SYNTHESIS AND CHARACTERIZATION OF SILVER NANOPARTICLES FOR ANTIMICROBIAL APPLICATION IN NATURAL RUBBER LATEX FOAM

By

W. G. INDRAJITH UDAYAKANTHA RATHNAYAKE

Thesis submitted in fulfilment of the requirements

for the degree of

Doctor of Philosophy

JULY 2014

DEDICATION

This thesis is dedicated to my treasured daughter Vinethmee Rathnayake and my beloved wife Niwanthi Rathnayake

ACKNOWLEDGEMENTS

This research has been accomplished owing to much devotion and dedication of many people who have contributed in numerous ways. Although it is difficult to mention all of them, it is a great privilege to extend my gratitude to all who endeavored.

First of all I would like to express my innermost gratitude to my main supervisor Professor Hanafi Ismail who made it possible for me to start my higher degree in Universiti Sains Malaysia. Your practical view and guidance on my research work was of the utmost importance. My sincere thanks go to my co-supervisor, Assoc. Prof. Dr. Baharin Azahari who always encouraged me to find new ways to do my research work. Thank you very much for both of you for the unending help throughout the course of my research.

I would like to give special thanks to my all the lecturers specially Dr. Susantha Siriwardena, Dr. Shantha Walopola, Professor Gamini Rajapakse and Dr. Sanath Rajapakse who understood my strength in research work and helped me to find new research arena. Thank you for your persevering support and encouragement.

Many thanks and appreciations go to my collaborative research partners, Dr. Channa R De Silva, Mr. Nalin Darsanasiri and Mr.Chaturanga Bandara for their valued support throughout the research work.

My gratitude also extends to previous and present members of my research group specially Dr. Kahar, Dr. Ragu, Dr. Viet, Dr. Mathi, Dr. Sam, Dr. Nik, Mr. Nabil, Miss. Maryam, Mr. Ooi, Miss. Shida, Mrs. Shazlin and Mr. Indra for their help in sharing ideas and friendship over the past three years. Their kind support made my research study a pleasant journey.

Not forgetting to thank the staff of School of Materials and Mineral Resources Engineering especially our respected dean and deputy deans, Prof. Zainal Arifin B. Ahmad, Assoc. Prof. Dr. Hashim B. Hussin and Assoc. Prof. Dr. Syed Fuad B. Saiyid Hashim, all the lecturers especially Professor Ahmad Fauzi, Dato' Profesor Ir. Eric K. H. Goh, Professor. Radzali B. Othman, Professor Hazizan B. Md. Akil, Professor Azizan b. Aziz, Professor. Azlan b. Ariffin, Prof. Ir. Mariatti bt. Jaafar Mustapha, Assoc. Prof. Dr. Zulkifli b. Mohamad Ariff, Assoc. Prof. Dr. Srimala, Assoc. Prof. Dr.Azura, Dr. Sivakumar, Dr. Zuratul and Dr. Norazharuddin, for giving me valuable advices throughout my research works. Also I would like to express my grateful thanks to our office staff and technicians especially Mr. Mior Zulbahri, Mrs. Nor Asmah Redzuan, Mr. Abdul Rashid, Madam. Fong, Mr. Kemuridan, Mr. Meor, Mr. Faizal, Mr. Mzaini, Mrs.Haslina, Mr. Azrul, Mr. Mokhtar, Mr. Shahril, and Mrs. Hasnah for training and helping me operate all the instruments.

Special thanks go to Universiti Sains Malaysia for financial support through the Research University Grant (RU Grant no. 1001/PBAHAN/814129).

Last but not least, I express my heartfelt gratitude to my parents Mr. W.G.P. Rathnayake and Mrs. K. Jayasinghe and my parents-in-law Mr. Dhanapala Hetiarachchi and Mrs. Rupa Hettiarachchi for giving me precious encouragement and companionship to make this research possible.

W. G. Indrajith Udayakantha Rathnayake

July 2014

TABLE OF CONTENTS

LIST OF TABLE

LIST OF FIGURES

LIST OF ABBREVIATIONS

ASTM	American Society for Testing and Materials
B,Clay	Bentonite Clay
BP	British patent
BR	Butyl rubber
CB	Conduction Band
CFU	Colony formation units
DNA	Deoxyribonucleic acid
DPG	Dipenyl guvanidene
DPNR	De-proteinized natural rubber
DRC	Dry Rubber Content
DTG	Derivative Thermo gravimetric Analysis
E.coli	*Escherichia coli*
EDX	Energy dispersive spectroscopy
ENR	Epoxide natural rubber
FTIR	Fourier Transform Infrared Spectrometry
G-	Gram negative
G+	Gram positive
GSNP	Green synthesized silver nanoparticles
HA-TZ	High ammonia TMTD and ZnO preserved
HRTEM	High resolution transmission electron microscope
ISO	International Standards Organization
IR	Isoprene rubber
KOL	Potassium oleate soap

LA-TZ	Low ammonia TMTD and ZnO preserved
MHA	Muller Hinton Agar
MIC	Minimum inhibitory concentration
MRSA	Methicillin-resistant *Staphylococcus aureus*
MST	Mechanical stability time
NBH	Sodium borohydrate
NBR	Acrylonitrile Butadiene rubber
NR	Natural Rubber
NRL	Natural Rubber Latex
NRLF	Natural Rubber Latex Foam
OD	Optical density
PCCS	Photon cross correlation spectroscopy
PEG	Polyethylene Glycol
PGN	Peptidoglycan
phr	Part per hundred of rubber
psi	Pound per square inch
PUF	Polyurethane foam
PVP	Polyvinyl pirrolidone
RF	Radio frequency
ROS	Reactive oxygen species
rpm	Round per minute
SA	*Staphylococcus aureus*
SBR	Styrene Butadiene Rubber
SEM	Scanning Electron Microscopy
SNPs	Silver nanoparticles

SPR	Surface Plasmon Resonance
SSF	Sodium silica fluoride
SWNT	Single-walled carbon nanotube
TEM	Transmission electron microscopy
TGA	Thermogravimetric Analysis
TrSC	Tri-sodium citrate
TSC	Total solid content
USP	United State patent
UV-Vis	Ultraviolet–visible spectroscopy
VB	Valance Band
VFA	Volatile fatty acids content
VOC	Volatile organic compound
XRD	X-ray diffraction
ZDEC	zinc diethyldithiocarbamate
ZMBT	zinc 2-mercaptobenzhiozolate

LIST OF SYMBOLS

ρ	Density (Kg/ m^3)
C_i	Molar concentration (mol/dm^3)
n_i	Amount of constitution (mol)
V	Volume (dm^3)
M	Molar mass (g/mol)
MW	molecular weight
n	mole
m	mass (g)
u	Atomic mass

SINTESIS DAN PENCIRIAN NANOPARTIKEL PERAK UNTUK KEGUNAAN ANTIMIKROB DI DALAM BUSA LATEKS GETAH ASLI

ABSTRAK

Di dalam projek penyelidikan ini bahan busa lateks getah asli (NRLF) telah dihasilkan dengan sifat-sifat antimikrob yang terdapat di dalam matriks busa lateks getah asli secara penyebatian bahan nano berasaskan perak menggunakan teknik-teknik yang berbeza. Kajian awal adalah untuk mengoptimumkan kaedah sintesis kimia nanopartikel perak (SNPs) dengan mengubah parameter-parameter proses seperti perkadaran bahan tindakbalas perak nitrat dan tri-sodium citrate (TrSC), masa tindakbalas dan suhu. Didapati apabila amaun TrSC meningkat, nanokoloid perak yang diperolehi adalah lebih stabil dan mengandungi SNPs bersaiz lebih kecil yang tersebar secara mono. Seterusnya, didapati penyebatian SNPs ke dalam matriks NRLF boleh dilakukan melalui beberapa teknik seperti pengenapan in-situ nanopartikel perak ke atas NRLF (kaedah 1), kaedah penyebatian terus (kaedah 2), menggunakan sabun oleat potassium tersebati nanopartikel sebagai bahan pembusaan dan pembawa (kaedah 3), sintesis hijau nanopartikel perak di dalam lateks getah asli (kaedah 4) dan yang terakhir dengan penyebatian perak terdop nanopartikel titanium (Ag terdop TiO_2) (kaedah 5). Didapati, kaedah 1 adalah kaedah terbaik untuk menyebatikan SNPs yang bersaiz lebih kecil dan disebarkan secara seragam di dalam busa lateks getah asli manakala kaedah 4 adalah cara yang lebih mudah dan novel untuk menyebatikan SNPs ke dalam NRLF. Di samping itu, kaedah terakhir menunjukkan aktiviti antimikrob yang paling tinggi walaupun kaedah ini sukar untuk

dilakukan secara sintesis berskala besar. Adalah diperhatikan yang NRLF yang terubahsuai menggunakan kesemua lima kaedah menunjukkan sifat-sifat antimikrob dan antikulat terhadap pelbagai jenis mikro-organisme patogen seperti Gram negative (G-) *Escherichia coli* (*E.coli*), Gram positif (G+) *Staphylococcus aureus* (SA), *Staphylococcus epidermidis* (SE) dan *Aspergillus niger* (A.niger). Keputusan yang diperolehi daripada kaedah 3 menunjukkan kaedah sintesis SNPs di dalam potassium oleat menghasilkan sabun yang boleh digunakan secara terus sebagai sabun karboksilat antimikrob. Keputusan daripada kaedah 4 menunjukkah kaedah sintesis hijau novel nanopartikel perak di dalam lateks getah asli boleh dilakukan tanpa agen penstabil atau agen penurun tambahan. Seterusnya, didapati perak terdop TiO_2 meningkatkan aktiviti antimikrob yang ketara walaupun di dalam keadaan gelap.

SYNTHESIS AND CHARACTERIZATION OF SILVER NANOPARTICLES FOR ANTIMICROBIAL APPLICATION IN NATURAL RUBBER LATEX FOAM

ABSTRACT

In this research project, natural rubber latex foam materials (NRLF) were developed with antimicrobial properties built-in within the natural rubber latex foam matrix by incorporating silver based nanomaterials using different techniques. The initial attempt was to optimize the chemical synthesis method of silver nanoparticles (SNPs) by varying the process parameters such as proportionate of reactant silver nitrate and tri-sodium citrate (TrSC), time of the reaction and the temperature conditions. It was found that, as the amount of TrSC was increased the obtained silver nanocolloid was more stable and consisted with mono-dispersed smaller sized SNPs. Next it was found that the incorporation of SNPs into the NRLF matrix can be accomplished via several techniques such as *in-situ* deposition of silver nanoparticles on NRLF (method 1), direct compounding method (method 2), using silver nanoparticles incorporated potassium oleate soap as both foaming and convenient carrier materials (method 3), green synthesis of silver nanoparticles inside natural rubber latex (method 4) and finally by incorporating silver doped titanium nanoparticles (Ag_doped TiO_2) (method 5). It was found that the method 1 is the best method to incorporate smaller sized and consistently distributed SNPs into the natural rubber latex foam whereas the method 4 shows novel and easy way to incorporate SNPs into the NRLF. In addition, the last method showed the highest antimicrobial activities even though that method is difficult to carry out in large scale

synthesis. It is observed that modified NRLF materials via all the five methods showed remarkable antimicrobial and anti-fungal properties against various kinds of pathogenic micro-organisms including Gram negative (G-) *Escherichia coli* (*E.coli*), Gram positive (G+) *Staphylococcus aureus* (SA), *Staphylococcus epidermidis* (SE) and *Aspergillus niger* (A. niger). Results obtained from the method 3, revealed the novel synthesis method of SNPs inside potassium oleate resulted soap material that can be directly used as an antimicrobial carboxylate soap. Results obtained from the method 4 confirmed that the novel green synthesis method of silver nanoparticles inside natural rubber latex can be easily carried out without using an additional stabilizing agent or a reducing agent. Furthermore it was found that the Ag doped TiO_2 enhanced antimicrobial activities of NRLF by a great extent even in dark conditions.

CHAPTER ONE
INTRODUCTION

1.1 Brief introduction of Natural Rubber Latex Foam (NRLF)

Natural rubber latex is a fascinating bio-polymeric material given to us by mother-nature. The milky white colour sap from a tree called *Hevea brasiliensis* often simply called as rubber tree is the main raw material for lots of useful products in our daily life. In this modern world, this naturally occurring raw material is used to produce a variety of products that make human life easy and comfortable. Surgical gloves, catheters and condoms made from natural rubber latex (NRL) prevent people from several life threatening diseases in numerous ways.

In the process of making NRLF from NRL, a stable dispersion of NRL and chemicals are being converted to a stable porous solid material. In this conversion several important steps should be followed such as making of air bubbles inside the liquid dispersion system, stabilizing the air bubbles in the dispersion, solidifying/gelling of the liquid dispersion phase without disturbing the air bubbles, vulcanizing of rubber particles of the dispersion phase and finally removing the remaining liquid phase while making a stable solid-gas system known as cellular/sponge material (Calvert et al., 1982).

1.2 Use of natural rubber latex foam materials

Enormous amount of foam materials are used in hospital environment as hospital mattresses and cushions in hospital furniture. Foam products can be divided in to two main categories such as polyurethane foam (PU foam) which is synthesized using chemicals and natural rubber latex foam (NRLF) derived from natural rubber latex. Natural rubber latex foam products have number of advantages than PU foam products. Natural rubber latex foam is widely used in bedding and furniture industries for manufacturing mattresses, pillows, sofa cushions, and in automobile products such as car seats, cushions, insulation materials (Madge, 1962).

Nanotechnology and nano scale materials have been touted as the "next industrial revolution". Nanotechnology is an emerging interdisciplinary technology that has been booming in many areas during the recent decade, including materials science, mechanics, electronics and aerospace. Its profound societal impact has been considered as the huge momentum to usher in a next industrial revolution (Lane, 2001).

1.3 Fundamentals of nanotechnology

The fundamentals of nanotechnology lie in the fact that properties of substances dramatically change when their size is reduced to the nanometer range. When a bulk material is divided into small sized particles with one or more dimensions (length, width, or thickness) in the nanometer range or even smaller, the individual particles exhibit unexpected and valuable properties different from those of the bulk material. It is known that atoms and molecules possess totally different behaviours than those of bulk materials; while the properties of the former are described by quantum mechanics, the properties of the latter are governed by classical mechanics. Between these two distinct domains, the nanometer range is a murky threshold for the transition of a material's behaviour. For example, ceramics, which normally are brittle, can easily be made deformable when their grain size is reduced to the low nanometer range. A gold particle with 1 nm diameter shows red colour. Moreover, a small amount of nano-sized species can interfere with matrix polymer that is usually in the similar size range, bringing up the performance of resultant system to an unprecedented level (Schmid, 2004).

1.4 Antimicrobial nanomaterials

The development in nano-technology has resulted in the application of nano-sized particles such as nano-sized silver (Chudasama et al., 2010; Martinez-Castanon et al., 2008; Prema and Raju, 2009; Shrivastava et al., 2007; Silvestry-Rodriguez et al., 2007; Sondi and Salopek-Sondi, 2004) titanium dioxide (Fu et al., 2005; Liu et al., 2008) and zinc oxide (Jones et al., 2008; Li et al., 2009; Padmavathy and Vijayaraghavan, 2008; Tam et al., 2008; Tayel et al., 2011; Xie et al., 2011; Zhang et al., 2010) to disinfect several types of pathogenic microbes such as *E.coli*, *Staphylococcus aureus*, *Salmonella typhus*, *Pseudomonas sp.*, *Salmonella sp.*, *Shigella sp.*, *K. pneumonia*.

1.5 Research Background of the Present Work

Metals and metal oxides are well known antimicrobial agents from the very old time (Stoimenov et al., 2002). Among so many types of antimicrobial metal and metal oxide nanoparticles such as, gold nanoparticles, aluminium nanoparticles, nanoparticles of TiO_2, MgO, ZnO and CuO, silver nanoparticles are well known and very prominent antimicrobial metal oxide nanoparticles due to their spectacular properties as explained below. Silver nanoparticles exhibit high thermal stability, little toxicity to human cells and tissues, higly toxic to vast range of pathegonic microbes and also it shows long-term activity (Monteiro et al., 2009). Synthesis of products based on silver nanoparticles that show antimicrobial properties is a well known research area among many resarchers from decades.

Synthesis of silver nanoparticles can be achieved from several techniques. Among them the most economically feasible and straightforward method is the chemical reduction method of a silver salt by using appropriate reducing agent. Silver nanoparticles can be obtained as a powder form or as a liquid form. There can be seen many research works on modifying polymers using silver nanoparticles to get variouse kind of functions and properties (Hang et al., 2010; Kim et al., 2010; Maneerung et al., 2008; Rifai et al., 2006). Polymers modified by silver nanoparticles have different types of applications such as antmicrobial, biomedical applications, applications in catalysts. Antimicorbial polymers based on silver nanoparticles are very momentous research area in modern polymer technology and modern nanotechnology. Combination of polymer technology together with nanotechnology present promising antimicrobial polymers not only to the academia but also to the modern market.

1.6 Problem Statements

The increase of health consciousness of consumers and the development of healthcare industry resulted in the increase in the demand of natural rubber latex foam (NRLF) having antimicrobial properties. As consumers are becoming more and more aware of bacteria and their harmful effects, manufacturers have to respond to their needs by offering antimicrobial solutions in a wide variety of applications, ranging from medical devices to construction materials and consumer goods (Brackett, 1992; McGowan, 1983). Similarly, the natural rubber based research area being benefited from antimicrobial technology by reducing microbes and increasing the service life of rubber materials (Bayston and Milner, 1981; Kaali et al., 2010). Antimicrobial solutions in NRLF would offer a win-win solution that assure consumers the way to a safer and a healthier life while helping manufacturers to save money and to conserve natural resources.

Natural rubber latex foam made by using natural rubber latex, latex compounding ingredients and silver nanoparticles can make very promising antimicrobial foam materials that can be used in many applications. The synthesis of stable silver nanoparticles in an aqueous media would be a very important step to achieve very good foam materials. Since the natural rubber latex is an aqueous alkaline colloid that can be de-stabilized by chemical and physical agencies. So it is very important to make a compatible dispersions or solid form of silver nanoparticles.

In addition, the long lasting stability of the silver nanoparticles in aqueous media is very much important to be added as an additive in the NRLF synthesis process. So SNPs have to be stabilized well in aqueous media or in a suitable media to keep the stability for long time. Also it has to be considered the viability of large scale synthesis as the applications of modified antimicrobial NRLF will be used in bulk form. Therefore, the incorporation of SNPs into the NRLF should find diverse ways that give the feasibility of large scale synthesis.

Combination of silver based nanomaterials with natural rubber latex to make antimicrobial natural rubber latex foam products would lead to a marvellous polymeric sponge material for healthcare mattresses, and other foam requirements in a wide spectrum of medical equipments in the healthcare industry. As explained above, foam materials having antimicrobial properties are very important not only in healthcare sector but also in many applications where the antimicrobial properties are more vital factor.

1.7 Objectives of Study

The foremost goal of this research work is to incorporate antimicrobial properties to the natural rubber latex foam using silver based nanoparticles. This study was deliberated and carried out to address the following sub-objectives in order to achieve the main objective:

1. To investigate the method of synthesizing silver nanoparticles using chemical reduction method and characterize their antimicrobial properties together with other characterization techniques in order to find the sizes of silver nanoparticles.

2. To attach silver nanoparticles on the surface of natural rubber latex foam by using chemical adsorbing method such as direct compounding of alkaline silver nano colloid with natural rubber latex and using a host material that can be carried stable silver nanoparticles into the natural rubber latex foam.

3. To investigate novel green synthesis method of synthesizing antimicrobial natural rubber latex foam using natural rubber latex as the media for stabilizing and reducing silver nanoparticles.

4. To develop a method to dope TiO_2 nanoparticles using silver nanoparticles and investigate the enhancement of antimicrobial activities of natural rubber latex foam by incorporating silver doped TiO_2 nanoparticles into the natural rubber latex foam matrix.

1.8 Organization of the Thesis

This thesis consists of ten chapters. Each chapter covers the research interest as declared under the objectives of study. An introduction of natural rubber latex foam and the importance of antimicrobial natural rubber latex foam to fight against pathogenic microbes are outlined in Chapter 1. It is followed by the development of natural rubber latex foam by incorporating silver related nanoparticles as a potential antimicrobial agent.

Chapter 2 provides the information on natural rubber latex technology, a brief introduction about products based on natural rubber latex technology and natural rubber latex foam technology. The historical development of natural rubber latex foam from natural rubber latex is discussed chronologically from the beginning of latex foam to the latest methods called “Dunlop” and “Talalay” method of making natural rubber latex foam. The detailed synthesize method of natural rubber latex foam by the “Dunlop” method is also summarized in this chapter. The introduction of antimicrobial agents using modern nanotechnology is described by using several examples and the use of silver nanoparticles as a potential antimicrobial agent is emphasized in the middle part of the Chapter 2. In later sections, several techniques of preparation of silver related nanoparticles using different types of techniques are described.

Chapter 3 explains the various kinds of chemicals and materials used in the entire research method. The preparation of natural rubber latex foam by the Dunlop method and synthesis of different types of silver nanoparticles are also described in this chapter. Final section of Chapter 3 mainly focuses on the characterization of fundamental properties of natural rubber latex, investigation of chemical and physical properties of synthesized nanoparticles, investigation of antimicrobial properties and other chemical properties of modified natural rubber latex and also evaluation of selected physical properties of resultant natural rubber latex foam.

In Chapter 4, the investigation of fundamental properties of pure natural rubber latex and the method of optimizing the size of pure silver nanoparticles by chemical reduction method are described. In the later part of the Chapter 4 is evaluated the antimicrobial properties of pure silver nanoparticles are evaluated together with some other properties such as particle sizes, UV-Vis data, and TEM image analysis.

Chapter 5 describes the first method of synthesizing antimicrobial natural rubber latex foam by in-situ deposition of silver nanoparticles on previously prepared natural rubber latex foam materials. In this Chapter, it is explained how the silver nanoparticles were adsorbed in an effective manner on the micro cavities of natural rubber latex foam. The properties of resultant natural rubber latex foam are described in detail in this Chapter.

Chapter 6 discusses the second method of preparing antimicrobial natural rubber latex foam by direct compounding method of natural rubber latex with alkaline colloidal solution of silver nanoparticles. It is explained that overcoming the unwanted brown colour of resultant natural rubber latex foam found in the first method can be successfully carried out by using this second method.

The third novel method explained in Chapter 7 describes the synthesis of convenient carrier material of silver nanoparticles into natural rubber latex foam matrix. In this chapter, it is explained that the method of synthesizing silver nanoparticles incorporated potassium oleate and it use of making silver nano particles incorporated NRLF. It was found that the resultant soap was acting as a foaming agent as well as a source of silver nanoparticles.

Chapter 8 discusses about a new method of making silver nanoparticles to be used as the main raw material in “Dunlop” production method of natural rubber latex foam making. It explains that the novel finding of green synthetic method of making silver nanoparticles inside aqueous dispersion of natural rubber latex. Further, it is explained that the resultant natural rubber latex can easily replaced pure natural rubber latex in the synthesis method of natural rubber latex foam. In the later part of the chapter, the evaluation of resultant natural rubber latex foam for antimicrobial properties and other properties is focused.

Chapter 9 explains the fifth method as well as the last method of making antimicrobial natural rubber latex foam. There it is described how to enhance the antimicrobial properties of TiO_2 nanoparticles by doping silver nanoparticles on the surface of TiO_2 nanoparticles. The use of silver doped TiO_2 nanoparticles as an antimicrobial agent in making antimicrobial natural rubber latex foam is also described in this chapter.

The main conclusions and recommendations for future research are outlined in the Chapter 10. The conclusions are written according to the results found in Chapter 3 to Chapter 9.

CHAPTER TWO
LITERATURE REVIEW

2.1 Introduction of Latex technology

According to the Blackley (Blackley, 1966c) the word of “latex” can be expressed as “a stable colloidal dispersion of a polymeric substance in an aqueous/non-aqueous medium”. Depending on the origin (synthetic/natural), physical nature of the polymeric substance, chemical nature of the polymeric substance and the polarity of any electrical charge that is bound with the polymeric substances, the latex can be classified to several types. Figure 2.1 shows the classification of latex based on origin of latex.

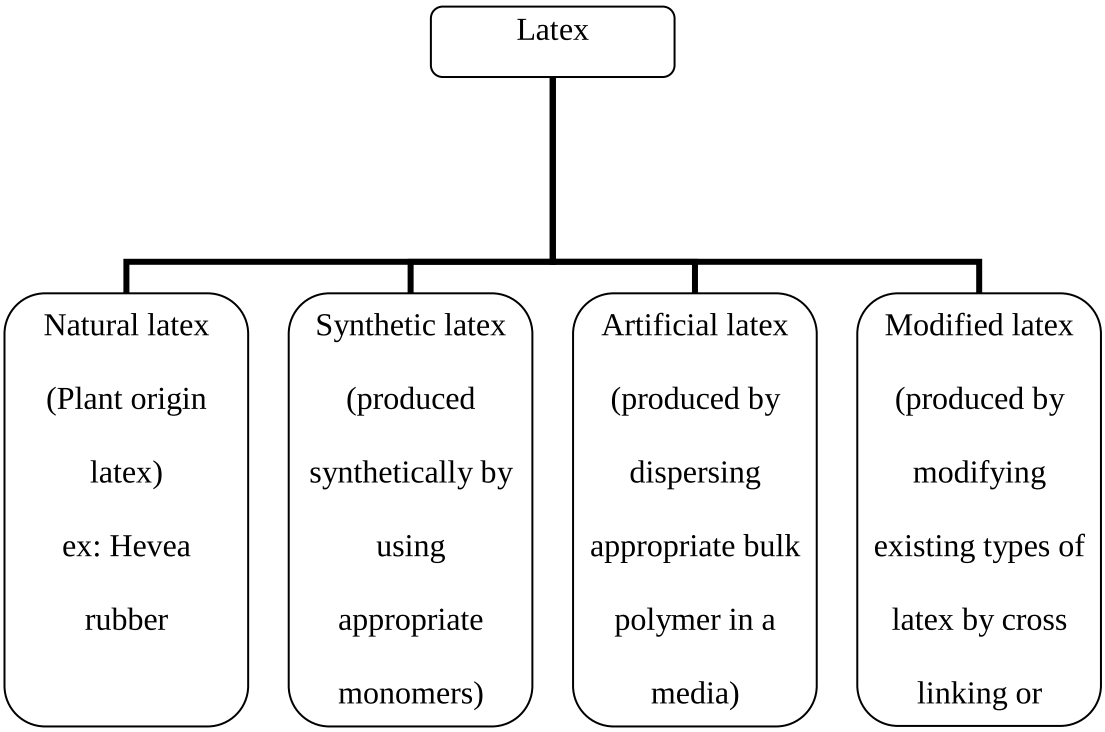

Figure 2.1: Different types of latex

Depending on the physical nature of the polymeric component, latex can be separated in to two main groups such as rubber latex which is the dispersed polymers are rubber at ambient temperature and resin or plastic latex where the dispersed polymers are glassy at normal temperature. Latex can be separated into several types according to the chemical nature of the dispersed polymer such as polysioprene latex where the main polymer is consisted with polyisoprene units, polystyrene latex where the main polymer is polystyrene, styrene butadiene co-polymer latex where the main polymeric chain is consisted with styrene as well as butadiene polymers Also the latex can be divided into three main types depending on the polarity of the bounded electrical layer which acts as the stabilizing layer of latex particles. Anionic latex is the latex that has the particles stabilized by a negative charge layer, cationic latex has latex particles that are surrounded by positive charge layer and the non-ionic latex is the latex that has particles that are enclosed by an uncharged layer (Blackley, 1966c).

As described in above paragraphs the natural rubber latex can be defined as follows "naturally occurred, anionically stable colloidal dispersion of polyisoprene polymer dispersed in an aqueous medium". In other words, natural rubber latex is naturally originated, anionic type polyisoprene rubber dispersion in an aqueous medium.

Liquid form of natural rubber latex that is preserved and centrifuged by several methods is used as the main raw material to make different kind of products such as gloves, condoms, foam, catheters, latex threads and casted products. The main use of centrifuged natural rubber latex can be summarized in Figure 2.2 (Blackley, 1966a).

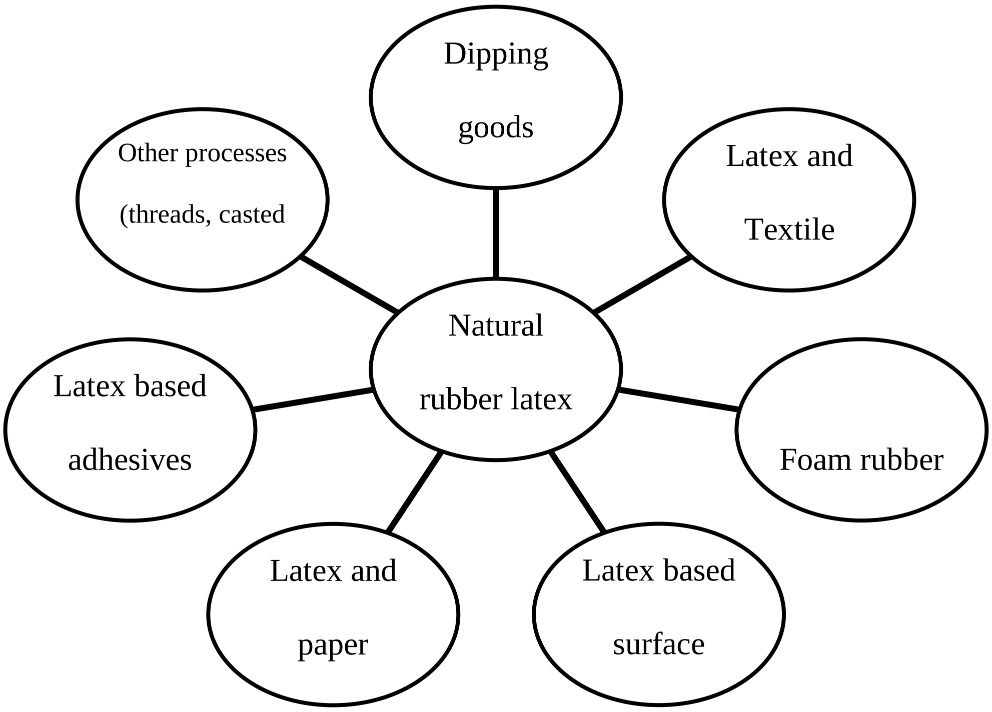

Figure 2.2: Different uses of latex

2.2 Introduction of the product based on Natural Rubber Latex Technology

As shown in the Figure 2.2, there are more than seven main categories of products that use liquid form of latex as the main raw material. In the present day market there are lots of products based on latex technology, however the main products are based on latex dipping technology, latex foam technology, latex thread technology, latex based adhesives, latex based surface coatings such as latex paints and the minor amount of products are based on latex and textile technology, latex and paper technology (Joseph, 2013).

In the latex dipping process, the thin walled articles are produced by means of using a required shaped former and appropriate latex compound. Latex dipping process can be classified into three main techniques such as straight dipping process, coagulant dipping process and heat sensitized dipping process. The main differences of these three techniques are based on the destabilization techniques that use to make the film on the former. In the straight dipping method, the destabilization process occurs without any external destabilizing agent. In this technique, the quality of the film on the former is achieved by several dipping cycles. In the coagulant dipping technique, a suitable coagulant agent is used to facilitate the destabilizing of the deposited latex film on the former.

Depending on the nature of the coagulant, this technique is further divided into two categories known as wet-coagulant dipping (the coagulating agent on the former is in liquid form) and dry-coagulant dipping (the coagulant agent on the former is in dry or semi dry form when the former dipped inside the latex compound). The most common technique used in glove manufacturing plants is the dry-coagulant technique or combination of these two techniques. Heat sensitized dipping process is achieved by means of using a heat sensitive compound and heated formers. The most common heat sensitized chemical that is mixed with natural rubber latex is polyvinylmethyl ether. This method also can be successfully carried out to make dipped products from foamed rubber latex (Blackley, 1966a; Joseph, 2013). Latex foam rubber technology is explained in detail in the section 2.3 onwards.

The next major technology based on latex technology is rubber thread manufacturing process. In the process of making thread using latex technology, suitably-compounded latex is constantly extruded through proper nozzles into a bath which is consisted of coagulating agents. The cross section of the thread is based on the cross section of the nozzle used. The main use of these threads is for elasticized bands in underclothes (Pisati et al., 1998).

Latex based adhesives are very popular nowadays due to their water based nature (Imam et al., 2001). However due to some allergic conditions of natural rubber in medical applications, the use of natural rubber latex to make adhesives is replaced by other types of materials such as silicon, polyvinyl ether, polyvinyl pyrrolidone (Webster, 1997).

Latex based surface coatings are widely known as water based latex paints. Most of water based latex paints are made out from emulsion polymerization of water insoluble monomers such as acrylonitrile, chloroprene, ethyl acrylates, vinyl acetate, vinyl chlorides (Henson et al., 1953; Hellgren et al., 1999). However the main draw backs of water based latex are; the time taken to dry the paint is comparatively higher than that of solvent based paint and the release of volatile organic compounds (VOC) to the environment (Hansen, 1974; Sparks et al., 1999; Silva et al., 2003).

Latex and paper technology is the other process that is used to make cellulose fibrous materials into useful products. In this technique, latex is added in the processing steps of paper making starting from the cellulose pulp to coating of the end paper (Blackley, 1966a). Latex coated textiles are also very useful materials nowadays as functional textiles that give many functions, as they are waterproof, fire retardant, temperature adapted fabrics, fragrance release fabrics (Sen, 2007). Figure 2.3 shows the pictures of some selected products that are made from different techniques of latex technology. Figure 2.3 (a) is the picture of natural rubber latex foam made out using foam rubber technology; (b) shows the products that are made out from latex dipping technology; (c) is the picture of rubber threads manufactured using latex thread technology; (d) is the latex based papers; (e) shows the picture of textile products that are made out using latex based textiles; (f) shows various kinds of flowers made out from latex casting technology; (g) is the latex based paint and (h) is a latex based adhesive.

Figure 2.3: Products based on natural rubber latex technology (adapted from http://jwlatexconsultants.com)

2.3 Natural Rubber Latex Foam

Natural rubber latex foam (NRLF) made from NRL gives ultra comfort to consumers due to its open cell structure and evenly distributed fine cells. Nowadays the NRLF plays a very important role in bedding and furniture industries, transportation industries such as automobile, aircraft and luxury ships. Furthermore, NRLF has many more advantages compared to other synthetic sponge materials such as polyurethane foam (PUF). A well-known advantage of NRLF against PUF is that NRLF is not producing any kind of harmful gas when it is burnt and it gives an ultimate soothing bed condition due to body heat dissipation through its open cell structure. NRLF beds have good air permeability, so body heat can be easily transferred to the environment and thus giving a better feeling to the consumer.

In the early stages of making sponge materials, rubber materials were synthesized by using solid rubber mixed with blowing agents. These blowing agents were used to make the gas phase inside the solid phase, but preparation of low density sponge materials and fine cell structured cellular product could not be achieved from this method (Straus, 1902).

2.4 Historical development of making foam by natural rubber latex

The preparation of sponge rubber from liquid latex dispersion can be found since the very early stages. In 1914, Schidrowitz and Goldsbrough reported in a British patent (BP) called "Improving rubber substance in making a porous or spongy rubber product using rubber latex and ammonium carbonate as the blowing agent" (Schidrowitz and Goldsbrough, 1914). Trobridoe and co-researchers published a patent about "Method of making articles from organic dispersions". They did investigate that the making of sponge articles directly from aqueous dispersions of rubber like organic materials. Further, they had reported details of a mould in very nice drawings. This special mould, except its heating elements, probably could be the first detailed diagram of a mould which later be used in modern manufacturing plants of foam rubber products (Trobridoe, 1931). Wilfred Henry Chapman and co-researchers assigned to Dunlop Rubber Company had reported that a sponge-like materials or cellular structure can be produced by natural, artificial or concentrated aqueous emulsions or dispersions of rubber or similar compositions. To make sponge materials, they used latex from a plant called Balata or Gutta Perchar. In addition, as a froth forming agent, they have used soap or soap forming ingredients or saponin (Chapman, 1932).

Ogilby had clearly drawn a flow chart of the synthesize steps of making shaped rubber sponge starting from stabilized latex containing Ammonium carbonate (Ogilby, 1938). Minor in 1939 published a USP to claim an apparatus for molding sponge rubber. In the invention, they have invented a mould which had removable walls and pipes to produce a desired shape of a foam rubber articles. They have also investigated the making of a sponge product having different densities by multiple layers of sponge rubber sheets. In this patent they have clearly drawn a diagram of different products having soft top layer and stiff bottom layer sponge rubber materials (Minor, 1939).

Other important investigation was done by Mitchell and his co-workers assigned to Dunlop Rubber Company, they had invented the composition of foaming agents and found that the concentration of rubber latex had an enormous influence on the quality of the structure of the final foam rubber products. Furthermore, they had found that the minimum concentration of rubber latex that can be used to produce a foam rubber was 45 % and the maximum concentration of rubber latex was 55 %. They had also mentioned that the possible ratio when incorporating air to rubber dispersion was 7 parts of air to one part of latex. Other than that, there were so many suggested quality parameters that the raw materials should have in the manufacturing of foam rubber. It can be said that this patent was the first published research work on controlling the parameters of raw materials as well as equipments used in the manufacturing of foam rubber articles from rubber latex dispersions. This was exactly like a quality manual for the production of NRLF (Mitchell, 1940).

A patent on preparation of sponge materials using both synthetic and natural rubber latex had been published in 1949 by Buskirk and Paul. With a list of six claims, they had published that the sponge rubber materials can be produced by natural rubber latex or by a mixture of both natural rubber latex and synthetic rubber latex by means of polymerization of butadinen-1,3 with styrene, which is now known as styrene butadiene latex (SBR latex) (Buskirk and Paul, 1949).

In 1962, Maclaran and Sons Ltd, London, published a book called "Latex foam rubber'. The book was mainly focused on the science and technology in the manufacturing of foam rubber articles using natural rubber latex and synthetic rubber latex. The author of the book was Madge and he had clearly described the main steps of making foam rubber from natural rubber latex compound. He also described the method of making foam rubber articles using synthetic rubber latex such as Styrene Butadiene Latex (SBR Latex). From his point of view, the synthetic rubber foam production started in 1945, when the Japanese invaded Malaya and they had stopped the production and shipping of NR latex to other countries. Then, both German and American scientists and technologists put their maximum efforts to make a large amount of synthetic rubber (Madge, 1962). In addition to the book published by Maclaren and Sons Ltd, another book was published on foam rubber production in 1966 by a well known publisher, "Chapman and Hall" from London, but the book not only explained about foam rubber production using natural rubber latex. In the book called "Polymer Latices and their applications" by Calvert, several authors from different areas of rubber technology had explained a broad spectrum of applications of natural rubber in manufacturing of various products. Since the authors were from different manufacturing plants, they explained relevant topics in a very practical manner. After giving an overall introduction to latex and their compounding ingredients, they had described the properties of natural rubber lattices as well as synthetic lattices. Then, chapter four was mainly focused on latex specifications and test methods for quality assurance of latex. In this chapter, the test method used to evaluate natural rubber latex and synthetic rubber latex is clearly explained. From chapter five to the end of the book, the applications of latex in various industries such as carpet, latex binders, adhesives, latex paints, dipped products, latex foam and finally miscellaneous applications of latex are described (Calvert et al., 1982).

The chapter written on latex foam rubber production is a very practical guide for the foam rubber manufacturing process using liquid mixer of latex as the main raw material. Since he was the Development Manager of Dunlopillo division in Dunlop Rubber Company, he described so many hands-on experience and practice of foam rubber products manufacturing method. He had explained the “Dunlop” process and the “Talalay” process separately by giving some typical formulation of both manufacturing processes. He clearly described the main difference of those two types of productions based on the gelling system. In Dunlop process, the gelling system is achieved by one-step operation by means of ZnO and SSF whereas in Talalay process gelling occurs in separate consecutive steps by freezing and using coagulant gasses like carbon dioxide (Calvert et al, 1982).

Furthermore, the “Dunlop” method was subdivided into eight major steps as follows;

a. Preparation of latex compound batch.
b. Foaming.
c. Addition of gelling agents.
d. Pouring the sensitized foam into a mould.
e. Foam gelling.

f. Foam curing.
g. De-moulding the foam.
h. Washing and Drying.

For each and every step, he had provided very practical guidelines, which he gained from the manufacturing environment of Dunlopillo plant (Calvert et al., 1982).

Also he explained the Talalay process in six steps viz.

a. Preparation of latex compound.
b. Foaming and vacuum expansion.
c. Moulding the foam.
d. Foam gelling and curing.
e. Foam de-moulding.
f. Washing and drying.

The history of making cellular rubber from natural rubber latex serum or dried rubber can be summarized using the above literature data. Even though the recent research works on latex foam are very few, the production of latex foam using NRL and Synthetic Latex are widely done in large scale production line all over the world due to its demand in so many applications. Scientific research works on natural rubber latex foam are very rare, whereas patent work on this field is ubiquitous. Zhu et al. (2012) published a paper on resilience of mattress foam and body pressure distribution characteristic of mattress. They have found that the resilience of latex foam mattress is better compared to that of the ordinary foam mattress. In addition, they also found that the latex foam sustains the body curves and contours while maintaining the spine in proper position. The research findings had confirmed the important of choosing the foam materials for constructing mattresses by investigating body pressure distribution properties.

2.5 Method of making natural rubber latex foam by the "Dunlop method"

Two types of latex foam manufacturing methods can be identified in literature. One method is called "Dunlop" method and the other is known as "Talalay" process. Talalay process is not a popular method in industries due to the high amount of capital investment and the complicated manufacturing techniques. Dunlop process is mostly used in industries due to its simple method of production and the low capital cost requirement of making a production line. Dunlop method can be divided into two major categories based on the foaming techniques known as batch process and continuous process. In the batch process, the foaming of the liquid compounded latex is done by an industrial type beater famously known as Horbart mixer. In the continuous manufacturing process, foaming of liquid compounded latex is done by continuous foaming machines. Today several brands of foaming machines can be seen in industries. Among them Oakes foaming machine is the most famous and a good quality foaming machine fabricated by the USA family company called "Oaks" (http://www.oakes.com).

The liquid foam is gelled using gellation by adding gelling agent and poured into required shaped mould. The mould can have many shapes and sizes depending on the end product of the latex foam product. The typical mould used for manufacturing mattresses in industries has aluminium pins made from alloy materials (Alloy and Temper: 1100-H14, Thickness Tolerance: 20 µm, Ultimate Strength: 15500 psi). The side walls of the mould would probably be the same material or stainless steel, but the stainless steel moulds are not the common type in industries due to the huge weight and unmanageable heat build-up. The sizes and the shapes of the moulds absolutely depend on the required sizes and the shapes of the final product of latex foam. The production of thicker products such as mattresses is carried out in very large moulds. A huge amount of aluminium pins is used to facilitate heat transferring inside the thick natural rubber foam products. The shapes, sizes and the distribution pattern of the pins mostly depend on the customer requirements. Figure 2.4 (a) shows the different sizes and shapes of the pins used in industrial type mattresses moulds, Figure 2.4 (b) shows the most common distribution pattern (square) of pins on the mould plates. The Figure 2.4 (c) shows the cross section of the moulds that have different top and bottom pin alignments. Mould design and mould construction for the manufacturing of products in natural rubber foam industries is a very important process (Blackley, 1966a).

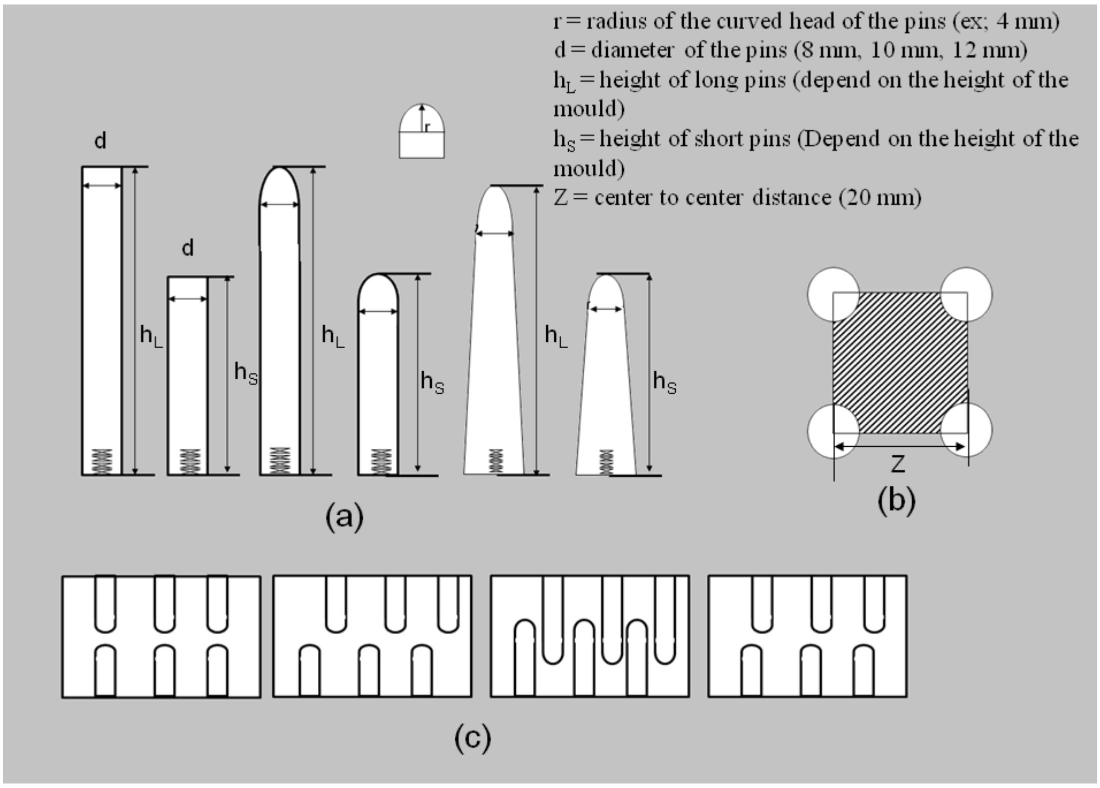

Figure 2.4: Mould design and mould construction in latex foam production (Blackley, 1966a; Madge, 1962)

The production process of a typical continuous natural rubber latex foam manufacturing plant can be seen in the Figure 2.5 (Blackley, 1966a; Joseph, 2013). It shows each and every step of the production process that is followed in a modern manufacturing plant. The first step of the manufacturing process starts with grinding of powdered raw materials into dispersion forms using water as the media. Then the dispersions are stored in storage tanks which are equipped with mechanical agitators that rotate 24 hrs to prevent from possible sedimentation of the dispersions. Next these dispersions are mixed with raw latex according to the formulation and stored in compounding tanks. Raw latex storage tanks also consisted with mechanical stirrers that rotate all the time to prevent separation of water from rubber in the latex. Then the compounded latex in the compounding tanks are matured up to 8-12 hrs and then transferred to the production plant and stored in the compounded batch tank. Detailed discussion of main steps of the synthesis of NRLF by "Dunlop" method will be discussed in chapter 2.5.1 onwards. The first main step of the manufacturing of natural rubber latex foam by a suitably compounded natural rubber latex batch starts from the preparation of dispersions.

2.5.1 Preparation of dispersions

Preparation of dispersion is a very important step in making a good quality natural rubber latex foam product. According to the theory of mixing chemicals to the latex dispersion, the size of the raw materials and the alkalinity of the raw materials should match with that of natural rubber latex dispersion (Blackley, 1966c). To match the particle sizes of raw materials with the particle size of natural rubber latex foam, the grinding of dispersions is a very important step. The grinding time of the dispersion totally depends on the required average sizes of the particles in dispersions. If the average particle sizes are below 2.5 μm, it is advisable to stop the grinding and unload the dispersions to storage tanks. Dispersion storage tanks are equipped with stirrers which run at a very low speed (5-10 rpm). Total solid content of dispersions is measured according to the ISO 124:1992 (E) methods in the lab and the densities of the dispersions are also measured by weighing a known volume of dispersions. The pH values are determined by the commercial pH meters. To make good quality dispersion, addition of a small amount of dispersion agent is required.

There are lots of surface active agents such as sulphonates (Sodium poly[(naphthaleneformaldehyde)sulfonate] commercially known as TAMOL), anionic organic Sulphates (Sodium dodecyl/lauryl sulphate commercially known as TAXAPON), cationic (Lauryl pyridiniun chloride), and amphoteric (c-celyl betaine). Non-ionic Condensation products of ethylene oxide with fatty acids, fatty alcohols or phenols (Synopol PEG 400, Polyethylene glycol) are used as dispersion agents in various industries. Among them sodium poly [(naphthaleneformaldehyde)sulfonate] commercially known as “TAMOL” is a famous dispersion agent in the preparation of stable dispersion in natural rubber latex foam industries. A small amount of Bentonite clay is also mixed with the dispersions to increase the colloidal stability of the dispersions.