents of the latex. The second attributes the effect of the liberation of fatty-acid anions through hydrolysis of the various lipid substances present in the

latex. Such anions are then thought to be adsorbed at the surfaces of the rubber particles, possibly partially displacing adsorbed proteins. They then interact with divalent metal ions, such as those of calcium and magnesium, which are either present in the latex initially or else are gradually released from complexes by the action of enzymes (Blackley, 1997).

2.2.2 Preservation of natural rubber latex (NRL) by ammonia

The ideal preservative for NRL should have the following criteria such as harmless both to people and to rubber, should not discolour latex or NRL films, should not impart an offensive odor to the latex, should not interfere with established latex processes, and finally should be cheap and convenient to handle.

Until this period, ammonia meets the above criteria. It is very effective as a bactericide, imparts alkalinity to the aqueous phase of NRL, and able to de-active some multivalent ions. On the other hand, AG also exhibited bactericidal activity based the extensive research that has been carried out on the pure glycerol that mainly known as antimicrobial and effective preservative (Triveni et al., 2015). Ammonia is not especially harmful to people if reasonable precautions are taken, unless it is inhaled in excessive quantities, or unless a concentrated aqueous solution meets the skin. It appears not to affect NRL, although it does cause significant changes to some non-rubber constituents of NRL (decreasing the proteins and resinous substances). It imparts no color to the NRL, or to the deposits obtained from the latex, from which it is eliminated during drying, but it imparts a strong odor. Ammonia has to be handled either as cylinders of anhydrous liquid or as concentrated aqueous solutions (Blackley, 1997).

2.2.3 Concentration of preserved natural rubber latex (NRL) by centrifugation method

It is standard practice to concentrate the latex so that the dry rubber content is 60% m/m or above. The concentration is done to make NRL more economically attractive for transportation, and the concentrated NRL is more suitable for industrial processes. The NRL latex can be concentrated by any of these methods; evaporation, creaming, centrifugation, and electrodecantation. Concentration by centrifugation is by far the most popular method. About 90% of the concentrated NRL used in the industry is produced by centrifugation, and the rest is produced either by creaming or an evaporation method. Concentration by electrodecantation is seldom used. Centrifugation is an effect of a type of accelerated creaming process, in which the motion of the rubber particles relative to the aqueous phase is affected through a centrifugal field rather than a gravitational field. Like creaming, successful concentration by centrifugation depends upon there being a significant difference between the density of the rubber particles and that of the aqueous phase (<https://learnbin.net/latex-concentration-in-latex-processing/>, January 2022).

After concentration, the concentrated NRL is treated with a specified quantity of preservatives; some dilution is made where necessary and left to mature once the laboratory report on it indicates that its dry rubber content (DRC), ammonia content, and the volatile fatty acid (VFA) number are within the specifications. Then the concentrated NRL is left to mature with periodic sampling to monitor the increase in its mechanical stability time (MST). Once all the parameters have been found to comply with the specifications, the concentrated NRL is then due for the next stage of handling. In most cases, the concentrated NRL is either packed within the factory premise in drums/containers/pallets or dispatched by road tankers or rail wagons to the

Port Installation before being exported abroad or to the latex processing industry (Yer and Lee, 1995).

2.2.4 Morphology of natural rubber latex (NRL) particles

The morphology of NRL particles is shown in Figure 2.2(A) taken from Atomic Force Microscope (AFM) images, obtained in tapping mode, of dip-coated slightly ammoniated NRL particles, taken one day after dipping. It could be seen that NRL particles are spherical and randomly distributed. The random distribution of the particles is the result of the NRL particles being very poly-disperse in size (Kanjaneer et al., 2011).

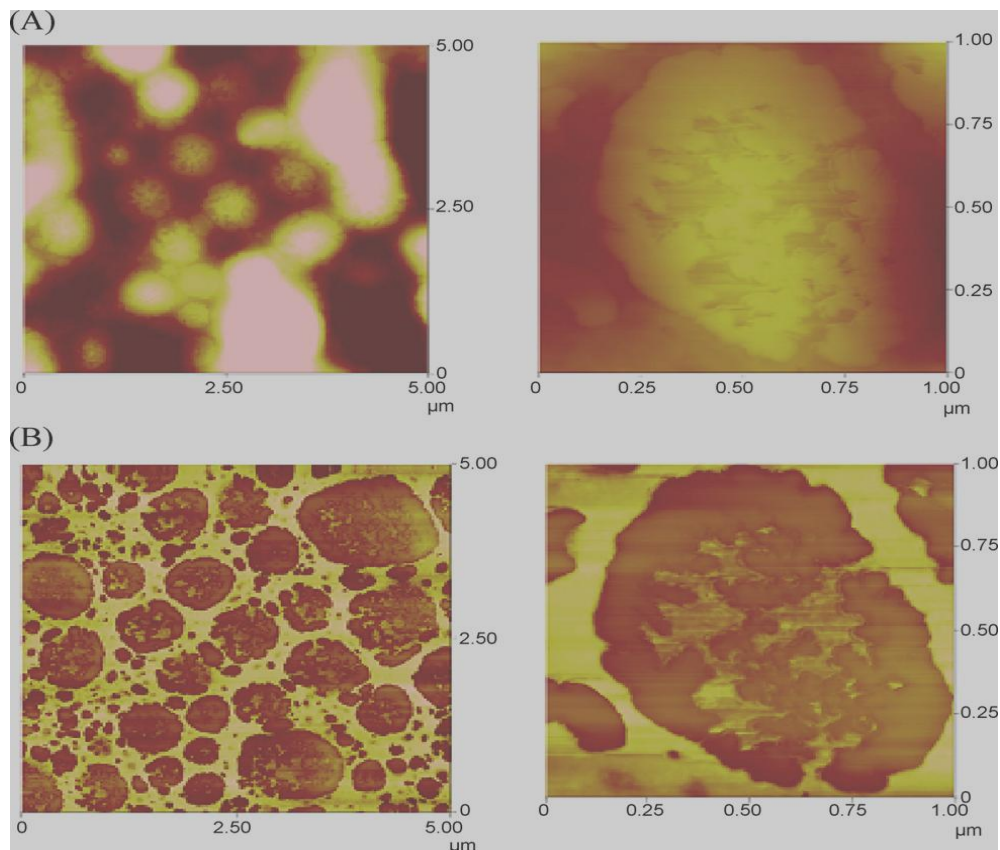


Figure 2.2 Micrographs from AFM in tapping mode of 20% (w/w) freshly tapped NR latex dip-coated on a glass substrate. The images were taken the day after the preparation of the NR film. (A) Two-dimensional images and (B) phase-contrast images of the same region (Kanjaneer et al., 2011)

The phase images of the NRL particle shown in Figure 2.2 (B) exhibited separate phases. The light and dark brown areas were indicative of the various components on the NRL particle surface. As depicted in Figure 2.1, the NRL particle is covered with proteins and phospholipids, the two areas with different phase contrast were inferred to areas of the adsorbed proteins and phospholipids.

The non-uniform phase-contrast images suggested that the NRL particles surface is surrounded by a layer made up of mixed domains of proteins and phospholipids (Figure 2.2 (B)), in contrast to the previously perceived structure of a double layer in Figure 2.3(A) (Tanaka et al., 1997, Cockbain and Philpott, 1963, Dupont et al., 1976). Here, the NRL molecule linked with proteins and phospholipids respectively at the ω - and α - terminal ends was believed to orientate themselves so that these hydrophilic ends are located on the particle surface as the thin layer. The polyisoprene molecules should then form the hydrophilic core, in essence, giving rise to the core-shell-like particle.

The proteins and phospholipids were phase-separated into domains on the surface of the NRL particle. A cross-sectional profile of the NRL particle surface was analyzed, and the result is depicted in Figure 2.3. The average difference in the vertical heights between the clusters was 5.4 ± 2 nm. This value was taken to represent the size difference of the protein and phospholipid molecules on the NRL particle surface. The proteins associated with the rubber particle have been reported to have molecular weights of about 14.5 and 24 kDa (Hasma, 1992, Dennis and Light, 1989).

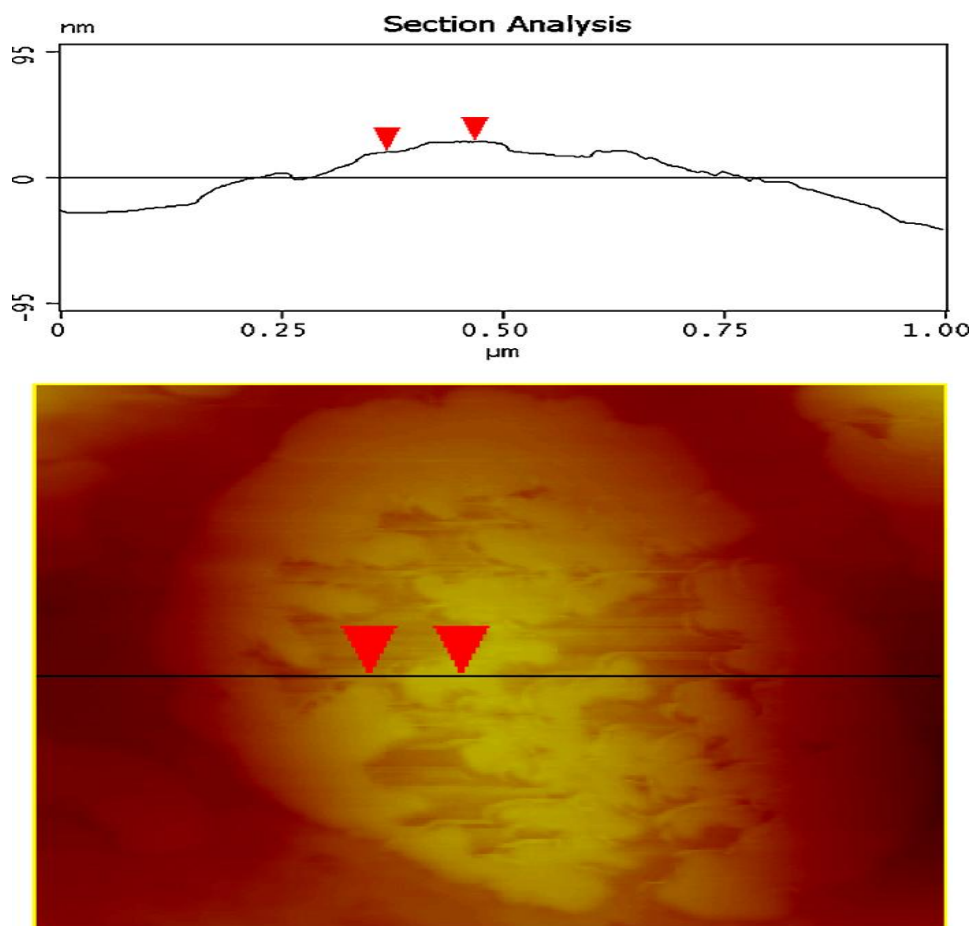


Figure 2.3 A cross-sectional profile of the rubber latex particle obtained by AFM (sample imaged one day after preparation) (Kanjaneer et al., 2011)

In contrast, phospholipids have approximate molecular weights of about 0.7-0.8 kDa. Hence, it was reasonable to assume the higher clusters on the NRL particle to be those of proteins, whereas the lower ones should correspond to the phospholipids. From the surface integral analysis of the cross-sectional data, the average surface area covered by proteins was approximately 84%, whereas that for the phospholipids was about 16%. This suggested that the major surface constituents of freshly tapped latex particles were proteins and their charges controlled the colloidal stability of the latex dispersion (Kanjaneer et al., 2011).

Confocal fluorescence microscopy was used to investigate the spatial distribution of proteins and phospholipids on the NRL particle surface. This technique rendered it possible to obtain information concerning the location of fluorescence molecules inside a particle-based on the presence of fluorescence molecules within the sample. As can be seen in Figure 2.4(A), numerous bright spots emanated from the fluorescence RB molecules (used to electrostatically bind the amine functional groups in proteins and phospholipids) and corresponded to the transmission image of the sample shown to the right. This indicated the presence of amino-functional groups on the exterior of the NRL particle. However, only dark spots were discernable in place of the bright red spot for the interior of the NRL particle at the same position as in Figure 2.4(B). This signified an absence of fluorescent molecules inside the NRL particles. In other words, no amino groups were present within the latex particles, which should contain only poly-isoprene hydrocarbon as the core. This result was in complete agreement with the proposed core-shell structure of the NRL particle surrounded by a shell layer of hydrophilic proteins and phospholipids (Kanjaneer et al., 2011).

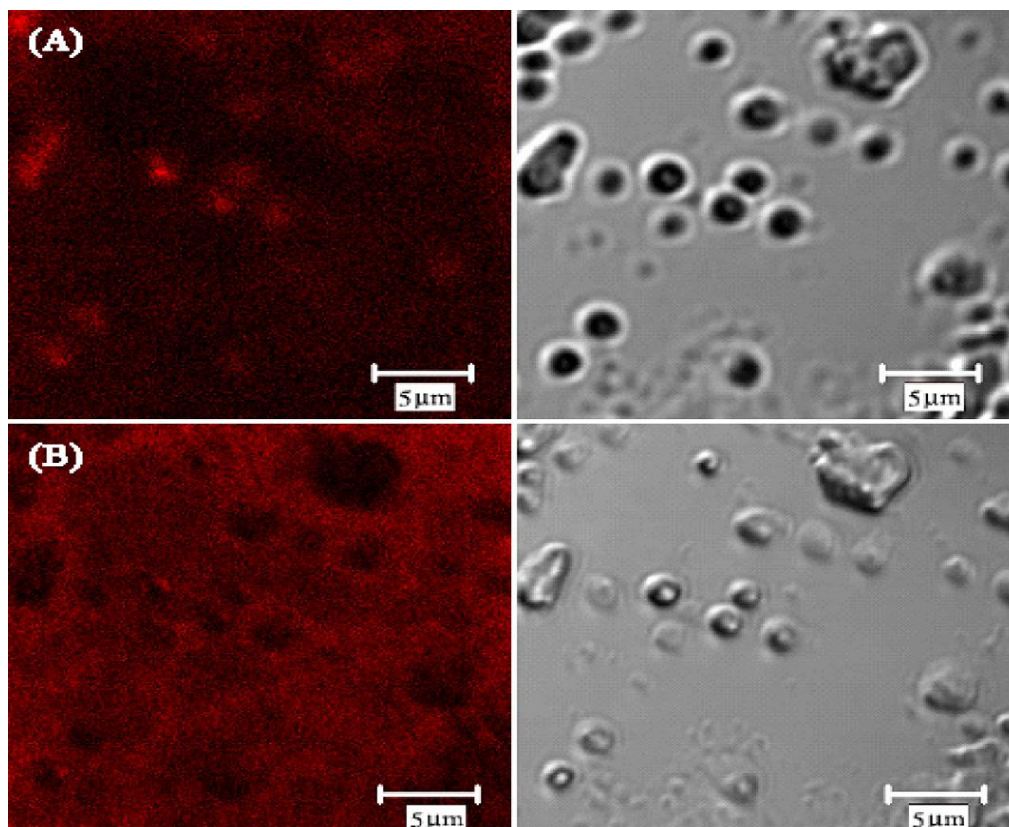


Figure 2.4 Confocal laser scanning micrographs (CLSM) of RB-labelled NR latex particles viewed (A) on the surface and (B) in the interior of the sample (Kanjaneet al., 2011)

2.2.5 Colloidal and rheological properties of natural rubber latex (NRL)

The colloid stability of high ammonia (HA) NRL concentrate is governed mainly by the negative charges on the surface of the latex particle as well as by the composition and nature of the dissolved substances in the aqueous serum phase. The negative charges on the latex particle surface are derived from the carboxyl groups of adsorbed proteins and adsorbed long-chain fatty acid soaps (Shinzo et al., 2021) the latter being products from the hydrolysis of phospholipids initially present in the field latex. Any attempt to remove this adsorbed layer of proteins and long-chain fatty acid soaps results inevitably in the immediate coagulation of the latex.

The colloidal properties of NRL dispersion systems are dependent on the composition at the interface between the dispersed particles and the dispersion

medium (Sansatsadeekul et al., 2011) and also the size of the disperse particles similar to other dispersion systems. They are subjected to interfacial and kinetic phenomena such as Brownian motion, surface adsorption, sedimentation, and diffusion properties. The NRL exhibit non-Newtonian flow; its viscosity varies with the shear rate and temperature. The material may exhibit shear-thickening, shear-thinning, pseudoplastic, thixotropy, or hysteresis.

The recent research proposed a new model of NRL particle consisting of a mixed layer of proteins and phospholipids surrounding the latex particles with polyisoprene rubber as the hydrophobic core (Nawamawat et al., 2011) as shown in Figure 2.5. As proteins could have dual characteristics similar to the stabilizers, it makes NRL partly embedded on the rubber core.

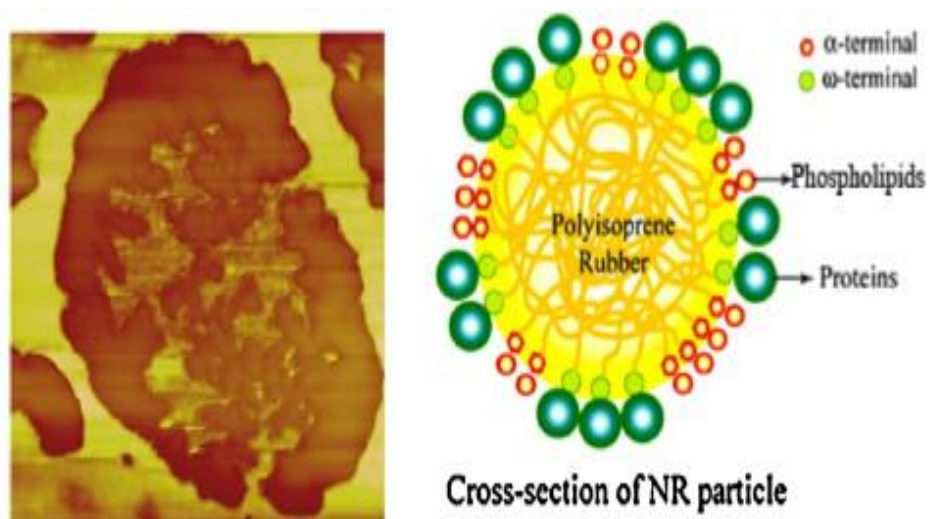


Figure 2.5 New model of NRL particle consisting of a mixed layer of proteins and phospholipids surrounding the latex particles with polyisoprene rubber as the hydrophobic core (Nawamawat et al., 2011)

Besides, the field latex particles are predominantly small spheres with a few larger pear-shaped or elongated particles, as shown in Figure 2.6(A). During the centrifugation process, the larger particles move more rapidly as compared to the smaller particles, as such the NRL concentrate tends to contain predominantly larger

and uniform particles as compared to field latex particles. The process also increases the proportion of the rubber in the latex and removes undesirable impurities.

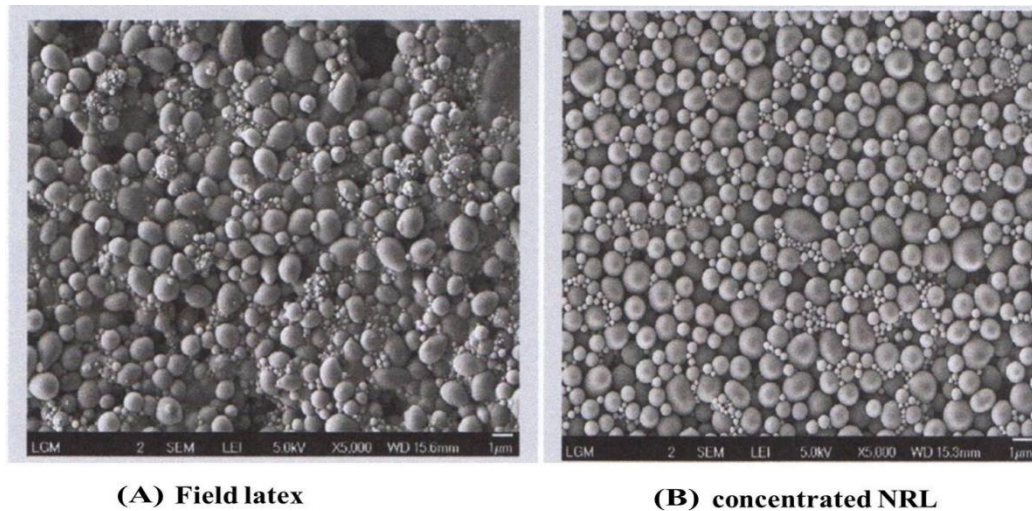


Figure 2.6 SEM micrograph of (A) field latex particles and (B) concentrated latex particles (Lim and Misni, 2016)

Colloid stability of NRL is a consequence of the presence of barriers between the particles, which discourages the close approach of the particles. These barriers arise from the balance between various attractive and repulsive forces, which are operative between two particles as they approach each other closely. Colloidal stability is conferred if the balance between the attractive and repulsive forces is such that a potential energy barrier confronts two particles as they approach each other closely as summarized in Figure 2.7. The higher this barrier, the more stable the colloid.

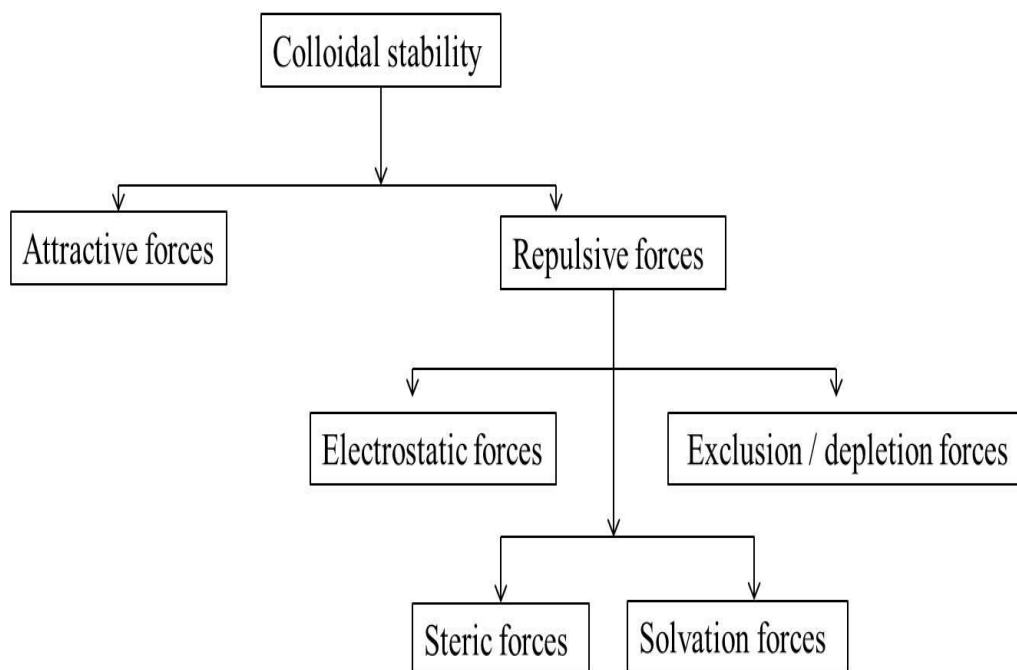


Figure 2.7 Colloid stability of NRL conferred by the balance between attractive and repulsive forces

2.2.5(a) Attractive forces

The forces of attraction that cause the particles in an un-stabilized lyophobic sol to aggregate are believed to be the same forces that cause the molecules in the condensed states of matter to cohere in the absence of primary valence forces between the molecules. There are also the forces that give rise to the phenomenon of interfacial free energy because they are the forces against which work has to be done to create a new interfacial area between two contiguous phases by bringing molecules from the bulk of the phases to the interface. That this must be so followed because the aggregation and coalescence of the particles in a lyophobic sol are accompanied by the loss of the interfacial area, which is created when the sol is formed. The forces of attraction between the particles in a lyophobic are relatively non-specific, in the sense that they do not depend greatly upon the nature of the atoms and molecules, which

comprise the particles. Forces of this type are known collectively as secondary valence forces or Van der Waals forces (Blackley, 1997).

The origins and natures of these forces are complex. Non-ionized molecules, they are believed to be three types: (1) attractions between permanent electric dipoles in the molecules, known as Keesom or orientation forces, (2) attractions between electric dipoles and those induced in one molecule by dipoles in others, known as Debye or induction forces and (3) attractions between fluctuating dipoles in the atoms which comprise the molecules, known as London or dispersion forces (Erik, January 2022).

The orientation and induction forces originate from classical electrostatic interactions. Meanwhile, dispersion forces are quantum mechanical in origin and amenable to a host of theoretical treatments of varying complexity, the most rigorous of which would take us into the world of quantum electrodynamics. The origin may be understood intuitively as follows: For a non-polar atom such as helium, the time average of its dipole moment is zero, yet at any instant, there exists a finite dipole moment given by the instantaneous positions of the electrons about the nuclear protons. This instantaneous dipole generates an electric field that polarizes any nearby neutral atom, including dipole moment in it. The resulting interaction between the two dipoles gives rise to an instantaneous attractive force between the two atoms, and the time average of this force is finite (non-zero).

Thus, all three types of force are essentially electrostatic in origin, the difference between them is how the charge-separation required to produce the electrostatic interaction is induced. All three types of secondary valence force give rise to an attractive potential which, relative to infinite separation as the datum of zero

potential, varies inversely as the sixth power of distance. For orientation and induction forces, this is the distance between the molecules, for dispersion forces, it is between the atoms. Notwithstanding that three types of intermolecular attractive forces are believed to operate between molecules, it is commonly assumed that, for microscopic portions of matter such as colloidal particles, the predominant contribution is from the dispersion forces. There are at least two reasons for this assumption, firstly, these forces have the requisite non-specific character, which orientation and induction forces do not have because they depend upon the chemical nature of the atoms and molecules which comprise the particles. The non-specific nature of dispersion forces is a consequence of their origin in the inherent electrical nature of the atoms which comprise the molecules, rather than from the particular arrangement of those atoms within the molecules. Secondly, the overall dispersion force of attraction between microscopic portions of the matter is believed to be approximately derivable by summation of the forces between individual pairs of constituent atoms. This is not true for orientation and dispersion forces (<https://courses.lumenlearning.com/wsusandbox2/chapter/intermolecular-forces/>, January 2022).

Latex particles are not dispersed in free space but in a dispersion medium. The attractive forces, which are significant for the colloid stability of lattices, are not those which the particles would experience if they were dispersed in free space, but those which the particles actually experience when dispersed in the appropriate dispersion medium. The effect of the dispersion medium is to reduce the attractive forces between the particles (Liang et al., 2007).