# STYRENE-METHYL METHACRYLATE-MODIFIED NATURAL RUBBER FROM DEPROTEINIZED NATURAL RUBBER LATEX

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# STYRENE-METHYL METHACRYLATE-MODIFIED NATURAL RUBBER FROM DEPROTEINIZED NATURAL RUBBER LATEX

**by**

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# LIST OF SYMBOLS

| | |
|---|---|
| w/w | Weight to weight ratio |
| Å | ångström |
| R• | Free radical |
| $M_1$• | Species |
| r | Reactivity |
| $A_1$ (g) | Mass of monomer used |
| $A_2$ (g) | Mass of non-reacted monomer |
| $M_1$ (g) | Mass of extract |
| $M_2$ (g) | Mass of specimen used |
| M | Mooney viscosity number |
| L | Indicates the use of large motor |
| $M_L$ (dNm) | Minimum torque |
| $M_H$ (dNm) | Maximum torque |
| $t_2$ (min) | Scorch time |
| $t_{90}$ (min) | Cure time |
| $T_g$ (°C) | Glass transition temperature |
| $M_{100}$ | Modulus at 100 % elongation |
| $M_{300}$ | Modulus at 300 % elongation |
| $\sigma$ | Stress |
| $F$ | Force |
| $A$ | Area |
| $\varepsilon$ | Strain |
| $l_1$ | Elongation |
| $l_0$ | Initial length |
| µ | micron ($10^{-6}$) |

# LIST OF ABBREVIATION

| | |
|---|---|
| ASTM | American Standard for Testing and Materials |
| CMC | Critical micelle concentration |
| CV | Conventional vulcanization |
| DPNR | Deproteinized natural rubber |
| MBTS | Dibenzothiazol disulfide |
| DSC | Differential Scanning Calorimetry |
| DVB | Divinylbenzene |
| DRC | Dry rubber content |
| EV | Efficient vulcanization |
| ENR | Epoxidized natural rubber |
| FL | Field latex |
| FTIR | Fourier Transform Infrared |
| HAL | High ammonia latex |
| HIPS | High impact polystyrene |
| MEK | Methyl ether ketone |
| MMA | Methyl methacrylate |
| NR | Natural rubber |
| NRL | Natural rubber latex |
| IPPD | N-isopropyl-N-phenyl-p-phenyllendiamine |
| phr | Part per hundred rubber |
| ppm | Part per million |
| PBD | Polybutadiene |
| PMMA | Polymethyl methacrylate |
| PP | Polypropylene |
| PS | Polystyrene |
| SNR | Polystyrene grafted DPNR |
| PVC | Poly(vinyl chloride) |

| | |
|---|---|
| $^1$H NMR | Proton Nuclear Magnetic Resonance |
| rpm | Round per minute |
| SEM | Scanning Electron Microscopy |
| SMR | Standard Malaysian Rubber |
| SMA | Stearyl methacrylate |
| SBR | Styrene butadiene rubber |
| TSR | Technically Specified Rubber |
| TGA | Thermal Gravimetric Analysis |
| TSC | Total solid content |

# GETAH ASLI TERUBAHSUAI STIRENA-METIL METAKRILAT DARIPADA LATEKS GETAH ASLI TERNYAHPROTEIN

## ABSTRAK

Kajian ini adalah mengenai pempolimeran *in situ* stirena (S) dan metil metakrilat (MMA) getah asli terubahsuai stirena-metil metakrilat di dalam lateks getah asli ternyahprotein menggunakan ammonium persulfat ($N_2H_8O_8S_2$) untuk menghasilkan getah asli terubahsuai S-MMA (S-MMA-NR) pada darjah ubahsuai yang berbeza, 10, 20 dan 30 % berat dengan berat monomer stirena dan MMA yang digunakan adalah sama (50/50 berat/berat). Kesan pelbagai faktor seperti masa tindakbalas, suhu tindakbalas, jumlah kandungan pepejal (TSC) dan kepekatan pemula terhadap penukaran monomer telah dikaji. Keadaan tindakbalas yang sesuai telah dikenalpasti iaitu pada suhu tindakbalas 65 $^{o}$C, 21 % jumlah kandungan pepejal, 5 % berat kepekatan pemula berbanding kepekatan monomer dan 6 jam masa tindakbalas berdasarkan peratus penukaran monomer tertinggi.

Kesan S-MMA-NR pada darjah ubahsuai yang berbeza terhadap kejadian dan darjah cantuman, sifat-sifat terma, kepekatan, pematangan, tensil dan morfologi telah dikaji. Kejadian cantuman telah disahkan melalui spektroskopi Infra Merah Jelmaan Fourier (FTIR) dan darjah cantuman telah ditentukan menggunakan spektroskopi Resonans Magnet Nukleus Proton ($^1$H NMR). Penyebatian telah dijalankan dengan menggunakan penggiling bergulung dua dengan sistem pemvulkanan separa cekap. Ciri-ciri pematangan telah ditentukan dengan menggunakan *Reometer Monsanto* manakala nombor *Viscometer Mooney* telah dikaji menggunakan *Viscometer Monsanto*.

Keputusan kajian menunjukkan peratus penukaran monomer bagi S-MMA-NR meningkat sehingga 99 % dengan peningkatan darjah ubahsuai. Sementara itu, darjah cantuman menunjukkan peningkatan ketara dengan peningkatan darjah ubahsuai dan sedikit berkurang pada darjah ubahsuai 30 % berat. Darjah cantuman tertinggi iaitu 49 % adalah pada darjah ubahsuai 20 % berat. Komposisi kopolimer S-MMA-NR telah ditentukan di mana komposisi stirena di dapati lebih tinggi berbanding komposisi MMA. Bagi sifat-sifat terma, keputusan Analisis Gravimetri Terma (TGA) telah menunjukkan peningkatan suhu perosotan maksimum getah terubahsuai dengan peningkatan darjah ubahsuai. Keputusan kalorimeter Pengimbas Pembezaan (DSC) pula telah menunjukkan hampir tiada kehadiran rantai bebas PS dan PMMA yang ketara di antara komponen-komponen dengan peningkatan darjah ubahsuai.

Penyebatian S-MMA-NR 10, 20 dan 30 % berat dengan dan tanpa hitam karbon telah dikaji terhadap sifat-sifat pematangan, kepekatan Mooney dan sifat-sifat mekanikal. Masa pematangan dan masa skorj bagi S-MMA-NR telah didapati meningkat dengan peningkatan darjah ubahsuai manakala tork$_{\text{mak-min}}$ telah berkurang dengan peningkatan darjah ubahsuai bagi kedua-dua vulkanisat tanpa pengisi dan berpengisi. Peningkatan dalam darjah ubahsuai juga telah menghasilkan getah yang lebih kaku dengan peningkatan modulus dan pengurangan bagi pemanjangan pada takat putus. Kekuatan tensil bagi getah terubahsuai itu juga berkurang. Mikrograf bagi Mikrograf Mikroskopi Pengimbas Elektron (SEM) menunjukkan kehadiran

agglomerat di dalam S-MMA-NR 30 % berat yang mungkin menjadi penyebab kepada kekuatan tensilnya yang paling rendah berbanding vulkanisat DPNR, S-MMA-NR 10 dan 20 % berat.

# STYRENE-METHYL METHACRYLATE-MODIFIED NATURAL RUBBER FROM DEPROTEINIZED NATURAL RUBBER LATEX

## ABSTRACT

The study reported here is concerned with the *in situ* polymerization of styrene (S) and methyl methacrylate (MMA) in deproteinized natural rubber latex using ammonium persulfate ($N_2H_8O_8S_2$) as initiator to obtain S-MMA-modified natural rubber (S-MMA-NR) at different degree of modification, 10, 20 and 30 wt% of equal amount of styrene and MMA monomer (50/50 w/w). Effect of various factors such as reaction time, reaction temperature, total solid content (TSC) and initiator concentration on the monomer conversion was investigated. Suitable reaction conditions at reaction temperature of 65 $^oC$, total solids content of 21%, initiator concentration of 5 wt% of monomer concentration and reaction time of 6 hours were identified based on the highest percent monomer conversion.

The effects of S-MMA-NR at different degree of modification on the grafting occurrence and efficiency, thermal, viscosity, curing, tensile and morphological properties were investigated. The grafting occurrence was confirmed by Fourier Transform Infra Red (FTIR) spectroscopy and grafting efficiency was determined using proton nuclear magnetic resonance ($^1H$ NMR) spectroscopy. Compounding of the modified rubber was carried out using a two roll mill based on semi-efficient vulcanization system. Cure characteristics were determined using a Monsanto Rheometer while Mooney viscometer number were examined using Monsanto Viscometer.

Results indicated that the monomer conversion of S-MMA-NR increased up to 99 % with the increase in degree of modification. Meanwhile, the grafting efficiency shows significant increment with the increase in degree of modification and slightly decreases at 30 wt % degree of modification. The highest grafting efficiency of 49 % was found at 20 wt % degree of modification. The copolymers composition of the S-MMA-NR was determined where the composition of styrene was found to be higher than that of MMA. On thermal properties, the Thermal Analysis Gravimetry (TGA) results indicated that the maximum rate of degradation temperature of the modified rubber increased with the increase in degree of modification. The Differential Scanning Calorimeter (DSC) results showed almost no significant free PS and PMMA chains presence in the component as the degree of modification is increased.

Compounding of S-MMA-NR 10, 20 and 30 wt % with and without carbon black were investigated in terms of cure characteristics, Mooney viscosity and mechanical properties. The cure and scorch time of S-MMA-NR increased with increasing degree of modification while the torque$_{\text{max-min}}$ decreases steadily with increasing degree of modification for both gum and filled vulcanizates. Increasing the degree of modification also resulted in stiffer rubber with increase in modulus and decrease in elongation at break. The tensile strength of the modified rubber decreased as well. Scanning Electron Microscopy (SEM) Micrographs showed the presence of agglomerates in S-MMA-NR 30 wt% which might be responsible for its lowest tensile strength compared to DPNR, S-MMA-NR 10 and 20 wt % vulcanizates.

# CHAPTER 1
# INTRODUCTION

## 1.1 Chemical Modification of NR

Natural rubber is an important material with unique and special characteristics used in wide range of engineering applications, i.e. tire, rubber springs, vibration mounts etc. Despite the increase in research on synthetic rubbers, natural rubber remains a practically irreplaceable elastomer. The fact that it comes from a renewable resource, coupled with the good properties, signifies that it is an important elastomeric material. The current increasing awareness of environmental issues has created a high level of interest in NR and its derivatives as compared to its synthetic counterparts, which are mostly manufactured from non-renewable oil-based resources. The current uncertainties in oil price issue also gives significant credit to the increase in research on NR.

NR is quite sensitive to heat and oxidation due to the presence of the double bond on its chains. These inherent drawbacks of NR have limited its application in industry. In efforts to extend its use, various methods have been developed to modify its properties through physical and chemical modifications. The inherent incompatibility at the molecular level posses by physical modification has been the main reason why chemical modifications of NR have gain interest among researchers. On chemical modification, modification of NR by bond rearrangement, grafting and attachment of new chemical groups onto the NR backbone have been reported (Blackley, 1997). Among these, the most relatively successful modification was Epoxidized Natural Rubber (ENR), which has currently been produced in pilot-plant quantities in Malaysia (Hashim et al., 2002a). Epoxidation of NR has been done since 1922, but commercial productions of ENR began at the end of 1988 and have been available in three grades, ENR-10, ENR-25 and ENR-50. Potential applications for ENR are in engineering components, the inner liner of tubeless tires, oil seals, and tire treads. ENR has good adhesive properties and can be used to bond poly(vinyl chloride) (PVC) to non-compatible materials and to bond rubber to metal.

These chemical modifications have not only been directed towards the enhancement of certain properties of NR, but also to introduce totally new properties not usually associated with NR like hardness, modulus, good oil, heat and solvent resistant, good aging properties etc.

## 1.2 Graft copolymerization of NR

The extension of applications of NR can be carried out by the grafting of a secondary polymer within the NR latex particle. A graft copolymer is a specialized type of block copolymer in which blocks of one monomer unit is covalently attached to a main-chain (backbone) polymer comprising exclusively units derived from the other monomer (Blackley, 1997). The grafting of NR with various monomers such as acrylonitrile, methyl methacrylate (MMA), stearyl methacrylate (SMA), divinylbenzene (DVB) and styrene using a range of initiator systems have been extensively studied (Hashim et al., 2002b and Dafader et al., 2005). For natural rubber, it was found that MMA and styrene are the most suitable monomers when polymerized to yields high level of grafting. Recently, grafting of binary mixtures of monomer has gained interest among researcher. In this regard, synergism during copolymerization reaction has been studied and investigated (El-naggar et al., 2001).

The graft copolymerization of styrene and MMA onto NR (Arayapranee et al., 2002) and SBR latex (Zhoa et al., 1994) have been studied and reported.

Many methods are available for the preparation of graft copolymers. Different polymerization procedures can yield different particle morphology which strongly influenced by the compatibility between the two polymers and by any grafting that occurs during the process. Among all these methods, free radical mechanism in emulsion polymerization has been the most widely applied system for the formation of graft copolymers, since it provides the simplest method and can be used with a wide variety of polymers and monomers (Morton, 1978). Generally, the compatibility between two grafted polymers is governed by grafting efficiency that occurs during the process. High grafting efficiency resulted in increasing the interfacial adhesion between the copolymers and consequently improved the mechanical properties. Chemical reactions or grafting directly of monomers onto NR backbone in the latex can be influenced by the presence of the proteins and other non-rubber substances. These proteins could act as free radical scavengers and terminate the free radicals species during the polymerization reaction and reduced the grafting efficiency. The proteins associated with natural rubber latex can also caused sensitizations or allergic reactions to human skin. The allergy caused by natural rubber latex products has become a serious problem and the removal of the protein was needed to lessen the problems (Pendle, 1993). Owing to the low grafting efficiency and the allergy caused by natural rubber latex products, therefore, DPNR latex is an obvious choice in graft copolymerization and in application where allergy is to be avoided (Thiraphattaraphun et al., 2001). For DPNR latex, the protein layer covering the latex is virtually removed and the protein's function in the latex is later replaced by the surfactant added.

The importance of this type of rubber structure is basically due to the fact that polymer chains of different chemical structure, which are normally incompatible, are chemically bonded to each other. The most obvious effect upon mechanical properties of such rubbers is increase in the stiffness and hardness. By far, the most commercially important product obtained by graft polymerization is Polymethyl Methacrylate grafted natural rubber which was first introduced in mid 1950s under the trade name Heveaplus. The main advantages of the poly (methyl methacrylate)-grafted NR lie in an ability to produce self reinforced vulcanisates and in adhesive applications. These rubbers are also stiff, non-tacky materials at ambient temperatures with degree of stiffness depending on the percentage of methyl methacrylate incorporated into the natural rubber.

Apart from the better mechanical properties resulted in the grafted rubber, such modified rubber also are used effectively as compatibilizer for polymer blends. The graft copolymers are very effective in reducing the interfacial adhesion by polymer chain entanglements and therefore bridging the interface (Altstadt et al., 2000). Thiraphattaraphun (2001) reported the incorporation of MMA grafted NR in PMMA blend by melt mixing method while Hashim and Neoh (2004) investigated the use of polystyrene grafted DPNR (SNR) as a compatibilizer for PS-SNR.

## 1.3 Problem Statement

The grafting of vinyl monomer onto NR has been extensively investigated and reported. However, only a few studies have been reported on grafting of binary mixtures of monomer. The graft copolymerization of styrene and MMA onto NR has been studied by Arayapranee (2002) and co workers by using cumene hydroperoxide/sodium formaldehyde sulfoxylate dehydrate/EDTA-chelated $Fe^{2+}$ as redox initiator. Zhoa et al. (1994) reported the graft copolymerization of these styrene and MMA monomers onto SBR latex with the benzoyl peroxide-ferrous salt (BPO-$Fe^{2+}$) redox initiator. Both works revealed that the polymerization process were very complicated and were dependent on process factors (amount of initiator, emulsifier, temperature, monomer to rubber ratio etc). However, the grafting of styrene and MMA monomers onto DPNR latex is yet to be reported so far.

In this study, the in situ polymerization of 50/50 (w/w) styrene/MMA mixtures in DPNR latex was carried out based on the principle of free radical emulsion polymerization. No surfactant was added during the polymerization reaction to avoid any formation of micelle which promotes homopolymerization. This is important to impart high degree of grafting to the modified rubber. The degree of modification was investigated at monomer (styrene and MMA) to rubber ratio of 10:90, 20:80 and 30:70, respectively. According to Hourston and Romaine (1989, 1990 and 1991), the polymerization of vinyl monomer in NR latex has been found feasible up to monomer to rubber ratio of 30:70. Above this ratio, the modified rubber is too stiff and does not behave like an elastomeric material. It was also reported that the highest grafting efficiency was observed between these ranges (Oliveira et al., 2005).

Parts of the study involved the curing or cross linking of the modified rubber. To achieve this, the rubber was cured with a typical sulphur based curatives using semi-efficient (semi – EV) curing system. Semi – EV curing system was chosen in this study because it gives good balance of cure characteristics and properties. The effect of incorporating filler (carbon black) into the rubber vulcanizate was also investigated.

## 1.4 Objective

The focus of the study reported here is concerned with the chemical modification of DPNR with styrene and methyl methacrylate (MMA). The main objectives of this study are:

1. To investigate the optimum parameter and reaction conditions of the *in situ* polymerization of styrene and MMA in DPNR latex for the purpose of preparing styrene-MMA (S-MMA) modified DPNR at different degree of modification, in this study different monomer to rubber ratio, 10:90, 20:80 and 30:70, respectively.
2. To characterize the resultant S-MMA modified DPNR in terms of degree of monomer conversion, grafting efficiency, thermal properties and morphology.
3. To investigate the cure behaviour and mechanical properties of the S-MMA modified DPNR prepared.

For simplicity and clarity, the term S-MMA-NR is used to refer to the S-MMA modified DPNR. Thus, S-MMA-NR at monomer to rubber ratio of 10:90, 20:80 and 30:70, will later be referred as S-MMA-NR 10, 20 and 30 wt%, respectively.

Monomer in this study refers to equal mixture of styrene and MMA monomer (50/50 (w/w)).

# CHAPTER 2
# LITERATURE REVIEW

## 2.1 Natural rubber

Natural rubber is an unsaturated hydrocarbon consisting solely of carbon and hydrogen with an empirical formula of $C_5H_8$. Isoprene is the repeating unit of natural rubber where one double bond unit existed for each $C_5H_8$ group. NR has a high average molecular weight. It is a straight chain polymer structure which almost all (90-95%) the isoprene have the cis-1,4 configuration. 1, 4 structure means that carbon atoms 1 and 4 are joined in forming the chain as shown in Figure 2.1 (Morton, 1973).

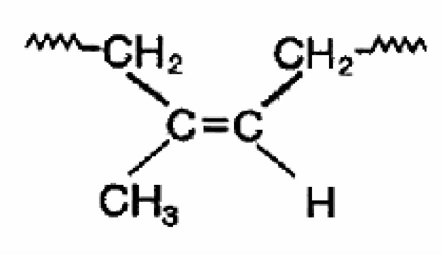

Figure 2.1: Chemical structure of cis-1,4-polyisoprene

### 2.1.1 Properties of natural rubber

Elasticity is one of the fundamentally important properties of NR due to the freely rotating links of its long chain molecules (Stern, 1967). Rubber is unique in the extend to which it can be distorted, and the rapidity to which it recovers to its original shape and dimensions. It is, however, not perfectly elastic. The rapid recovery is not complete. Part of the distortion is recovered more slowly and another part is retained. The extent of this permanent distortion is known as permanent set which depend on the rate and duration of applied force. The slower the force, and the longer it is maintained, the greater is the permanent set (Ciullo and Hewit, 1999).

The elastic nature of NR also account for the resilience of NR product. This resilience means less kinetic energy is lost as heat during repeated stress deformation. Resilience and hysteresis go hand in hand. In a highly resilience rubber little of the energy of deformation is lost thus resulted in low hysteresis and little heat is developed as a result of deformation (Stern, 1967).

As being indicated earlier, almost all of the NR structure consist of a string of long and uninterrupted cis-1,4-polyisoprene unit. Due to its high structural regularity, NR tends to crystallize spontaneously at low temperature or when it is stretched. Low temperature crystallization causes stiffening, but it is easily reversed by warming. The strain induced crystallization results in the polymer greatly with high tensile strength and resistance to cutting, tearing and abrasion (Eng and Ong, 2001). It is also found that both saturated and unsaturated fatty acid found in the NR had a synergistic effect on the acceleration of the rate of crystallization of NR.

Another important property of uncured NR compounds is building tack. When two fresh surfaces of milled rubber are pressed together they bond into a single piece. This facilitates the building of composite articles from separate components. In tire manufacturing for example, the building tack property is important to hold together the separate pieces of uncured tire. During cure they fuse into a single unit (Ciullo and Hewit, 1999). During storage, the hardness of NR will increase and this will show with increasing value of Mooney viscosity. Mooney viscosity is a test to measure the toughness of the rubber. The higher value of Mooney viscosity will give the better resistance of that rubber to elongation (Ismail and Hashim, 1998).

### 2.1.2 Natural rubber latex

Natural Rubber latex occurs in more than 2000 species of higher plants but is mostly obtained from hevea brasiliensis tree (Heng and Ong, 2001). Freshly tapped NR latex is a whitish fluid with a density of between 0.975 and 0.980 g/ml and a pH of 6.5 to 7.0. Basically, NR latex is a dispersion of rubber and non rubber particles in an aqueous serum. The composition of these rubber and nonrubber particles including proteins, lipids, carbohydrates, acids, amines and some inorganic constituents varies depending on its source (Hourston and Tabe, 1996). The data in table 2.1 are typical for the analysis of NR latex (Hourston and Tabe, 1996). The rubber particles size ranges from about 50 Å to about 30 000 Å (3μm). In young trees the particles are spherical in shape but in matures tree the larger particles are often pear-shaped (Heng and Ong, 2001).

Table 2.1: Typical composition of NR latex

| | |
|---|---|
| Total solid content (%) | 36 |
| Dry rubber content (%) | 33 |
| Proteineous substances (%) | 1 – 1.5 |
| Resinous substances (%) | 1 – 2.5 |
| Ash (%) | < 1 |
| Sugars (%) | 1 |
| Water (%) | 60 |

The latex is collected from the trees and processed into commercial rubber latex. The low rubber content and high non-rubber solids found in NR latex has severely limits its usefulness as an industrial raw material. Hence it is necessary to concentrate the field latex to increase its dry rubber content (DRC). Three concentration methods available are creaming, evaporation and centrifugation. Among these three, the latter are the most widely used and the NR latex is usually concentrates to 60% DRC. The latex concentrates must be preserved to inhibit bacterial growth that could destabilize the latex. Therefore, ammonia is usually added to the latex as a preservative to increase the alkalinity (pH) and retard microbial growth. The additional benefit from adding ammonia is the increase in stability of the NR latex due to the increase in negative surface charge of the rubber particles (Blackley, 1997).

### 2.1.3 Classification of natural rubber

Natural rubber is normally processed into either latex or dry rubber, depending on its application. Rubber products such as dipped goods, foam, and thread produced from latex, whereas other products such as tires are made from dry rubber. About 90% of natural rubber is sold as solid, dry rubber in different grades according to their methods of production. Generally, natural rubber can be classified as latex (liquid) and cuplump (solid latex which coagulated naturally in the field) as shown in Figure 2.2. The types and grades of natural rubber processed depend greatly on the raw material input (Eng and Hong, 2001).

For many years, the conventional grades were listed and specified by the Booklet International Standards of Quality and Packing for Natural Rubber or also called the green book. The green book describes more than 31 standards which are under seven main grades (Ribbed Smoked Sheet, Pale Crepes etc). Classification of this grade is made entirely on appearance visual aspect has caused difficulties in interpretation (Stern, 1967). In an effort to deal with the situation the Rubber Research of Malaya introduced the so called Technically Specified Rubber (TSR). The bales are based on the rate of curing and are marked with colours to indicate the curing rate (red for slow, yellow for medium, blue for fast).

Dry rubber content scheme was launched in 1965 whereby Malaysian rubber could be marketed in either conventional or new process form. The scheme introduced mandatory specifications for the technical parameters such as dirt content, volatile matter content, ash content, nitrogen content and plasticity tests. The natural rubber processing and packing were also modernized by inclusion of size reduction equipment, dryers and compressed into $33^1/_3$ kg polyethylene-wrapped bales (Loganathan, 1998).

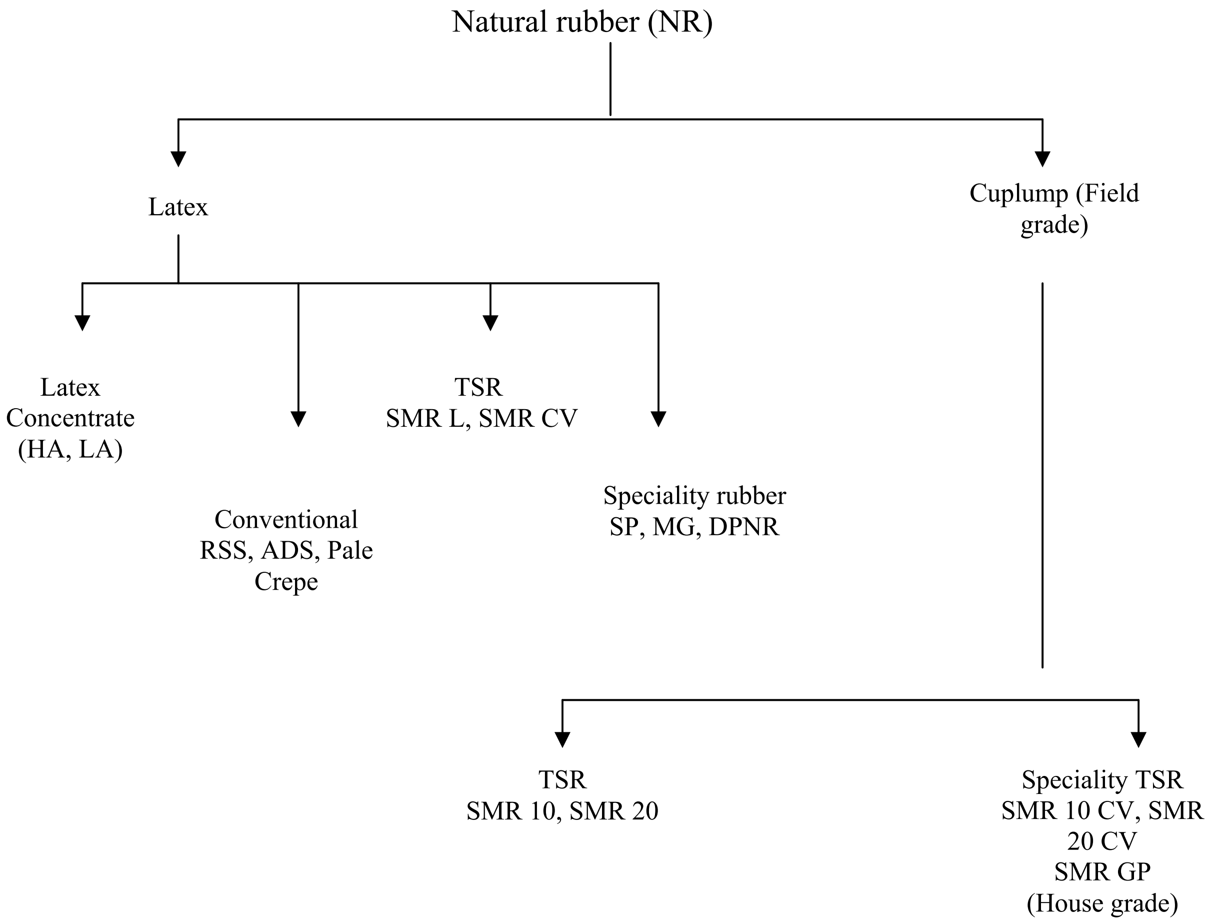

Figure 2.2: General natural rubber types and grades (Eng and Hong, 2001)

### 2.1.4 Deproteinized natural rubber latex

NR plays an important role in production of rubber goods like gloves, condoms, balloon and some parts of medical and dental equipment. However, the presence of the protein in the latex can cause sensitization or allergic reaction to human skin. The sweat can dissolve protein and allows contact with skin. The allergy caused by natural rubber latex products has become a serious problem and the removal of the protein was needed to lessen the problems (Pendle, 1993). Therefore, DPNR latex is an obvious choice in the application where allergy is to be avoided. DPNR is a special grade of NR latex with low protein content. Its maximum nitrogen content is 0.15 % which represents a reduction of the protein content by up to 3%. This grade of NR latex also has low water affinity and is suitable for applications such as cable insulation and engineering uses which require low creep

In NR latex, proteins make up about 1 – 2 % fresh weight of NR latex. The protein component is believed to be exclusively associated with particle surface as an adsorbed layer and help to maintain the latex colloidal stability during collection and transport prior to processing. Protein is an organic substance that contains carbon, hydrogen, nitrogen, oxygen and sulphur. Since the NR latex is not a homogenous fluid, the latex protein is not homogenously dispersed. Latex proteins are found in the latex serum and are also associated with the bottom fraction. About 70 % of the proteins are soluble while the remaining is associated with membranes (Blackley, 1997). Deproteinized Natural Rubber (DPNR) latex can be prepared in many ways from field latex or commercial high ammonia (HA) latex. However, the two most common methods are by washing with non-ionic surfactant and enzymatic treatment which are further described below (Ichikawa et al., 1993):

Method 1: Washing with surfactant. The latex is diluted with deionised water to 10 % DRC and stabilized with 1 % w/v non ionic surfactant. Then, the latex is centrifuged for 30 minute at 1.1 x $10^4$ r.p.m. The cream fraction is re-dispersed into deionised water containing 1 % w/v of the surfactant to make 10 % DRC latex and subjected to centrifugation. The procedure is repeated one to five times and the total solid content of the final latex is adjusted to 60 %.

Method 2: Enzymatic treatment. The latex is diluted with deionised water to 10 % DRC and stabilized with 0.12 % sodium naphthenate. The pH is adjusted to 9.2 by the addition of sodium dehydrogenphosphate into the diluted latex. Alkaline protease, alcalase 2.0T is then added and the pH is again adjusted to 9.2. The mixture is allowed to stand at 37$^{o}$C for 27 h. The deproteinised rubber is stabilized by adding surfactant and centrifuged three times in a similar way as method 1.

The protein extraction can also be done using irradiation. Rigero et al. (2003) was irradiating the NR latex with different doses of gamma ray to reduce the water soluble protein content and the concentration of extracted proteins increased with increasing radiation dose. The protein content of the films obtained by casting method was extracted with phosphate buffer solution, pH 7 and was measured using Micro BCA Protein Assay kit.

Consequently, when proteins are degraded or removed from the latex, other problem such as destabilization of the latex and changes in its coagulation properties occurs. Hence, the surfactant (e.g. sodium dodecyl sulphate) is added to the latex during deproteinization process to maintain the latex stabilization as shown in Figure 2.3. The degree of protein removed during the deproteinisation is indicated by the amount of nitrogen content in the NR. The NR latex after the deproteinisation contain lower amount of nitrogen as compared to untreated NR latex.

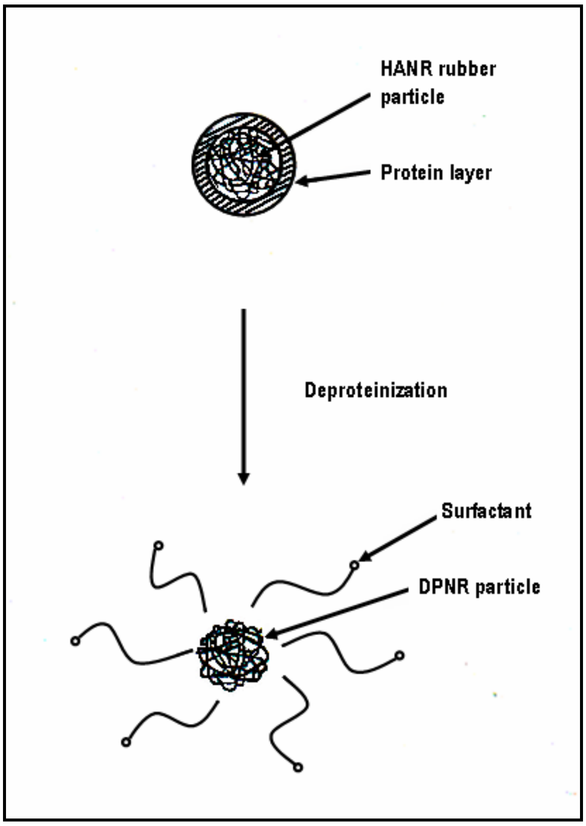

Figure 2.3: Rubber particles of HANR latex and DPNR latex

Table 2.2 shows the nitrogen content of untreated latex and deproteinized latex which indicates the amount of protein using centrifugation and enzyme method (Ichikawa et al., 1993).

Table 2.2: Nitrogen content of untreated and deproteinized latex

| Item | Nitrogen content (%) |
|---|---|
| FL. Untreated | 0.87 |
| FL. Once centrifugation | 0.09 |
| FL. 5 times centrifugation | 0.03 |
| FL. Enzyme method | 0.009 |
| HAL. Untreated | 0.56 |
| HAL. Once centrifugation | 0.08 |
| HAL. 5 times centrifugation | 0.03 |
| HAL. Enzyme method | 0.008 |

Perella and Gaspari (2002) reported that enzyme treatment of NR latex effectively reduces the protein content throughout the latex. The enzyme treatment of NRL alters the antigenic proteins associated with NRL by cutting them into smaller pieces and rendering them into less immunogenic. Even this method adds marginally to the production cost, it is still quite cost effective when compared with post washing NR latex products or the use of synthetic latex. Moreover, enzyme-treated latex maintains the excellent physical properties and performance of the latex. The vulcanized DPNR rubber showed almost similar tensile strength and a slight decrease in modulus compared to untreated rubber (Ichikawa et al, 1993). Aging properties also were found not affected by deproteinization process. These finding demonstrate that high deproteinization of latex has no significant negative effect on physical properties.

The thermal properties and crystallization behaviour of highly DPNR latex was investigated by Kawahara et al. (1999). The density of NR latex decreased after the removal of protein and linked fatty acid groups, while the thermal expansion coefficient increased. The $T_g$ of the rubber was slightly reduced by deproteinization and transesterification which resulted in the decrease of gel content. The overall crystallization rate of the untreated rubber was significantly influenced by the linked fatty acid group and the untreated rubber showed the most rapid crystallization among all the samples which were examined.

### 2.1.5 Vulcanization of Natural Rubber

Vulcanization is a process by which the long chains of the rubber molecules become crosslinked by reactions with the vulcanization agent to form three-dimensional structures. The three dimensional structure produced restricts the free mobility of the molecules and transforms the soft and weak plastic-like material into strong elastic product (Stephens, 1973). This vulcanisation process also give a product having reduced tendency to crystallise, improved elasticity, better resistivity toward solvent and substantially constant modulus and hardness characteristics over a wide temperature range (Blow, 1982). The major effects of vulcanization on properties of vulcanized rubber are summarized in Figure 2.4 (Coran, 1978).

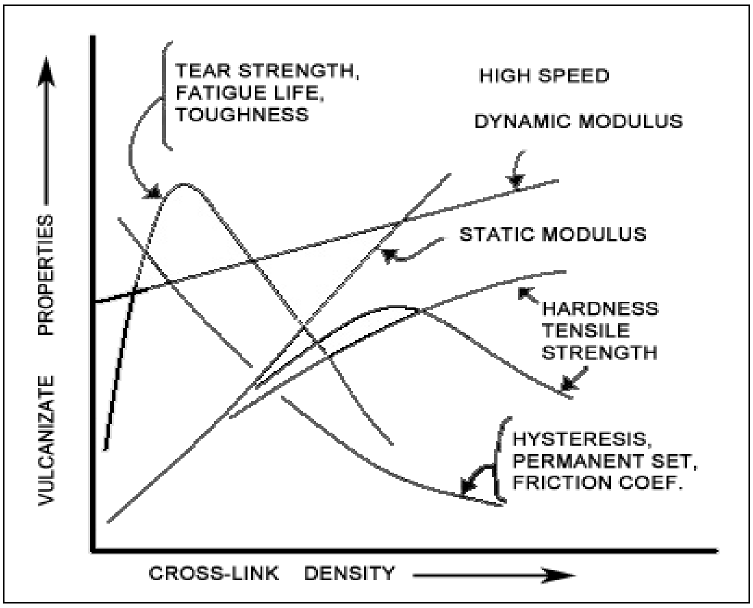

Figure 2.4: The effects of vulcanization on properties of vulcanized rubber

From the figure it is noted that the vulcanizate properties (tensile strength, modulus etc) are increased as the number of crosslinks is increased. However, with further increase in crosslink density resulted in decrease of most of the vulcanizate properties. This process is called reversion. Reversion is a term applied to the loss of network structures by nonoxidative thermal aging. The compounder must recognize this dynamic nature of the cure system and optimize the choice of ingredients to produce a stable vulcanizate. However it should be noted that the properties in Figure 2.4 are not functions of crosslink density only. They are also affected by the type of crosslink, the nature of polymer, the type and amount of filler (Coran, 1978).

NR can be vulcanized using sulphur, which is by far the most used crosslinking agent in rubber industry owing to its low cost, easy availability, good processing and physical properties. Other crosslinking systems are peroxides which are very occasionally used, particularly where freedom from staining by metals such as copper are important. Sulphur reacts chemically with the raw rubber forming crosslinks between the rubber chains. The crosslinks of rubber and sulphur in the vulcanization network can be in many ways as monosulphide, disulphide or polysulphide as shown in Figure 2.5(a). It may also present as pendent sulphides (Figure 2.5(b)), or cyclic monosulphides and disulphides (Figure 2.5(c)) depending on the recipe and vulcanizing system used (Morrell, 1982).

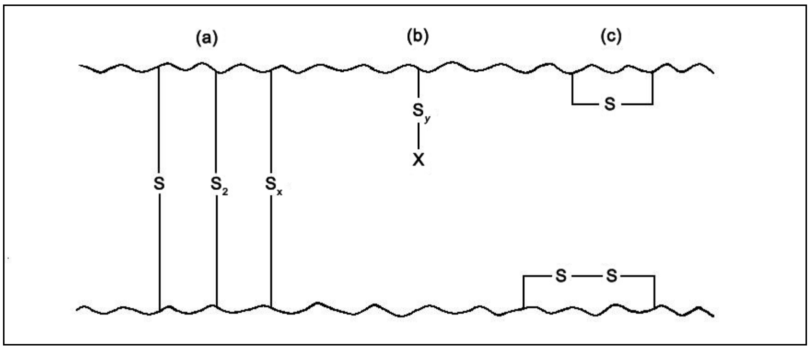

Figure 2.5: Types of sulphide crosslinks formed in vulcanized rubber

With sulphur alone, the curing process may take hours and inefficient. Therefore, the addition of accelerator (such as thiurams, thiazoles, guanidines and sulfenamides) is needed to reduce the curing time. Accelerator is ingredients used to control the rate of cure as well as crosslink density in rubber. The control of scorch, cure rate, cure state and reversion also depends to a large extent on the accelerators. In order to ensure the effectiveness of accelerators, the presence of activators (zinc oxide and stearic acid) in the system is required to activate the accelerators so that it performs more effectively. It is believed that they react in some manner to form intermediate complexes with the accelerators. The complex thus formed is more effective in activating the sulphur present in the mixture, thus increasing the cure rate (Ciesielski, 1999). Table 2.3 shows the typical rubber compound formulation expressed in parts per hundred rubber (phr).

Table 2.3: Typical rubber compound formulation

| Materials | Parts per hundred rubber |
|---|---|
| Raw rubber | 100 |
| Sulphur | From 0 to 4 |
| Zinc oxide | 5 |
| Stearic acid | 2 |
| Accelerators | From 0.5 to 3 |
| Antioxcidant | From 1 to 3 |
| Filler | From 0 to 150 |
| Plasticizer | From 0 to 150 |
| miscellaneous | |

Accelerated sulphur systems can be classified based on accelerator-sulphur ratio into: conventional vulcanization (CV) systems, semi-efficient vulcanization (semi-EV) systems and efficient vulcanization (EV) systems. In CV system, the level of sulphur and accelerator is in the range of 2.0 - 3.0 phr and 0.5 - 1.0 phr, respectively. The structures of its vulcanizate are dominantly polysulphide crosslink. EV system can be achieved by using small amounts of sulphur, about 0.3 to 0.8 phr, together with larger amounts of accelerator (2 - 5 phr). This system produces vulcanizate structures with dominantly mono and disulphide crosslink. In between these two systems lies the semi-EV system using about 1.5 phr of sulphur and almost similar amount of accelerator.

Rattanasom et al. (2005) reported the effect of CV and EV system on the mechanical properties and heat aging resistance of NR/tire tread reclaimed rubber (RR) blends. The results revealed that most mechanical properties, except for the tensile retention, of the CV vulcanizates are generally higher than those of the EV vulcanizates. It is also appears that the CV vulcanizates give slightly lower heat build up than EV vulcanizates. EV vulcanizates exhibit better heat aging resistance than CV vulcanizates, particularly when RR content is less than 50 phr, due to the greater thermal stability of mono and disulphide crosslink compared to the polysulphide ones. However, at higher filler loading, the properties tend to become independent of the vulcanization system due to the polymer-filler attachment effect. The similar findings were also reported by Joseph et al. (1988) who studied the vulcanizate properties of NR/SBR blend.

### 2.1.6 Reinforcement with carbon black

#### 2.1.6.1 Definition and classifications of filler

Fillers may either reinforced, extend, dilute or impart certain processing properties. Generally, fillers for rubber can be divided into two classes which are inert filler (clay, whiting and barites) which make the rubber mixture easier to handle before vulcanization but have little effect on its physical properties and reinforcing filler (carbon black, silicate and silica) which do improve the properties of vulcanized rubber (Billmeyer, 1984). Nonreinforced vulcanized rubbers, sometimes called pure-gum vulcanizates, are relatively soft, pliable and extensible and are most useful for items as rubber bands, tubing and gloves. Inert fillers also incorporated primarily to make the final product less expensive since it is significantly cheaper. Reinforcing filler stiffens and strengthens the structure by introducing a network of many relatively weak points. Generally, the reinforcing effect of a filler depends upon its nature, the type of elastomer with which it is used and the amount of filler present.

### 2.1.6.2 Carbon black

Carbon black is the most important filler in rubber formulation. Its loading can vary between 30-70 phr. Tire and mechanical goods consume about 65% and 25% of total black production, respectively. Carbon blacks consist of elemental carbon (90–99%), hydrogen and oxygen and are composed of aggregated particles. Carbon blacks are produced by converting either liquid or gaseous hydrocarbons (generally oil and gas) to elemental carbon and hydrogen by partial combustion or thermal decomposition (Horn, 1982). Commercially, carbon black is categorized as furnace black, thermal black, channel black or lamp black according to the process by which they are manufactured. Lamp black is the oldest type of carbon black, having been used as a pigment for centuries. Channel black, a highly reinforcing types of carbon black produced from natural gas, was introduced in the late nineteenth century and was the major carbon black used worldwide in the early twentieth century for rubber and pigment applications. Furnace and thermal blacks have been produced since the early twentieth century and most of all carbon black produced today is furnace black (Ciesielski, 1999 and Horn, 1982).

The particles of carbon black are not discrete but are fused or ‘clusters’ of individual particles and the fusion is more pronounced with very fine blacks (Horn, 1982). Carbon black surface contain functional groups capable of reacting with polymer molecules to form grafts during processing and vulcanization. When carbon black is incorporated into a rubber matrix, the strength related properties (modulus, mooney viscosity, ball rebound and abrasion resistance) of the rubber can be largely improved, depending on the nature of the carbon black (particle size, structure, surface area and surface activity).

In general, the reinforcement imparted to an elastomer increases as the particle size of the carbon black is decreased. If the filler particle greatly exceeds the rubber interchain distance, it introduces an area of localized stress. This can contribute to elastomer chain rupture on flexing or stretching. However, the finer carbon blacks are generally more difficult to process (Donnet and Wang, 1996). The blackness of a carbon black in general runs parallel to its particle size. The smaller it is, the blacker the colour. Blackness of a carbon black can be measured by a nigrometer (Stern, 1967).

The term structure of carbon black refers to the joining together of carbon particles into long chains and tangled three-dimensional aggregates or the tendency of a carbon black to agglomerate. This aggregation of particles occurs in the flame during the manufacture of carbon black. The higher the structure of a carbon black, the more irregular the shapes of the aggregates, resulted in less aggregates are capable of packing together. A high structure carbon black has aggregates favouring high particle count, with those particles joined in chain-like clusters formed which random branching of additional particle chains may occur and low-structure carbon black consist of relatively few prime particles, forming a more compact unit. The higher the structure, in turn, the greater it's reinforcing potential (Ciullo and Hewitt, (1999). Structure is normally measured by determining the total volume of the air spaces between aggregates per unit weight of carbon black.

The surface area that is accessible for reaction with rubber molecules, probably another important property of carbon black. Surface area is generally the inverse of particle size. A filler must make intimate contact with the elastomer chains if it is going to contribute to reinforcement. Fillers that have a high surface area have more contact area available, and therefore have a higher potential to reinforce the rubber chain (Ciullo and Hewitt, 1999). The surface area of rubber grade carbon blacks varies from 6 to 250 $m^2/g$ and generally can be determined by nitrogen adsorption using the ASTM standard test method (Lyon, 1990).

Another factor affecting the rubber reinforcement is the surface activity of the carbon black particles. A filler can offer high surface area and high structure, but still provide relatively poor reinforcement if it has low specific surface activity. The surface activity is determined by the physical and chemical nature of the filler in relation to that of elastomer. In carbon black particles, the presence of carboxyl, lactone quinine and other organic functional groups which promote a high affinity of rubber to filler. This, together with the high surface area of the carbon black means there will be intimate elastomer-carbon black contact (Ciullo and Hewitt, 1999). The carbon atoms also can be relatively unreactive if they are an integral part of the layer plane, more reactive if attached to hydrogen atom, and very reactive if present as a resonance-stabilized free radical. An increase in surface reactivity results in higher modulus, higher abrasion resistance, higher adsorptive properties, higher ‘bound rubber’ and lower hysteresis (Boonstra, 1982).

The old classification of carbon black is informal and according to its various performances including level of abrasion resistance, level of reinforcement, processing properties, general usefulness, particles size and electrical properties. It designated them by lettering code, and this system is still in use even though it is inconsistent and confusing (Ciullo and Hewitt, 1999).