IMPROVING THE DUCTILITY AND ELASTIC RECOVERY OF BITUMEN -NATURAL RUBBER LATEX BLEND

By

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ABSTRACT

IMPROVING THE DUCTILITY AND ELASTIC RECOVERY OF BITUMEN-NATURAL RUBBER LATEX BLEND

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In this study, styrene monomer was grafted onto natural rubber (NR) via emulsion polymerization, using redox initiator as the initiation system. The grafted NR (NR-*g*-PS) was added as a modifier into bitumen emulsion to investigate its effect on low temperature pavement cracking. The effect of the level of styrene monomer, processing temperature, and the type and level of initiator used in the grafting of NR latex, on the ductility properties of the cationic bitumen-NR latex blend was investigated. The optimum level of NR-*g*-PS content to the bitumen emulsion, and the effect of amphoteric surfactant and acidification during charge conversion of the modified latex on ductility properties were determined.

NR-*g*-PS with 25 parts per hundred rubber (phr) of styrene monomer was prepared in the presence of tetramethyltriuram disulfide using redox initiator *tetra*-butyl hydroperoxide / tetraethylene pentamine at the processing temperature of 40 °C. It was then converted to cationic latex and acidified by hydrochloric acid. A blend of 4% of the cationic NR-*g*-PS latex with slow setting (SS-1K) type of bitumen emulsion gave the highest mean ductility value of 23.7 cm at 5 °C. The percentage of elastic recovery (ER) of the bitumen/NR-*g*-PS blend at 7 °C increased with the increase of latex dosage from 2 to 6 phr. The highest percentage of ER obtained was 41%.

The properties of the NR-*g*-PS prepared at various processing temperature (28-60 ºC), such as colloidal property, grafting efficiency, free residual styrene monomer and total monomer conversion, chemical, mechanical, thermal and swelling properties were determined. Grafting efficiency obtained was between 91.0 and 92.0 %. Gas chromatography analysis showed that the highest monomer conversion and lowest free styrene monomer was obtained at processing temperature of 40 °C. NR-*g*-PS films obtained from different processing temperature had similar tensile strength of ~about 21 MPa. The swelling results confirmed that NR-*g*-PS was a lightly vulcanized NR.

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PERMISSION SHEET

It is hereby certified that **TINAVALLIE A/P GRUMOORTHY (**ID No.: **11ADM06206)** has completed this thesis entitled **"IMPROVING THE DUCTILITY AND ELASTIC RECOVERY OF BITUMEN-NATURAL RUBBER LATEX BLEND"** under the supervision of **ASSISTANT PROFESSOR DR. CHEE SWEE YONG** (Supervisor) from the Department of Chemical Science**,** Faculty of Science.

I hereby give permission to my supervisors to write and prepare manuscript of these research findings for publishing in any form, if I did not prepare it within six (6) months' time from this date provided that my name is included as one of the authors for this article. Arrangement of the name depends on my supervisors.

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This dissertation entitled "**IMPROVING THE DUCTILITY AND ELASTIC RECOVERY OF BITUMEN-NATURAL RUBBER LATEX BLEND"** was prepared by TINAVALLIE A/P GRUMOORTHY and submitted as partial fulfillment of the requirements for the degree of Master of Science at Universiti Tunku Abdul Rahman.

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DECLARATION

I TINAVALLIE A/P GRUMOORTHY hereby declare that this project report is based on my original work except for citations and quotations which have been duly acknowledged. I also declare that it has not been previously and concurrently submitted for any other degree or award at UTAR or other institutions.

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ASTM	American Society for Testing Materials
CHPO	Cumene Hydroperoxide
CRM	Crumb Rubber Modifier
DCPO	Dicumyl peroxide
DPNR-*g* -PS	Styrene grafted Deprotenized Natural Rubber
DRC	Dried Rubber Content
DSC	Differential Scanning Calorimetric
DTG	Differential Thermo Gravimetric
ER	Elastic Recovery
EVA	Ethyl-Vinyl-Acetate
FTIR	Fourier Transform Infrared
GC	Gas chromatography
ISO	International Organization for Standardization
KN	Kilo Newton
MEK	Methyl Ethyl Ketone
MMA	Methyl Methacrylate
MPa	Megapascal
MW	Molecular Weight
NR	Natural Rubber
NR-*g*-PS	Styrene Grafted Natural rubber
NRL	Natural Rubber Latex
PE	Polyethylene

PIP	Polyisoprene
phr	Parts per Hundred Rubber
phs	Parts per Hundred Solid
PMB	Polymer Modified Bitumen
PS	Polystyrene
SEM	Scanning Electron Microscopy
SBR	Styrene Butadiene Rubber
SBS	Styrene–Butadiene–Styrene
SDS	Sodium Dodecyl Sulfate
TBHPO	*Tetra*-butyl hydroperoxide
TEPA	Tetraethylenepentamine solution
TGA	Thermo Gravimetric Analysis
TMTD	Tetramethyltriuramdisulfide Dispersion
TSC	Total Solids Content
WP	Waste Plastic
wt %	Weight percent

CHAPTER 1.0

INTRODUCTION

1.1 Bitumen in Road Construction

In the past, unmodified bitumens were able to cope with the traffic volumes and loads exerted on them. Nowadays, the burden placed upon road system has reached a critical stage in many developed and developing countries where the increased volume in heavy vehicles coupled with an appreciable increase in allowable axle weights for these vehicles has lead to a dramatic increase in level of stresses exerted on bitumen surface. Due to the sharp increased of stresses exerted on bitumen surface, most of the road system experience distress and deteriorate before it can achieve the design service life.

The use of polymer modified bitumen (PMB) offers a promising way to improve pavement performance, hence to prolong the service life of the road system even though the road experience unexpected increasing number of traffic volume. PMB pavement exhibits greater resistance to rutting and thermal cracking and decrease fatigue damage, stripping and temperature susceptibility. Typically, PMB are more viscous compared to unmodified bitumen and tend to show improved adhesive bonding to aggregate particles (Shafii et al., 2011).

1.2 Types of Bitumens

1.2.1 Paving Grade Bitumens

Paving grade bitumens are refined and blended to meet road engineering and industrial specifications that take into account different climatic conditions. Typically, paving bitumens are specified based upon specific physical properties related to consistency, adhesion properties, viscosity, hardness, or brittleness at a specified temperature. It's most widely used as parent bitumen from which other types, as listed below, are produced (BP Bitumen Australia, 2012).

Paving grade bitumens are specified by the penetration (British standards Institution, 2000a) and softening point test (British standards Institution, 2000b). In Europe and elsewhere, paving bitumens are denoted by the permissible range of penetration value (expressed as a "pen grade," e.g. 40/60 pen grade, 100/150 pen grade), which is indicative of the consistency of the material at a temperature of 25 ºC. In the USA and elsewhere, a performance grade ("PG") system has been in use since the mid-1990s. Under this system, both traffic levels and climatic conditions are taken into account. For example, a PG designation of PG 64-22 represents the high and low temperatures (in terms of degrees Centigrade) at which the bitumen would be expected to perform satisfactorily (Central European Normalization, 2000).

The standard penetration grades bitumen include 40/50, 60/70, 85/100, 120/150 and 200/300, which have penetrations of 40 to 50, 60 to 70, 85 to

100, 120 to 150, and 200 to 300, respectively. The Asphalt Institute recommends the use of 120/150 or 85/100 penetration bitumens in the bitumen concrete for cold climatic condition with a mean annual temperature of 7 °C or lower. For warm climatic condition with a mean air temperature between 7 and 24 °C, 85/100 or 60/70 penetration bitumens are recommended. For hot climatic condition with a mean annual air temperature of 24 °C or greater, the use of a 40/50 or 60/70 penetration bitumens are recommended (Asphalt Institute, 1991).

1.2.2 Oxidized Bitumens

Oxidized bitumen (industrial grade bitumen) is made by vigorous air blowing (normally beyond 180 °C) through hot paving grade bitumen. In the process the asphaltene content is increased which in turn results in higher softening points and very low penetration number (HP Bitumen Handbook, 2008). The softening points of oxidized grade of bitumen are much higher than those of the corresponding paving grade bitumen. It also has more rubberlike properties and its viscosity is much less affected by changes in temperature than in the case with paving grade bitumen (BP Bitumen Australia, 2012).

1.2.3 Cutback Bitumens

Cutback is a free flowing liquid at normal temperatures and is obtained by fluxing bitumen with suitable solvents (HP Bitumen Handbook, 2008). The fluidity of cutback bitumens (or cutbacks as they are known) depends on the degree of hardness of the bitumen and the proportion of diluents. Cutbacks are classified according to the time it takes for them to cure, or become solid due to the evaporation of the diluents. Classifications are rapid curing (RC), medium curing (MC) or slow curing (SC). A cutback varies in behaviour according to the type of cutter or flux used as the diluents, with white spirit commonly used for RC grades, kerosene for MC and diesel for SC (BP Bitumen Australia, 2012).

1.2.4 Bitumen Emulsions

Bitumen emulsions are heterogeneous, two-phase systems consisting of two immiscible liquids, bitumen and water, stabilised by a third component, the emulsifier (Stein, 1980; Asphalt Institute, 1990; Speight, 1992; Roberts et al., 1996). The bitumen is dispersed throughout the continuous aqueous phase in the form of discrete droplets, typically 0.5 to 5 microns in diameter, which are held in suspension by electrostatic charges (Morgan and Mulder 1995).

Bitumen emulsions can be divided into three classes, which are cationic emulsions, anionic emulsions and non-ionic emulsions. The terms cationic and anionic refer to the overall particle charge on the bitumen droplet imparted by the emulsifier (Morgan and Mulder, 1995). An anionic bitumen emulsion has negatively-charged bitumen particles, and is usually more suitable for use with calcareous aggregates, which tend to have positive surface charges. A cationic bitumen emulsion has positively charged bitumen particles, and is usually more suitable for use with siliceous aggregates, which tend to have negative surface charges. A non-ionic bitumen emulsions contains bitumen particles that are electrically neutral. Non-ionic bitumen emulsions are not used in pavement applications. Example of non-ionic emulsion is clay emulsions (Tia, 2012).

Bitumen emulsions further graded according to their setting rate (i.e., rapid, medium, and slow). Rapid-setting (RS) grades are used for surface treatment, seal coating, and penetration macadams. Medium-setting (MS) grades are used for premix jobs and patch repair work. Slow-setting (SS) grades are used for mix-in-place road mixtures, patch mixtures, tack coats, fog coats, slurry seals, and soil stabilization (Speight, 1992; Roberts et al., 1996). Slow setting emulsions are preferred in rainy season.

An RS emulsion is designed to demulsify (to break away from the emulsion form such that bitumen particles are no longer in suspension) upon contact with an aggregate, and thus has little or no ability to mix with an aggregate. It is best used in spraying applications where mixing is not required but fast setting is desirable. An MS emulsion is designed to have good mixing characteristics with coarse aggregates and to demulsify after proper mixing. It is suitable for applications where mixing with coarse aggregate is required. An SS emulsion is designed to be very stable in the emulsion form, and is suitable for use where good flowing characteristics are desired or where mixing with fine aggregates are required. The three types of cationic bitumen emulsions are denoted as CRS, CMS and CSS. The absence of the letter "C" in front of the emulsion type denotes an anionic type (Tia, 2012).

Within each type, bitumen emulsions are graded by the viscosity of the emulsion and the hardness of the bitumen. The lower viscosity grade is designated by a number "1" and the higher viscosity grade is designated by a number "2", which is placed after the emulsion type. A letter "h" that follows the number "1" or "2" designates that harder bitumen is used. For example, a "CSS-1h" designates a slow-setting cationic type having a relatively lower viscosity and containing hard base bitumen (Tia, 2012).

1.3 Modified Bitumens

Certain additives or blend of additives called as bitumen modifiers can improve properties of bitumen and bituminous mixes. Bitumen treated with these modifiers is known as modified bitumen (Tia, 2012).

For the modifier to be effective and for its use to be both practicable and economic (Morgan and Mulder, 1995; Read and Whiteoak, 2003), it must:

a. be readily available
b. resist degradation at process and application temperature
c. blend with bitumen
d. improve resistance to flow at high service temperature without making the bitumen too viscous at application temperature or too stiff or brittle at low temperature in service

e. be cost effective

The modifier, when blended with bitumen, should have the following characteristics (Morgan and Mulder, 1995; Read and Whiteoak, 2003):

a. maintain its premium properties during storage, application and in service
b. be capable of being processed by conventional equipment
c. be physically and chemically stable during storage, application and in service
d. achieve a coating viscosity at normal application temperatures

The additives or modifiers can be loosely classified into five groups (Morgan and Mulder, 1995; Read and Whiteoak, 2003) as below:

a. inert filler
b. mouldable filler
c. chemical agents, wetting/ adhesion agents
d. solvents (including hydrocarbon extracts)
e. polymers

1.4 Classification of Polymers

Polymers can be divided into two groups in term of the basis of source (Bower, 2002):-

a) Natural polymers

   - These polymers are obtained from natural sources. For example, protein, cellulose, starch, rubber, and so on.

b) Synthetic polymers

   - These polymers are synthesized by chemical reactions. For example, nylon, teflon, polyethylene, styrene butadiene rubber and so on.

Polymer modifier for bitumen modification can be divided into two major groups: elastomers and plastomers based upon their strain performance characteristics at low temperatures. Rubber products are classic examples of elastomers. Their identifying property is their elasticity over a wide temperature range. Elastomeric polymers can be stretched up to ten times without cracking, but quickly return to original configuration once that load has been released. The bitumen engineer has had to carefully choose from a broad range of bitumen grades to meet each specific climatic and traffic condition. The introduction of natural or synthetic rubbers such as styrene-butadiene rubber (SBR), styrene-butadiene block copolymer (SB, SBS), styrene-isoprene (SI), and polychloroprene gives the bitumen increased flexibility, particularly at the climatic extremes where most pavement damage occurs (King and Johnston, 2012).

Plastomers are employed to take advantage of the strength imparted by a rigid three-dimensional chemical network. Plastics are stronger but less flexible than their elastomeric counterparts. Products such as ethyl-vinyl-acetate (EVA), polyethylene/polypropylene, ethylene propylene (EPDM) and polyvinyl chloride (PVC) significantly raise the stiffness of a bitumen without sacrificing the low temperature performance (King and Johnston, 2012).

Elastomeric and plastomeric polymer modifiers are further classified as either thermoset or thermoplastic, based upon their temperature-dependent structural formation and reformation characteristics. When initially heated, thermoset polymers develop a complex, cross-linked structure, which is retained upon cooling, but which cannot be reversed when reheated. In contrast, thermoplastic polymers also develop a well-defined, linked matrix when cooled, but the resultant structures can be reversed or "reset" with reheating (King and Johnston, 2012).

1.5 Natural Rubber (NR)

Natural rubber (NR) is a sustainable and renewable resource. A variety of synthetic counterparts are made to meet some specific requirements such as for high temperature applications or for oil-in contact products. However, these synthetic rubbers are mostly manufactured from nonrenewable oil-based resources. Under an increasing awareness of environmental issues and fuel shortage in the future, NR is undoubtedly backed into play (Kalkornsurapranee et al., 2009).

1.5.1 Constitution of Fresh Latex

Natural rubber latex (NRL) is isolated from the tiny latex vessels present in the tree beneath the bark and over the cambium tissues without damaging the tree by the process known as tapping (Karak, 2009) (Figure 1.1). Field latex (freshly-tapped NRL) is a white or slightly opaque liquid with density varying from 0.974 to 0.986 g/ml (Sarkar, 1994) and neutral or slightly alkaline (NIIR Board, 2000) and with variable viscosity. Latex is a natural product thus; the proportion of these constituents may vary with the type of tree, the tapping method, nutrition, climate conditions, stimulation, stability of latex and the time of collection (Mathew, 2001). NRL is composed of about average 36 % of rubber fraction, 5 % of non-rubbers components such as protein, lipid, carbohydrates, sugar, with water accounting for the remaining 59 % (Bonner and Galston, 1947; Sansatsadeekul et al., 2011).

Sansatsadeekul et al. (2011) reported that, in young trees the particles are spherical in shape but in mature trees the larger particles are often pear-shaped (Bonner and Galston, 1947; Wititsuwannakul et al., 2003). The rubber particles exist in the latex form of small globules, having diameters in the range 0.02 - 3.0 µm (Wititsuwannakul et al., 2008; Kurian and Mathew, 2011), suspended in a watery liquid or serum. The other particles in latex comprise of lutoids and Frey-Wyssling particles (Mathew, 2001; Wititsuwannakul et al., 2003; Priyadarshan, 2011). The lutoids are subcellular membrane bound bodies ranging in size from 2 to 5 µm, containing a fluid serum known as β-serum (Kurian and Mathew, 2011), which is a destabiliser for rubber particles. Frey- Wyssling particles are spherical, larger in size and are yellow coloured. Their high carotenoid content suggests that they might contain enzymes for isoprenic synthesis pathways (Priyadarshan, 2011).

Figure 1.1: Tapping the latex of the rubber tree (adapted from http://www.kew.org/plants/rubber.html on 20 may 2012)

Quebrachitol (methyl-1-inositol), sucrose and glucose are the major carbohydrates in latex (Kurian and Mathew, 2011). The total protein content of fresh latex is approximately 1 - 1.5 %, of which about 20 % is adsorbed on the rubber particles and similar proportion is associated with the bottom fraction, with the remainder dissolved in the serum phase (Archer and Sekhar, 1955). The adsorbed proteins and phospholipids impart a negative charge on the rubber particles, thereby improving the stability of the colloid (Mathew, 2001; Kurian and Mathew, 2011). Bowler (1953) stated that proteins from fresh latex particles have isoelectric points ranging from pH 4.0 to 4.6. Lipids in fresh latex consist of fats, waxes, sterols, sterol ester and phospholipids (Mathew, 2001).

Sansatsadeekul et al. (2011) reported that, the lipids associated with NR are comprised mainly of neutral lipids and phospholipids. The lipids associated with rubber and non-rubber particles play a key role in the stability and colloidal behavior of latex. Latex also contains amino acids, nucleotides, and low molecular weight thiols. The nucleotides are cofactors and intermediates in the biosynthesis of rubber (Kurian and Mathew 2011). Thus, it's proven the non-rubber components play an important role in stabilizing the latex particles and in contributing to the outstanding properties of NR (Wititsuwannakul et al., 2003; Sansatsadeekul et al., 2011). The composition of fresh latex and the function of these components in NR are summarized in Table 1.1.

Table 1.1: The constituent percentage and function of components in NRL (adapted from Karak, 2009)

Components	Percentage (%)	Function of components
Rubber hydrocarbon	36	Main component of NR
Protein	1.4	Act as activator to accelerator and also act as filler
Lipids	1.6	Act as activator to accelerator
Carbohydrates	1.6	Reduce stability of latex
Inorganic constituents	0.5	Prooxidants
Other	0.4	β-carotene causes oxidation and storage hardening
Water	58	Medium of latex

1.5.2 Concentration of NRL

The main reasons for concentration of latex include a preference for high dried rubber content (DRC) by consuming industry, economy in transportation and purification of latex. The four major methods to concentrate NRL were described below:

a. Creaming method

   Creaming is usually done by adding small quantity of gum such as ammonium alginate, tamarind seed powder or Irish moss into latex (Dinesh, 2005; NIIR Board, 2000). Creaming agents are well mixed into the preserved latex and allowed remaining for a few days. The creaming agents slow down the Brownian movement of the latex and separation takes place within 4 - 5 days. Since rubber is lighter than water, rubber floats on the top. Water is removed from the bottom and cream is collected and the ammonia content is adjusted to 0.7 percent (Dinesh, 2005).

b. Evaporation method

   Evaporation involves the removal of water only. Therefore, the ratio of non-rubber constituents to rubber and the particle size distribution remain unaffected (Mathew, 2001). Addition of chemicals such as stabilizers, alkalis and soap are needed for this process. Concentration is done in a rotating drum in which smaller drum furnishes addition evaporation and agitates the latex. Latex with high solids content (75 %) is produced by this process (Dinesh,2005).

c. Electrodecantation method

Latex is added to a rectangular tank with an electrode at each end and many grooves, about 1 cm apart, in which sheets of cellophane are placed. When an electric current is applied particles build up on the cellophanes and float to the top as cream. Fresh latex is added continuously from the top of the cell. Latex with 60 - 62 % concentration is produced by this process (Dinesh, 2005).

d. Centrifuge method

Centrifuging is a more popular process and it is done by centrifugal machine (Mathew, 2001). This method is based on the differences in specific gravities between the rubber and the serum. The bowl of the machine rotates at a high speed, while the water content in the latex is reduced to the required levels. Centrifuging removes water content and also purifies the latex by removing the water soluble non-rubber particles (NIIR Board, 2000). The cream fraction is further stabilized with the addition of preservatives and the DRC is adjusted to 60 % before sending to customer.

1.5.3 Applications of NR

The common techniques for manufacturing useful products from NRL are dipping, casting/ moulding, foaming, extrusion, and coating. Wide range of rubber products are made by latex dipping. The most significant of these are condoms, various types of balloons and various types of gloves such as surgical gloves, household gloves, electrician gloves and heavy industrial gloves (Blackley, 1997c). Hollow castings and replicas can be manufactured by various types of moulding or casting techniques. NR foam is an excellent cushioning material. The most important applications of foam are in mattresses, pillows and seating in all kinds of vehicles. Latex is also used as a binder for nonwoven fabrics, and as carpet backing. Elastic thread manufactured from NRL is an indispensable component of many types of garments (Kurian and Mathew, 2011).

Medical applications of the NR include dialysis tubing, hypodermic syringe seals, and baby dummies. Fabric coatings for inflatable boats, balloons, and footballs are examples of the applications of NR in sports and recreational activities. Flooring, adhesives for pressure sensitive tapes, door/barrier mats, footwear are familiar examples of household rubber products (Kurian and Mathew, 2011).

NR is a very versatile material that has been successfully used in engineering applications for over a century. NRL cement formulations are used in civil engineering applications. Anti-vibration mountings, flexible couplings, bridge bearings, rail pads, power transmission and conveyer belts, rubber covered rollers, cable covering, hoses, tubing, tank liners, extruded products, and components for domestic and industrial machinery are some of the industrial and engineering rubber products (Kurian and Mathew, 2011).

1.5.4 NR for Bitumen Application

The foremost attempt of using rubber as road material to modify bituminous binder was carried out in 1899 by Caudenberg, who originated a process to manufacture rubber-bitumen. Rubber was in the form of solid blocks when it was first used in the mixture of road materials that gave very durable surfacing but were also expensive and slippery at the same time. Therefore, in the early year’s only relatively small amount of rubber additives were used practically in bituminous road mixtures (Greysmith, 1962). Use of rubber by a French bitumen company for laying pavements as early as in 1902 has been documented.

Addition of NR to bitumen has been attempted in different ways. One of the earliest methods is the addition of latex, stabilized with alkali, to molten bitumen under vigorous stirring. Water evaporates and NR gets mixed with the bitumen. Fermando and Nadarajah (1992) had carried out improvement on bitumen properties by various kinds of NRL such as field latex, concentrated latex, and skim latex.

Addition of rubber in powder form has also been attempted. These include rubber powder from the rejections of various dry rubber and latex products. Vulcanized and lightly vulcanized powders are convenient to use. Smoked sheet or crepe rubber can be used, by masticating and dispersing it in fluxing oil. NRL is the most effective additive to bitumen, but difficulties arise due to its water content (Fermando and Nadarajah, 1992).

1.6 Problem Statement

Bitumen is a single-phase homogeneous mixture of many different molecules, which may be differentiated into two broad classes: polar and non-polar. The non-polar molecules serve as a matrix or solvent for the polar molecules, which form weak “networks” of polar-polar associations that give elastic properties to bitumen (Jones and Kennedy, 1992). The polar molecules interact and primarily give bitumen its elastic characteristics. The non-polar molecules mainly contribute to the viscous behavior of the bitumen and control the low temperature properties of the bitumen (Youtcheff and Jones, 1994).

In road paving industry, bitumen emulsion is used for cold mix application such as chip seal, slurry seal, microsurfacing, cold recycled mixture. Bitumen emulsion has several advantages compared to normal bitumen such as eco-friendly, easy to handle at ambient temperature and it is an energy saving material because it does not need any heating process in its application. The history of bitumen emulsions and its application in road construction begin in the early part of 20th century (Shafii et al., 2011).

For a flexible pavement, one of the failure modes is low-temperature cracking. This is a consequence of the thermal contraction or shrinkage of the bitumen pavement under freezing conditions, and it occurs when the thermal stress induced at low temperatures exceeds the tensile strength of the bituminous mixture. Bituminous mixtures with a high stiffness modulus at low temperatures are most prone to low-temperature cracking. To reduce the risk of this type of cracking, the binder should have good flexibility (low stiffness and high ability of stress relaxation) at the lowest pavement temperature (Isacsson and Zeng, 1998).

Many researchers suggested that PMB may have a beneficial effect with regard to resistance to the low-temperature cracking (Isacsson and Zeng, 1998; Chappat, 1999; Isacsson and Lu, 1999). Polymer modified bitumen emulsions offer improvements in mitigation of pavement distress and reduce life cycle costs when compared to unmodified bitumen emulsions. In addition, polymer modified bitumen emulsions also exhibit reduction in rutting and thermal cracking related problem and increased resistance to many forms of traffic-induced stress (Shafii et al., 2011).

Cationic styrene-butadiene polymer and NRL are widely used to blend at 2 to 4 % by weight into bitumen emulsion for road construction. The synthetic latex blended bitumen emulsion has better ductility and elastic recovery properties at lower temperatures compared to the latter. NRL is a sustainable and renewable resource and the production cost of synthetic latex is high. Therefore, modification of NRL to give better ductility and elastic recovery at low temperature after blending with bitumen emulsion is important.

Centrifuged latex and pre-vulcanized latex are the type of NRL available in the market with variety of grades. These NRL can be modified by physical and chemical reactions. Chemical modification of NR by grafting with vinyl monomers with various initiator systems has gained considerable importance (Arayapranee and Rempel, 2008). The thermoplastic elastomers improve the oil resistance of NR. Thermoplastic elastomers are a relatively new class of materials that combine the physical properties of elastomers, that is, elasticity, and the excellent processing characteristic of thermoplastics (Derouet et al., 2009). The modified NRL should be in cationic form so that it can mix with cationic bitumen emulsion and bind well with negative charge aggregates.

1.7 Objectives

The aims of this study are:-

a) To prepare cationic NRL which can meet the ductility requirement of > 20 cm at 5 ºC and elastic recovery > 60 % at 7 ºC after blended with cationic bitumen emulsion.

b) To determine the effect of the type and level of monomers, processing temperature, and the type and level of initiator of the grafted NRL, on the ductility and elastic recovery properties of the blended cationic bitumen emulsion.
c) To determine the optimum NR content in modified bitumen based on ductility properties.
d) To investigate the colloidal, grafting efficiency, percentage of free styrene monomer and total monomer conversion, chemical, thermal, swelling and mechanical properties of that particular modified NRL.
e) To examine the morphology of the modified NRL that gives good ductility and elastic recovery properties.

1.8 Scope of Work

The study conducted will focus on the application of NRL as a modifier in bitumen emulsion and its effect on low temperature pavement cracking. The low temperature ductility and elastic recovery of NRL modified bitumen emulsions will be tested with the aid of a ductilometer.

The ductility of the existing cationic NRL (1497C/65)– bitumen blend as well as the effect of the type and level of surfactant in the latex will be investigated. Styrene monomer grafted NR using redox initiator system will be prepared and tested on its ductility and elastic recovery properties in the NRL-bitumen blend. The effect of the level of monomers, processing temperature, and the type and level of initiator of the grafted NRL, on the ductility and elastic recovery properties of the blended cationic bitumen emulsion will be investigated. The optimum modified NR content to the bitumen emulsion and the effect of level of amphoteric surfactant and acidification during charge conversion of the modified latex on ductility properties will also be investigated.

The properties of the modified NRL such as colloidal, grafting efficiency, percentage of free styrene monomer and total monomer conversion, chemical, thermal, swelling and mechanical will be studied. The morphology of modified NRL will be examined using Scanning Electron Microscope (SEM).

CHAPTER 2.0

LITERATURE REVIEW

2.1 Bitumen

2.1.1 Physical Properties of Bitumen

Bitumen is a non-crystalline viscous material, black or dark brown, which is insoluble in water at 20 ºC, soluble in aliphatic organic solvents; and soluble in carbon disulphide (CS_2), chloroform, ether, and acetone; possessing adhesive and water- proofing qualities (Sax and Lewis, 1987). Density of bitumen lies between 1.01 to 1.04 g/cm^3 at room temperature and it depends on the crude source and paving grade (Read and Whiteoak, 2003). When referring to a natural source, a heavy crude oil is generally termed bitumen when its density over passes 1 g/cm^3 at 15.6 ºC (Speight, 1999).

Bitumen exhibits a glass transition around -20 ºC, although it varies in a very wide range from +5 ºC down to -40 ºC depending essentially on the crude origin and somewhat less on the process. The transition range, typically spans 30 to 45 ºC and -20 ºC, corresponds to the typical midpoint value (Turner and Branthaver, 1997). Therefore, on a thermodynamical standpoint bitumen is a very viscous liquid at room temperature.

2.1.2 Chemical Composition of Bitumen

Bitumen composition depends on the crude source and the refining process (Polacco et al., 2006; Garcia-Morales et al., 2006). The chemical analysis cannot be used to define the exact chemical structure or chemical composition of bitumen, elemental analyses indicates that most bitumen contain 82 - 88 weight percent (wt %) of carbon, 8 - 11 wt % of hydrogen, traces of 0 - 1 wt % nitrogen, traces of 0 - 1.5 wt % oxygen and traces of 0 - 6 wt % sulphur (Morgan and Mulder, 1995).

While heteroatom make up only minor component of most bitumen, the heteroatom profoundly influence the differences in the physical properties of bitumen from different crude sources (Speight, 1992; Robert et al., 1996). Trace amount of metals such as vanadium, nickel, iron, magnesium and calcium may be found in bitumen in the form of inorganic salts and oxides or in porphyrinic structures (Morgan and Mulder, 1995).

The chemical composition of bitumen is extremely complex (Polacco et al., 2006); therefore, a complete analysis of bitumen would be extremely laborious and would produce a large amount of data that correlation with the rheological properties would be impossible (Morgan and Mulder, 1995). However, bitumen compound can be separated into 4 groups (SARAs): saturates, aromatics, resin and asphaltenes (Morgan and Mulder, 1995; Polacco et al., 2006; Lesueur, 2009; Naskar et al., 2010).

The main characteristics of these four broad component groups are as follows:

2.1.2.1 Saturates

Saturates comprise of very straight and branch chain aliphatic hydrocarbon together with alkyl-naphthenes and some alkyl-aromatics (Morgan and Mulder, 1995). They are non-polar viscous oils (Cobett, 1969; Morgan and Mulder, 1995) which form a colourless or lightly coloured liquid at room temperature because of a very low glass transition temperature around -70 °C, which is typically 40 °C below the glass transition of their parent bitumen (Lesueur, 2009). 5 - 15 wt % of a paving grade bitumen contains saturates (Cobett, 1969). The average molecular weight range is similar to that of aromatics and the components include both waxy and non-waxy saturates (Morgan and Mulder, 1995). Their solubility parameter lies between 15 and 17 MPa and their density at 20 °C is around 0.9 g/cm^3 (Speight, 1999).

2.1.2.2 Asphaltenes

Asphaltenes represent between 5 - 25 wt % of paving grade bitumen (Cobett, 1969). Asphaltenes are insoluble in n-heptane but soluble in toluene. The black or brown amorphous solids contain, in addition to carbon, hydrogen, some nitrogen, sulphur and oxygen. The structure of asphaltene is shown in Figure 2.1. Asphaltenes are generally considered as highly polar and complex aromatic materials of fairly high molecular weight. The asphaltenes content has a large effect on the rheological characteristics of bitumen.

Increasing the asphaltenes content produces harder, more viscous bitumen with a lower penetration, higher softening point and consequently higher viscosity (Morgan and Mulder, 1995). Asphaltenes contain more condensed aromatic rings and more polar groups (Zhao et al., 2001) but the presence of fused aromatic structure seems to be the fundamental feature differentiating the asphaltenes from the rest of the bitumen molecules. Because of so many condensed aromatics rings, asphaltenes form almost planar molecules that can associate through π→π bonding to form graphite-like stacks (Lesueur, 2009). The structure of asphaltenes is not fixed. Thus, the gel structure is destroyed on heating and reforms on cooling. Asphaltenes micelles may break down if strong or more prolonged heating is applied (Morgan and Mulder, 1995).

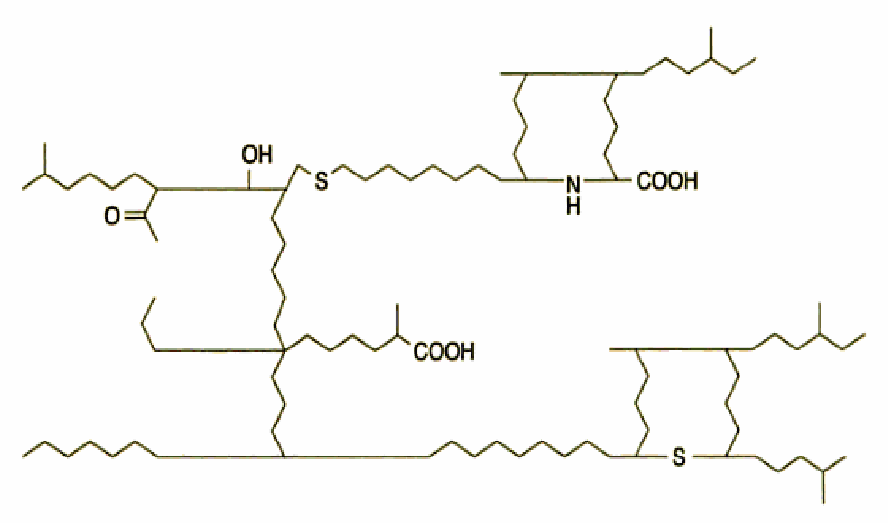


Figure 2.1: Asphaltene structure (Read and Whiteoak, 2003)

2.1.2.3 Resins

Resins are soluble in n-heptane and very polar in nature (Morgan and Mulder, 1995); black in colour, solid at room temperature (Cobett, 1969). This particular characteristic makes them strongly adhesive. They are dispersing agents or peptisers for the asphaltenes and the proportion of the resins to asphaltenes governs the degree of solution (Sol) or gelatinous (Gel) type character of the bitumen. Resin separated from bitumens are found to have molecular weight ranging from 500 to 50,000, with particle sizes of 1 nm to 5 nm and an H/C atomic ratio of 1.3 to 1.4 (Morgan and Mulder, 1995). Lesueur (2009) showed that resin can sometimes be more polar than asphaltenes, but with less condensed aromatic rings. They typically contain fused aromatic rings, with a most probable structure corresponding to 2 - 4 fused rings.

2.1.2.4 Aromatics

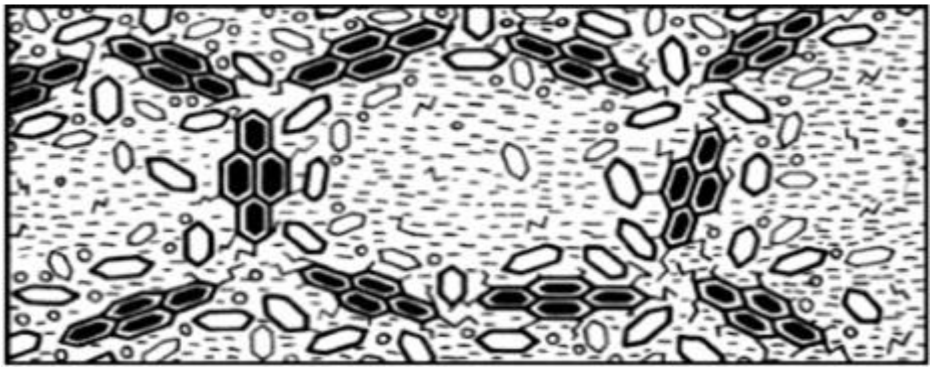
Aromatics, also called naphthenes aromatics, are the most abundant constituents of bitumen together with resin (Corbett, 1969). Aromatics represent the major proportion of the dispersion medium for the peptised asphaltenes. They constitute 40 to 65 % of the total bitumen (Morgan and Mulder, 1995). They form yellow to red liquid at room temperature (Corbett, 1969). They are more viscous than saturates at the same temperature, because of a higher glass transition temperature around -20 ºC, which is similar to the parent bitumen (Claudy et al., 1992). The average molecular weight range is in the region of 300 to 2000, they consist of non-polar carbon chains in which the unsaturated ring system dominates and they have higher dissolving ability than other high molecular weight hydrocarbons (Morgan and Mulder, 1995).

2.1.3 Bitumen Structure

Bitumen is traditionally regarded as a colloidal system (Girdler, 1965) consisting of high molecular weight asphaltenes micelles dispersed or dissolved in a lower molecular weight oily medium (maltenes). The micelles are considered to be asphaltenes together with an absorbed sheath of high molecular weight aromatics resins which act as a stabilising solvating layer. Away from the centre of the micelle, there is a gradual transition to less polar aromatic resins, these layers extending outwards to the less aromatic oily dispersion medium (Morgan and Mulder, 1995).

If the aromatic/resin fraction is not present in sufficient quantities to peptise the micelles, or has insufficient solvating power, the asphaltenes can associates together further. This can lead to an irregular open packed structure of linked micelles in which the internal voids are filled with an intermicellar fluid of mixed constitution. These bitumens are known as ‘GEL’ type, as depicted in Figure 2.2(a). In the presence of sufficient quantities of resins and aromatics of adequate solvating power, the asphaltenes are fully peptised and the resulting micelles have good mobility within the bitumen. These are known as ‘SOL’ type bitumens and are illustrated in Figure 2.2(b) (Morgan and Mulder, 1995; Read and Whiteoak, 2003).

a.) Gel type bitumen



b.) Sol type bitumen

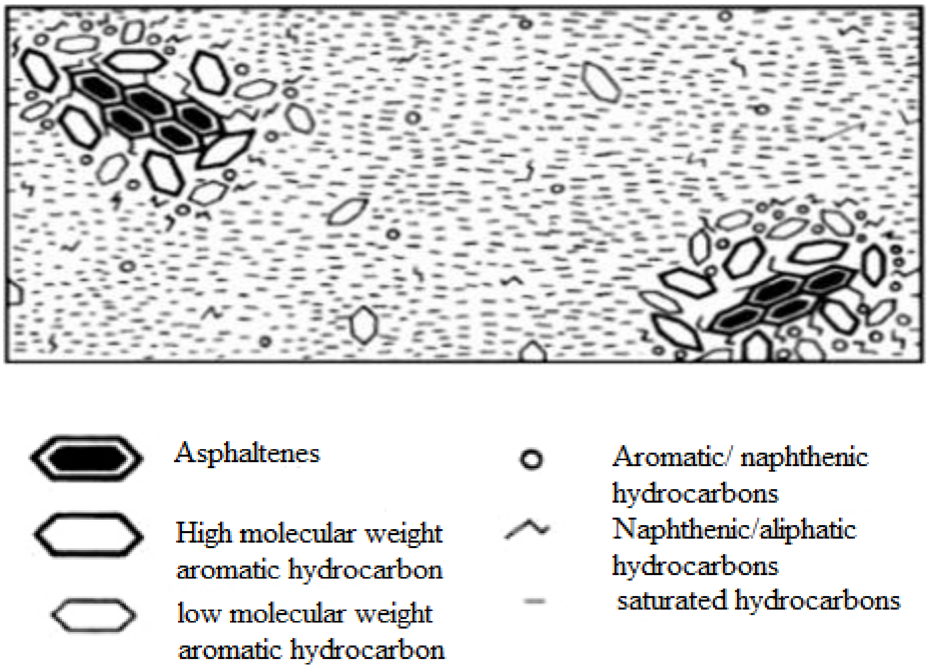


Figure 2.2: (a) Gel and (b) Sol type bitumen structure (Morgan and Mulder, 1995; Read and Whiteoak, 2003; Lesueur, 2009)

Sol bitumens exhibit Newtonian behaviour, whereas gel bitumens are highly non-Newtonian. In practise, most bitumen are of intermediate character due to sol-gel structure. In modern terms, non-Newtonian behaviour would be described as delayed elasticity together with some non-linearity in the viscoelastic properties (Morgan and Mulder, 1995).

2.2 Polymer Modified Bitumen (PMB)

Bitumen behaves as a viscoelastic material at usual in-service temperatures, showing mechanical/rheological properties suitable for traditional paving and roofing applications (Navarro et al., 2009). However, bitumen has the characteristics of high temperature rutting (Navarro et al., 2009; Galooyak et al., 2010), crack initiation, and propagation in the low temperature region are due to its severe temperature susceptibility (Galooyak et al., 2010). Moreover, fatigue and aging of bitumen limit its industrial application (Galooyak et al., 2010).

The lifetime of pavements reduces (Navarro et al., 2009), due to the thermal susceptibility of bitumen, increasing number of vehicles and load weight of some of them (Navarro et al., 2009; Galooyak et al., 2010). Since last decades the properties required to road pavements have become more and more exigent (Navarro et al., 2009). Therefore, modifications of bitumen with binders are important for road paving applications.

Modification of bitumen with rubbers has been conducted since the earliest times. The first patent on the addition of rubber to bitumen was fitted in 1843 by Henry Austin who specified a glue for fixing wooden pavements blocks comprising “pitch or lae and caoutchouc dissolved in naptha and poured in” (Morgan and Mulder, 1995; Read and Whiteoak, 2003) but the objective was more to find a substitute for rubber than to modify bitumen (Thomson, 1964). Also in 1843, Thomas Hancock was granted a patent for

"Preparing caoutchouc in combination with other substances", including bitumen (Morgan and Mulder, 1995).

Bitumen binders for road paving experience a variety of thermo-mechanical demands. Many modifiers such as carbon black, sulfur, fly ash, amine and polymers have been employed to improve physical and rheological properties of bitumen (Sun and Lu, 2007). At the turn of the 20th century, field trials with rubber modified bitumens were performed and continued for several decades until polymer modified bitumen (PMB) gained significant commercial interest in the late 1970s (Thomson, 1964; Cong et al., 2006).

Polymer additives to reinforce bitumen are now widely used in the industry as commercial products. Many types of naturally occurring and man-made rubbers have been used for the modification of bitumen including polybutadiene, polyisoprene (PIP), NR, butyl rubber, chloroprene and styrene-butadiene rubber (SBR). The principle effect of these materials is to increase the viscosity of bitumen (Morgan and Mulder, 1995).

Polymers may be added either directly to the bitumen prior to the mixing with the aggregate (wet process) or to the mix, at the same time bitumen is blended with the aggregates (dry process). The latter gives mixes with different properties than those obtained via the wet process (Yildirim, 2007). PMBs have been used with success at locations of high stress, such as intersections of busy streets, airports, vehicle weigh stations, and race tracks (Yildirim, 2007). Desirable characteristics of PMB include greater elastic recovery, a higher softening point, greater viscosity, greater cohesive strength and greater ductility (Yildirim, 2007). The pavement with PMB exhibits higher resistance to rutting and thermal cracking, lower fatigue damage, stripping, aging and temperature susceptibility (Lu and Isacsson, 1997). The properties of PMB are dependent on polymer characteristics and content, bitumen nature, compatibility of polymer with bitumen as well as the blending process (Yildirim, 2007).

Nowadays, PMB technology is used by researcher and manufacturer in bitumen emulsion to improve the performance of bitumen emulsion. Polymer modified bitumen emulsion is used for cold mix especially for chip seal, slurry seal, surface dressing and microsurfacing.

2.2.1 Type of Polymer Modifier Used in PMB

2.2.1.1 Styrene–Butadiene–Styrene (SBS)

Styrene–butadiene–styrene (SBS) block copolymers are classified as elastomers that increase the elasticity of bitumen and they are probably the most appropriate polymers for bitumen modification (Becker et al, 2001; Sengoz and Isikyakar, 2008). SBS copolymers derive their strength and elasticity from physical cross-linking of the molecules into a three dimensional network (Airey et al., 2003). Rutting resistance of mixes with SBS modified bitumen was found to be higher (Tayfur et al., 2007; Anjan and Veeraragavan, 2010) when compared to mixes with NR, crumb rubber, waste plastic modified bitumen binder and unmodified bitumen binder (Anjan and

Veeraragavan, 2010). At constant bitumen binder content, mixes with rubber modified bitumen binder yielded better performance when compared to mixes with unmodified bitumen binder (Anjan and Veeraragavan, 2010).

Serfass et al. (1992) found that emulsified SBS modified bitumens show excellent adhesion to various types of aggregate compare to hot applied SBS modified binder and it can even be sprayed on damp surfaces. Moreover, emulsified bitumen applications also show to tolerate higher SBS dosing levels than modified hot mixes, resulting in improved stone retention, cohesion and viscoelasticity, especially in crack sealing applications (Serfass et al., 1992).

2.2.1.2 Styrene–Butadiene–Rubber (SBR)

SBR has been widely used as a bitumen modifier, usually as dispersion in water (latex) (Yildirim, 2007). SBR latex particles in a polymer modified bitumen emulsion remain in the aqueous phase and spontaneously transform into a continuous microscopic polymer film surrounding bitumen particles upon curing (Takamura, 2001). The benefit of latex is that the rubber particles are extremely small and regular. When they are exposed to bitumen during mixing they disperse rapidly and uniformly throughout the material and forma reinforcing network structure (Becker et al., 2001).

According to Becker et al. (2001), SBR latex polymers increase the ductility of bitumen pavement, which allows the pavement to be more flexible and crack resistant at low temperatures. SBR modification also increases elasticity, improves adhesion and cohesion, and reduces the rate of oxidation, which helps to compensate for hardening and aging problems (Yildirim, 2007).

Water-based SBR latex has been widely used to improve chip retention in emulsions, but SBS has gradually replaced latex because of its effect of greater tensile strength at strain, and because it is compatible with a broader range of bitumens (King at al., 1999).

Takamura (2001) has demonstrated the benefits of SBR modification of bitumen emulsions and microsurfacing mixes, with significant increases in rutting resistance temperatures observed with increasing polymer content. Bitumen emulsions modified with 3 percent SBR latex performed significantly better than unmodified emulsions or neat non-emulsified bitumen (Johnston and Gayle, 2009).

From the study conducted by Qinqin et al. (2011), it was found that the temperature susceptibility of SBR latex modified bitumen emulsion became lower, which was more favorable for practical application, such as slurry seal and micro-surfacing. Furthermore, the increase of equivalent softening point indicated that the thermal stability and the heat resistance of bitumen were significantly enhanced by SBR modification. Compared to unmodified bitumen emulsion, the increase of 5 °C ductility and decrease of equivalent brittle point revealed that anti-cracking performance of bitumen was also enhanced considerably by SBR modification (Qinqin et al., 2011).

2.2.1.3 Crumb Rubber

‘‘Crumb rubber modifier’’ (CRM) is the term that refers to applications in which ground recycled rubber and paving bitumen are combined (Yildirim, 2007). CRM are not pure polymers, but represent blends of SBR latex, NR, carbon black, and other additives (Holleran et al., 1997). Usually, the rubber is recycled from used automotive tires, which has the additional benefits of saving landfill space that would otherwise be occupied by tyres and thus reducing cost (Becker et al., 2001).

Characteristics of CRM are dependent on rubber type, bitumen composition, size of rubber crumbs, and time and temperature of reaction (Becker et al., 2001). CRM is extensively crosslinked and is not very compatible with the bitumen nor is it readily swollen. Devulcanization and use of high shear both reduce molecular weights and open up the polymer structure, thereby improving the solubilization/emulsification (Sabbagh and Lesser, 1998).

Recycled tire rubber reduces reflective cracking, which increases durability. Due to its high molecular weight, it has problems of low compatibility (Yildirim, 2007). There are some practical problems in using crumb rubber: it needs high temperatures and long digestion times in order to be dispersed in the bitumen (Becker et al., 2001).

2.2.1.4 Ethylene Vinyl Acetate (EVA)

Ethylene Vinyl Acetate (EVA) is commonly used as a plastomeric modifier which represents a copolymer of ethylene and vinyl acetate. EVA polymers have been used in road construction for more than 20 years in order to improve both the workability of the bitumen during construction and its deformation resistance in service (Zhang and He, 2007). There has not been much record on polymer modified bitumen emulsion using EVA. Normally, EVA is used in bitumen modification that is purposely used for hot application. Study conducted by Panda and Mazumdar (1999) confirmed that bitumen mixture using EVA modified bitumen increased the value of Marshall Stability and air voids and at the same time decreased the flow and unit weight value.

2.2.1.5 Natural Rubber Latex (NRL)

NRL is an elastomeric hydrocarbon polymer that exists as a natural milky sap produced by several species of plants. NR is produced from NRL by coagulation to form a solid material (Johnston and Gayle, 2009). In 1929, the first ever application of NRL in road construction took place in Singapore. In UK, Europe and USA, the use of NRL in bitumen modification had been studied extensively in the 1950’s and 1960’s.

In 1970’s a patented process known as ‘Ralumac’ process was develop to modify bitumen emulsion with NRL. This process involves mixing naturally anionic NRL in aqueous phase with cationic surfactants and emulsifying the resulting liquid with bitumen using a colloid mill (Ruggles, 2005). This type of NRL modification is usually a two-stage process using a continuous-feed emulsion plant to achieve the desired results. However, when compatible NRL is used (with respect to bitumen microstructure) the process can be reduced to a single stage, and the latex was added pre- or post-emulsification (King et al., 1998; Ruggles, 2005).

Since its introduction, NRL modified bitumen has been found to enhance the thermal stability of bitumen in two fundamental ways (Ruggles, 2004):

a. NRL at high temperatures increases the bitumen’s viscosity (thickening) making road surface more resistant to deformation under heavy loads during hot weather.
b. At low temperatures the NR reduces thermal cracking associated with bitumen.

The resulting cationic emulsion is attracted to the anionic surfaces of the aggregate, latex, and filler material; this increases the oil wet ability and ensures better adhesion of the coagulated bitumen to the mineral grains once cured (Takamura, 2002). Figure 2.3 shows the surfactant action in NRL modified bitumen. This breaking process is essential in ensuring rapid adhesion and strength development. The polymer component of a properly formulated and stabilized emulsion is dispersed throughout the bituminous cement to form an elastic lattice upon curing (King and Johnston, 2012).

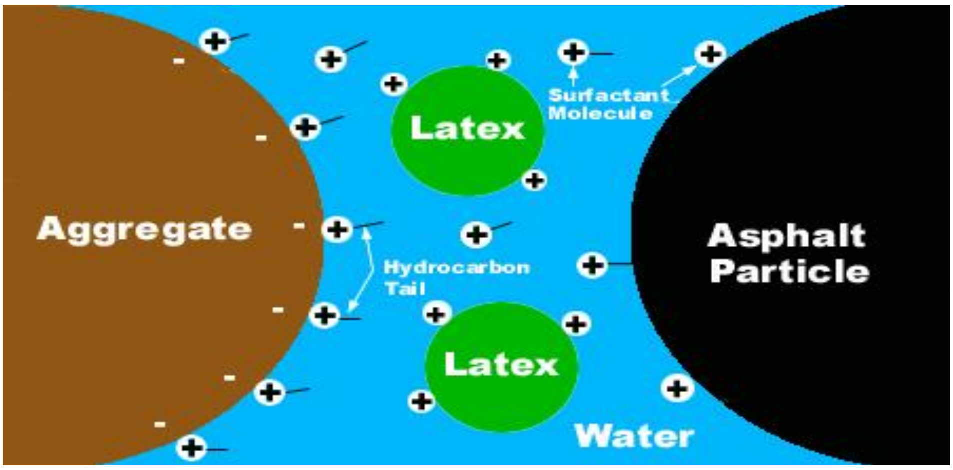


Figure 2.3: Surfactant action in NRL modified bitumen emulsion (King and Johnston, 2012)

NRL modified bitumen yields similar performance benefits to those obtained in hot mix, including increased thermal stability, higher resistance to load deformation, and reduced thermal cracking (Ruggles, 2005). The resulting rubberized bitumen acts like an elastic membrane, which holds residual bitumen particles together, thereby retarding crack propagation and increasing stone retention (Figure 2.4). Crack pinning also contributes to retarding the crack growth. At higher temperatures, the NRL's lattice resists flow in the bitumen matrix, which increases the pavement's resistance to deformation. Micro surfacing, slurry seals, chip seals, and tack coats all may benefit from the use of NRL modified bitumen emulsions. Figure 2.4 illustrates the distribution of latex within the bitumen binder used in a typical chip seal (King and Johnston, 2012).

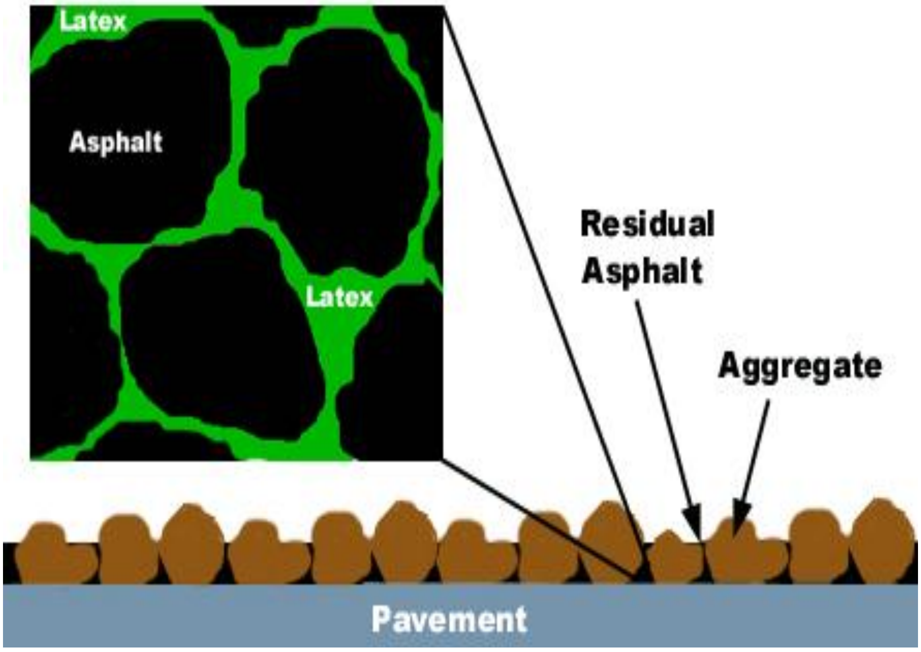


Figure 2.4: Polymer modified chip seal (King and Johnston, 2012)

Study conducted by Malithong and Thongpin (2010) showed that pre-vulcanized NRL could be added to modify bitumen emulsion and improve properties of bitumen better than NRL. Pre-vulcanized NRL bitumen emulsion possesses acceptable properties of modified bitumen emulsion for highway construction application.

2.2.2 Polymer Content in PMB

The dosage of polymer varies but is generally one to five percents of polymer by weight of bitumen, and two to three percents is the most common dosage for chip seal and slurry seal applications (King and Johnston, 2012).

Johnston and Gayle (2009) stated that the range of polymer content recommended for most applications generally varies between about 2 – 10 % by weight of the residual bitumen content, with most research, standard, and manufacturer specifications calling for a polymer concentration of approximately 3-5 %. The optimal percentage depends upon the specific polymer, specific bitumen and their interaction.

Study conducted by Anderson et al. (1992) shows that the addition of polymer between 2.8 - 3 % had little effect on the stress-strain response of the emulsion residue at low temperatures and had moderate increases in stiffness of the emulsion at temperatures above 25°C. Takamura (2000) used 3 - 3.5 % of SBR latex for microsurfacing formulation that consists of 100 parts of aggregates, 8-15 parts of water and 0.5 - 2 parts of Portland cement.

According to Naskar et al. (2010), the optimum waste plastic (WP) content was found to be 5 wt % based on the thermal stability results. Differential Scanning Calorimetric (DSC) results showed that the crystalline fraction increases with increasing in polymer content. At lower wt % of WP content, the interaction between bitumen and WP was significantly high because of the better swelling of polymer particles which further enables interaction of polymer particles with bitumen phase (Naskar et al., 2010). A summary of polymer modification method and polymer dosage is shown in Table 2. 1.

Table 2.1: Summary of polymer modification method and polymer dosage

Type	Method	% of polymer content	Application	References
SBR or Butanol LS 198®)	Soap pre batching No post or Field addition	2-6 % of residual bitumen content, Usually 3 %	various	(Turk et al., 1999; Ruggles, 2005)
SBR, NRL, Neoprene,	Pre-blend solids with bitumen using a high shear blender. For latex-soap pre-batching	2 % of residual bitumen content	microsurfacing	(Jones et al., 1989)
SBS	Pre- blended With bitumen	4 % by weight of bitumen content	Various low temperature applications	(Gerard et al., 2001)
NRL (1497C)	Ralumac Process - soap Pre-batching	4 % of total emulsion by weight	various	(Ruggles, 2005)
PE (Tyrin® 2552)	Pre-blend directly with binder	3-5 % of residual bitumen content	various	(Morrison et al., 1994)

2.2.3 Bitumen-Polymer Blending Method

Polymer modified bitumen emulsion is a product made from bitumen emulsion that has been modified with polymer emulsion or a product made by means of emulsifying bitumen that has been modified by polymer (Forbes et al., 2001). Several techniques can be used to produce polymer modified bitumen emulsion. The polymers or modifiers may be added into hot bitumen before emulsification process take place, added to the finished emulsion product or “co-milled” at the colloid mill with various component streams during production.

Different blending method to add polymer has important influence on polymer network distribution and will affect the performance of polymer modified bitumen emulsions (Zhang and He, 2007). Forbes et al. (2001) studied the effect of four polymer modification techniques on bitumen binder microstructure at high temperatures. The emulsion modification techniques tested include (Figure 2.5): -

a. Pre-blending – The polymer modifier is added directly to the bitumen prior to emulsification. This method is required for solid forms of polymer.
b. Co-milling – Separate streams of polymer, bitumen, and emulsifier solution (soap) are co-milled together simultaneously.
c. Soap pre-batching – The polymer modifier is added to the soap solution (water and emulsifier) prior to milling with the bitumen.

d. Post-blending – The polymer modifier is added to the final bitumen emulsion either at the plant or in the field.

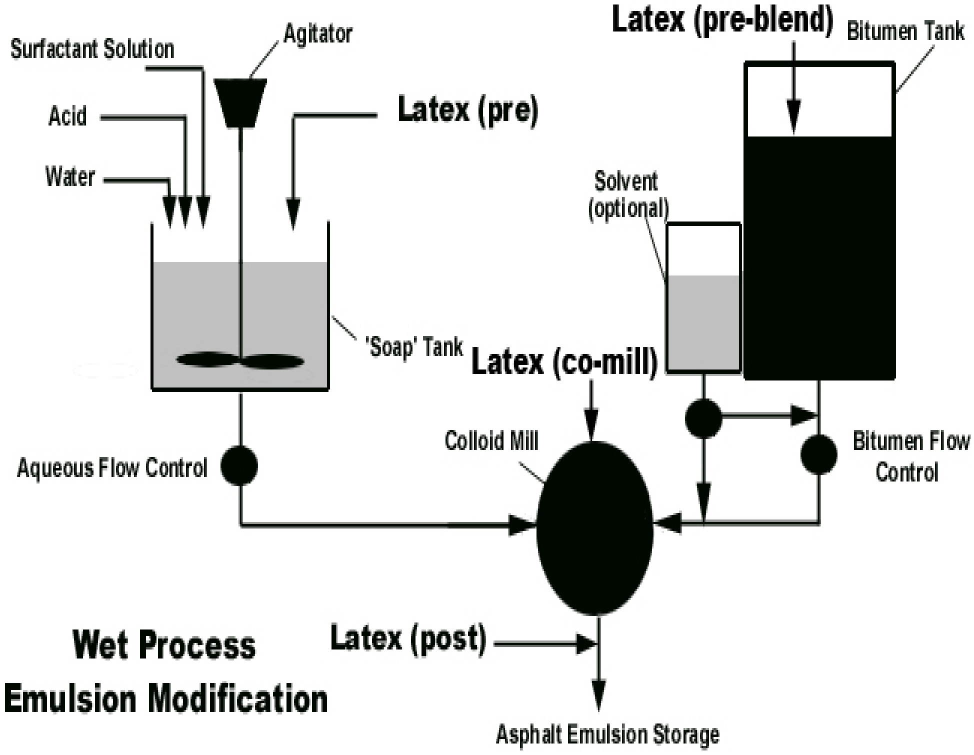


Figure 2.5: Typical emulsion modification processes (Ruggles, 2005)

From the study, Forbes et al. (2001) found that, pre-blending method produced a monophase emulsion where a single phase of polymer modified bitumen droplets could be seen(Figure 2.6(a)). The other methods produced bi-phase emulsions (Figure 2.6(b)) which were a combination of two phases of bitumen droplets and polymer droplets. However, in bi-phase emulsion manufacture, the polymer was not exposed to temperatures above 85 - 90 °C.

In monophase emulsions, the pre-blended bitumen and polymer is processed at temperatures up to 180 °C to allow adequate dispersion of the polymer in the bitumen. At high temperatures approaching 200 °C there is an increased risk of both polymer and bitumen degradation occurring. This may cause an adverse effect upon the quality of the PMB residue and present a major advantage with bi-phase emulsions. When bitumen emulsions are prepared by soap pre-batching or co-milling, latex particles are prevented from coalescing in the presence of the soap solution, but result in the formation of a thin film or matrix around the bitumen particles upon drying as shown in Figure 2.6(c) (Forbes et al., 2001).

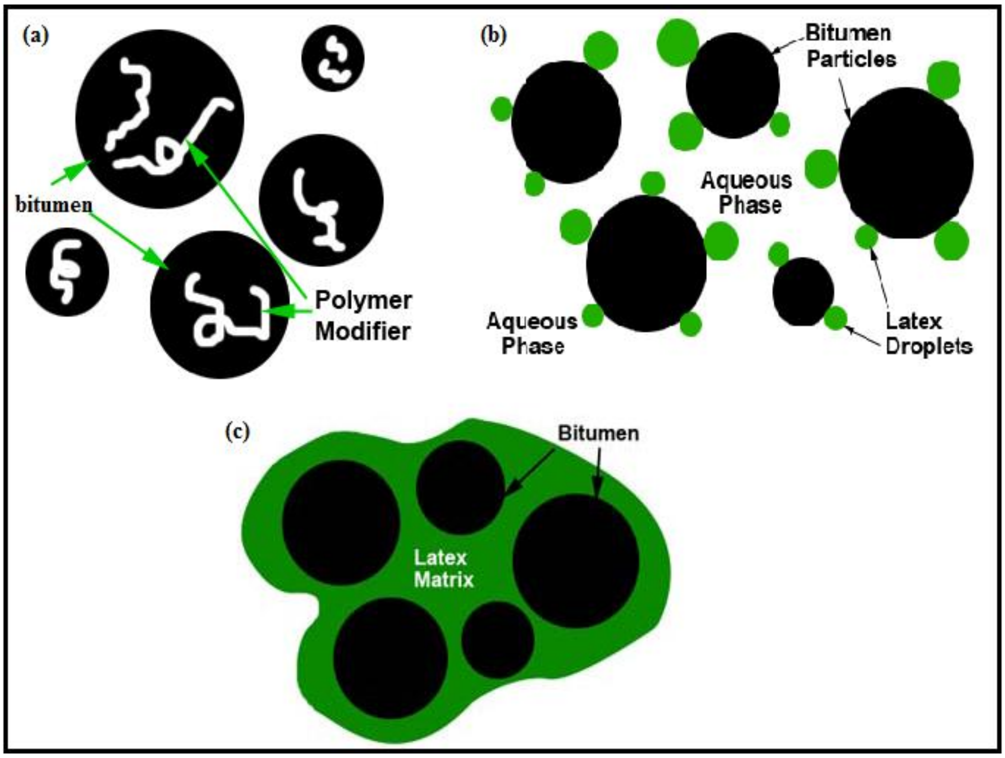


Figure 2.6: (a) Pre –blended bitumen-polymer monophase (b) Bi-phase modified emulsion (c) Polymer network in cured, co-milled emulsion (Takamura, 2000; Forbes et al., 2001)

Some of the polymers such as SBR latex and NRL have an advantage in manufacturing polymer modified bitumen emulsion due to its physical form. It can be co-milled, added into emulsifier or even can be post-blended into the prepared emulsion (Takamura and Heckmann, 1999). Sometimes, post-blending method is discouraged due to the need for vigorous, continual and thorough mixing to ensure proper and homogeneous polymer dispersion (Johnston and Gayle, 2009). Becker et al. (2001) observed that the phase separation and stability problems associated with using solid polymer modifiers generally necessitate pre-blending the solid polymer in the bitumen at elevated temperatures prior to emulsification process (Johnston and Gayle, 2009).

In general, bitumen and polymer are mixed together and blended at elevated temperatures for differing periods of time prior to using them as a paving binder. Lee et al. (2006) reported that a longer reaction time was ineffective in increasing the high temperature viscosity of the control PMB. Mashaan et al. (2011) also found that the blending time has an insignificant effect in the case of 30 and 60 minutes on rheological properties of rubberized bitumen.

2.2.4 How Polymers are Incorporated into Bitumen

The way polymer usually influences the bitumen characteristics is by dissolving into certain component fractions of the bitumen itself, spreading out its long chain polymer molecules to create an inter-connecting matrix of the polymer through bitumen. It is this matrix of the long chain molecules of the added polymer that modifies the physical properties of bitumen (Summer, 2002).

Due to the thermoplastic nature of the polymers, some polymers actually break up into their constituent molecular blocks at high temperatures, during mixing and laying and recombine into their polymer chains at lower temperatures (Summer, 2002).

Basically rubberized bitumen comprises of a bituminous compound into which rubber in a suitable form and proportion is incorporated using an appropriate technique. The two materials interact once the bitumen components migrate into the rubber causing it to swell. Initially, the bitumen-rubber interaction is a non-chemical reaction, where the rubber particles are swollen by the absorption of the aromatic oils of bitumen (Bahia and Davies, 1995). However, the base bitumen should be carefully selected to ensure that the content of light fractions of bitumen is high enough at the end of the curing process (Ould-Henia and Dumont, 2006). Bouldin et al. (1990) indicated that softer bitumens would be more compatible with rubber polymers and crumb rubber modification would be more effective with stiffer bitumens.

The absorption of bitumen components by rubber inevitably depletes the bitumen of the absorbed components and, consequently, modifies its properties by making it stiffer and more brittle (Green and Tolonen, 1977; Singleton et al., 2000; Artamendi et al., 2002; Airey et al., 2003). Furthermore, the rubber particles may also suffer some form of degradation (mainly devulcanization and depolymerization) when they are mixed with bitumen at high temperatures for prolonged periods of time (Green and Tolonen, 1977;

Billiter et al., 1997). The extent of swelling and degradation depends on the nature of rubber, the chemical composition of bitumen and the mixing conditions such as time, temperature and degree of agitation (Green and Tolonen, 1977; Huang and Pauli, 2008).

A re-vulcanization phenomenon may occur when mixing bitumen with pre-vulcanized rubber. The rubber vulcanization requires the use of sulfur and other agents, which may not react completely during this process. When rubber is mixed with hot bitumen, the vulcanization process will be reactivated and may continue for some time, depending on the interaction temperature (Green and Tolonen, 1977) and on the rubber volume fraction. During the rubber-bitumen interaction, other phenomena may also occur (Peralta et al., 2010):

a. Some components of the rubber, as extender oils, carbon black and other additives can be dissolved in the bitumen;
b. The rubber particles swell, due to the diffusion of small molecules of the bitumen in the reticulated molecular structure of rubber;
c. The molecules of bitumen diffused in rubber structure also induce a relaxation of the links between the rubber atoms, thus decreasing the rubber bulk density;
d. The rubber particles saturated with bitumen molecules change into a brittle gel, which can split by stirring and heating (occasional depolymerization may occur).

It has been clearly established that for maximum effectiveness, rubber must be dissolved in bitumen. Different forms of NR like preserved field latex, pre-vulcanized latex, sheet rubber, powdered rubber and ground-vulcanized rubber were used for rubberization and of these the best performance was observed with NR latex (Indian rubber board, 2002).

2.2.5 Sulfur as an Additive in PMB

The use of sulfur in bitumen and paving technology dates back to the early 20th century when sulfur was used to modify the properties of paving bitumen composition. The presence of sulfur was shown to improve the properties of bitumen-concrete mix (Colvin and Moore, 2002). Sulfur is expected to improve the surface adherence of modified bitumen to inorganic materials in concrete. Sulfur modification of polymeric materials for further use in improving the properties of bitumen binder or in rejuvenating distressed roads gained momentum in the last two decades (Takamura et al., 2001; Takamura, 2003). Many USA patents appeared since 1990s in which sulfur was used in the modification of different polymers that are later used in the modification of bitumen binder or other road maintenance applications.

Current practice is to add the desired level of polymer, along with a reactant which promotes cross-linking of the polymer molecules until the desired bitumen properties are met. This reactant typically is sulfur in a suitable form for reacting. These processes are discussed in various patents (Bellomy and McGinnis, 1994). When added to bitumen at 140 °C, sulfur is finely dispersed in bitumen as uniform small particles; coagulation and settlement of sulfur particles become noticeable after three hours (Kennepohl et al., 1975). Therefore, the sulfur extended bitumen mixtures had to be produced directly in the mixing plant just before the laying of the bitumen mixture.

One major concern in handling sulfur-bitumen mix is the fear of the evolution of hydrogen sulfide during production and laying. According to Kennepohl et al. (1975) and Fromm and Kennepohl (1979), H_2S evolution only start at temperatures higher than 150 °C, hence the application at temperature up to 150 °C should not cause pollution and safety problems.

Wen et al. (2002) carried out rheological characterization study of the storage-stable SBS modified bitumen. The bitumen-SBS mix was prepared at 160 °C and a maximum of 5 wt % of SBS (based on 100 parts bitumen) and 10 wt % of sulfur (based on the SBS) were added. Below 120 °C, neither the reaction of the bitumen and sulfur nor the vulcanization of the sulfur of the SBS/sulfur blend could take place according to the literature (De Filippis et al., 1997). The addition of sulfur to SBS modified bitumen resulted in the formation of a chemically vulcanized SBS network structure in the modified bitumen, and the high temperature performance of the bitumen was improved and their temperature susceptibility was reduced to a great extent (Wen et al., 2002).

2.2.6 Physical Properties of PMB

2.2.6.1 Ductility Properties

Ductility is a distinct strength of bitumen, allowing it to undergo notable deformation or elongation. Ductility is defined as the distance in centimeter, to which a standard sample or briquette of the material will be elongated without breaking (Mashaan et al., 2012). It is generally considered that bitumen with a very low ductility will have poor adhesive properties and thus poor performance in service (Tia, 2012). Low temperature ductility can reflect the low temperature property of binder (Liu et al., 2008).

The study of Mashaan et al. (2011) concluded that finer rubber particles resulted in higher ductility elongation and also, that toughness would increase as rubber content increases. Elastic recovery (ER) value was improved with a maximum time of 2 hours at 24 °C (Jensen and Abdelrahman, 2006). The bitumen-rubber modification resulted in better rutting resistance and higher ductility but the modifier is sensitive to decomposition and oxygen absorption (Yildirim, 2007).

Liu and coworkers (2008) tested four types of crumb rubber with two different particle sizes with base bitumen. They concluded that with increasing crumb rubber content from 16 to 24 %, the ductility at 5 °C decrease significantly. The particle size of crumb rubber did not influence much on ductility at low temperatures. They suggested avoiding the use of agriculture tire crumb rubber- bitumen modifier in cold region because it gave the worst ductility at 5 °C. The 16 % blending of tread rubber – crumb rubber (60 meshes – particle size) with bitumen gave 25.7 cm ductility at 5 °C.

Anjan and Veeraragavan (2010) reported that, the ductility of SBS polymer and NR modified bitumen at 27 °C were 100+ cm and 78.5 cm respectively. Galooyak and co-workers (2010) conducted the ductility test at 15 and 4 °C (ASTM D113) on base bitumen (85/100 penetration grade) as well as on SBS modified samples. SBS modified bitumen gave ductility results of 114 cm and 28 cm at 15 and 4 °C, respectively. The ductility at 4 °C for the PMB was obviously better than the base bitumen.

Elastomers such as SBR and SBS have significant effect on ductility at both 4 and 25 °C; while SBR modified bitumens have high ductility at all temperatures, SBS modified bitumens tend to give lower ductility (Yildirim, 2007). Naskar et al. (2010) used 60/70 penetration grade (VG-30 viscosity grade) bitumen to blend with 0 - 7 % content of WP. The ductility of the WP modified bitumen was tested at 25 °C. The ductility value decreased from 100 cm to 31 cm as the WP content increased from 0 to 7 % in modified bitumen.

2.2.6.2 Elastic Recovery (ER) Properties

ER (or elasticity) is the degree to which a substance recovers its original shape following application and release of stress. Some degree of ER is desirable in pavement to avoid permanent deformation (Yildrim, 2007). When a tire passes over a section of pavement, it is desirable for that pavement to have the ability to ‘give’, but it is equally important for it to recover to its original shape (Asphalt institute, 2003).

ER of bitumen, a measurement widely used to test PMB, can be measured by elongating bitumen sample, cutting it, allowing it to rest, and determining the degree to which the elongated specimen returns to its original length. The ER test has been shown to be a good measurement of polymer contribution to bitumen performance, although no relationship appears to exist between rutting resistance and ER. ER and other conventional measurements are inconsistent in ranking PMB performance. These measurements may only indicate whether a modifier is present in bitumen specimen, but not its contribution to the bitumen performance (Yildrim, 2007).

According to the study of Jensen and Abdelrahman (2006), the ER property is very important in both fatigue and rutting resistance selection and evaluation. Oliver (1981) concluded from his study that the ER of rubberized bitumen led to an increase as the rubber particle size decreased. Modified bitumen showed a significant enhancement on the ER, and, in contrast, the ductility decreased with respect to unmodified bitumen (Mashaan et al., 2011). Anjan and Veeraragavan (2010) reported that, the ER of SBS polymer and NR modified bitumen at 15 °C were 77 % and 55 % respectively.

2.2.7 Advantages of Rubber Modified Bitumen

The application of NR by mixing it with bitumen materials in roadwork is an alternative that may help increase domestic consumption of NR. Proper blending of bitumen with NR in a fixed proportion confers good ER to the blend. Incorporation of 2 - 4 % of NR into bitumen thus improves the properties of the latter substantially and rubberized bitumen is found to be an excellent binder for rubble and sand. The rubberized bitumen formed minimizes permanent deformation due to overload on the road (Indian rubber board, 2002).

The NR modified bitumen is unaffected by changes in atmospheric temperature. It improves skid resistance due to increased aggregate retention and elimination of bleeding. Rubber increases the resistance to flow of bitumen at high temperature and improves the resistance to brittle fracture at low temperature (Nair, 2003). The above properties increase the service life of rubberized roads in many cases to more than 100 % when compared to that of bituminous roads. Thus, rubberization of roads will combine savings with safety (Indian rubber board, 2002). The advantages of the use of rubber modified bitumen in road construction may be thus summarized as below (Lewandowski, 1994):-

a. Increase in useful service life
b. Improved resistance to cracking at low temperature

c. Better resistance to fatting up or bleeding of bitumen under hot condition
d. Improved skid resistance
e. Increased fuel economy
f. Better grip and cornering
g. Low repairs and maintenance cost (about 33 % savings)

2.3 Natural rubber (NR)

2.3.1 Structure of NR

Faraday discovered in 1826 that NR was composed of a hydrocarbon with a ratio of five carbons to eight hydrogen atoms (Grave, 2007). In 1860, Greville Williams isolated isoprene by collecting the distillate from the heating of NR (Grave, 2007). The fundamental structure of NR consists of isoprene units, C_5H_8 with the empirical formula equivalent to $(C_5H_8)_n$.

In 1925, J.R. Katz found that NR crystallized on stretching and could be characterized by wide angle X-Ray diffraction (White, 1995). Nyburg (1954) and Dinesh (2005) stated that, using the stretch direction X-ray repeat distances, that the chain configuration across the double bond in NR had a *cis* configuration. Figure 2.8 showed the structure of NR and gutta percha.

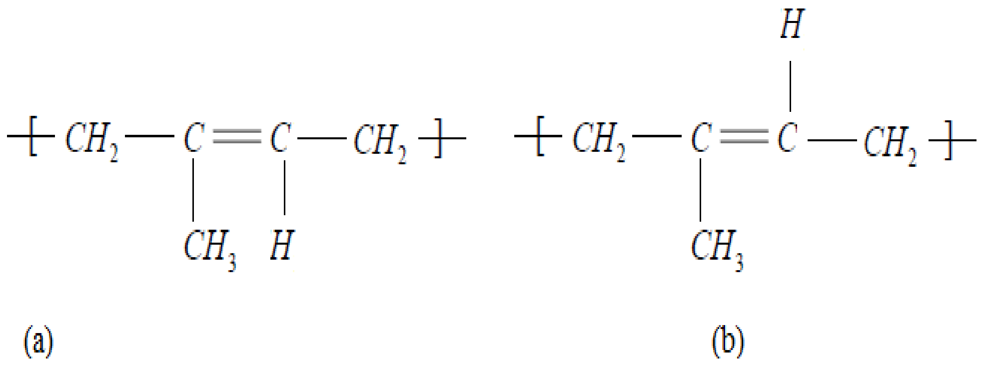


Figure 2.8: Structure of NR (Nyburg, 1954; Dinesh, 2005)

By the use of ^{1}H-NMR and ^{13}C-NMR spectroscopy, Tanaka et al. (1989) showed that the second and third units of *Hevea* rubber are *trans*, followed by repetitive *cis* enchainment. The terminal groups are believed to be $–CH_2OH$ or a fatty acid ester. Figure 2.9 showed the microstructure of natural *Hevea* rubber. The different structures of possible enchainments in polyisoprene (PIP) are shown in Figure 2.10.

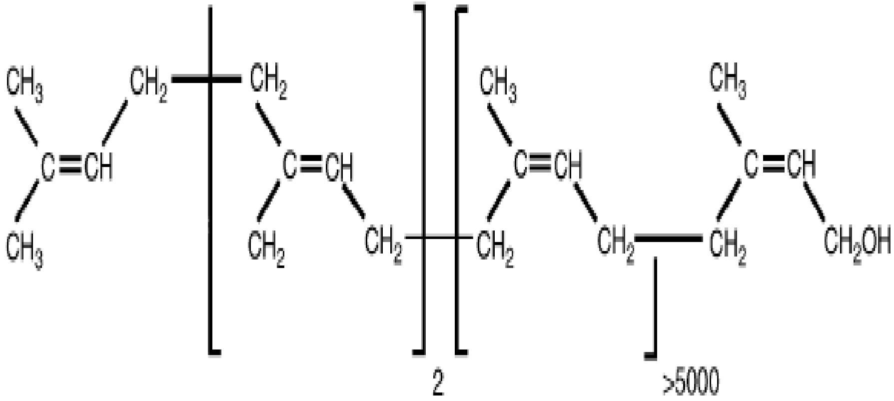


Figure 2.9: The microstructure of natural *Hevea* rubber (Puskas et al., 2006)

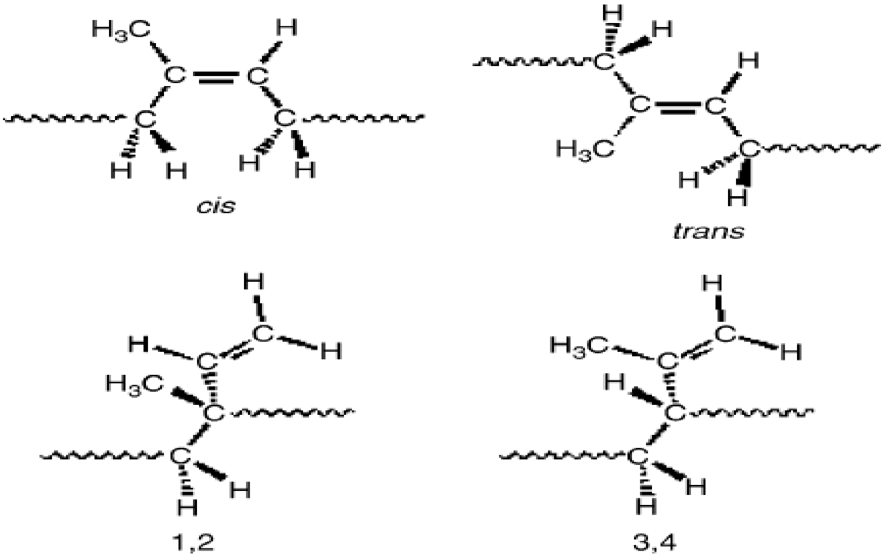


Figure 2.10: Possible enchainment in polyisoprene (PIP) (Dinesh, 2005)

The presence of cyclized polyisoprene (*c*PIP) sequences in NR was also detected. Other chemical groups, termed ‘‘abnormal’’ were also identified (aldehydes, epoxides and amines) however, their origin remains unknown (Puskas et al., 2006). The chemical structure of natural *cis*-PIP rubbers obtained from different plant species (Russian dandelion, golden rod, Jelutong) differs only in the number of the initial *trans* units (0 to 3) following the 1,1-dimethylallyl head group. Only a relatively few species, such as balata and Gutta percha, produce gutta or *trans*-1,4 PIP (Puskas et al., 2006).

2.3.2 Properties of NR

The physical and chemical properties of the NR are influenced by the presence of the non-rubber substances. The properties of NR depend very much upon the degree of cross linking. The NR polymer is nearly 97 % *cis*-1,4 PIP (Ciullo and Hewitt, 1999a; Karak, 2009). The linear hydrocarbon chain with a methyl group in each repeating unit is the characteristic of the structure. The molecular weight and its distribution are high (average molecular weight = 1-2 x 10^6 g/mol and MWD=5[10]). The high molecular weight distribution (MWD or PDI) may be due to natural production of NR, where the external conditions vary widely. However, this wide MWD is helpful in its processing as the low molecular weight polymer molecules act as plasticizer for high molecular weight polymer chain (Karak, 2009).

High molecular weight results in high viscosities. The Mooney viscosity of fresh dry NR is in the range of 55 - 90. During storage the viscosity of NR increases to 70 - 100 Mooney units depending on the length of the storage periods (Kurian and Mathew, 2011). The natural storage hardening is believed to be due to cross linking reaction between aldehyde groups present in the rubber molecule with the amino groups of free amino acids and proteins (Subramaniam, 1975). The aldehyde groups can be deactivated and storage hardening reaction can be inhibited by treating the rubber with 0.15 % hydroxylamine salt. This is the technique used for the production of viscosity stabilized rubber grades, also known as constant viscosity rubbers (Kurian and Mathew, 2011).

A small percentage of rubber undergoes cross linking even when present within the latex vessels of the tree (Mathew, 2001). This is evident from the 5 - 10 % of gel content in freshly prepared NR. The gel content increases during storage and it is known as the macrogel. The macrogel is responsible for increased viscosity of NR during storage (Kurian and Mathew, 2011). The macrogel breaks down almost completely during mastication of the rubber, and dissolves completely in aliphatic and aromatic solvents, chlorinated hydrocarbons, tetrahydrofuran and carbon disulphide (Mathew, 2001; Kurian and Mathew, 2011).

NR particles of the field latex are stabilized via adsorbed proteins and phospholipids, which render them amphoteric behavior. Hydrolysis of the phospholipids resulted in changes of the chemical composition of the rubber/water interface with time in latex concentrates well after production (Blackley, 1997a).

NR has a flexible molecular chain due to its amorphous mass of coiled structures that make it too soft to be used for any useful purpose. Elasticity is one of the fundamentally important properties of NR. Rubber can be substantially deformed and will automatically return to its original configuration after the stress is removed. It is, however not perfectly elastic. The rapid recovery is not complete. Part of the distortion is recovered more slowly and part is retained. The extent of this permanent distortion, called permanent set, depends upon the rate and duration of the applied force. The slower the force, and the longer it is maintained, the greater is the permanent set. Because of rubber elasticity, however the permanent set may not be complete even after long periods of applied force (Ciullo and Hewitt, 1999a).

Because of high stereo specificity, NR has high tendency to crystallize on cooling at low temperature or by stretching in a particular direction (Mathew, 2001; Karak, 2009; Kurian and Mathew, 2011). The unstrained polymer has a maximum rate of crystallization at about -26 ºC; even orientation of polymer chains is possible by cooling at 0 ºC. The maximum degree of crystallinity which is possible to achieve is 25 - 30 %. The un-stretched raw rubber shows a crystalline melting point (T_m) of +25 ºC (Mathew, 2001).

Crystallization limits movement between neighbouring molecular chains and results in a large increase in hysteresis and ultimate strength. Thus, NR does not require reinforcing filler for high tensile strength and it can be compounded without or with only moderate amounts of carbon black and mineral filler, to give highly resilient and durable products (Elliott, 1979). All polymeric materials will undergo a glass transition (T_g) and change from glassy to a rubbery state. Specific volume measurements on NR have established a T_g -72 ºC, though the methyl group in each repeating unit stiffen the chain, which increases the T_g (Mathew, 2001; Karak, 2009). Glass transition of NR is higher than that of *cis*-1,4 polybutadiene (Kurian and Mathew, 2011).

The hydrocarbon nature of the polymer indicates that NR swells by close solubility parameter hydrocarbons solvents. The solubilisation or dissolution of NR is very difficult to achieve as it has very high molecular weight and entangled structure. Further, the presence of some microcrystalline structures and possible little cross linked structures retard the dissolution process. Toluene, benzene, xylene can slowly solubilise NR at very low concentration of polymer after a long time of exposure (Karak, 2009).

The rheological properties of NR are strongly influenced by long chain branching. The slow rate of stress relaxation of *Hevea* rubber compared to guayule and synthetic PIP rubber has been attributed to chain branching (Mathew, 2001). Although NR is hydrocarbon in nature, the presence of active double bond in each repeating unit, makes it chemically similar to alkene and the electron density of this double bond in each repeating unit is further enhanced by the +I (inductive) effect of methyl group attached with it. Thus, NR undergoes chlorination, oxidation, hydrohalogenation, epoxidation, cyclization, halogenation and other reactions (Karak, 2009).

NR has good dielectric properties, an excellent resilience, a good tear resistance and an elevate damping capacity. NR is chemically resistant to non-oxidizing dilute mineral acids, alkalis and salts. However, they are readily attacked by oxidizing chemicals, atmospheric oxygen, ozone, oils, benzene, and ketones and as a general rule they also have poor chemical resistance to petroleum and its derivatives and many organic chemicals in which the material soften (Cardarelli, 2008). Table 2.2 shows the summary of NR properties.

Table 2.2: Summary of NR properties (adapted from Karak, 2009)

Item	**Attribute**	**Properties**
Molecular behaviour	Glass transition temperature	-70 ºC
	Hardness range	30-100 Shore A
	Maximum tensile strength	27.58 MPa at 21.11 ºC
	Maximum elongation	50 % at 21.11 ºC
Advantages	Physical resistance	Excellent resilience Excellent tear strength Excellent abrasion resistance Excellent impact strength
	Environmental resistance	Good compression resistance Excellent water resistance Good low temperature flexibility Good oxidation resistance
	Chemical resistance	Good resistance to alcohols and oxygenated solvents
Limits	Environmental resistance	Poor ozone resistance Poor sunlight resistance
	Chemical resistance	Poor oil and petrol resistance Poor resistance to hydrocarbon solvents

2.3.3 Modification of NRL

Interest in modifying NR has dampened after the emergence and development of the plastics and synthetic rubber industries and bottom fell out of the NR market. As mentioned earlier, NR possesses excellent physical properties including its high resilience, strength and fatigue resistance (Lee et al., 2002). Moreover, it is a renewable resource. However, NR is poor resistance to oil and petrol, ozone, oxidation, weathering and a wide range of solvents due to unsaturated nature of NR chains and its non-polarity (Derouet et. al, 2009). Improvements based on compounding alone are not always sufficient to meet these targets. Therefore, a more fundamental alteration of NR molecule is required. This can be achieved by chemical modification (Blackley, 1997b).

2.3.3.1 Chemical Modification of NR

In the efforts to extend the use of NR, there have been various methods developed in order to modify its properties such as hydrochlorinated NR (Nghia et al., 2008), epoxidized NR (Van Zyl et al., 2003), cyclization of NR in latex form, halogenations of olefinically - unsaturated polymers in latex form (Blackley, 1997b) and grafting copolymerization in lattices (Kumar and Kothandaraman, 2008). New materials that can compete both technically and economically with oil-based synthetic elastomers can be produced by chemical modification of NR. Chemical modification must obey certain criteria to have a chance of technological and commercial feasibility (Romaine, 1988):-

a. The reagent should be specific and not induce changes in the NR molecule
b. Reaction should be capable of being carried out with high efficiency in the latex or during conventional mixing or curing
c. No catalyst that is poisoned by non-rubber should be employed
d. Reagent and processes should be cheap

2.3.4 Graft Copolymer Synthesis

Graft copolymers are branched molecules where the main chain is made entirely of a repeated unit of one monomer, while the branched chains are of another monomer (Dafader et al., 2006). One of the most practical modification methods is grafting the second monomer onto the NR backbone (Lee et al., 2002). Synthesis of graft copolymers from NR has been carried out in solution, solid rubber and latex phases (Blackley, 1997b; Kongparakul et al., 2009). However, the most economical and practical method is possibly that of latex modification (Kongparakul et al., 2009). Chemical modification of NR in the latex state is more challenging than in the solid rubber state.The quantities of grafted monomer on NR molecules are affected by various parameters such as monomer, emulsifier and initiator concentrations, reaction time and reaction temperature.

Considerable work has been done on techniques of graft copolymerization of different monomers on polymeric backbones. These techniques include chemical, radiation, photochemical, plasma-induced techniques and enzymatic grafting (Bhattacharya and Misra, 2004).

2.3.5 Factors Affecting Grafting Efficiency

Gasperowicz et al. (1982) investigated the grafting of ST onto poly(butylacrylate) in emulsion form. The grafting efficiency was found weakly affected by the temperature of polymerization. It was found that, the grafting efficiency decreased with increasing reaction time, the monomer/polymer ratio, and emulsifier and initiator concentration. The same conclusions were also drawn by Xu et al. (1999) for the grafting of ST onto poly(ethyl acrylate) in a seed emulsion process and by Merkel et al. (1987) for the graft copolymerization of MMA onto polybutadiene latex.

Cameron and Qureshi (1980) studied the grafting reaction of ST onto PIP in benzene solution at 60 °C. They found that the graft copolymer amount was independent of the initiator concentration. Enyiegbulam and Aloka (1992) investigated the grafting of MMA onto SBR in methyl ethyl ketone (MEK)/toluene solution initiated by benzoyl peroxide. Grafting efficiency decreased with an increase in the monomer concentration. However, the grafting efficiency was weakly affected by the concentration of benzoyl peroxide initiator.

Arayapranee and Rempel, (2004) investigated the graft copolymerization using NR as the core and ST and MMA as the shell monomers in the seeded emulsion process. The increase in grafting efficiency with increasing temperature resulted in the higher chain mobility afforded by lower viscosity of the reaction medium at a high temperature level. The grafting efficiency increased with increasing rubber-to-monomer ratio. This suggests that the periphery of the latex particle was the site of the grafting reaction. The grafting efficiency slightly increased with increasing ST-to-MMA ratio over the range investigated. In addition, the grafting efficiency decreased with increasing initiator concentration.

Pukkate et al. (2007) reported the graft copolymerization of styrene onto deproteinized natural rubber to form nano-matrix structure and the styrene conversion and grafting efficiency were found to be dependent on the styrene/rubber ratio. Arayapranee and Rempel (2008) grafted MMA or ST monomer onto NRL via emulsion polymerization with cumene hydroperoxide (CHPO) as an initiator at 50 °C for 5 hours. It was found that, the grafting efficiency of ST in the graft copolymer was higher than that of MMA.

2.3.6 Monomer

Vinyl monomers such as styrene (ST), methyl methacrylate (MMA), stearyl methacrylate, divinylbenze, acrylonitrile, dimethylaminoethyl methacrylate and mathacrylic acid have been grafted onto NR by researchers (Nakason et al., 2006; Man et al., 2008). It was found that ST and MMA are the most suitable monomers for graft copolymerization on NR because it produces useable rubber with a high level of grafting efficiency (Arayapranee et al., 2003; Kochthongrasamee et al., 2006).

The nature of monomer is a very important factor in determining the polymeric radicals. The most reactive monomers give the least reactive polymeric radicals and the least reactive monomers yield the most reactive polymeric radicals. Thus, the reactivity of ST and MMA is in the following order: ST > MMA, and the reactivity of polymeric radicals formed from these monomers is in the reverse order: polystyryl < PMMA radicals (Arayapranee et al., 2003; Arayapranee and Rempel, 2004). Aerdts et al. (1994) reported a large difference in reactivity ratios, namely, a MMA reactivity ratio of 0.19 ± 0.05 and a ST reactivity ratio of 0.73 ± 0.05, at 323 K.

Regardless of the origin of the radical site on the backbone polymer, the ability of this site to participate in a grafting reaction is dependent on its reactivity. If the radical site on the backbone polymer is much more stable than is the polymeric radical generated from the monomer, then the monomer does not readily add onto the backbone polymer and this radical is not effective as a grafting site. Thus, it is important to distinguish between the reactivity of all the radical species relative to their tendency to react with the monomer (Arayapranee et al., 2003).

2.3.7 Initiator

Generally, the synthesis of graft copolymers using free radical polymerization can be divided into groups of related processes: chain transfer and copolymerization, redox polymerization, high-energy radiation techniques and photochemical synthesis (Halasa et al., 2005). Graft copolymerization of vinyl monomer onto NR molecule has been performed by free radical polymerization using various initiator systems including thermal initiators and redox initiator (Kalkornsurapranee et al., 2009). Benzoyl peroxide, potassium persulfate and azobis(2-methylproprionitrile) are the usual type of thermal initiator used for grafting (Kalkornsurapranee et al., 2009). The three main redox initiators used by researcher for grafting monomer onto NR are cumene hydroperoxide (CHPO) /tetraethylenepentamine (TEPA), *tert*-butyl hydroperoxide (TBHPO) /tetraethylenepentamine (TEPA) and potassium persulfate ($K_2S_2O_8$) /sodium thiosulfate ($Na_2S_2O_3$) (Kochthongrasamee et al., 2006; Kalkornsurapranee et al., 2009).

A number of research investigations have been reported on the grafting of vinyl monomers such as MMA or ST onto NRL using an amine activated hydroperoxide initiator (Arayapranee and Rempel, 2004). During graft copolymerization, radical formation for initiation reaction can occur either on the NR backbone or on the monomer to be grafted. The radical formation on the monomer results in homopolymerization. Therefore, initiators capable of creating radicals on the NR backbone are preferred (Arayapranee and Rempel, 2004)

Graft copolymerization of ST and MMA onto NRL using a CHPO redox initiator was studied by using a two-level fractional factorial design (Kalkornsurapranee et al., 2009). It was suggested that grafting reactions occurred mainly on the surface of latex particles (Luankeaw, 2002; Kalkornsurapranee et al., 2009). Researchers used CHPO/TEPA and TBHPO/TEPA in 1: 1 molar ratio with a total amount of 1 phr for the purpose (Arayapranee and Rempel, 2004; Arayapranee and Rempel, 2008; Satraphan et al., 2009).

According to Kochthongrasamee and co-workers (2006), the graft copolymer initiated with CHPO/TEPA gave the highest percentage grafting efficiency and percentage of grafted NR. The more hydrophobic initiator (CHPO) was more efficient than those of TBHPO and $K_2S_2O_8$ for grafting a relatively polar monomer onto NR. It is expected that the radical concentration from CHPO/TEPA on the NR particles would be higher than those of TBHPO and $K_2S_2O_8$, since TBHPO/TEPA is soluble in both the organic and aqueous phase, while $K_2S_2O_8/NaS_2O_3$ is only soluble in the aqueous phase. The $K_2S_2O_8/Na_2S_2O_3$ initiating system reduces significantly the amounts of gel fraction and the polymer molecular weights in the sol fraction (Kochthongrasamee et al., 2006).

A redox-initiating system consisting of TBHPO and TEPA proved to be very effective for emulsion polymerization in NRL. That is, it was not sensitive to oxygen and works well with ammonia present (Schneider et al., 1996; Arayapranee and Rempel, 2004; Nakason et al., 2003). Bipolar redox initiator couple consisting of TBHPO and TEPA was used to promote core-shell morphology (Schneider et al., 1996). Moreover, NR-*g*-PMMA has been market since the mid-1950s under the trade name *Heveaplus* via graft copolymerization using TBHPO as the initiator (Satraphan et al., 2009).

2.3.8 Emulsifier

The addition of vinyl monomer can cause instability in NRL. Thus, addition of emulsifier with the monomer is important in order that the latex can achieve stability. Previous researcher used sodium dodecyl sulfate (SDS) (Arayapranee et al., 2003; Arayapranee and Rempel, 2008; Kongparakul et al., 2009) and oleic acid (Lehrle and Willist, 1997) as emulsifier to prepare styrene grafted NRL (NR-*g*-PS).

2.3.8.1 Emulsion polymerization

Emulsion polymerization is one of several, and probably the most widely used, method of effecting addition polymerization. The most important group of compounds participating in addition polymerization is compounds containing one or more double bonds. As this study involved the use of vinyl monomers in the stage II polymerization (free radical polymerization occurs in the micelle), with preformed latex, this method of polymerization was utilized (Romaine, 1988).

A typical aqueous emulsion polymerization is carried out by agitating water, monomer (which is usually sparingly soluble in water), water soluble initiator and surfactant. The surfactant is usually a long chain fatty acid or salt with hydrophilic head and hydrophobic tail. In aqueous solution, these molecules aggregate to form micelles which exist in equilibrium with free molecules.

The emulsifier is adsorbed on the surface of growing latex particles and functions as a protective colloid preventing the latex from flocculating. Polymerization then occurs at a steadily decreasing rate until all the remaining monomer has been converted to polymer (Romaine, 1988).

2.3.9 Application of NR-*g*-PS

A specific application for rubber particles, where improvements in compound properties may arise, is in the modification of brittle plastics such as polystyrene (PS). Actually PS is conventionally toughened by a rubber dispersed phase. Conventional wisdom holds that a good adhesion between the rubber particles and the surrounding glassy matrix is necessary to achieve enhanced impact strength. The adhesion is usually promoted by formation of PS chains grafted on the rubber, which are believed to be collected at the interface thus stabilizing the system (Serena et al., 2006).

Pukkate et al. (2007) reported that grafted NR can be used as a compatibilizer or an impact modifier in polymer blending. In polymer blends, the rubber core of the graft product acts as a toughening agent, whilst the glassy layer is used as a compatibilizer with glassy materials. Thus, the grafted product enhances the adhesion between two phases of the blend to improve the mechanical properties. ST grafted NR could be used as a compatibilizer between NR and PS blends and the addition of grafted NR can improve the compatibility and thermal stability of the blends (Asaletha et al., 1998).

Hinchiranan et al. (2007) investigated the application of ST or MMA graft NR by adding grafted NR into acrylic sheet. The mechanical properties of the modified acrylic sheet increased with an increase in the amount of grafted NR addition. Luankeaw (2002) reported that the ST grafted NR could be used as an impact modifier for PVC blends.

CHAPTER 3.0

MATERIALS AND METHODS

3.1 Materials Used

3.1.1 Material Used for NRL Modification

Table 3.1 lists the materials used to modify NRL in this study.

Table 3.1: Materials used to modify NRL

Materials	Manufacturer	Purity
Centrifuged NRL	Synthomer (M) Sdn. Bhd	61.50%
Revultex 1497C	Synthomer (M) Sdn. Bhd	65.50%
Revultex HCE68	Synthomer (M) Sdn. Bhd	68.75%
Revultex LR	Synthomer (M) Sdn. Bhd	60.50%
Graftex 15	Synthomer (M) Sdn. Bhd	50.00%
Ammonia solution	QrëC®	28.00%
Styrene	IdemitsuSm (M) Sdn. Bhd.	99.70%
Cumene hydroperoxide (CHPO)	Nippon oil & Fats Cooperation	73.00%
Tetra-butyl hydroperoxide (TBHPO)	Akzo Nobel	70.00%
Tetraethylenepentamine solution (TEPA)	Huntsman Corporation	95.00%
Dicumyl peroxide (DCPO)	Akzo Nobel	45.00%

Table 3.1 (continued): Materials used to modify NRL

Materials	**Manufacturer**	**Purity**
Tetramethyltriuramdisulfide Dispersion (TMTD)	Synthomer (M) Sdn. Bhd	50.00%
Sulfur dispersion	Synthomer (M) Sdn. Bhd	50.00%
Enzyme alcalase	Novozymes	100.00%
Surfactant LCU	Synthomer (M) Sdn. Bhd	30.00%
Surfactant empigen BB	Huntsman Corporation	35.00%
Surfactant nonylphenolethoxylate (NPEO)	Akzo Nobel	70.00%
Surfactant X	Synthomer (M) Sdn. Bhd	45.00%
Redicote E-11	Akzo Nobel	53.00%
Hydrochloric acid (HCl)	MERCK	35.00%
Nitric acid	MERCK	65.00%
Petroleum ether	QrëC®	99.50%
Acetone	Bendosen	99.50%
Methylethylketone (MEK)	Bendosen	99.50%

3.1.2 Type of Bitumen Emulsion Used

Bitumen emulsion was supplied by ACP DMT Sdn. Bhd. The properties of the bitumen emulsion were not revealed by the supplier. The penetration grades of the bitumen emulsion are 80 – 100 penetration. Table 3.2 shows the detail of bitumen emulsion used.

Table 3.2: Type of cationic bitumen emulsion used and its application

Type	**Grade**	**Application**
Slow setting	SS-1K	Prime coating, slurry seals
Rapid setting	RS-1K	Tack coating, penetration macadam

3.2 Apparatus

Stainless steel container with cooling jacket and cover, mechanical stirrer, beakers, hot plate and magnetic bar, weight balance, petri dish, glass plate, retort stand with clamp, mini dipping tank, mini leaching tank, 80-120 mesh sieve, round bottom flask, condenser, extractor chamber, cellulose thimble, heating mantle, sample bottles (1-2 kg), thermometer, aluminium cans, oil free papers, ductilometer mould, rotary evaporator, small paint brush

3.3 Procedure

3.3.1 Chemical Modification of NRL

The graft emulsion polymerization reaction was carried out in 2 kg stainless steel container equipped with a stirrer, cooling jacket and cover. The NRL was diluted with ammonia solution and DI water to the TSC of 45 %. The mixture was stirred for 10-15 minutes and the pH was maintained above 10. The temperature was maintained at 28 ºC (room temperature).

3.3.1.1 Effect of Amount of ST Monomer in Grafted NRL

ST monomer, emulsifier and initiator TBHPO were incorporated into a 1-L beaker and was stirred for 20 minutes. This solution mixture was added drop wise to the latex with vigorous stirring. The latex agitated for another 15 minutes. The reaction was left undisturbed for 2 hours at 28 ºC. TEPA solution was added drop wise into the latex with continuous gentle stirring for 15 minutes. The temperature was maintained at 28 ºC for another 3 hours without agitation. The mixture was left in room temperature for 24 hours.

TMTD dispersion was added to this mixture and stirred for 15 minutes. Finally, the ST grafted latex (NR-*g*-PS) was filtered using 80 mesh sieve, collected in sample bottles and labelled. This process was carried with amount of ST ranging from 3 to 45 phr. The charge of the latex were converted to cationic with the addition of 2.5 phs of Surfactant LCU and followed by 0.1 phs of deproteinized agent.

3.3.1.2 Effect of Acidification of NR-*g*-PS

Acidification of latex is an important step for the latex charge to convert from anionic to cationic. NR-*g*-PS latex synthesized from 3.3.1.1 with various ST content (3 to 25 phr) was acidified with two types of acid, namely 17 % HCl acid and 17 % nitric acid (HNO_3), to drop the pH to 5.0-5.5.

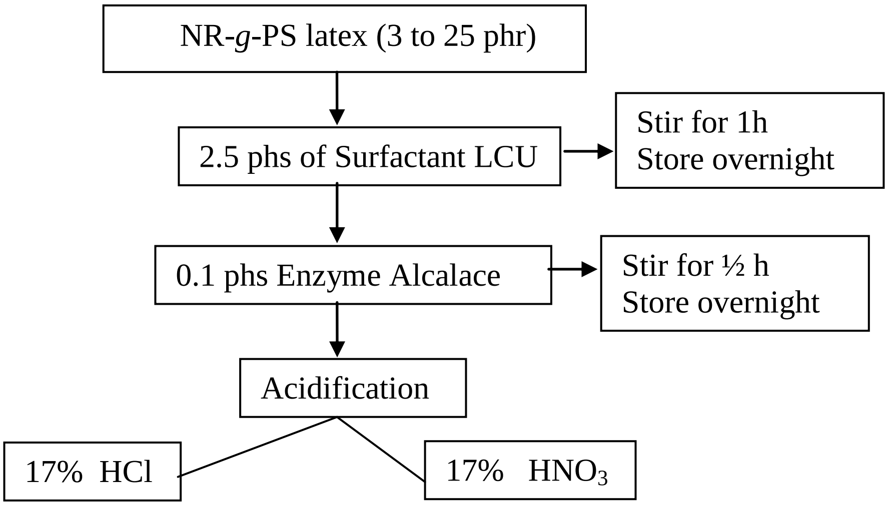


Figure 3.1: Flowchart of NR-*g*-PS latex charge conversion and acidification steps

3.3.1.3 Effect of Level of Surfactant LCU in NR-*g*-PS

Various amount of Surfactant LCU (1.7, 2.0 and 2.5 phs) was added into a 25 phr ST grafted NR which was acidified by HCl acid and tested on ductility.

3.3.1.4 Effect of Addition of TMTD to NR-*g*-PS

A 25 phr ST grafted latex was prepared as mentioned in 3.3.1.1 with and without TMTD. The charge of the latex was converted to cationic as mentioned in the Figure 3.1 by HCl acidification and tested on ductility by blending it with SS-1K bitumen emulsion.

3.3.1.5 Effect of Type of Bitumen Emulsion/NR-*g*-PS Blend

SS-1K and RS-1K were the two types of cationic bitumen emulsion used to blend with a 25 phr ST grafted latex, Revultex 1497C-65 and NS198.

3.3.1.6 Effect of Initiator Ratio of NR-*g*-PS

Emulsifier, activating agent TEPA, TMTD amounts were fixed as used in 3.3.1.1. ST contents were fixed to 25 phr. The various TBHPO/CHPO initiator ratio range from 0.345/0, 0.291/0.064, 0.173/0.203, 0.054/0.336 and 0/0.345 phr were tested on this parameter. The charge of the latex was converted to cationic as mentioned in the Figure 3.1 by HCl acidification.

3.3.1.7 Effect of Sulfur in NR-*g*-PS/Bitumen emulsion Blend

Cationic NR-*g*-PS latex from 3.3.1.6 which gave better ductility at lower temperature was selected for this parameter. Sulfur dispersion (50 %) ranging from 0.1 to 0.8 phs based on the solid weight of rubber was added into latex/bitumen emulsion mixture. Mechanical stirrer with 450 rpm speed was used to mix the mixture for 30 minutes. The NR-*g*-PS/bitumen emulsion/sulfur dispersion mixture was dried in an oven at 50 ºC to complete dryness so that it can be easily peeled off from oil free paper.

3.3.1.8 Effect of Processing Temperature of NR-*g*-PS

NR-*g*-PS latex (25 phr) synthesized in section 3.3.1.1 gave the best ductility result. Therefore, the same formula was used to synthesize NR-*g*-PS latex at different processing temperatures. The process was repeated at 40 ºC, 50 ºC and 60 ºC with the charge converted to cationic by HCl acidification.

3.3.1.9 Effect of Dosage of NR-*g*-PS

The latex from section 3.3.1.8 which gave the highest ductility result was tested in this parameter. So far only 4 parts of the modified latex was blended with 100 parts of bitumen emulsion. Thus, 2 and 6 parts of modified latex was blended with SS-1K bitumen emulsion to further test on its ductility.

3.4 Application Test

3.4.1 Preparation of Cationic Bitumen Emulsion-Modified NRL Blend For Ductility and ER Testing

Four parts of cationic modified NRL was added into 100 parts of cationic bitumen emulsion. The mixture was stirred well with mechanical stirrer at 500-550 rpm for 15-20 minutes.

The rubberized bitumen emulsion was poured on oil free paper folded into rectangular shape and dried in an oven overnight at 50 ºC. The rubberized bitumen emulsion was placed in a 250 ml aluminum can and heated on a hot plate until it turned fluid.

Glycerin and kaolin (china clay) mixture (1:1 ratio) was applied on the surface of a brass plate and the inferior surface of the ductility mould before the bitumen mixture was poured into it. This is to prevent the rubberized bitumen from sticking to the mould surface. The rubberized bitumen was poured in a thin stream back and forth from end to end of the mould until the mould is more than level full.

The test specimen was allowed to cool at room temperature for 30 minutes. Then, the mould and the plate with test specimen were placed in the water bath which was set at 5 ºC for ductility test and 7 ºC for ER test.

After 30 minutes, the plate and the mould with test specimen were removed from the water bath; the excess rubberized bitumen emulsion was removed with a hot straight edged putty knife.

The mould, the plate with the test specimen were then placed back in the water bath for 85 minutes at 5 ºC for ductility test and 7 ºC for ER test. Then, the test plate was removed from the test specimen and the side pieces were detached. The ring at each end of the clips was attached to the pins in the testing machine. Figure 3.2 shows the flowchart of the preparation of cationic bitumen emulsion- NRL blend.

3.4.2 Ductility Test Based on ASTM D113-99

Ductility is defined as the distance in cm, to which a standard sample or briquette of the material will be elongated without breaking. Ductility is the property of bitumen that permits it to undergo great deformation or elongation. The two clips were pulling apart at uniform speed of 5 mm/min at 5 ºC until the rubberized bitumen rupture where the thread has practically no cross-sectional area. The distance up to the point of breaking of thread is the ductility value which is reported in cm. The average of two normal tests was reported as the ductility of samples. The ductility value gets affected by factors such as pouring temperature, test temperature and rate of pulling. Figure 3.3 shows the ductility mould and the way of measuring ductility.

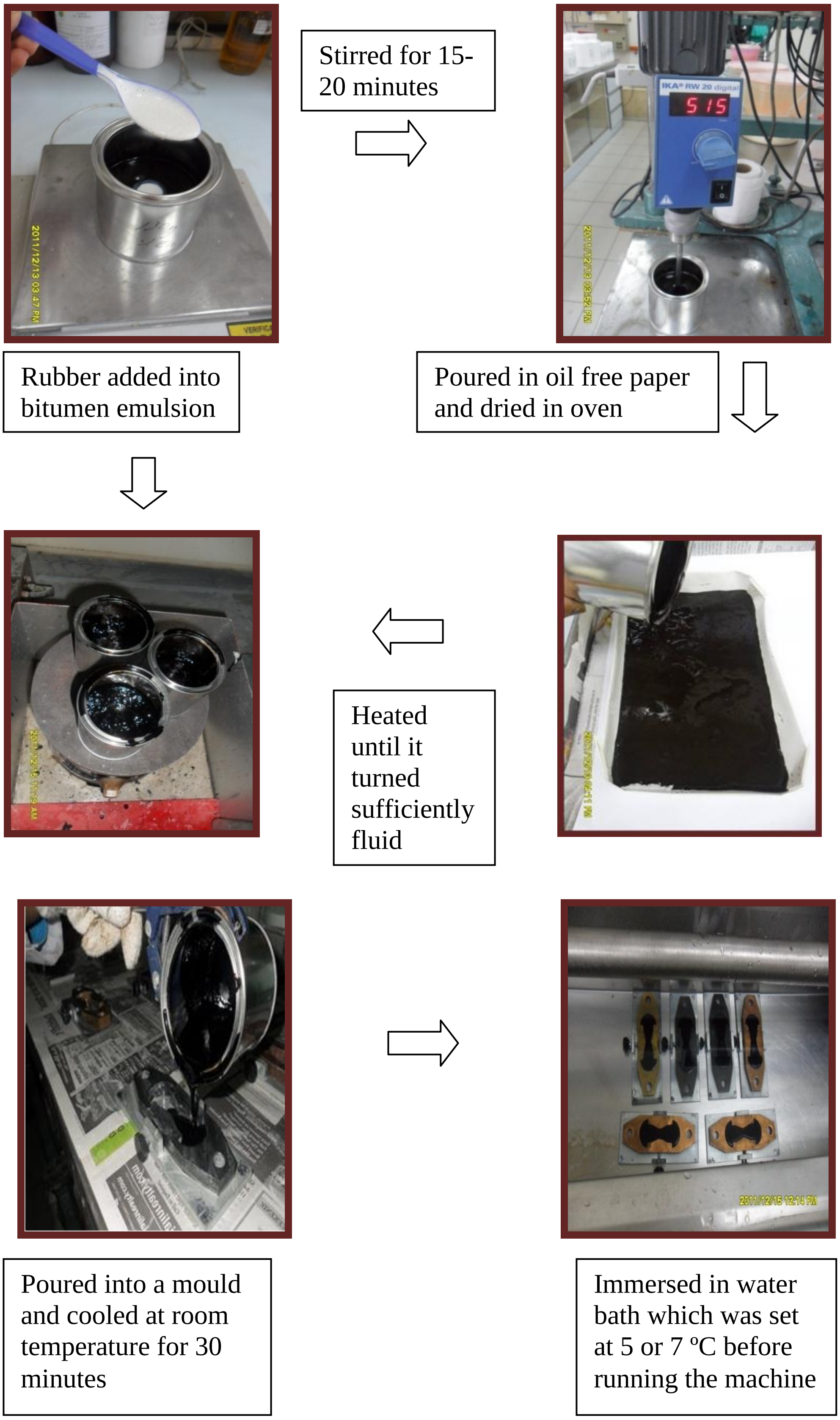


Figure 3.2: Flowchart of preparation of bitumen emulsion-NRL blend

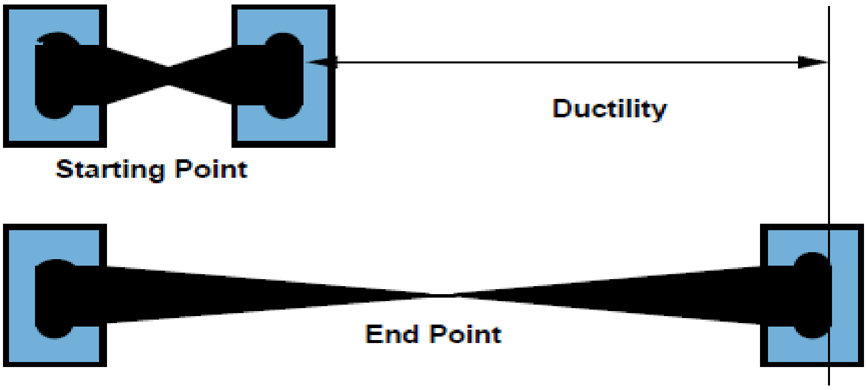


Figure 3.3: Ductility mould and the way of measuring ductility

3.4.3 ER Test Based on ASTM 6084-97

The ER was measured by the percentage to which the rubberized bitumen emulsion will recover based on its original length after it has been elongated to a specific distance (20 cm) at a specified rate of speed (5 mm/min) then cut into halves in the middle. Figure 3.4 briefly explains the ER test.

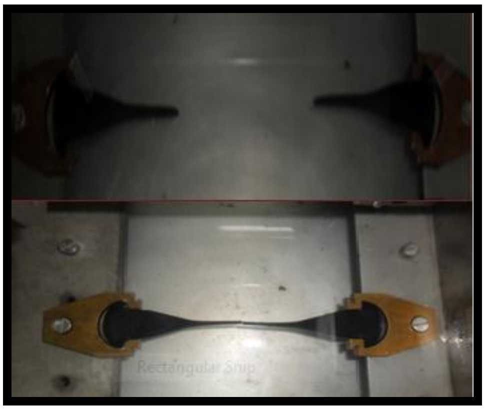
The ER is a measure of the tensile properties of the polymer modified emulsified bitumen. The temperature of the water bath of ductilometer machine was maintained at 7 ºC. The percentage of elastic recovery was calculated by the following formula:

$$\text{Percentage of elastic recovery} = \frac{20 - x}{20} \text{x} 100 \qquad \textbf{Eq.3.1}$$

where x = final reading in cm after bringing the two broken ends together

- The test specimen was elongated to 20 cm at a rate of 5 mm/min
- Then, the testing machine was stopped and the test specimen was held in this stretching position for 5 minutes.

- The testing specimen was cut into halves using a pair of sharp scissors.
- The specimen was left undisturbed for one hour.



- After 1 hour, one half sample specimen was retracted until the two broken ends touched.
- The new pointer reading was recorded in centimetres.

Figure 3.4: Flowchart of ER test of rubberized bitumen emulsion

3.5 Characterization of NR-*g*-PS Latex

Except for mechanical properties, NRL grafted with 25 phr of ST (2.4 mol kg^{-1} NR) at various processing temperature was used throughout the following characterization.

3.5.1 Colloidal Properties Based on ASTM D1076 (ISO9001)

3.5.1.1 Total Solids Content (TSC)

2.5 g ± 0.5 g of latex was poured into Petri dish (W_0). The Petri dish was gently swirled to ensure that the latex covers the bottom of the dish. The content was dried in the oven at 105 ^{0}C for 2 hours. The Petri dish was removed from the oven and allowed to cool at ambient temperature in a dessicator before weighing. The drying procedure was repeated until the loss in mass between two successive weighing is <1 mg (W_1). The results of the duplicate determination shall not differ by more than 0.15 % (w/w) and the average of the two determinations shall be taken as the result. Total solids content was calculated and expressed as a percentage by mass, using the equation below:-

$$\text{Total solid content} = \frac{\text{mass of dried films } (W_1)}{\text{mass of test portions } (W_0)} \text{ x } 100 \qquad \textbf{Eq. 3.2}$$

3.5.1.2 pH

pH meter was calibrated. The electrode was rinsed with distilled water. The sample was stirred thoroughly to ensure that it is homogeneous. The convenient size of the sample was taken and the temperature of the latex was maintained at 23 ± 2 °C by mildly agitating the sample container in a water bath at that temperature. The pH meter electrode was immersed into the latex sample and the reading was recorded. The step above was repeated. If the new reading does not differ from the first by > 0.1 pH unit, the determination is complete. If the two readings differ by > 0.1 pH unit; two further determinations make. The electrode was immersed in a bath of distilled water when not in use.

3.5.1.3 Brookfield Viscosity

The sample was strained through an 80 mesh sieve. The specimen was conditioned to the desired test temperature of 25 ± 2 °C in a suitable bath for a period of 2 hours in order to eliminate air bubbles. The latex sample was poured into 600 ml beaker. Spindle no. 2 was attached onto the viscometer motor shaft and the guard was attached securely to the motor housing of the viscometer. The instrument was tilted slightly while immersing the spindle to avoid tapping air bubbles on the disc surface. The spindle of the viscometer was immersed into the latex until the surface of the latex was at the notch of the spindle. Do not hit the spindle against the side of the beaker while it is attached to the viscometer because it will damage the shaft alignment. A suitable speed (60 rpm) was selected before turning on the viscometer. The viscosity was recorded in centipoise which is equivalent to millipascal. second (mPa.s).

3.5.1.4 Coagulum and Microcoagulum

200 ± 1 grams of latex were accurately weighed into a beaker (W_o) and 200 ml of 5 % potassium oleate solution was added and mixed well. The test filter (80 mesh for coagulum and 300 mesh for microcoagulum) was dried in an oven controlled at 100 ± 5 °C, and the mass was recorded as W_1. The test filter (wire gauze) was clamped between the stainless steel rings and washed with 5 % potassium oleate before the latex/surfactant mixture was poured through it. The residue in the test filter was washed with the same surfactant until it is free from latex, followed by washing with water. The test filter which contains the wet coagulum was removed from the clamp and the underside was swabbed with filter paper. It was then dried together with the wet coagulum/microcoagulum in an oven at 100 ± 5 °C for 30 minutes.

After drying, it was allowed to cool in a dessicator and weighed until the loss in mass between successive weighing is less than 1 mg (W_2). The test was conducted in duplicate. Further two determinations would be carried out if the results of duplicate determination do not agree within 0.01 % (w/w). The amount of coagulum and microcoagulum which is expressed as a percentage by mass of the latex, is calculated by the formula

$$\frac{W_2 - W_1}{W_o} x\ 100 \qquad \textbf{Eq. 3.3}$$

Where,

W_o is the mass, in grams, of the test portion

W_1 is the mass, in grams, of the test filter

W_2 is the mass, in grams, of the test filter plus the dried coagulum

3.5.1.5 Mechanical Stability Test (MST)

If the TSC of the latex is lower than 55 %, MST test is conduct as it is, without any dilution with ammonia solution. 100 g of NRL was warmed with gentle stirring at 36 - 37 °C in a hot water bath. The warmed latex was filtered through a wire mesh (80 mesh size) and 80 ± 0.5 g of the filtered latex was weighed into a container. The temperature of the latex should be around 35 ± 1°C. Without delay, the container was placed in position and the Klaxon machine was started. Meanwhile, the timer was switched on. A tachometer is used to confirm the speed of the stirrer of the machine is fixed at 14000 ± 200 rev/mm.

The end point of the sample was determined by dripping the sample gently on the surface of water contained in a Petri dish at intervals of 15 seconds. The timer was stopped once small pieces of coagulated rubber were deposited. The end point should be confirmed by the presence of an increased amount of coagulated rubber deposition after 15 seconds of additional agitation. The results were recorded in the number of seconds between the commencement of stirring and the end point. The mean of two replicates was calculated. If the results of the duplicate determinations do not agree within 5 % of the mean value, the test shall be repeated.

3.5.2 Free ST Monomer Analysis by Gas Chromatography

Gas chromatography (GC) from Agilent Technologist Model 6820 System was used to quantify the amount of free ST monomer in the grafted sample.

GC conditions were set as follows: Capillary column (DB wax) at 30 ºC, carrier gas helium flow rate of 1.1 ml/min. Flame ionization detector was employed with hydrogen and air flow rates of 40 and 400 ml/min, respectively.

Headspace operating conditions were: 5 min strong shaking for sample equilibration at a temperature of 110 ºC, vial pressurization time of 0.2 min, sample loop fill time of 0.2 min, and loop equilibration time of 0.05 min.

Sample preparation and measurement procedure were as follows: 1 g of modified latex was diluted with 4 g of DI water and 1000 µL of intermediate cyclohexanone was added and mixed well. 1 cc/ml of this mixture was injected into a closed vial by micro syringe and placed in the headspace sample tray for headspace GC measurement.

3.5.3 Grafting Efficiency (Solvent Extraction)

The NR-*g*-PS latex samples were cast onto Petri dish and dried in an oven at 70 ºC for 24 hours. The NR-*g*-PS films consisted of free NR, free homopolymer (PS) and grafted NR were cut into small pieces (5 mm x 5 mm x 0.5 mm). The grafting properties of NR-*g*-PS were determined by double-step extraction. A known weight of the grafted NR film (W_0) was extracted with petroleum ether in a Soxhlet extractor for 24 hours to ensure non-grafted NR was removed from the sample.

After that, extraction the undissolved part of the rubber was dried in oven at 100 ºC for 2 hours and weighed (W_1). It was then extracted by a methyl ethyl ketone (MEK): acetone (50:50) mixture for 24 hours to eliminate the free PS. The final product was dried at 100 ºC for 2 hours and weighed (W_2). The percentage of free NR, free homopolymer and grafting efficiency (GE) were determined according to the equations below:-

$$\text{GE,\%} = \frac{\text{The residual weight after two extractions}}{\text{The total weight of polymer formed}} \times 100 \qquad \textbf{Eq.3.4}$$

$$\text{\% of free NR} = \frac{W_1 - W_0}{W_0} \times 100 \qquad \textbf{Eq.3.5}$$

$$\text{\% of homopolymer PS} = \frac{W_2 - W_1}{W_1} \times 100 \qquad \textbf{Eq.3.6}$$

3.5.4 FTIR Analysis

Fourier transform infrared spectrophotometer was used to determine the functional groups of grafted NR. The infrared spectra were obtained by using a Thermo Fisher Avatar 360 spectrophotometer in a range of 4000-400 cm^{-1}, with the scan time of 20 and resolution of 4 cm^{-1}. Samples were prepared by casting latex film of 1 mm thickness on AgCl cell and dried.

3.5.4 Mechanical Properties (ASTM D412)

Dumbbell shaped specimens (25 mm x 6 mm) were punched out from the dipped film using a C-type die. Thickness gauge was used to measure the thickness of the film. The physical property of unaged NR-g-PS film was tested using Testometric M350-5kN tensiometer, at a crosshead speed of 50 mm/min. The tensile strength, modulus at 100 % elongation and elongation at break of the samples were determined with the operation condition at 25 ºC and 45-55 % relative humidity according to ASTM D 412 specification. Five specimens were tested for each property and average of these values was reported.

3.5.4.1 Preparation of Test Specimen for Physical Testing

The dip-foam (glass plate) was washed with liquid detergents and dried in an oven at 70 ºC for 2 minutes. The latex samples were stirred well with perforated stirrer before use. 900 ml of well mixed latex was sieved through a 120 mesh sieve into a 1000 ml beaker. The latex was decanted into mini dipping tank from the beaker. The mini dipping tank was covered and allowed undisturbed for at least 1 hour.

Aqueous calcium nitrate solution (50 %) was stirred gently. The glass plates were immersed to a depth of 16 cm and withdrawn immediately (Make sure that the glass plate was covered well with coagulant). The dipped form was left in inverted position by clamping on a retort stand to drain off the excess coagulant and the tip of glass plate was wiped with tissue paper to clear off the excess coagulant. The dipped form was dried at 70 ºC for 2 minutes.

Pieces of paper were used to skim the surface of latex in the mini dipping tank in order to remove the air bubbles and skin formed on the surface. The glass plate was immersed into the latex and dwelled there for 35 seconds. The depth of immersion of the glass plate into the latex is about 16 cm. The glass plate was withdrawn slowly and steadily in order to obtain an even film. Then, the dipped form was clamped on a retort stand in inverted position to drain off the excess latex for 1-2 minutes.

Both the lower corners of the dipped latex were pinched off for better leaching before drying in an oven at 70 ºC for 2 minutes. The partially dried film was leached in warm DI water (50-60 ºC) for 15 minutes before the dipped latex film was further dried in an oven at 70 ºC for 4 hours. The latex film was conditioned in the tensile room at 21 ± 2 ºC with a humidity of 45-55 % for a maximum of 20 hours before tensile testing.

3.5.6 Thermal Studies

Two techniques were used to study the thermal behaviour of NR-*g*-PS. They were thermogravimetric analysis **(**TGA) and Differential Scanning Calorimeter (DSC).

3.5.6.1 Thermogravimetric Analysis (TGA)

TGA is a technique in which the mass of a substance is monitored as a function of temperature or time as the sample specimen is subjected to a controlled temperature program in a controlled atmosphere. Thermogravimetric analyses were carried out using the Mettler Toledo (TGA/SDTA851) themogravimeter. Samples (~2.5-5.0 mg) in alumina crucible were heated at a constant heating rate of 10 °C min^{-1} at temperature ranges between 25 and 600 °C. The measurements were performed with a nitrogen gas flow rate of 20 ml min^{-1}. The temperature at which the rate of mass loss at its maximum was determined from the differential thermogravimetry (DTG) curves and the decomposition temperature (T_{max}) were obtained.

3.5.6.2 Differential Scanning Calorimeter (DSC)

The thermal behaviour of unmodified and modified NRL was studied using a Mettler-Toledo 823DSC thermal analyzer. The heating and cooling rate was 10 ºC min^{-1}. About 2.5 - 5.0 mg sample of a dried latex film was placed into an aluminium pan. The unmodified or modified rubber was first cooled in a cell to -100 ºC by means of a refrigerated cooling system and then heated up to 150 ºC. The midpoint of the baseline shift was taken as the glass transition temperature (T_g).

3.5.7 Equilibrium - Swelling Test (Modified from Blackley 1997b)

The NRL was mixed well with some colour dye. A thin rubber film was coated on a glass plate using wire coater. The film was dried at room temperature. Talc or corn starch powder was applied to facilitate the remove of rubber film. Circular die punch with a diameter of 25 mm was used to punch the powdered film. Petri dish containing 20-30 ml of toluene was placed on a calibrated graph paper. The round film was placed into the Petri dish which was covered with a watch glass. The circular film was immersed in the solvent for 20 minutes. After 20 minutes of immersion, the diameter of the film was measured by reading the graph paper underneath the Petri dish. The percentage of swelling of the film was calculated based on the equation below:-

$$\text{Percentage of swell} = \frac{\text{swollen diameter} - \text{unswollen diameter}}{\text{unswollen diameter}} \text{ x } 100\ \%$$

The relation of percentage of swell with crosslink density for NR film in toluene is broad as given in Table 3.3.

Table 3.3: Categories of crosslink density based on percentage of swell

Categories	**Percentage of swell**
Unvulcanized	160 %
Light vulcanized	100-160 %
Moderately vulcanized	80-100 %
Fully vulcanized	75 %

3.5.8 Morphology Analysis

The morphology of the latex samples was determined using Field Emission Scanning Electron Microscopy (FESEM Model JEOL JSM-6701F). The test portion of samples was stained with 2 % osmium tetraoxide. Excess osmium tetraoxide solution was removed from the latex by centrifugation process. The staining not only enhanced the contrast for the microscope viewing of' the NR-*g*-PS but also hardened the rubber phase. Latex stains with osmium tetraoxide were placed onto the specimen stub with aluminium tape and fractured in liquid nitrogen to avoid the possibility of phase deformation.

Specimen was then prepared for examination by evaporative coating with ultra-thin layer of platinum under high vacuum. This provided a conducting layer that permits SEM examination. SEM was operated at 5KV, with 15 mm working distance and was tilted at 0° viewing angle.

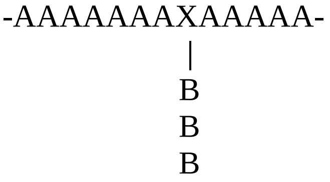
CHAPTER 4.0

RESULTS AND DISCUSSION

4.1 Grafting

Grafting is a process that allows for the development of new materials that feature unique properties. The introduction of new functional groups on a substrate surface improves properties such as hydrophilicity, adhesion, biocompatibility, conductivity and antifogging, among others.

A graft copolymer is a polymer comprising molecules with one or more species of blocks connected to the main chain as side chains, having constitutional or configurational features that differ from those in the main chain, exclusive of branch points in a graft copolymer. The simplest case of a graft copolymer can be represented by structure, where a sequence of A monomer units is referred to as the main chain or backbone, the sequence of B units is the side chain or graft, and X is the unit in the backbone to which the graft is attached.



$$-\mathrm{AAAAAAA}\underset{\substack{|\\ \mathrm{B}\\ \mathrm{B}\\ \mathrm{B}}}{\mathrm{X}}\mathrm{AAAAA}-$$

In graft copolymers the backbone and side chains may both be homopolymeric, the backbone may be homopolymeric and the side chains copolymeric or vice versa, or both backbone and side chains may be copolymeric but of different chemical compositions. Branching in one or more stages and cross-linking may also occur. Cross linked structures usually cannot be fully characterized because they are insoluble and frequently infusible (Riess et al., 2002).

4.2 Preparation of NR-*g*-PS Latex

Chemical modification of NR by grafting with vinyl monomers with various initiator systems has gained considerable importance in the modification of the properties of NR (Schneider et al., 1996; Arayapranee et al., 2002; Anancharungsuk et al., 2007). In this work, NR-*g*-PS was synthesized via emulsion polymerization, using bipolar redox initiator.

4.2.1 Centrifuged NRL

Chemical grafting in an aqueous dispersion or emulsion such as in the latex form has several advantages than in dry state, with the following reasons:

a. Homogeneous distribution of monomer in rubber
b. The rate of grafting can be expected to be higher than that in dry state due to the influence of the free radicals generated in water phase which diffuse more easily to polymer particles.

Core–shell particles may be prepared by graft copolymerization of NR in latex form because NR, an unsaturated elastomer with double bonds in its chains, can be readily grafted with a variety of monomers with the well-established technique of seeded emulsion polymerization. Latex particles with a soft core and a hard shell are modified as impact modifiers, whereas particles with a hard core and a soft shell are usually used in the coating and adhesive fields (Zhao et al., 1994). The graft copolymers of different vinyl monomers, such as methyl methacrylate (MMA or $C_5H_8O_2$) or styrene (ST or C_8H_8) onto NR, comprising an inner soft polymer sphere, the core, and an outer hard polymer, the shell, can be expected to have better impact-resistance properties (Arayapranee and Rempel, 2008).

Before the grafting reaction was started, the pH of the centrifuged NRL was increased to above 10. It has been found that the stability of graft copolymerization became better when the pH value of the reaction system was increased by adding concentrated ammonia. With the addition of ammonia, the degree of hydrolysis and solubility of amine group are reduced and thus flocculation of amine group would decrease (Liu and Yang, 2003).

Most vinyl polymerizations are sensitive to oxygen which frequently causes induction period and retardation. In this work, dissolved oxygen from centrifuged NRL was not removed by nitrogen purging. Therefore, it might have affected the grafting efficiency of the reaction mixture at elevated temperatures with consequent bubble formation.

4.2.2 Monomer

This experiment was concentrated on free radical graft polymerization of monomers onto NR in NRL, where the NR particles served as the seed particles and the monomer was added in an emulsion form. There are basically two possible states in which the free radical graft copolymerization could occur. In one state, monomers such as butyl acrylate are hardly soluble in NR particles. Butyl acrylate normally has a maximum solubility of only 3 phr in rubber particles. In this state, the monomer is largely located in the monomer droplets, and polymerization occurs in the water phase (Wang, 1996). In another state, monomers such as ST and MMA are fully soluble in NR particles. In this state, the monomer is largely located inside NR particles, with only a small amount of it found in water (Fried, 1995; Brandrup and Imergut, 1995).

ST was chosen for graft polymerization with NR in this study in view of the fact that the modified NRL would be blended with bitumen emulsion which contained aromatic compounds for ductility test.

Another reason for choosing ST as the monomer is that, the reactivity of the polystyryl radical is about the same as the polyisoprenyl radical with both of them stabilized by resonance (Arayapranee and Rempel, 2004). The chemical nature of isoprene is similar to ST; this leads to the assumption that grafting can take place via abstraction or addition of a hydrogen atom from the polymer backbone as shown in Figure 4.1 (Arayapranee et al., 2003; Arayapranee and Rempel, 2004).

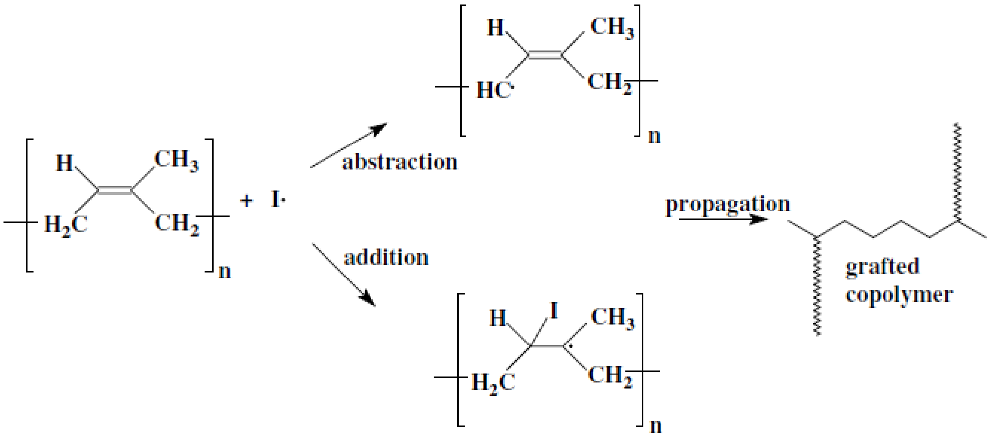


Figure 4.1: Abstraction and addition reactions which can lead to grafting in a system with labile hydrogen

Non-purified monomer exhibited a slight increase of free homopolymer and hence a slight decrease of grafting efficiency (Kalkornsurapranee et al., 2009). Therefore, in this work purified ST monomer was used to produce NR-*g*-PS latex. Purified ST monomer was supplied by Synthomer (M) Sdn. Bhd.

Man et al. (2008) grafted 10-30 wt % of MMA and ST monomer mixture (50:50 ratio) onto DPNR latex to prepare ST-MMA grafted DPNR latex. Nakason et al. (2003 and 2006) grafted 5-40 % molar ratios of MMA to NR. ST-feed of 1.5 (Pukkate et al., 2007; Suksawad et al., 2011), 3.0 (Arayapranee and Rempel, 2008), 5.5 (Suksawad et al., 2011) and 6.0 mol/kg-rubber (Arayapranee et al., 2008; Suksawad et al., 2011) were used to prepare NR-*g*-PS latex. Kawahara et al. (2003) reported that NR particles with about

0.5 µm in diameter were dispersed in a PS matrix of 1.5 mol ST per kg of DPNR to carry out the graft copolymerization which was initiated by TBHPO/TEPA at 30 °C. In this work, 3-45 phr of ST monomer was used to graft onto NRL to prepare the graft copolymer.

4.2.3 Emulsifier

Usually SDS or oleic acid is used as emulsifier to prepare NR-*g*-PS latex. The surfactant has two functions: first, as an emulsifier for the monomer prior to synthesis, and second, to provide colloid stability to the final product. Direct addition of vinyl monomer can cause instability in NRL. NRL might gel or coagulate if a hydrophobic monomer is added directly. Thus, it is important to add emulsifier to the monomer in order to stabilize the latex. The presence of emulsifier can avoid coagulation and renucleation of particles. In this work, different types of anionic emulsifiers were tried in order to find the most powerful and stable emulsifier in a wide range of pH and applications.

The excess use of an emulsifier can lead to the formation of particles that composed entirely of the PS homopolymer. As found in literature, only 1-2 parts per hundred rubbers (phr) of emulsifier is needed to prepare NR-*g*-PS or DPNR-*g*-PS. According to Arayapranee et al. (2003), the emulsifier has little effect on the grafting efficiency when the amount of the emulsifier used was between 1 phr and 2 phr. The amount of emulsifier used in this work was less (< 0.5 phr) than that reported in literature.

4.2.4 Redox Initiator

A redox-initiating system consisting of TBHPO or CHPO and TEPA proved to be very effective for emulsion polymerization in NRL. This initiation system is not sensitive to oxygen and works well in the presence of ammonia (Schneider et al., 1996; Nakason et al., 2003; Arayapranee and Rempel, 2004). Bipolar redox initiator couple consisting of TBHPO and TEPA was used to promote core-shell morphology (Schneider et al., 1996). Schneider and co-workers used 1:1 ratio of TBHPO and TEPA while in this work 1.6:1.0 ratio was used. Higher concentration of initiator yields lower latex molecular weight.

ST monomer and the initiator were emulsified with an anionic emulsifier before they were added into NRL. This was to prevent the NRL from flocculating. After adding the mixture of emulsifier/monomer/initiator to the diluted NRL (45 % TSC), the mixture was left undisturbed for 2 hours at a specified temperature. This was to allow ST monomers to swell in the NR particles before grafting was initiated. Then, the co-initiator TEPA was added to initiate the grafting reaction. TEPA was diluted to 10 % with distilled water before use.

4.2.4.1 Grafting Mechanism by Redox Initiator

Reactions involving free radicals have been most widely apply in grafting processes, and such reactions have been used with a wide range of polymers and monomers (Lehrle and Willist, 1997; Kumar and Kothandaraman, 2008). In the grafting reaction of monomer onto NR, the locus where polymerization occurs is of much importance. The initiators initiate the reaction via two loci in the mixture (Kochthongrasamee et al., 2006):-

a. Partition of the initiator between the monomer-swollen NR and the aqueous phase is different for each initiator.
b. Partition nucleation in the aqueous phase could take place

In the preparation of the grafted NR, initiation of polymerization is due to free radicals produced by the interaction of CHPO / TBHPO dissolved in the monomer swollen rubber particles and TEPA in the aqueous phase of the latex. With such a hydrophobic– hydrophilic catalyst combination, it is probable that the CHPO / TBHPO decompose to yield alkoxy radicals (RO•) formed at the particle–water interface, which would interact with the monomer or the rubber molecule producing a macroradical that initiates grafting (Arayapranee and Rempel, 2004).

For the PIP molecule, the two methylene groups in the isoprene residue are not equivalent and it seems likely that the attack occurs preferentially at carbon 4, so that the methyl group exerts the greatest stabilizing influence on the resulting allylic radical. In the grafting system, the attack of the alkoxy radical on *cis*-PIP most likely occurred by chain transfer to form the polyisoprenyl radical. The reactivity of the polystyryl radical is about the same as that of the polyisoprenyl radical (both are stabilized by resonance) (Arayapranee and Rempel, 2004).

The alkoxy radicals not only can add to double bonds or abstract *α*-methylenic hydrogen atoms to produce polyisoprenyl radicals, but also initiate monomers to form polymeric radicals, which combine with polyisoprenyl radicals. Some of the free polymer radicals would form free copolymers (Arayapranee and Rempel, 2004). Figure 4.2 explains the possible reaction sites in the modified NRL in the bipolar redox initiation systems.

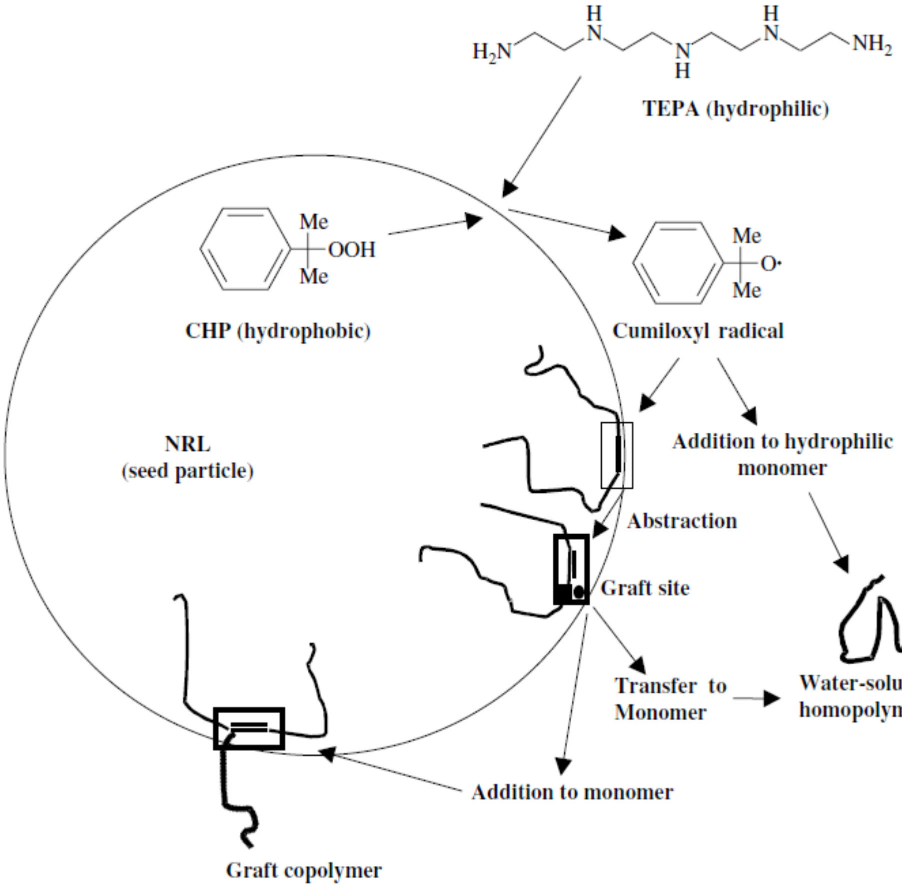


Figure 4.2: Possible reaction sites in the modified NRL in the bipolar redox initiation system (Arayapranee and Rempel, 2004)

The following reaction scheme is proposed for the graft polymerization of vinyl monomers onto NR by free-radical method.

Initiation:

Attacking monomer: $RO^{\bullet} + M \rightarrow M^{\bullet}_1$

Attacking rubber: $RO^{\bullet} + NR\text{-}H \rightarrow NR^{\bullet} + ROH$

Reinitiation: $NR^{\bullet} + M \rightarrow NR\text{-}M^{\bullet}_1$

Propagation:

Propagation of free polymerization: $M^{\bullet}_1 + nM \rightarrow M^{\bullet}_{n+1}$

Propagation of graft polymerization: $NR\text{-}M^{\bullet}_n + nM \rightarrow NR\text{-}M^{\bullet}_{n+1}$

Chain transfer to macromolecules:

Transfer to monomer: $M^{\bullet}_n + M \rightarrow M^{\bullet}_1 + M_n$

$NR\text{-}M^{\bullet}_n + M \rightarrow M^{\bullet}_1 + NR\text{-}M_n$

Transfer to rubber: $NR\text{-}M^{\bullet}_n + NR\text{-}H \rightarrow NR^{\bullet} + NR\text{-}M_nH$

$M^{\bullet}_n + NR\text{-}H \rightarrow NR^{\bullet} + M_nH$

Termination:

Free copolymers : $M^{\bullet}_n + M^{\bullet}_m \rightarrow M_{n+m}$

Graft copolymers : $NR\text{-}M^{\bullet}_n + NR\text{-}M^{\bullet}_m \rightarrow NR\text{-}M_{n+m}\text{-}NR$

Graft copolymers : $NR\text{-}M^{\bullet}_n + M^{\bullet}_m \rightarrow NR\text{-}M_{n+m}$

Here, $RO^{\bullet}$ represents the initiating free radical. M and $M_n^{\bullet}$ are the monomer and monomer radical. NR and $NR^{\bullet}$ and $NR\text{-}M_m^{\bullet}$ are PIP, PIP radical and grafted PIP.

4.2.5 Addition of TMTD to NR-*g*-PS

TMTD is an organic accelerator and sulfur donor. Figure 4.3 shows the structure of TMTD. The addition of TMTD dispersion into the NR-*g*-PS latex at the end of the process is to maintain the viscosity and stability of the graft copolymer during storage. When TMTD is used without sulfur the amount incorporated should be 2.5 to 3.5 parts by weight, calculated based on 100 parts of rubber (Hofmann, 1967). However, the amount used in this work was 0.04 phr, which was very much lesser than the amount recommended.

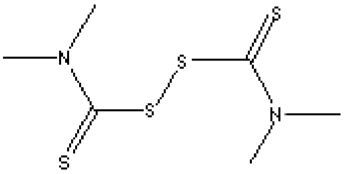


Figure 4.3: Structure of TMTD

Initially, centrifuged NRL contained low amount of TMTD and ZnO. TMTD dispersion could react with ZnO from the unvulcanized NRL and form zinc dithiocarbamate, or TMTD splits up into two dithiocarbamate acid radicals in a vulcanization temperature. It has been confirmed in several occasions that dithiocarbamate residues are bound to rubber hydrocarbon chains. TMTD without the presence of sulfur could form C-C crosslinking to

NR. Thiuram vulcanizate based on *cis*-PIP is completely soluble after a curing time of 15 minutes. Modern opinions are now beginning to assume that the crosslinks are sulfur bridges, whose structure are more uniform than the compound which is cross-linked with sulfur. Without the participation of ZnO, thiuram crosslinking is almost impossible (Hofmann, 1967).

4.3 Structure of NR-*g*-PS

The graft copolymer of NR-*g*-PS consists of two structurally different polymer chains, namely rigid PS and rubbery NR segments in the same molecule as portrayed in Fig. 4.4 (Nanthaporn et al., 2008).

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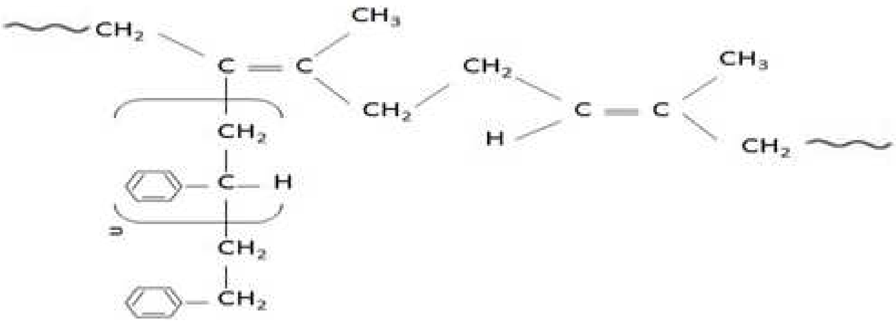


Figure 4.4: NR-*g*-PS structure (Nanthaporn et al., 2008)

4.4 Pre-treatment of Modified NRL

NR-*g*-PS latex is anionic. NR-*g*-PS latex particles need to acquire the same surface polarity as the particles in cationic bitumen emulsion, in order to mix well without forming coagulates. Hence, pre-treatment such as charge conversion, enzyme treatment and acidification of NR-*g*-PS is required.

4.4.1 Charge Conversion of NR-*g*-PS

As a part of a colloid stabilization system the ammonia-preserved NRL comprises proteinaceous substances which are anionic in alkaline medium and cationic in acidic medium (Blackley, 1995a). Usually NRL particles are negatively charged. However, it is possible to reverse the charge on NRL particles by rapid acidification. According to Blackley (1995a), reversal of charge polarity by acidification is not feasible for conventional synthetic lattices, because the colloid stabilizer used is not amphoteric.

NR-*g*-PS latex particles need to acquire the same surface polarity as the particles in cationic bitumen emulsion. Therefore, excess amphoteric surfactant (LCU) was added into anionic NR-*g*-PS latex and mixed well before undergoing acidification. Figure 4.5 shows the structure of surfactant LCU. Surfactants influence the interactions of the particles with other materials, such as cationic bitumen emulsion, to which the latex is added. Excessive use of surfactants can cause a reduction in water resistance and adhesion.

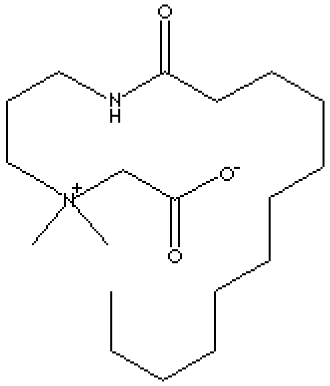


Figure 4.5: Structure of Surfactant LCU (Lauryl aminopropylbetaine)

So these positively charged NR-*g*-PS latex particles repel with the positively charged cationic bitumen emulsion. Cationic NR-*g*-PS latex is able to mix well with cationic bitumen emulsion without forming coagulates.

4.4.2 Enzyme Treatment

Certain enzymes, when added to NRL, have the ability to chemically digest the proteins, reducing them to smaller units and rendering them unable to cause allergic reactions. This enzyme treatment of NRL is in use today, but not universally (Perrella et al., 2002).

Alcalase is a liquid enzyme preparation containing a protease which is suitable for use in high temperature and moderate pH. Proteases are produced from the fermentation of selected nonpathogenic strains of bacteria. Proteases are a form of hydrolytic enzymes that cleave peptide bonds.

The enzyme treatment of NRL alters the antigenic proteins associated with NRL by cutting them into smaller pieces and rendering them less immunogenic. The use of proteolytic enzymes to digest NRL proteins has broad application in the rubber industry. Chemists at Synthomer (M) Sdn. Bhd. blend enzyme and non-eznyme treated NRL with bitumen emulsion before testing its ductility at low temperature. They have found that enzyme treated NRL gave slightly higher ductility at 5 °C. This was the main reason for maintaining this particular step in this study.

4.4.3 Acidification of NR-*g*-PS Latex

Acidification of NRL can be done with various types of acid. According to Synthomer's NR Technical team, acetic acid can be used to acidify NR-*g*-PS latex but it will produce rotten egg smell during storage. Therefore, we avoid using acetic acid for acidification purpose. According to Siti Maznah et al. (2008), acidified NRL with different pH value gives different values of extractable protein. Therefore, the pH value of the acidified latex was fixed between 5.0-5.5 to make it similar to the pH of cationic bitumen emulsion.

Treating NRL with acid denatures the proteins, making them insoluble by reducing protein solubility (Siti Maznah et al., 2008). Siti Maznah and coworkers (2008) stated that the extractable protein content of the films was reduced with reducing pH. The crosslink density, tensile strength and the elongation at break of acid treated films were slightly lower than that of the untreated films.

4.5 Preparation of Cationic Bitumen Emulsion/ NR-*g*-PS Blend

Polymer modified bitumen emulsion are normally produced with 80/100 penetration grade bitumen. NRL consists of polymerized isoprene monomers will increase the elasticity of bitumen. However, NRL is more sensitive to heat and is therefore mainly used in the modification of cold bituminous binder. For cold applied products, the rheological properties of bitumen emulsion can be modified either by pre-modification or by post-modification of the bitumen emulsion (Road Pavement Forum, 2007).

“Ralumac” is Revertex1497C/HS modified cationic bitumen emulsion found in the market. For “Ralumac” preparation, NRL is added into cationic bitumen emulsion through either pre- or post-blending method. Revertex 1497C/HS is mixed with emulsifier acid in aqueous phase and then converted to cationic bitumen emulsion in the pre-blending method. This product allows NRL to be used in both batch and continuous bitumen emulsion plants (Ruggles, 2005). In this work, cationic NR-*g*-PS was blended with cationic bitumen emulsion through post-blending. In South Africa, post-modification of bitumen emulsion is the most popular practice (Road Pavement Forum, 2007).

Some rubber particles are absorbed by bitumen, but most of them are only partially digested and hence increase the viscosity of the bitumen dramatically. Digestion of rubber is a continuous process which occurs at higher rate at higher temperature. NRL modified bitumen emulsions are sensitive to heat. They can undergo significant changes in their properties if they are exposed to high temperature for extended period as this could lead to degradation and/or separation of NRL from the base bitumen. Hence, improper heating of the samples can affect the properties of the binders and provide non-representative results of the actual modified bitumen (Road Pavement Forum, 2007). To avoid disparity in test results, it is important to ensure that the modified bitumen emulsion samples undergo a minimum and controlled amount of heating.

In literature, high shear mixer (3000-5000 rpm) with shearing time of 40-50 min and mixing temperature of 160-175 °C is used to prepare SBR modified bitumen (Zhang et al., 2009 ; Zhang and Yu, 2010). In this study, mechanical stirrer with 500 – 550 rpm was used to blend bitumen and NR-*g*-PS mixture at 28 °C. After drying, the bitumen- ST grafted NR mixture was heated at 100-120 °C for 20 minutes in an aluminium container until it has become fluid; the stirring speed used was 400 rpm. The use of mechanical stirring will prevent the segregation of different components during storage (Road Pavement Forum, 2007).

Shorter mixing time and lower temperature required in post-blending are convenient to be carried out in bitumen plant or field. The method for adding cationic NR-*g*-PS latex to bitumen is very simple. Moreover, processing NR in latex form is low cost, fast, highly efficient and, most importantly, safe. Other than that, it saves energy and it is eco-friendly.

On blending two lattices, it is not uncommon for some destabilization and flocculation of one or both of the lattices to occur. This could happen with cationic NR-*g*-PS latex and a bitumen emulsion. In practice, such an effect is normally accompanied by a significant change in viscosity. However, there was no change in viscosity after NR-*g*-PS was blended with bitumen.

When cationic NR-*g*-PS latex was blended with a cationic bitumen emulsion, there was no evidence of a major emulsion incompatibility. The NR-*g*-PS latex was compatible with cationic bitumen emulsion. There was no phase separation observed after blending. The degree of compatibility varies with bitumen and the type of polymer used in the formulation of the polymer modified sample. Compatibility also varies with the concentrations of the polymer. The higher the concentration of the polymer, the lower the degree of compatibility will be (Road Pavement Forum, 2007).

No phase separation of the styrene grafted latex from bitumen was observed during the cooling process. However, microscopy observation is needed to confirm the homogeneous distribution of rubber particles in bitumen emulsion. For this work, SEM analysis could not be done because the dried rubberized bitumen emulsion form bubbles during the analysis even with the lowest accelerating voltage.

Modern theory states that NR is believed to form a foam-like lattice structure within the bituminous phase. This lattice structure forms irrespective of how rubber and bitumen are blended. However, other experiments found that NR only shows its effect on the modified bitumen when it is fused with bitumen, forming a ‘gel’ state (Ruggles, 2005).

The introduction of a proprietary modified NRL suitable for direct addition to cationic bitumen emulsions has increased its use enormously.

4.6 Ductility of NR Modified Bitumen

The ductility of bitumen is expressed as the distance in centimeters by which a standard briquette can be elongated before the thread breaks under the conditions specified. Ductility test is utilized as a measure of the cohesive strength of the bitumen. Cohesion is a measure of the tensile stress required to break the bond between the molecules in bitumen and the polymer used for the modification (Road Pavement Forum, 2007). Low-temperature ductility is an important property of paving bitumen, which is very much related to the low-temperature resisting cracking property of pavement (Zhang and Yu, 2010).

4.6.1 Effect of Amount of ST Monomer

ST monomer from 3 to 45 phr was used to graft onto NRL. However, literature shows that 20-25 wt % ST was used with SBR. The recipe used to prepare NR-*g*-PS latex with 3 phr of ST monomer is shown in Table 4.1. Table 4.2 shows the ductility results of bitumen modified with NR grafted with various amounts of ST and Figure 4.6 shows the graph of the results obtained. The ductility value increased as the amount of ST monomer increased from 3 phr to 25 phr. Ductility value decreased significantly, from 20.3 cm to 15.5 cm, when the ST amount in NR-*g*-PS latex was further increased from 25 to 45 phr.

Table 4.1: Recipe of 3 phr of NR-*g*-PS latex (sample SG3)

Formulation	SG3 (gram)
Part A	
NRL (matured)	663.70
Ammonia	69.90
DI water	154.10
Part B	
ST	**11.75**
Emulsifier	2.31
TBHPO	1.97
CHPO	-
Part C	
TEPA	0.63
DI water	5.67
Part D	
TMTD	0.60

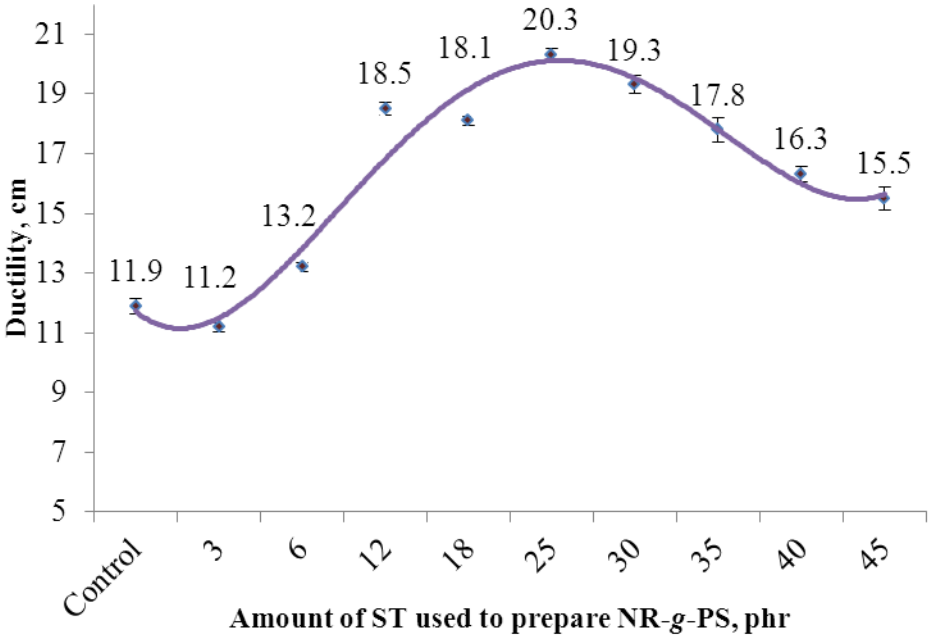


Figure 4.6: Effect of amount of ST monomer on ductility of bitumen-grafted NR blend (Control was bitumen emulsion alone)

The bitumen emulsion-styrene grafted NR blend looked like chewing gum at the mixing temperature of around 90 - 100 °C. During the ductility testing at 5 °C, the bitumen emulsion- styrene grafted NR blend with 25 to 45 phr ST had been pulled out from the mould. Therefore, repeated test on these samples were carried out to obtain average readings. Bitumen-modified NR developed a chewing gum characteristic consistently with the tendency of being pulled out from the mould during testing. This is presumably due to the blend was very high in modulus.

Overall, bitumen emulsion modified with NR-*g*-PS gave higher ductility than base bitumen (Control). At lower temperature, where the base bitumen could not sustain large extensions and the NR-*g*-PS enhanced the flexibility of the bitumen and thus the ductility increased. The inherent strength, tenacity and toughness of the bitumen emulsions were improved by modification with NR-*g*-PS. Hence, greater force or tensile stress is required to break the molecular bonds of modified bitumen emulsion. Ductility is a property of bitumen which is partly related to its ability to flow (Morgan and Mulder, 1995). It is therefore not surprising that NR-*g*-PS modified bitumen did not necessarily lead to higher ductility value.

The addition of NR-*g*-PS latex to bitumen made a significant change to its properties even at fairly low concentrations. NRL grafted with 25 phr ST gave the highest ductility value at low temperature and eventually met the main objective of this research work. The improvement in ductility could be due to the presence of ST or due to the peroxide grafting. For the latter, if there was any un-reacted TBHPO after the ST grafting, it could form cross-linking or grafting in between NR-*g*-PS latex and bitumen. However, the ductility decreased when the amount of ST decreased from 25 phr to 3 phr, while same amount of peroxide was used in the formulation. This indicated that residual peroxide in the system was not the main cause for the improvement in ductility.

Another reason that the ST level may be important could be related more to the nature of the NR-*g*-PS latex. The grafting technique is very likely to result in a graft block copolymer together with some free PS. This block copolymer structure could well mimic and results in it being very similarly to an SBS block thermoplastic elastomers. SBS is widely used as an effective modifier for hot melts bitumens, with the phase separated PS domains acting as physical, pseudo cross-links for the rubber chains. The effectiveness of phase separation and hence the influence of pseudo cross-linking on SBS performance decreases markedly if the ST content in an SBS is below 15 wt % and molecular weight of the PS blocks drop much below ca. 10, 000.

The properties of the blend of bitumen and thermoplastic polymer depend on the amount and size of the asphaltenes, the amount and size of the modified latex and the aromaticity of the maltenes phase (Morgan and Mulder, 1995). Therefore, the ST content in the grafted NR indirectly influences the maltenes phase of modified bitumen. Excess aromatic compound in bitumen-ST grafted blend could affect the properties. NR grafted with more than 25 phr ST showed a decrease in ductility which was likely due to excessive content of

ST. In conclusion, 25 phr of ST was the optimum level to graft on NR to improve the ductility of the blend.

4.6.2 Effect of Acidification of NR-*g*-PS

According to Lesueur (2009), bitumen could be reacted with other compounds such as sulfur, chlorine or various acids (nitric, acid sludge, fatty acids and so on) in normal storage tank. Cationic emulsifiers in cationic bitumen emulsion are typically mono-, di- or polyamine derivatives of fatty acids and may be functionalized by ethoxylation. The emulsifier must be mixed and reacted with acid to attain water solubility. The emulsifier solution is prepared by reacting the emulsifier with dilute hydrochloric acid (HCl) or acetic acid, with the pH of the solution being carefully controlled so as to produce the amine salt as below (Morgan and Mulder, 1995):-

$$R\text{-}NH_2 + HCl \rightarrow R\text{-}NH_3^+ + Cl^- \quad \ldots\ldots\ldots\ldots\ldots \textbf{Eq. (4.1)}$$

Fatty amine + hydrochloric acid → amine hydrochloride

Most of the bitumen plants used HCl to dilute the cationic emulsifier. Ruggles (2005) added 0.15 and 0.5 % of HCl, emulsifier, Revultex 1497C latex and water into bitumen. The concentration of HCl used by Ruggles was 36 %. Some bitumen plants do add latex to soap tank prior to emulsification, of course it is best if soap, emulsifier and acid are added first before latex is discharge into soap. Therefore, acidification of NRL can be an important part to improve its compatibility with cationic bitumen emulsion.

Acidification of NRL can be done with various types of acid. Nitric acid (HNO_3) and HCl were used in this study. Acetic acid can also be used to acidify NRL but it produces rotten egg smell during storage. Therefore, acetic acid was avoided in this work.

Concentrated HCl acid (33-35% w/v) is far too corrosive and irritating since it fumes owing to the high volatility of the HCl gas, thus rendering it practically too hazardous to handle in ordinary use without adequate safety measures. Therefore, it was necessary to try out varying dilutions of the acid so as to ascertain the highest concentration, which could be conveniently used without being too hazardous. The concentration was found to be 17-20 % (w/v); at which concentration there is no unbearable fuming. The final concentration used was fixed at 17 % (w/v).

Among the NR-*g*-PS latex, 25 phr ST monomer grafted latex gave the highest ductility value in both acid media of HCl and HNO_3. Table 4.3 and Figure 4.7 show that the ductility of NR-*g*-PS latex which was acidified with HCl was generally higher than that with HNO_3. This could be due to that the acid used in both the modified NRL and cationic bitumen emulsions are of the same type that they are able to form compatible blending mixture.

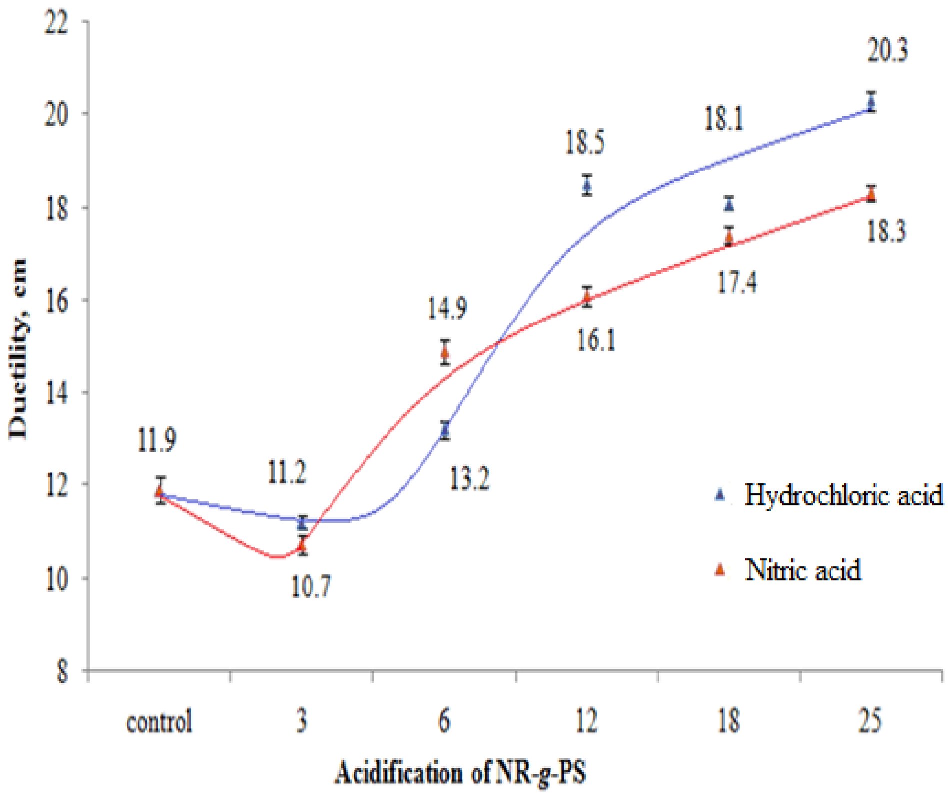


Figure 4.7: Effect of acidification of NR-*g*-PS (Control was bitumen emulsion alone)

Another reason could be that HCl is stronger than HNO_3. As a result, the quantity of protein denatured by HCl would be higher than that by HNO_3. As mentioned earlier, treating NRL with acid denatures the proteins which then reduces the tendency of high molecular weight proteins to degrade on heating and thus prevents the regeneration of the extractable protein (Siti Maznah et al., 2008). Therefore, the distance between the grafted NR particle and free PS particles could have been shortened and their miscibility improved, resulted in the ductility being slightly higher.

4.6.3 Effect of Level of Amphoteric Surfactant (LCU) in NR-*g*-PS

Table 4.4 shows the effect of level of surfactant LCU on the ductility results. Figure 4.8 shows that the mean ductility value increases as the level of the amphoteric surfactant was increased. The control was bitumen emulsion alone. 2.5 phs of LCU surfactant in NR-*g*-PS latex gave the highest ductility (20.3 cm) than the others. Surfactant level more than 2.5 phs surfactant LCU was not tried in this work. The rationale for not using surfactant above 2.5 phs was that when higher level of surfactant is used, the soap level in the latex will be higher. This may create too much bubble in the system and thus affect the ductility of the blend.

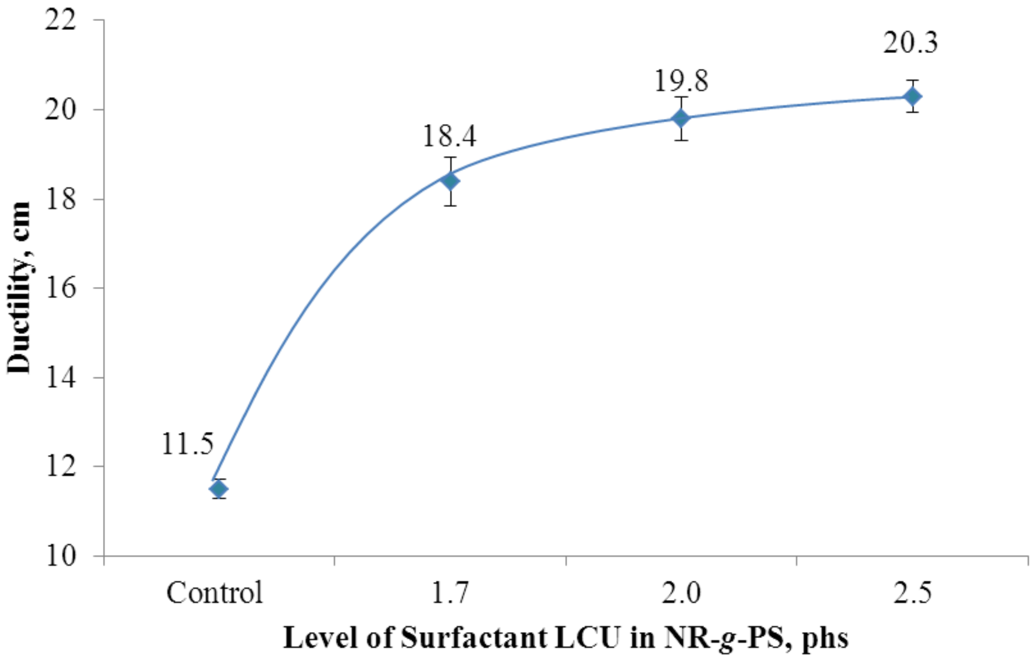


Figure 4.8: Effect of level of surfactant LCU on NR-*g*-PS (SG25)

4.6.4 Effect of TMTD

TMTD was added at the end of the grafting reaction. NRL grafted with 25 phr ST was tested with slow setting type (SS-1K) bitumen emulsion with and without the addition of TMTD dispersion. Table 4.5 and Figure 4.9 show the ductility results for 25 phr NR-*g*-PS latex with and without addition of TMTD dispersion. The control used was bitumen emulsion. The addition of TMTD into NR-*g*-PS latex had slightly improved the ductility at room temperature. The un-reacted TMTD could actually form crosslink between cationic bitumen emulsion and NR-*g*-PS sample when the mixture was blended at 90-100 °C (Hoffmann, 1967).

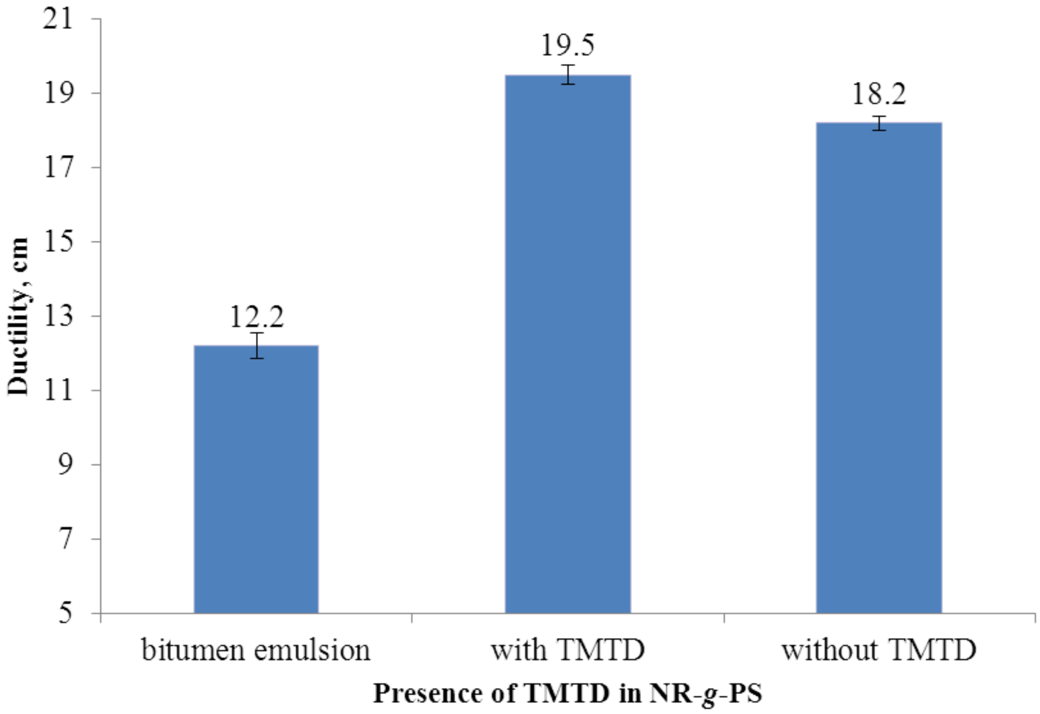


Figure 4.9: Effect of addition of TMTD into NR-*g*-PS (SG25) on the ductility of the bitumen blend

4.6.5 Effect of Type of Bitumen Emulsion

Slow setting type (SS-1K) and rapid setting type (RS-1K) of cationic bitumen emulsion were blended with 25 phr NR-*g*-PS latex (sample SG25), Revultex 1497C-65 and NS198 (SBR) respectively. Revultex 1497C-65 and NS198 were included to compare with SG25 sample (Table 4.6).

Sample NS198 gave a ductility of > 150 cm in both types of bitumen emulsions. Revultex 1497C-65 in RS-1K bitumen was slightly better in ductility compared to RS-1K control, whereas Revultex 1497C-65 in SS-1K bitumen was slightly poorer than SS-1K control. NR-*g*-PS latex gave higher ductility value in SS-1K bitumen emulsion compared to RS-1K. The mean ductility values of SG25 latex in SS-IK and RS-1K were 22.4 cm and 18.2 cm, respectively (Figure 4.10).

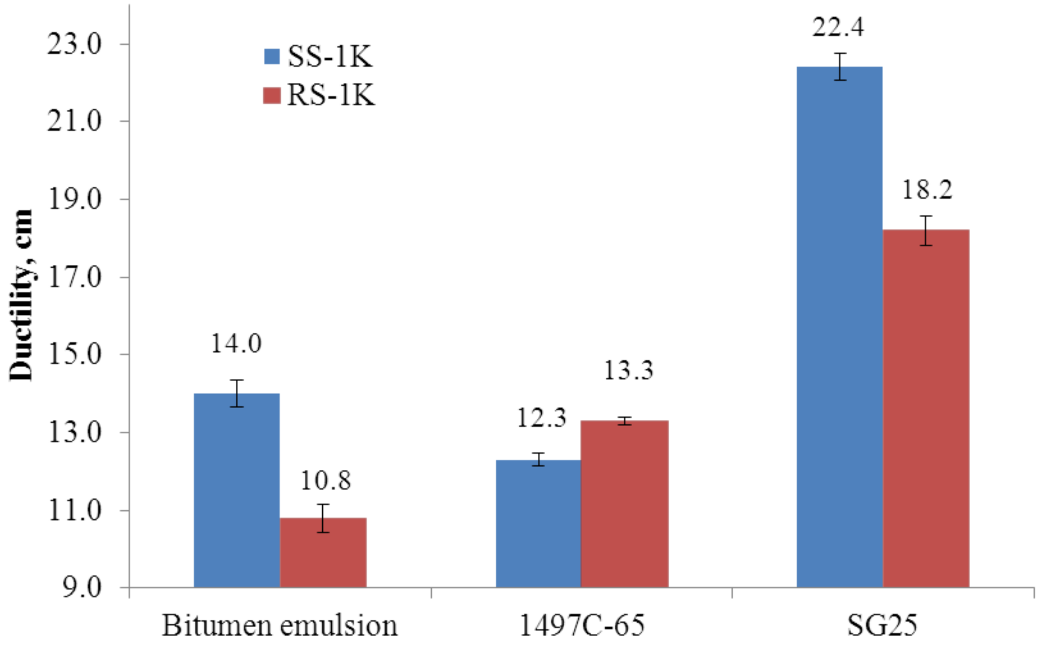


Figure 4.10: Effect of type of bitumen emulsion

In the modified bitumen emulsion, there is competition between the NR-*g*-PS particles and the naturally occurring asphaltenes for the available maltene portions (resins and aromatics) of the bitumen (Road Pavement Forum, 2007). The competition varies with the type and source of both bitumen and NR-*g*-PS; this will affect the compatibility of the final product.

Therefore, any changes in the crude type and the refining process used during the manufacture of the base bitumen emulsion could affect the compatibility of the bitumen and NR-*g*-PS latex system (Road Pavement Forum, 2007). Different compositions of bitumen emulsion are a factor which influences the ductility properties. Slow setting bitumen emulsions are softer than rapid setting bitumen emulsion. Based on the results obtained, we concluded that NR-*g*-PS latex (SG25) blended with soft bitumen emulsion (higher penetration grade) was more suitable for improving ductility at low temperature.

4.6.6 Effect of Initiator Ratio in NR-*g*-PS

In redox initiation system, TBHPO and CHPO were the oxidising agents used to graft ST onto NRL. A fixed amount of TEPA was used as a co-initiator or reducing agent. Table 4.7 shows the ductility results at various initiator ratios.

According to Kochthongrasamee et al. (2006), the graft copolymer initiated with CHPO/TEPA gave the highest percentage of grafting efficiency on NR. More hydrophobic initiator (CHPO) was more efficient than TBHPO for grafting a relatively polar monomer onto NR. It is expected that the radical concentration from CHPO/TEPA on the NR particles would be higher than those of TBHPO, since TBHPO/TEPA is soluble in both the organic and aqueous phase. However, from the ductility results obtained from this study, grafting NR using TBHPO alone as oxidizing agent gave higher ductility than that with CHPO (Figure 4.11). The presence of CHPO in the grafting of ST onto NRL gave lower ductility value.

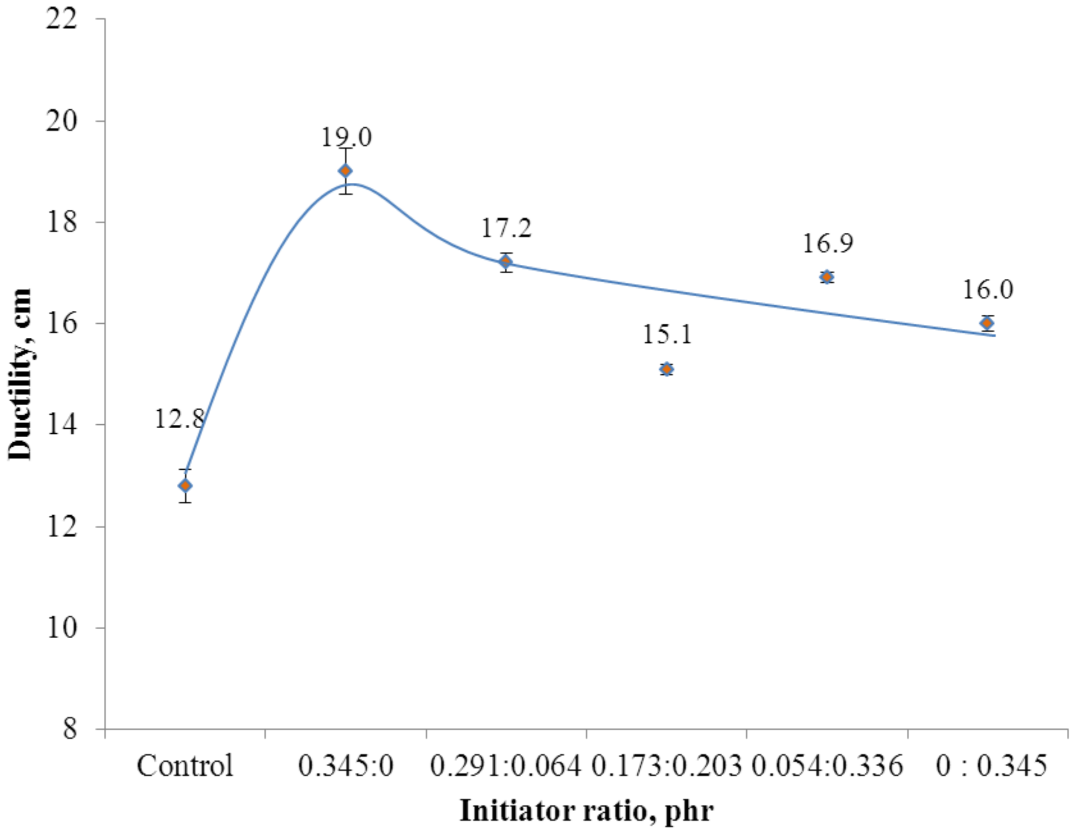


Figure 4.11: Effect of initiator (TBHPO: CHPO) ratio used in NR-*g*-PS (SG25)

4.6.7 Effect of Addition of Sulfur

Sulfur modification of polymeric materials in improving the properties of bitumen binder or in rejuvenating distressed roads gained momentum in the last two decades (Takamura et al., 2001; Takamura, 2003). Zang and Yu (2010) modified bitumen with SBR, polyphosphoric acid and 0.34 or 0.67 parts of sulfur to improve low temperature ductility. In this study, the desired level of NR-*g*-PS latex was added with sulfur to promote cross linking in the NR-*g*-PS latex and the ductility of the modified bitumen was investigated.

Sulfur was added in dispersion form to facilitate the crosslinking reaction. When added to bitumen at 100-120 °C, sulfur dispersion was finely dispersed in bitumen as uniformly small particles. However, coagulation and settlement of sulfur particles became noticeable after the blending mixture was dried. The NR-*g*-PS/sulfur/ bitumen mixture was too soft to be pulled off from oil free paper after drying.

Table 4.8 and Figure 4.12 show that the addition of sulfur dispersion from 0.1 phs to 0.8 phs did not improve the ductility properties of the modified bitumen at 5 °C. Overall low temperature ductility of the modified bitumen decreased slightly in the presence of sulfur dispersion.

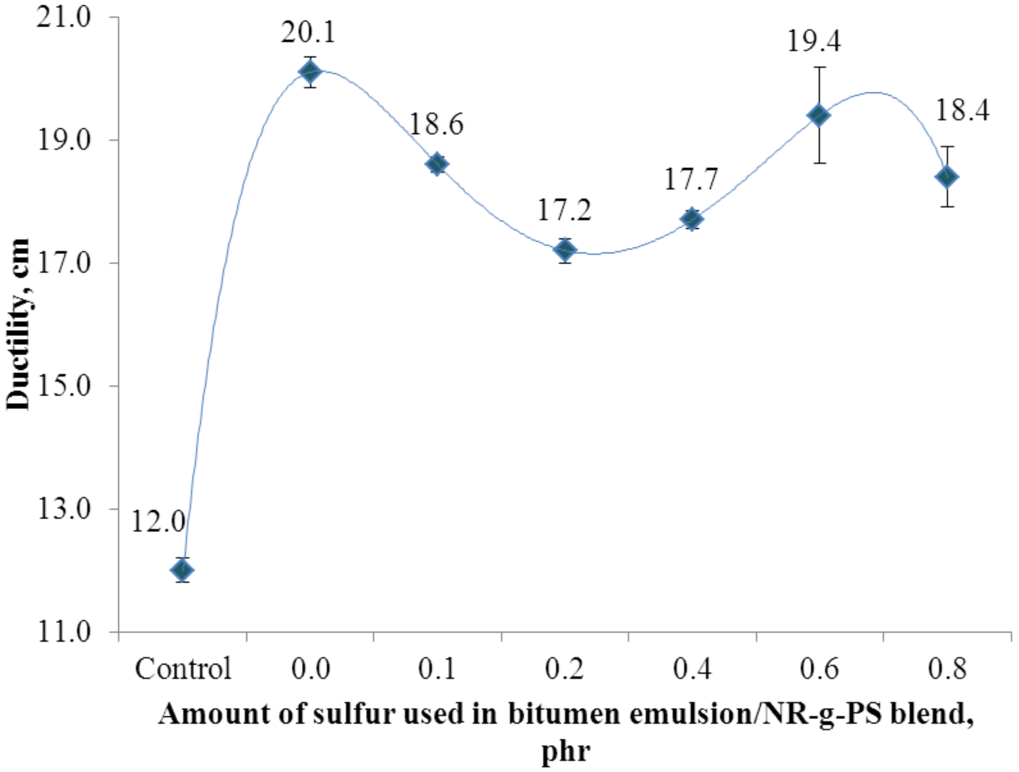


Figure 4.12: Effect of addition of sulfur on the ductility of bitumen emulsion/NR-*g*-PS (SG25) blend

4.6.8 Effect of Processing Temperature of NR-*g*-PS

According to Nakason et al. (2003) and Kalkornsurapranee et al. (2009), maximum grafting efficiency and conversion value were reached at the reaction time of 3 hours and the grafting efficiency slightly decreased beyond 3 hours. Arayapranee et al. (2003) reported that the conversion of monomer is constant after the first 2-3 hours of reaction. There were no newly generated active sites on the rubber molecules at longer reaction time. Homopolymers formed more readily than the graft copolymers if the reaction time was beyond 3 hours.

Arayapranee and Rempel (2008) studied the grafting of MMA or ST monomer onto NR backbone at 50 °C using CHPO/TEPA initiator. They studied the effect of reaction time (0 - 8 hours) on grafting efficiency, free polymer and graft copolymer. It was found that, grafting efficiency increased continuously with increasing reaction time up to 3 hours, and then, it increased slightly with further increases in reaction time up to 5 hours; beyond 5 hours the result was constant. A constant percentage of free polymer and grafted copolymer was observed after 3 hours of reaction time.

Kalkornsurapranee and co-workers (2009) reported that the highest grafting efficiency was achieved at reaction temperature 50 °C. The percentage of conversion and grafting efficiency were found to constant at about 95 %. Nakason et al. (2003) investigated the effect of temperature from 40 to 70 °C on deprotonized MMA grafted NRL synthesis. According to their research, a higher temperature caused a higher conversion. This may be attributed to the increasing trend of the initiator decomposition. Therefore, an increased number of radicals and rate of polymerization occurred.

The highest grafting efficiency was observed at a reaction temperature of 50 °C. An increase in the reaction temperature beyond 50 °C caused a decreasing trend in the grafting efficiency. This may be attributed to radical recombination and other side reactions, such as the homopolymerization of MMA and NR. Kochthongrasamee et al. (2006) also suggested the reaction temperature in a range of 30–60 ºC, and found that the raise of reaction temperature beyond 60 ºC resulted in a decrease of grafting efficiency.

Therefore, in this work the processing temperature from 28-60 °C was used to prepare 25 phr of NR-*g*-PS latex. The processing temperature was maintained for 3 hours after the addition of activating agent, TEPA. Based on Table 4.9 and Figure 4.13, NR-*g*-PS prepared at 40 °C (sample TM40) gave good ductility result which passed the main objective of this research.

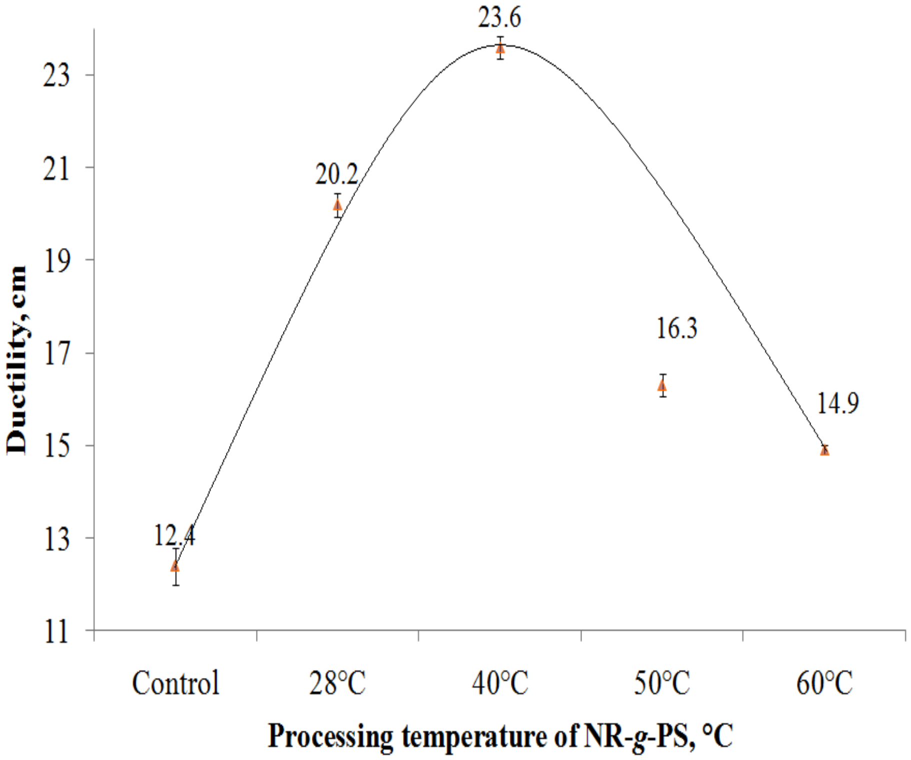


Figure 4.13: Effect of processing temperature of NR-*g*-PS (SG25)

Table 4.9: Effect of processing temperature of NR-*g*-PS on ductility

Sample Code	Description	1st, cm	2nd, cm	3rd, cm	Mean, cm	Standard Deviation
Control	Cationic SS-1K Bitumen Emulsion	12.0	12.8	12.4	12.4	0.40
TM28	4phr TM28 latex + 100 phr of Control	20.5	20.2	20.0	20.2	0.25
TM40	4phr TM40 latex + 100 phr of Control	23.8	23.3	23.6	23.6	0.25
TM50	4phr TM50 latex + 100 phr of Control	16.0	16.5	16.3	16.4	0.25
TM60	4phr TM60 latex + 100 phr of Control	15.0	14.8	14.9	14.9	0.10

TM40 sample had the tendency to come out of the mould during testing due to its very high modulus. This could be due to more grafting or cross linking in the TM40 latex-bitumens. The improvement in ductility is at least partly due to cross-linking of the rubber in the presence of the bitumen, which is what we had been attempting to achieve, and which could result in an interpenetrating network of bitumen and rubber to effectively improve their compatibility. It is also possible that there is some grafting of rubber onto the bitumen or vice versa, giving a similar compatibilising effect.

The effect of peroxide was observed clearly in the samples with higher processing temperatures, namely TM40, TM50 and TM60. TBHPO is peroxide which needs a relatively high decomposition temperature. Further increase in the processing temperature of above 60 °C, for 25 phr NR-*g*-PS latex, seemed to lead to decrease in ductility; possibly due to less residual TBHPO in the higher processing temperature. Furthermore, Arayapranee and Rempel (2004) stated that the actual concentration of monomer in the particle could be very low at higher temperatures. Therefore, NR-*g*-PS prepared at processing temperature above 40 °C did not improve the low temperature ductility of bitumen. The optimum processing temperature of NR-*g*-PS would be 40 °C which gave higher ductility in this study.

4.6.9 Effect of Dosage of NR-*g*-PS in Bitumen Blend

Johnston and Gayle (2009) stated that the range of polymer content recommended for most applications generally varies between 2 – 10 % by weight of bitumen content, with most researches, standards, and manufacturer specifications calling for a polymer concentration of approximately 3 – 5 %. The optimal level depends upon specific polymer, specific bitumen and their interaction. At lower wt % of polymer content, the interaction between bitumen and polymer was significantly high because of better swelling of polymer particles which further enables interaction of polymer particles with bitumen phase (Naskar et al., 2010). In this work, the dosage of latex used in bitumen blend was fixed between 2-6 wt %.

Table 4.10 shows the ductility of TM40 (NR-*g*-PS prepared at 40 °C) and NS198 (SBR) at various dosages in SS-1K bitumen emulsion. NS198 was tested for comparison purpose. For the TM40 – modified bitumen, as shown in Figure 4.14, the low temperature ductility increased significantly when the bitumen/TM40 ratio was 100/4 (4 wt %) compare with the base bitumen, which implied a good improvement by TM40 on the low-temperature ductility of base bitumen. When the bitumen/TM40 ratio was 100/6 (6 wt %), the low temperature ductility decreased slightly but not significantly compared to that of 100/4 ratio. The highest mean of ductility obtained was 23.6 cm with 4 wt % of TM40 in the blend (Figure 4.14).

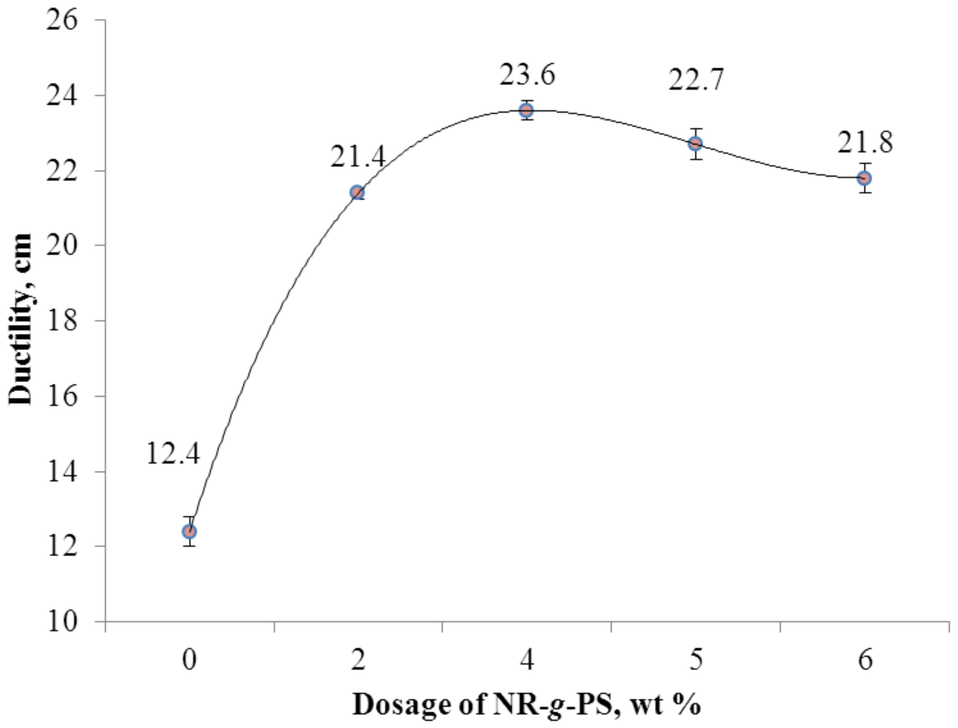


Figure 4.14: Effect of dosage of NR-*g*-PS (TM40) in bitumen blend

The results showed that 2 to 6 wt % of NS198 gave the maximum ductility of >159 cm. During the test, bitumen-NS198 blend was pulled to become as thin as a fine thread and it managed to reach the end of the ductility machine without breaking. The fine thread was found to be in coil form. Although the ductility of TM40 modified bitumen was far lower than NS198 modified bitumen, the main objective of this work, to obtain a ductility of >20 cm, was achieved.

4.7 ER of Modified Bitumen

The elastic behaviour of a binder indicates how much the binder recovers most or all of its initial shape when the load that caused the deformation is removed. ER of a binder is commonly used to measure the fatigue resistance of a binder or its ability to absorb large stress without cracking or deforming. The elastic property of bitumen is generally influenced by the type of modifier as well as the degree of modification involved. It is determined by measuring the recovery of a sample which has been extended in a low temperature ductilometer, e.g. at 7 °C. In general, there is a direct relationship between ER and the degree of modification.

An important requirement for polymer modified cationic bitumen emulsion is an improvement in the ER properties of the bitumen. European Standard includes ER as part of requirements for road application.

SBR latex from BASF, namely NS198 latex was used as a control against NR-*g*-PS latex in this test because of its excellent ductility properties. Table 4.11 compares the ER results of NS198 and NR-*g*-PS lattices (Sample TM40) in SS-1K bitumen emulsion. The ER property of the modified bitumen was tested according to ASTM 6084-97.

Table 4.11: ER results of NS198 (SBR) and NR-*g*-PS latex (TM40) blended with 100 wt % of SS-1K bitumen emulsion

Description	**Percentage of ER (%)**				
	1st,%	**2nd,%**	**3rd,%**	**Mean, %**	**Standard deviation**
2 wt % of NS198	38.50	38.00	39.00	38.50	0.50
4 wt % of NS198	47.50	48.80	47.90	47.50	0.50
6 wt % of NS198	53.65	54.00	53.20	53.62	0.40
2 wt % of TM40	34.00	33.00	33.50	33.50	0.41
4 wt % of TM40	37.50	38.00	37.00	37.50	0.50
6 wt % of TM40	41.00	40.50	41.50	41.00	0.50

On blending two lattices, it is not uncommon for some destabilization and flocculation of one or both of the lattices to occur and this could happen with cationic NR-*g*-PS latex and a bitumen emulsion. In practice, such an effect is normally accompanied by a significant change in viscosity. However, the viscosity of both TM40 and NS198 blended bitumen were almost unchanged after mixing. When cationic TM40 was blended with a cationic bitumen emulsion in various proportions, there was no evidence of a major emulsion incompatibility. No phase separation of the NR-*g*-PS latex from bitumen was observed during cooling. The drying rates and sample appearance of both the latex modified bitumen were also found similar.

However, the percentage of ER of NR-*g*-PS latex (TM40) was lower than NS198 modified bitumen emulsion (Figure 4.15). It is believed that NS198 contains a much higher level of surfactant and it is more strongly cationic than NR-*g*-PS (TM40).

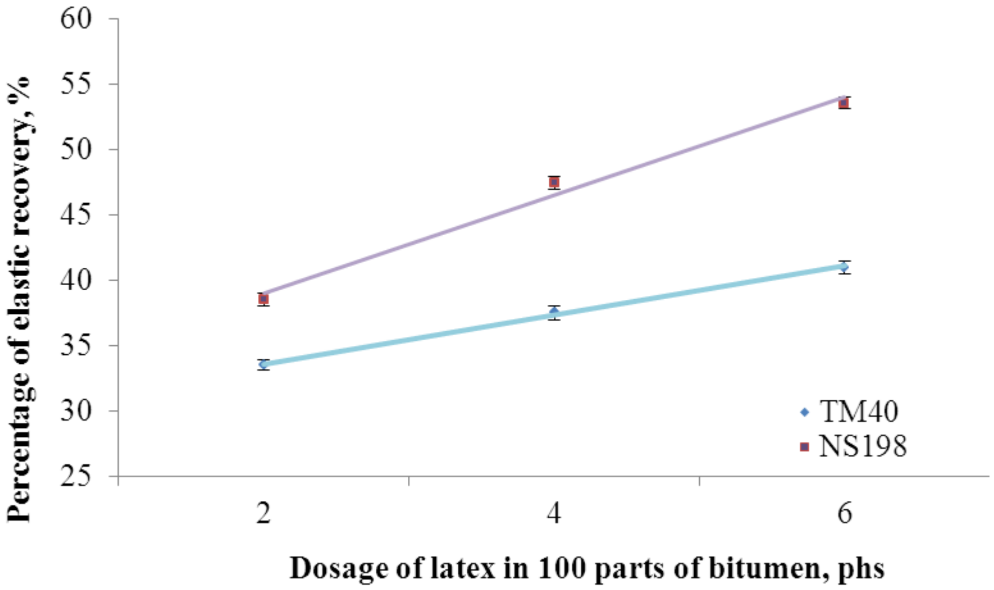


Figure 4.15: Comparison of ER of NR-*g*-PS (TM40) and NS198 at 7°C

As an emulsion polymerized SBR, the MW of the soluble portion of NS198 is likely to be very much lower than the soluble portion of NR-*g*-PS. Gel permeation chromatography (GPC) analysis has found that the soluble NS198 had the number average MW values of ca. 50,000-100,000 compared to 400,000-600,000 for NRL. GPC analysis could not be carried out for TM40 because it did not dissolve in THF solvent. This indicated that TM40 must be much higher in MW which might have affected its miscibility with the bitumen emulsion. Hence, the elastic behaviour of the blend was affected.

If the latex particle size of NR-*g*-PS latex was considerably larger than NS198 it could be anticipated that the efficiency of surrounding the bitumen droplets and the formation of a fused rubber filament network would be considerably reduced, particularly given the cube root relationship of particle volume (weight) to diameter. The charge inversion process during the production of cationic NR-*g*-PS latex may result in significant particle flocculation as well, based on the observed creaming tendency of NR-*g*-PS latex.

The visco-elastic effects involved in determining the ER properties of the modified bitumens are relatively weak and likely to be very stress-strain and time dependent.

Apart from possible factors noted above the ER result could also be significantly affected by the parameters set by the test method itself. For example, strain stress, degree of extension and uniformity of the sample elongation and relaxation times. It also seemed probable that different standard test methods (ASTM versus EN) will give different absolute results, although hopefully in the same order.

4.8 Characterization

Except for mechanical properties, NRL grafted with 25 phr of ST (2.4 mol kg^{-1} NR) at various processing temperature was used throughout the following characterization.

4.8.1 Colloidal Properties

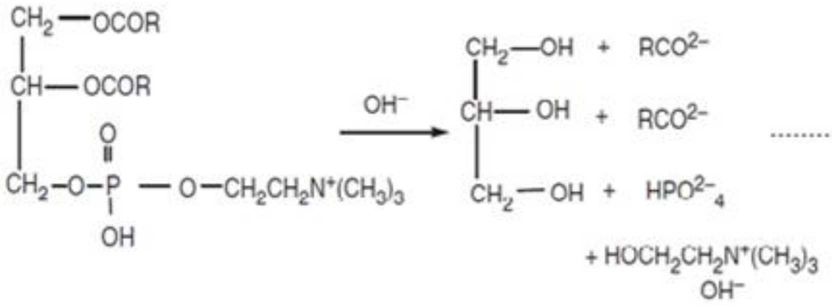
Table 4.12 shows the differences in colloidal properties of ungrafted and grafted NR at various processing temperature. The colloidal properties of the grafted latex were tested without further purification. While the ungrafted latex had been diluted to 45 % TSC initially, NRL grafted with 25 phr of ST showed an increase in TSC to around 51 %.

As the processing temperature increased, the pH of the grafted latex decreased slightly. This was due to evaporation of ammonia. As the processing temperature increased, the links between the particles ruptured and thus reduced the interactions among these particles. As a result, the viscosity of the grafted latex decreased. The results revealed that the viscosity of the compound is dependent on the accelerator type. Latex mixture without any organic accelerator gave the highest viscosity due to lack of formation of crosslinks (Elhamouly et al., 2010).

Table 4.12: Colloidal properties of ungrafted and NR-*g*-PS latex processed at various processing temperature

Colloidal properties	NR	NR-*g*-PS at different processing temperature			
		28 °C	**40 °C**	**50 °C**	**60 °C**
TSC (%)	45.0	50.8	51.0	50.5	51.6
Viscosity (centipoises) Spindle no.2 at 60 rpm	35.0	51.3	51.0	48.5	47.0
pH	11.00	10.97	10.66	10.56	10.58
MST (s)	950	>1800	>1800	>1800	>1800
Coagulum (ppm)	6	10	8	7	8
Micro-coagulum(ppm)	26	38	33	35	32

The graft copolymer produced at various processing temperature showed very high stability toward high shear, as its mechanical stability (MST) was very much higher than that of the ungrafted NRL (Kalkornsurapranee et al., 2009). The addition of an anionic emulsifier increased the latex stability by increasing the negative charge on the surface of the particles. Besides, the presence of an anionic emulsifier may accelerate the hydrolysis of proteins and phospholipids adsorbed on the surface of the rubber particles during heating, thereby producing fatty acid soap in the system (Sasidharan et al., 2005). Furthermore, most of the phospholipid reacted with ammonia solution to form fatty acid soap as shown in equation 4.2 (Yumae et al., 2010).



………… **Eq. (4.2)**

The fatty acid soap, which contains hydrophilic and hydrophobic parts in one molecule, is adsorbed at the surface of the rubber particle to form hydration layer to envelope the latex particles (Blackley, 1997a; Yumae et al., 2010). This enhances the colloidal stability of the latex and hence results in higher MST (Yumae et al., 2010). However, although the presence of coagulum remained low, the amount of microcoagulum found was slightly higher in the grafted latex than the ungrafted latex.

4.8.2 Free ST Monomer Residue and Total Monomer Conversion in NR-*g*-PS

Recently, the advanced analytical techniques such as FTIR and Raman spectroscopy have been developed for on-line or in-line monitoring of the compositions in emulsion polymerization process. However, all these methods provide a relatively poor accuracy in monomer quantification for the samples with very high conversion (Chai et al., 2004). Therefore, a method for accurate determination of residual monomer is highly needed. Gas chromatography

(GC) is widely used for monomer quantification in emulsion polymerization sample since most of the monomers are highly volatile (Guyot et al., 1981). GC analysis provides a relatively high accuracy in monomer quantification.

GC can accurately determine very low level of residual monomer in liquid samples. In polymer latex, the residual monomer is distributed between the aqueous phase and the solid, polymer particle phase. Therefore, a sample pretreatment is needed before GC analysis. Solvent extraction is a common technique used in such sample pretreatment. However, it has several problems in the practical application. A full evaporation (FE) headspace GC is particularly suitable for liquid sample analysis. This method uses a very small sample size to achieve a near-complete transfer of solutes from a condensed matrix or solids into a vapor phase in a very short period of time. Therefore, it does not need any sample pretreatment; it also eliminates the unknown extraction efficiency problem (Chai et al., 2004).

Monomer conversion can be calculated from the free monomer result. It is defined as the fraction of monomer at a given time that has converted to polymer (Arayapranee and Rempel, 2008). Table 4.13 shows the percentages of free ST monomer and monomer conversion in NR-*g*-PS prepared at various processing temperatures. The percentage of ST monomer conversions in the grafting process was above 90 %.

Table 4.13: Percentage of free ST monomer residual and monomer conversion in NR-*g*-PS

Sample	Free ST monomer, g	Total amount of ST used, g	Free ST monomer, %	Monomer conversion, %
TM28	6.59×10^{-3}	0.13	5.07	94.93
TM40	3.66×10^{-3}	0.13	2.82	97.18
TM50	4.33×10^{-3}	0.13	3.33	96.67
TM60	5.41×10^{-3}	0.13	4.16	95.84

The conversion was 94.90 % at 28 ºC and increased to 97.18 % at 40 ºC; it was 96.69 % at 50 ºC and decreased to 95.87 % at 60 ºC. The percentages of free ST monomer found in NR-*g*-PS processed at 40 ºC and 50 ºC were the lowest with a difference of about 0.5 % between them. This suggests that the optimum processing temperature is between 40 ºC and 50 ºC. The decline of monomer conversion at 60 ºC was possibly due to radical decomposition at higher processing temperature.

4.8.3 Grafting Efficiency

In order to determine the presence of graft copolymer in the final product was dried in a vacuum oven to remove water and ST monomer. Upon treating it with MEK and petroleum ether respectively, ungraft or free PS and free NR were extracted from the product. The remaining specimen was the reaction products which are not soluble in petroleum ether and MEK.

Table 4.14 shows the results of solvent extraction and the grafting efficiency of the grafted NR samples grafted at temperature between 28 ºC and 60 ºC. The grafting efficiency obtained was between 91.0 and 92.0 %. Free NR and free PS homopolymer contents found in the grafted NR differed by about 1% at most, as the grafting temperature was varied. As the reaction temperature increased, more *tert*-butyl hydroperoxyl radicals were produced, transferred to the rubber chain and then polymerized to form the graft copolymers (Suriyachi et al., 2004). However, the processing temperature of the grafted latex did not show very significant effect on the grafting efficiency of NRL. This might be due to the limitation of the *cis*-1,4 configuration of PIP. The grafting site of *cis*-PIP might not be available any more after a certain percentage of grafting has taken place (Man et al., 2008; Kalkornsurapranee et al., 2009). However, these results prove that the TBHPO/TEPA redox initiator system was able to produce radicals even at room temperature and was effective up to at least 60 ºC.

Table 4.14: Effect of processing temperature on grafting properties

Sample	**Free homopolymer (%)**		**Grafting efficiency (%)**
	NR	PS	
TM28	3.05	5.65	91.47
TM40	3.53	5.97	90.70
TM50	3.70	4.94	91.54
TM60	2.75	5.39	92.00

It is known that the rate of decomposition of the initiator depends on the reaction temperature (Suriyachi et al., 2004). In this work, TBHPO/TEPA redox initiator was able to produce radicals at low temperature (Suriyachi et al., 2004) and was effective in other processing temperature, even up to 60 °C. Dissociation of TBHPO initiators has faster at higher processing temperature which accelerated the formation of the more radicals to the rubber backbone. The collision between the radicals and styrene monomer caused the rate of polymerization and grafting efficiency to increase.

Besides the swelling ability of rubber, the solubility of monomer and its diffusion rate into NR particles could be the other factors that affect grafting efficiency (Arayapranee et al., 2003; Arayapranee and Rempel, 2004). Nevertheless, the results indicated that the solubility of ST monomer and its diffusion rate were not influenced significantly within the temperature range employed in this study.

In addition, the viscosity of the latex reduces at higher processing temperature which increased the mobility of the molecular chain to initiate the grafting reaction (Arayapranee et al., 2003; Arayapranee and Rempel, 2004).

According to literature, the grafting efficiency decreased if reaction temperature is beyond 60 °C. This is due to the rapid decomposition of the initiator yielding a high instantaneous radical concentration. The radical might be acting as radical scavengers. The radicals either underwent recombination, or other side reaction, and the initiator efficiency was thus reduced. Therefore, the appropriate reaction temperature to give a high grafting efficiency is 60 °C (Suriyachi et al., 2004).

4.8.4 Chemical Analysis by FTIR

The ungrafted and NR-*g*-PS were characterized by FTIR spectroscopy (Figure 4.16). Since each type of covalent bonds has a different natural frequency of energy vibration, the identification of absorption peak in the vibration portion of infrared (IR) region will give a specific type of covalent bonding (Ahmad et al., 2012).

The IR spectrum of the unmodified NRL (Figure 4.16(a)) shows important characteristic absorption bands related to the functional groups present in NR. The significant vibration modes attributed to *cis*-1,4 PIP are summarized as follows: 3035cm^{-1} (olefinic C-H stretching), 2961, 2927, 2855 cm^{-1} (aliphatic C-H stretching), 1449 cm^{-1} (C-H deformation of $–CH_2$-), 1376 cm^{-1} (C-H deformation of $–CH_3$) and 837 cm^{-1} (C-H deformation of *cis* C=C-H) (Anancharungsuk et al., 2007). The weak transmittance bands at 3285 cm^{-1} correspond to >N–H of the protein impurities in NR (Kongparakul et al., 2008). Protein found in latex acts as free-radical scavengers (Nakason et al., 2003; Nakason et al., 2006; Man et al., 2008). Nitrogenous substance existing in protein terminates the activity of free radicals during the initiating and propagating steps of graft copolymerization and reduced the grafting efficiency (Man et al., 2008). Moreover, the spectrum also displays a peak at

1662 cm^{-1} corresponding to a C=C stretching vibration (Kongparakul et al., 2009).

The IR spectrum of the ST grafted NR (Figure 4.16 (b)) shows two additional peaks at 760 and 698 cm^{-1}, which are characteristic of monosubstituted benzene ring (Colthup et al., 1990; Asaletha et al., 1995a; Asaletha et al., 1995b; Kongparakul et al., 2009). The absorption band at 1082 cm^{-1} is assigned to the C–H in-plane band of the aromatic ring (Hershenson, 1964). These absorption bands are important evidences of the presence of ST in the polymer matrix (Moura et al., 2011).

The grafted NR also shows medium sharp peaks at 3026 and 2855 cm^{-1}, which correspond to aromatic C-H stretching in PS. Besides, the spectrum also displays the peaks of C=C stretching of the aromatic ring of PS at 1600 and 1492 cm^{-1} (Asaletha et al., 1995b). The peaks at 2927 and 2855 cm^{-1} are sharper for grafted NR compared to ungrafted NR due to overlapping between aromatic C-H stretching in PS and aliphatic C-H stretching of NR. NR-*g*-PS prepared at other processing temperatures gave similar pattern of IR peaks as Figure 4.16 (b). These results indicate that grafting of ST onto PIP backbone was been successful.

The summaries of FTIR bands of ungrafted NR and NR-*g*-PS at various processing temperature are listed in Table 4.15.

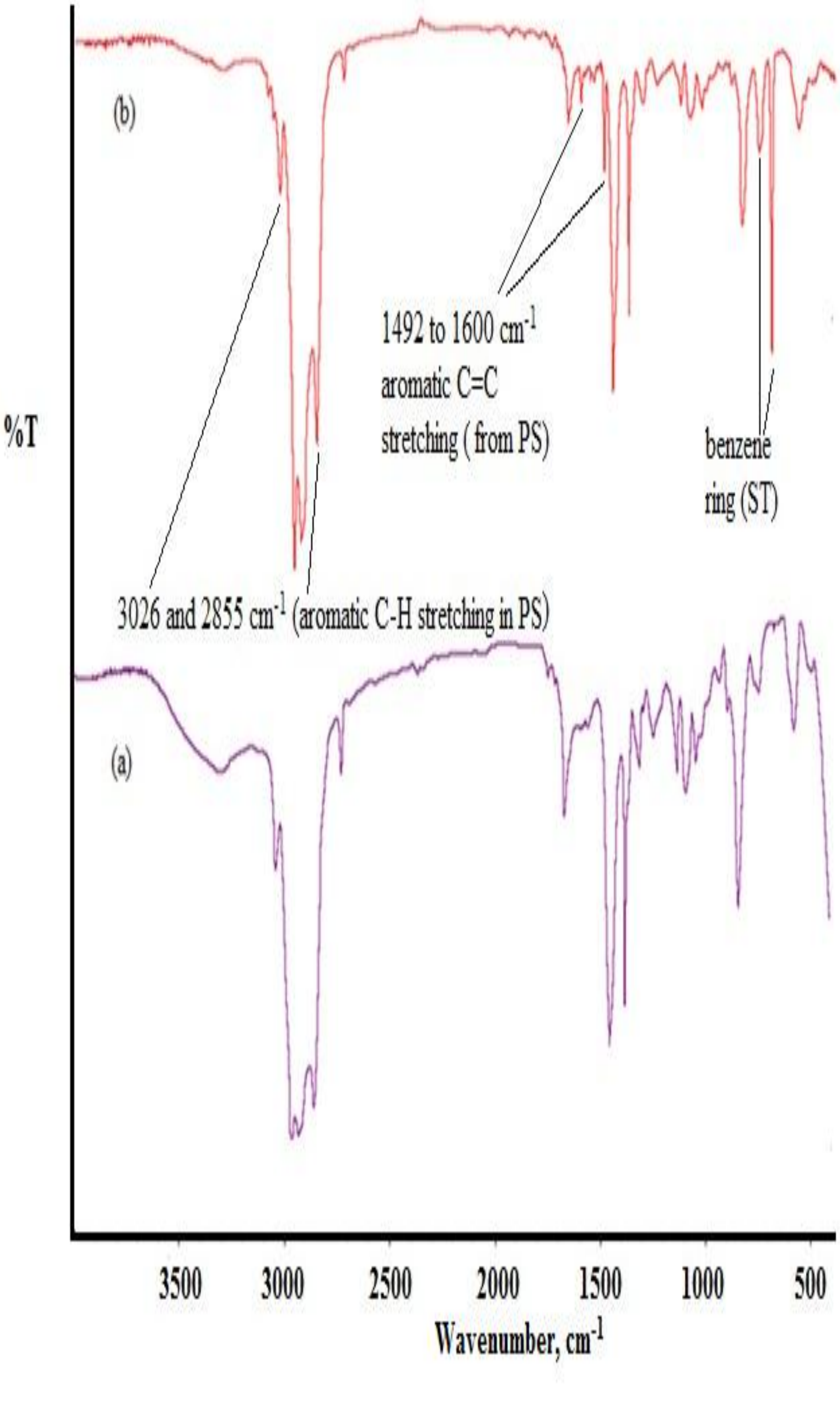


Figure 4.16: FTIR spectra of (a) ungrafted NR and (b) NR-*g*-PS at 40 °C

Table 4.15: FTIR analysis of ungrafted NR and NR-*g*-PS prepared at various processing temperature

NR	NR-*g*-PS at 28 °C	NR-*g*-PS at 40 °C	NR-*g*-PS at 50 °C	NR-*g*-PS at 60 °C	Attributions
3285	3287	3287	3289	3286	N-H of protein of NR (Kongparakul et al., 2008)
3035	-	-	-	-	stretching vibration of olefinic = C-H (Nallasamy and Mohan, 2004)
-	3026	3026	3026	3026	Aromatic C-H stretching ring of PS
2961	2961	2961	2961	2961	CH_3 asymmetric stretching (Nallasamy and Mohan, 2004)
2927	2927	2926	2927	2927	CH_2 asymmetric stretching (Nallasamy and Mohan, 2004) Aromatic C-H stretching ring of PS
2855	2855	2854	2854	2854	CH_2 asymmetric stretching (Nallasamy and Mohan, 2004) Aromatic C-H stretching ring of PS
-	2000-1670 (4 weak peak)	2000-1670 (4 weak peak)	2000-1670 (4 weak peak)	2000-1670 (4 weak peak)	Different benzene ring substitution (C-H deformation of out of plane)
1663	1663	1662	1662	1662	C=C stretching vibration
-	1601	1601	1601	1601	C=C stretching of the aromatic ring of PS

Table 4.15 (continued): FTIR analysis of ungrafted NR and NR-*g*-PS prepared at various processing temperature

NR	NR-*g*-PS at 28 °C	NR-*g*-PS at 40 °C	NR-*g*-PS at 50 °C	NR-*g*-PS at 60 °C	Attributions
-	1492	1492	1492	1492	C=C stretching of the aromatic ring of PS
1238	1242	1242	1242	1242	CH_2 twisting (Nallasamy and Mohan, 2004)
1128	1128	1128	1127	1127	C–C stretching (Nallasamy and Mohan, 2004)
-	1082	1082	1082	1082	C–H in-plane band of the aromatic ring (Hershenson, 1964).
1031	1029	1029	1029	1029	CH_3 rocking (Nallasamy and Mohan, 2004)
893	893	893	893	893	CH_3 wagging (Nallasamy and Mohan, 2004)
837	837	837	837	837	C–H out of plane bending of *cis* C=C-H (Arayapranee and Rempel, 2004; Nallasamy and Mohan, 2004)
-	758	758	758	758	monosubstituted benzene ring (Arayapranee and Rempel, 2004)
740	-	-	-	-	CH_2 rocking (Nallasamy and Mohan, 2004)
-	699	699	699	699	monosubstituted benzene ring (Arayapranee and Rempel, 2004)

4.8.5 Film Preparation and Mechanical Properties

It is well known that NRL has excellent film forming properties and its film is soft and tacky (Arayapranee and Rempel, 2008); whereas grafted NRL normally has poor film forming properties and the film is usually stiffer. Poor film formation means that the film cracks upon drying, which is a sign of high concentration of the secondary polymer at the surface of the particles (Schneider et al., 1996). It was reported that NR-*g*-PS usually has poor film forming properties. For this reason, NR-*g*-PS latex has to be blended with NRL in order to prepare a film for mechanical test (Arayapranee and Rempel, 2008).

However, the NR-*g*-PS latex produced in this study had shown excellent film forming properties. We were able to prepare dipped films following the standard dipping process for NRL. This indicated that the styrene domains distributed evenly within the NRL. As a result, the film formed was without any cracking (Schneider et al., 1996). Powder talc or corn starch was applied when removing the film from dipping form to reduce surface friction of rubber film. However, this caused serious contamination in electronic and biomedical applications. It is therefore of great interest to coat a polymer having high glass transition temperature, e.g., PS on the rubber substrate to increase the film surface hardness and to reduce surface friction of rubber film (Anancharungsuk et al., 2007). Thicknesses of the films obtained were in the range of 0.40 -0.45 mm. The samples thus obtained were kept in a conditioning room prior to mechanical testing.

Few researchers vulcanized the grafted latex by semi-efficient sulfur formulation (Man et al., 2008) or blended with NRL followed by semi-efficient vulcanization (Arayapranee and Rempel, 2008) before casting the film for mechanical testing. Suksawad et al. (2011) obtained a stress at break of 20 MPa for DPNR-*g*-PS which has similar to crosslinked NR due to nano-matrix structure and effect of physical crosslinking. NR-DPNR mixture was used to graft ST and then blended with fresh NRL followed by semi-efficient vulcanization (Sresungsuwan and Hansupalak, 2013). In this work, the mechanical properties of the grafted latex were determined without any addition of fillers, antioxidants and vulcanizing agents.

The influence of the amount of ST used in the grafting reaction at room temperature on the ultimate tensile strength of the NR-*g*-PS produced is shown in Figure 4.17. The amount of ST monomer used was in the range of 3-35 phr (0.3-3.4 mol kg^{-1} NR). Fixed amount of initiator, emulsifier and activating agent were used throughout this study. It is clear that increasing ST concentration up to 25 phr led to an increase in the tensile strength of NR-*g*-PS film. However, as the monomer concentration increased from 25 to 35 phr, a decline in the tensile strength is evident.

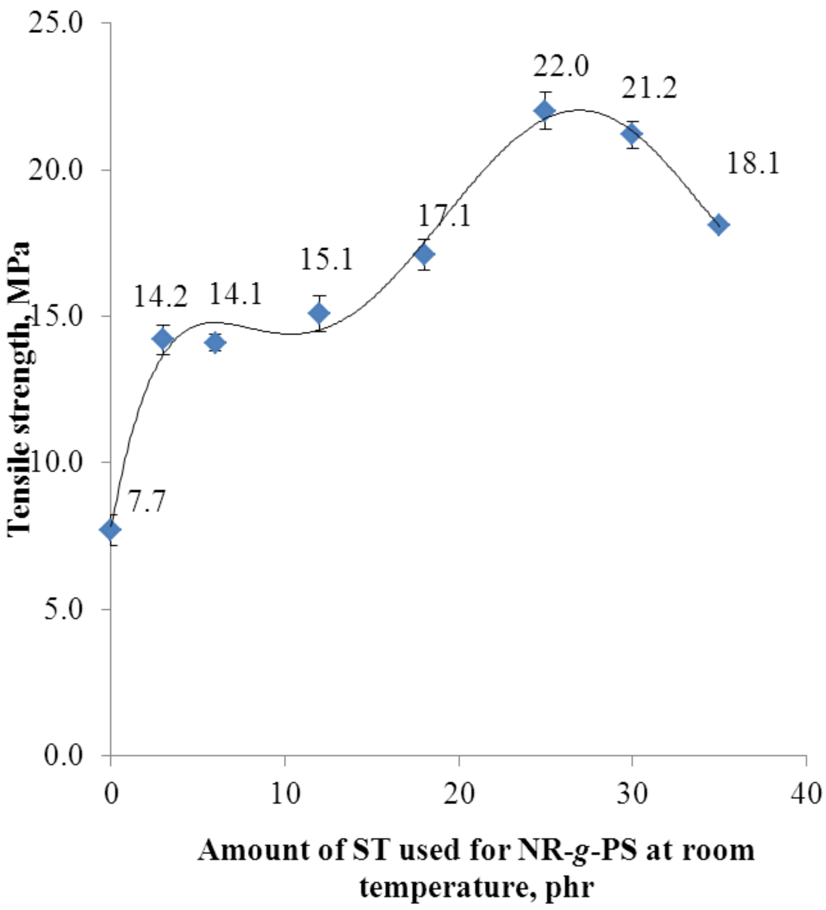


Figure 4.17: Effect of amount of ST grafted at room temperature on the tensile strength of NR-*g*-PS

Figures 4.18a, 4.18b and 4.18c show the effect of processing temperature on tensile strength, elongation at break and modulus at 100% elongation of the NR-*g*-PS (with 25 phr of ST) unaged film, respectively. Unvulcanized NRL has lower tensile, lower modulus and higher elongation at break (Blackley 1997a). It's proven again from our results. NR-*g*-PS films obtained from different processing temperature had almost similar tensile strength of ~21 MPa (Figure 4.18 (a)). In this temperature range, the difference is only 1 MPa, which is likely due to measurement error.

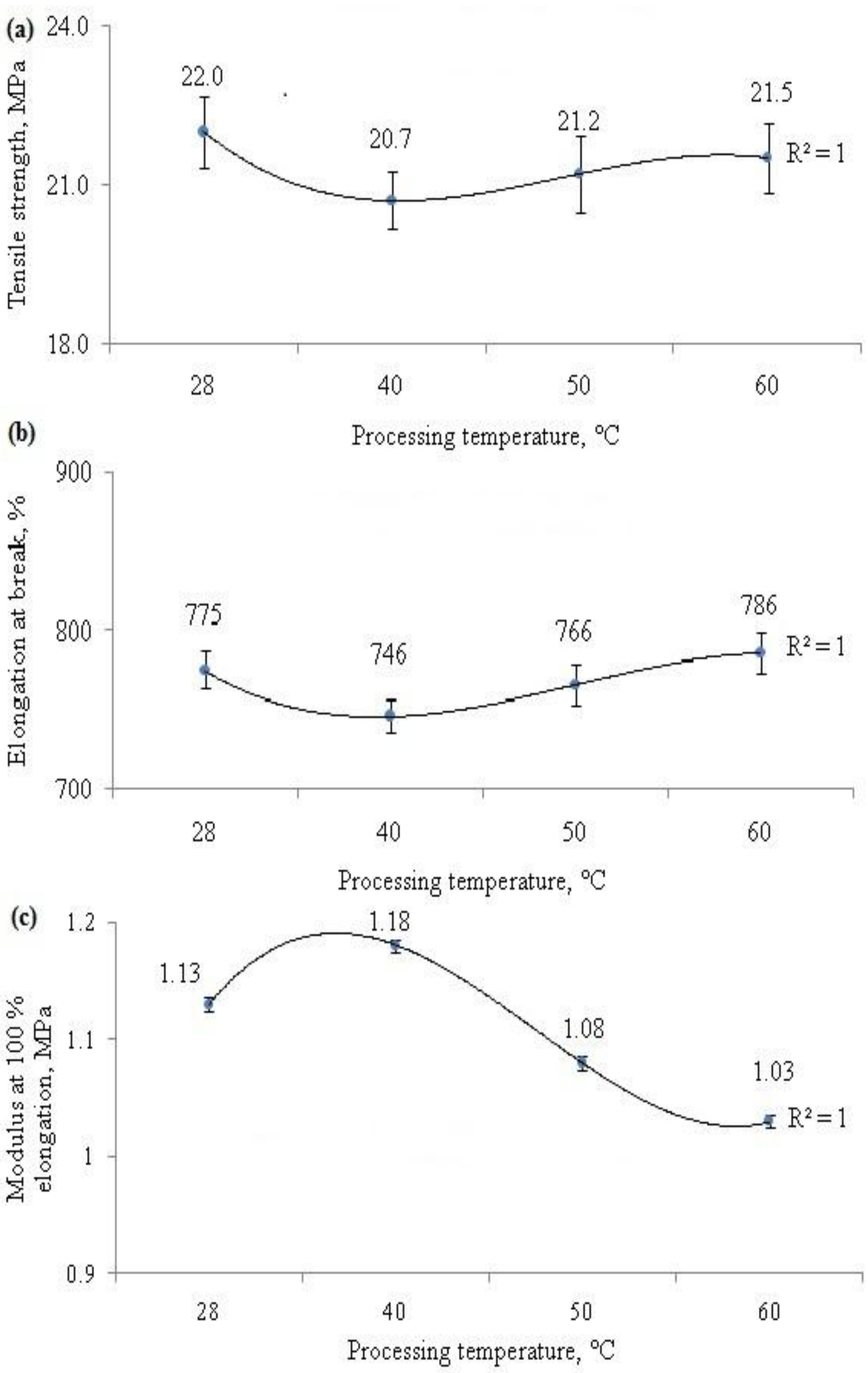


Figure 4.18: Effect of processing temperature on tensile strength (a) and elongation at break (b) and modulus at 100 % elongation (c) of the NR-*g*-PS

The effect of processing temperature on elongation at break of these samples showed a similar trend as that on tensile strength (Figure 4.18 (b) cf. Figure 4.18 (a)). Whereas, processing temperature above 40 ºC had reduced the modulus at 100 % elongation of the NR-*g*-PS films (Figure 4.18 (c)). The tensile strength, elongation at break and modulus at 100 % elongation of the unmodified NR were 7.7 MPa, 1008 % and 0.45 MPa, respectively.

PS is a glassy thermoplastic with rigid, hard and brittle characteristics. The presence of PS polymer onto PIP backbone reduced the elasticity and increased the stiffness of the material. Thus, higher force is required to elongate the specimen. However, the results showed that the processing temperature did not have much significant effect on the tensile strength and elongation at break of the NR-*g*-PS films, although it had affected the modulus at 100 % elongation of these films. The modulus at 100% elongation of NR-*g*-PS produced at 50 ºC and 60 ºC had decreased by 8 and 13 %, compared with the grafted NR produced at 40 ºC. This suggested that the PS branches distribute more evenly along PIP backbones when the graft polymer was produced at higher temperature, thus reducing its stiffening effect on the film (Ismail et al., 2009).

The polar attraction between grafted molecules is another factor contributing to the increased in modulus (Man et al., 2008). NR-*g*-PS prepared at 40 ºC has higher content of grafted PS compared to the other processing temperature grafted latex. Therefore, NR-*g*-PS prepared at 40 ºC has lower tensile strength, elongation at break and has a higher modulus at 100 %

elongation. Hence, we can conclude that the grafting efficiency of the monomers is directly related to the mechanical properties of the resulting NR-*g*-PS.

4.8.6 Thermal Properties

4.8.6.1 Thermogravimetric Analysis (TGA)

Thermogravimetric analysis (TGA) is one of the most commonly used techniques to study the primary reactions of the decomposition of polymers and other materials. TGA is also useful for the characterization and evaluation of polymer thermal stability (Rohana Yahya et al., 2011). Although NR has excellent mechanical properties, these properties may interfere with its low thermal stability. This may cause the polymer chain to be more susceptible to degradation. Degradation usually starts from a head-to-head structure, a site of unsaturation or a tertiary carbon atom (Gamlin et al., 2000).

The thermal stability of the NR-*g*-PS and ungrafted NR was investigated using TGA and DTG. The integral (TGA) and differential thermogravimetry (DTG) curves provide information on the number of stage of breakdown, weight loss of the material at each stage and threshold temperature (Asaletha et al., 1998). The DTG curve shows the temperatures where the thermal degradation processes take place with maximum rate.

Figure 4.19(a) shows that the degradation temperature of the grafted NR was slightly higher than the ungrafted NR. The pure NR decomposed at the temperature range of 300–450 °C. No degradation was observed in NR film below 250 ºC because solid rubber is quite stable (Asaletha et al., 1998). At 435 ºC, about 82 % of the materials related to *cis*-PIP molecules were degraded (Sekharan et al., 2012) (Table 4.16). Weight loss and volatilization of degradation products take place rapidly at this stage. In organic ashes such as oxides, carbonates, phosphates and metal silicates represent the 4.68 % of residual mass recorded at 540 °C in the thermal degradation of NR (Agostini et al., 2008) (Table 4.16).

From the DTG curves in Figure 4.19 (b), while NR film shows only one $T_{\max}$ at 397.4 ºC, NR-*g*-PS film prepared at 40 ºC shows an additional shoulder at higher temperature, around 453-456 °C (Table 4.16). The first degradation peak of NR-*g*-PS was similar to the ungrafted NR, but the end set temperature of the first degradation dropped by ~10°C compared to pure NR as it is clearly shown in Table 4.16. Since $T_{\max}$ depends on the heating rate, the heating rate in this study was maintained at 10 °C min^{-1} to eliminate any discrepancy caused.

Mathew et al. (2001) stated that neat PS decomposes twice: the first stage of weight loss due to the loss of benzene rings occurs in the range of 200–350 °C, and the second stage, due to the decomposition of the polymer’s backbone, occurs in the range of 400–450 °C. The second peak of NR-*g*-PS could be observed clearly; because PS has higher oxygen permeability (Schneider et al., 1996). The second stage of degradation that occurred at higher temperature was obviously due to the presence of PS in the modified

NR. The increase in chain stiffness increases the thermal stability of modified NR (Man et al., 2008).

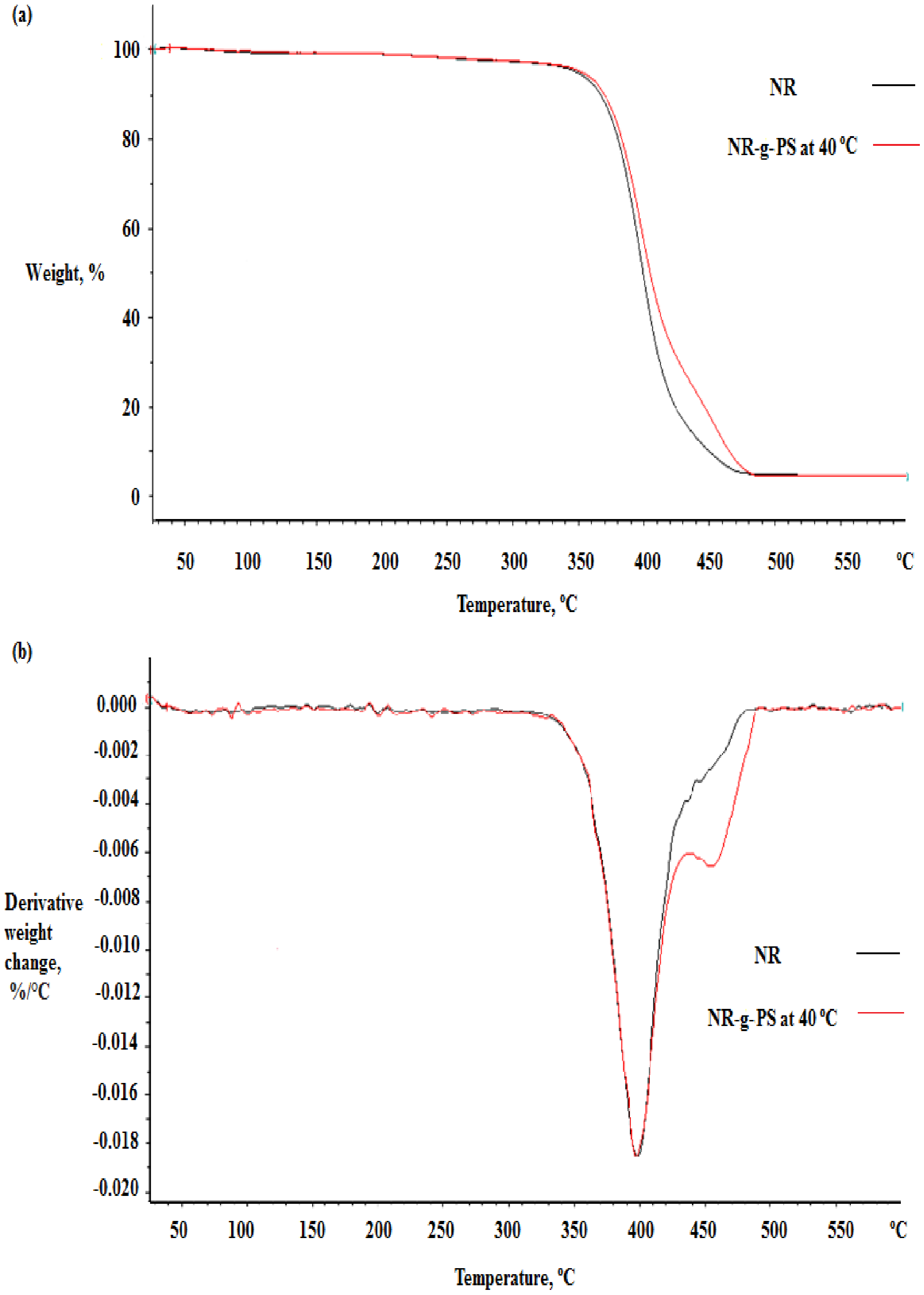


Figure 4.19: (a) TGA thermogram and (b) DTG curves of NR and NR-*g*-PS processed at 40 °C

4.8.6.2 Differential Scanning Calorimetry (DSC)

To investigate the structure of the graft copolymers, DSC was used to explore the macromolecule chains' motion (Arayapranee et al., 2003). DSC provides information concerning the glass transition temperature, a second order event which manifests itself in a DSC curve as a step change corresponding to the change in the heat capacity of the system (Sekharan et al., 2012). To investigate the glass transition, more accurately, T_g was determined as a point of the inflection of the curves. Many of the important technical properties of elastomers such as resilience and abrasion resistance can be correlated to T_g (Martins et al., 2008). Table 4.17 shows the DSC results of neat NR and NR-*g*-PS prepared at various processing temperature.

Table 4.17: Transition temperature of NR and its grafted copolymers prepared at various processing temperature

Sample	**Transition temperature, °C**			
	T_{g1}		T_{g2}	
	Onset	Midpoint	Onset	Midpoint
NR	-65.8	-64.1	-	-
TM28	-66.8	-64.9	39.09	40.76
TM40	-65.9	-64.3	31.44	33.04
TM50	-66.2	-64.4	34.30	36.33
TM60	-66.1	-64.4	36.84	38.34

T_g is affected by the size of the side groups and the mobility of the chain (Arayapranee et al., 2003; Satraphana et al., 2009). Any factor disturbing the closest packing of the main chain will lower the T_g; any factor stiffening or increasing the interaction between chains will increase the T_g (Arayapranee et al., 2003). This behavior was not observed in the DSC results. In the previous research, miscibility of the multicomponent systems was evaluated by T_g measurements. It was classified into the following three: one T_g for the miscible system, closed two T_g's for compatible system, and distinct two T_g's for immiscible system (Kosugi et al., 2012).

The DSC thermograms of copolymers with PIP-rich composition showed T_g originated from PIP backbone to appear between -64.5 °C, whereas those originated from grafted NR chain appeared between 33-41 °C. Man et al. (2008) stated that the expected T_g for MMA and ST grafted rubber is around 60 °C. However, obtained lower T_g compare to that; this might be due to shorter PS branch length along the NR main chains. The peak represents PS around 100 °C was not observed for NR-*g*-PS samples. This indicated that very low amount of un-grafted copolymer of PS was present in the modified rubber (Man et al., 2008). The presence of separate thermal transitions in the DSC curve of PS grafted NR may be attributed to the poor compatibility between NR and grafted PS.

With increasing processing temperature of NR-*g*-PS from 28 °C to 40 °C, there was no obvious change in T_{g1}; while T_{g2} decreased to 33 °C. The DSC results suggest that there was improvement in the miscibility between the

NR and PS components at higher processing temperatures, especially at 40 °C. These results also confirmed the existence of graft copolymers in NRL particles.

4.8.7 Swelling Properties

This method is widely used in latex industry to measure the swelling properties and it is approved by Lembaga Getah Malaysia (LGM). This method provides a quantitative, if the test is carried out with care and accurate measurement of the degree of vulcanization of latex. However, it is time consuming. A few hours are required for drying the film and attaining swelling equilibrium. The time required to attain of equilibrium swelling depends greatly upon the thickness of the film. Some reduction of time is possible if very thin films are prepared. However, handling of such films, e.g. those with less than 0.1 mm in thickness, is difficult (Blackley, 1997b). Therefore, the size of the coating bar used and the time of swelling were fixed by LGM. The graph paper used to measure the swelling was also calibrated by LGM.

The unvulcanized rubber does not swell in toluene and cracking on the film can be observed in a few minutes. The solvent is absorbed by the material until it loses its inner cohesion and the molecules enter the solution. No state of equilibrium is reached during the process. Swelling does not take place because the osmotic pressure exerted on the rubber by the solvent is lesser than the cohesive mechanisms of the molecules of the unvucanized rubber (Blackley, 1997b).

Figure 4.20 reveals that the swelling percentage decreased significantly, from 152 % to 143 %, when the processing temperature of NR-*g*-PS increased from 28 °C to 40 °C. With the processing temperature at 50 °C, the swelling percentage decreased only a little from 143 % to 140 % and it remained unchanged at 60 °C. These results indicated that 28 °C could be too low and 40 °C was sufficient for the process. Further increase of the processing temperature from 40 °C to 60 °C reduces the swelling of NR-*g*-PS significantly.

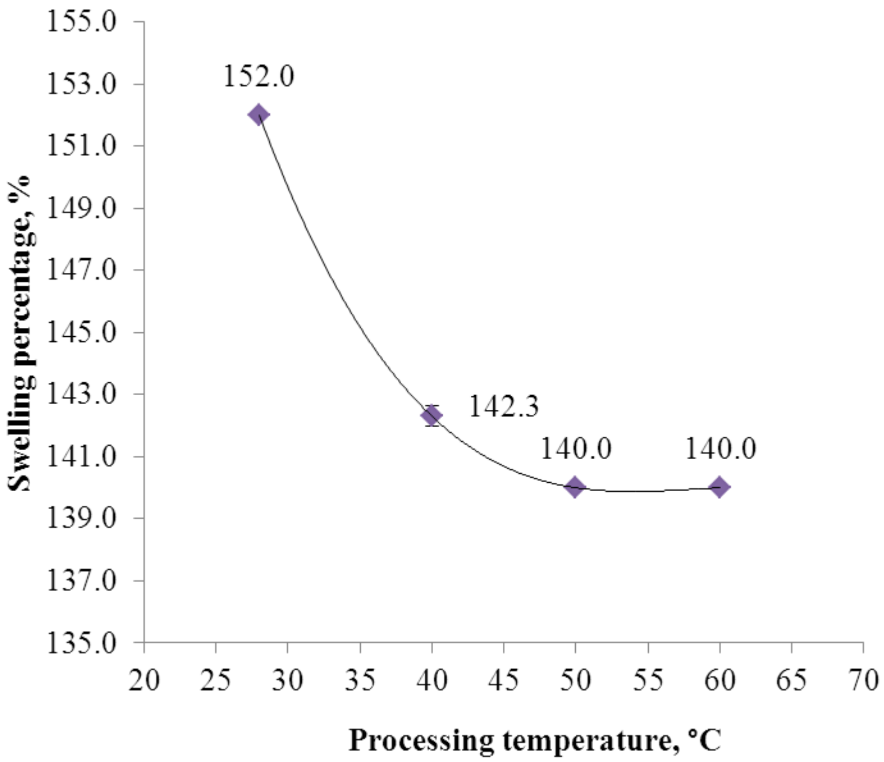


Figure 4.20: Swelling of NR-*g*-PS films prepared at various processing temperatures

It is widely accepted that the swelling percentage of NR film in toluene is inversely proportional to crosslink density (Elhamouly et al., 2010). The swelling percentage decreases with the increase of processing temperature of NR-*g*-PS due to higher crosslink density obtained. The rubber particles became swelled, due to the cross-linking among PIP of NRL with the grafting of ST onto PIP backbones. Elhamouly et al. (2010) reported that TMTD gave a better crosslinking density than other accelerators. Mixture that didn't contain organic accelerator showed a weak resistance to toluene (Elhamouly et al., 2010). Hence, the presence of TMTD in NR-*g*-PS could have caused the increase in the crosslink density of the grafted latex.

Unvulcanized and vulcanized NR could be broadly classified by the percentage of swelling of NR film in toluene or heptane as follows: unvulcanized (160 %), lightly vulcanized (100-160 %), moderately vulcanized (80-100 %), and fully vulcanized (75 %). The swelling percentages of NR-*g*-PS at various processing temperatures were in the range of 140-152 %. Thus, the results suggest that the grafted NR was a lightly vulcanized NR.

4.8.8 Morphology of NR-*g*-PS

The surface morphology of the grafted rubber was obtained by OsO_4 staining at the carbon–carbon double bonds of the NR to increase the contrast and gradation of the NR particles. Grafting between plastic (PS) and elastomer (NR) components leads to compatibility of the two domains, resulting in a favourable state of the dispersion and some possible chemical bonds linking the two domains together (Arayapranee et al., 2003). NRL particle is spherical in nature with a smooth surface. The NRL particles grafted with PS show an irregular surface spotted with many nodules of much smaller particle size (Figure 4.21). This is due to the growing macroradical chains, which were being generated on the surface of NR particles that continued to propagate to form nodules at the outer layer (Kochthongrasamee et al., 2006).

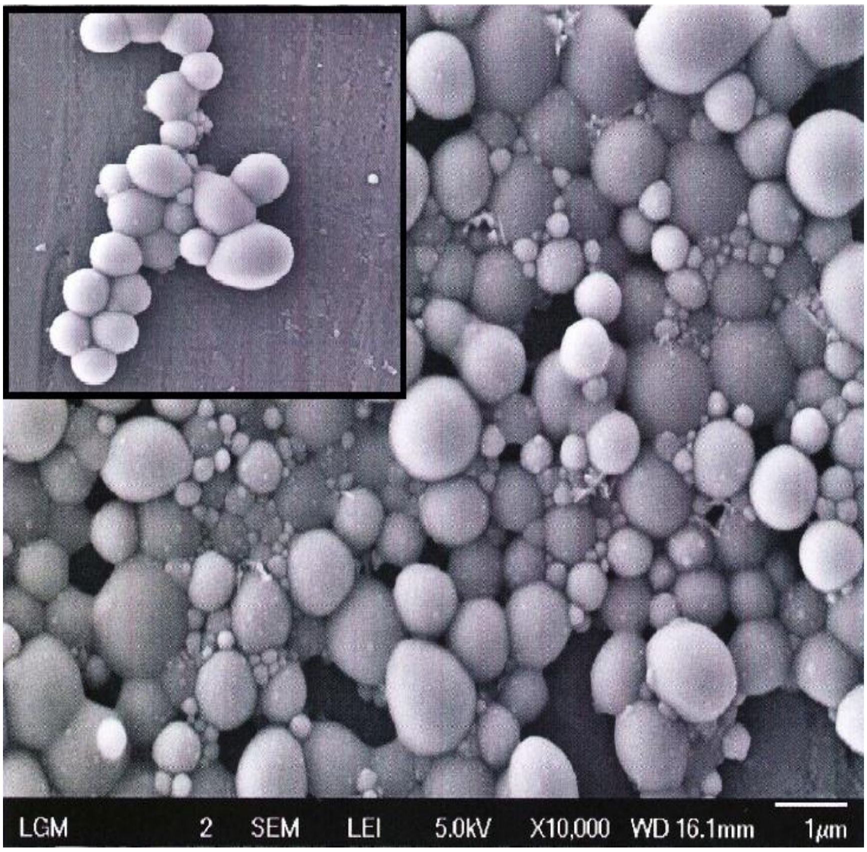


Figure 4.21: Morphology of NR-*g*-PS at 10,000 times of magnification

CHAPTER 5.0

CONCLUSION

In this research study, graft copolymerization of NRL with ST (25 phr) at various processing temperatures (28-60 °C) had been carried out using TBHPO/TEPA bipolar redox initiator. It was then, converted to cationic latex by adding 2.5 phs of Surfactant LCU, and acidified by 17 % HCl. A blend of 4% of the cationic latex processed at 40 °C with SS-1K type of bitumen emulsion gave a mean ductility value of 23.7 cm at 5 °C. The percentage of elastic recovery (ER) of the bitumen/NR-*g*-PS blend at 7 °C increased with the increase of latex dosage from 2 to 6 wt %. The highest percentage of ER obtained was 41 %. The ductility results for SBR latex is remarkably high (>150 cm) compared to unmodified/ NR-*g*-PS latex bitumen blend.

The TSC and MST of the grafted NRL increased; while the pH and viscosity of the modified latex decreased as the processing temperature was increased. The styrene grafted NR film could be prepared by conventional dipping technique. The grafted NR had good film formation ability with no cracking upon drying. The tensile strength of the NR-*g*-PS films obtained from different processing temperatures had similar tensile strength of ~21 MPa, which was about 1.5 times higher than ungrafted NR, while its modulus at 100 % elongation nearly doubled than that of the ungrafted NR.

The grafting efficiency of NR-*g*-PS obtained was between 91.0 and 92.0 %. It increased slightly with the increase in processing temperature. The presence of two medium peaks at 760 and 698 cm^{-1}, which are characteristic of monosubstituted benzene ring of styrene, in the infrared spectrum of the modified NR, indicated successful grafting of styrene onto NR backbone. TGA results showed that NR-*g*-PS has enhanced thermal stability compared to the unmodified NR. GC analysis showed that PS grafted NR with the highest monomer conversion and the lowest free styrene monomer was produced at 40 °C. The swelling results confirmed that NR-*g*-PS is a lightly vulcanized NR. DSC results confirmed the presence of PS in NR-*g*-PS.

Ductility test is a very simple test which gives no real information on the properties of the bitumen other than its elongation at break. The ER test is possibly a little more informative with respect to the visco-elastic properties of the bitumen but again it relates to a result under only one test condition and also provides data only on the strain and not the associated stress in the sample. Therefore, in order to have a more in-depth understanding as well as to explore the full potential of modified NRL, other test such as penetration, softening point, Fraass breaking point, penetration index and viscosity may be conducted and investigated in future study. In addition, the grafting of butyl acrylate and ST monomer onto NRL can be explored as well.

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Table 4.2: Effect of amount ST monomer on ductility of rubberized bitumen

Sample code	Description	1st , cm	2nd , cm	3rd , cm	Mean, cm	Standard deviation
Control	Cationic bitumen emulsion (SS-K1)	11.70	12.20	11.80	11.90	0.26
SG3	4phr of cationic SG3 latex + 100 phr of Control	11.00	11.30	11.20	11.17	0.15
SG6	4phr of cationic SG6 latex + 100 phr of Control	13.40	13.10	13.20	13.23	0.15
SG12	4phr of cationic SG12 latex + 100 phr of Control	18.70	18.30	18.50	18.50	0.20
SG18	4phr of cationic SG18 latex + 100 phr of Control	18.10	18.30	18.00	18.13	0.15
SG25	4phr of cationic SG25 latex + 100 phr of Control	20.10	20.30	20.50	20.30	0.20
SG30	4phr of cationic SG30 latex + 100 phr of Control	19.60	19.00	19.30	19.30	0.30
SG35	4phr of cationic SG35 latex + 100 phr of Control	17.40	18.20	17.80	17.80	0.40
SG40	4phr of cationic SG40 latex + 100 phr of Control	16.00	16.50	16.30	16.27	0.25
SG45	4phr of cationic SG45 latex + 100 phr of Control	15.20	15.90	15.30	15.47	0.38

Table 4.3: Effect of acidification of NR-*g*-PS latex on ductility

Sample code	Description	1st ,cm	2nd ,cm	3rd, cm	Mean, cm	Standard deviation
Control	Cationic Bitumen Emulsion (SS-K1)	11.7	12.2	11.8	11.9	0.26
	a) Acidified with 17% HCl acid					
SG3	4phr of cationic SG3 latex + 100 phr of Control	11.0	11.3	11.2	11.2	0.15
SG6	4phr of cationic SG6latex + 100 phr of Control	13.4	13.1	13.2	13.2	0.20
SG12	4phr of cationic SG12latex + 100 phr of Control	18.7	18.3	18.5	18.5	0.20
SG18	4phr of cationic SG18latex + 100 phr ofControl	18.1	18.3	18.0	18.1	0.15
SG25	4phr of cationic SG25latex + 100 phr of Control	20.1	20.3	20.5	20.3	0.2
	b) Acidified with 17% HNO_3 acid					
SG3	4phr of cationic SG3latex + 100 phr of Control	10.9	10.5	10.8	10.7	0.21
SG6	4phr of cationic SG6latex + 100 phr of Control	15.0	15.0	14.8	14.9	0.25
SG12	4phr of cationic SG12latex + 100 phr of Control	16.0	15.9	16.4	16.1	0.20
SG18	4phr of cationic SG18 latex + 100 phr of Control	17.0	17.8	17.5	17.4	0.20
SG25	4phr of cationic SG25latex + 100 phr of Control	18.5	18.0	18.3	18.3	0.16

Table 4.4: Effect of level of surfactant LCU in NR-*g*-PS on ductility

Level of LCU, phs	**Description**	**1st, cm**	**2nd, cm**	**3rd, cm**	**Mean, cm**	**Standard Deviation**
Control	Cationic Bitumen Emulsion	11.7	11.4	11.3	11.5	0.20
1.7	SG25 latex prepared **with 1.7 phs LCU**+ Control	18.9	18.4	17.8	18.4	0.55
2.0	SG25 latex prepared **with 2.0 phs LCU** + Control	20.0	19.2	20.1	19.8	0.49
2.5	SG25 latex prepared **with 2.5 phs LCU** + Control	19.9	20.6	20.4	20.3	0.36

Table 4.5: Effect of addition of TMTD to NR-*g*-PS on ductility

Sample code	**Description**	**1st, cm**	**2nd, cm**	**3rd, cm**	**Mean, cm**	**Standard Deviation**
Control	Cationic Bitumen Emulsion	12.5	11.8	12.2	12.2	0.35
SG25	SG25 latex prepared **with TMTD** + Control	19.8	19.5	19.3	19.5	0.25
SG25(W/O)	SG25 latex prepared **without TMTD** + Control	18.0	18.4	18.2	18.2	0.20

Table 4.6: Effect of type of bitumen emulsion on ductility

Sample code	Description	1st , cm	2nd, cm	3rd , cm	Mean, cm	Standard Deviation
Control (1)	New batch SS-1K cationic bitumen emulsion	13.8	14.3	14.0	14.0	0.35
Control (2)	RS-1K cationic bitumen emulsion	10.7	10.5	11.2	10.8	0.36
1497C-65 (SS-1K)	Cationic 1497C-65 latex + Control (1)	12.2	12.5	12.2	12.3	0.17
1497C-65 (RS-1K)	Cationic 1497C-65 latex + Control (2)	13.4	13.2	13.3	13.3	0.10
SG25(SS-1K)	SG25 latex + Control (1)	22.4	22.0	22.7	22.4	0.35
SG25 (RS-1K)	SG25 latex + Control (2)	17.8	18.4	18.5	18.2	0.38
NS198(SS-1K)	NS198+ Control (1)	159.0	159.0	159.0	159.0	0.00
NS198(RS-1K)	NS198+ Control (2)	159.0	159.0	159.0	159.0	0.00

Table 4.7: Effect of various initiator ratio on ductility

TBHPO:CHPO ratio, phr	Description	1^{st}, cm	2^{nd}, cm	3^{rd}, cm	Mean, cm	Standard Deviation
Control	SS-1K cationic bitumen emulsion	13.2	12.5	12.8	12.8	0.32
0.345:0	4 phr of SG25/A + 100 phr of control	19.6	19.0	19.5	19.4	0.32
0.291:0.064	4 phr of SG25/B latex + 100 phr of control	17.0	17.4	17.2	17.2	0.20
0.173:0.203	4 phr of SG25/C latex + 100 phr of control	15.0	15.2	15.1	15.1	0.10
0.054:0.336	4 phr of SG25/D latex + 100 phr of control	16.8	17.0	16.9	16.9	0.10
0:0.345	4 phr of SG25/E latex + 100 phr of control	16.2	15.9	16.0	16.0	0.15

Table 4.8: Effect of addition of sulfur on the ductility of bitumen emulsion/NR-*g*-PS blend

Amount of S, phs	Description	1^{st}, cm	2^{nd}, cm	3^{rd}, cm	Mean, cm	Standard Deviation
Bitumen	SS-1K Cationic Bitumen Emulsion (Control)	11.8	12.0	12.2	12.0	0.20
0.0	4 phr of SG25 latex + Control	19.9	20.1	20.4	20.1	0.25
0.1	4 phr of SG25 latex + Control + 0.1 phs sulfur dispersion	18.5	18.7	18.5	18.6	0.12
0.2	4 phr of SG25 latex + Control + 0.2 phs sulfur dispersion	17.0	17.2	17.4	17.2	0.20
0.4	4 phr of SG25 latex + Control + 0.4 phs sulfur dispersion	17.8	17.5	17.7	17.7	0.15
0.6	4 phr of SG25 latex + Control + 0.6 phs sulfur dispersion	20.3	19.2	18.6	19.4	0.78
0.8	4 phr of SG25 latex + Control + 0.8 phs sulfur dispersion	18.9	18.2	18.0	18.4	0.47

Table 4.10: Effect of Dosage of NR-*g*-PS latex on ductility of rubberized bitumen

Sample Code	Description	1st, cm	2nd, cm	3rd, cm	Mean, cm	Standard Deviation
Control	Cationic SS-1K Bitumen Emulsion	12.0	12.8	12.4	12.4	0.40
TM40 (2 wt %)	2 wt% of TM40 sample + 100 wt% of control	21.6	21.3	21.4	21.4	0.15
TM40 (4 wt %)	4 wt% of TM40 sample + 100 wt% of control	23.8	23.3	23.6	23.6	0.25
TM40 (5 wt %)	5 wt% of TM40 sample + 100 wt% of control	22.0	21.3	22.0	21.8	0.40
TM40 (6 wt %)	6 wt% of TM40 sample + 100 wt% of control	22.9	22.2	22.9	22.7	0.40
NS198(2 wt %)	2 wt% of NS198 sample + 100 wt% of control	159.0	159.0	159.0	159.0	0.00
NS198(4 wt %)	4 wt% of NS198 sample + 100 wt% of control	159.0	159.0	159.0	159.0	0.00
NS198(6 wt %)	6 wt% of NS198 sample + 100 wt% of control	159.0	159.0	159.0	159.0	0.00

Table 4.16: Comparison of thermal properties of NR and NR-*g*-PS

Sample	First step				Second step			
	Onset, °C	T_{max}, °C	Endset, °C	Residue mass at 435 °C, %	Onset, °C	T_{max}, °C	Endset, °C	Residue mass at 540 °C, %
NR	375.10	397.42	422.93	18.25	-	-	-	4.68
TM28	373.32	397.31	411.91	22.21	445.62	455.91	471.55	0.48
TM40	373.03	395.21	411.54	26.85	445.68	456.49	474.99	6.14
TM50	373.44	398.50	412.66	27.67	449.73	453.06	473.67	7.07
TM60	374.90	397.73	412.23	25.56	447.91	452.84	471.49	4.32