# CHAPTER II

THEORY AND LITHERATURE REVIEW

2.1 Natural Rubber

Natural rubber (NR) occurs in over 200 species of plant. The *Hevea brasiliensis* tree accounts for over 99% of the world's natural rubber production. Other plants that contain rubber are guayule, balata and gutta percha tree.[2,4]

It has already been noted that natural rubber has the chemical name of polyisoprene. The rubber from *Hevea brasiliensis* is a polymer colloid largely comprising cis-1,4-polyisoprene. The structure of cis-1,4-polyisoprene is shown as follows :
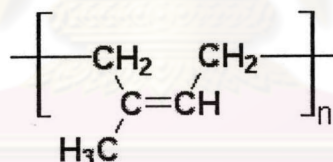
Cis-1,4- polyisoprene

2.1.1 Natural Rubber Latex

The latex of the *Hevea brasiliensis* tree has been described as a cytoplasmic system containing rubber and non rubber particles dispersed in an aqueous serum phase.

Freshly tapped natural rubber latex has a pH of 6.5-7.0, a density of 0.98 g/cm^3, and a surface free energy of 4.0-4.5 μJ/cm^2(0.96-1.1 μcal/cm^2).[2] The production of composition in natural rubber latex varied between wide limits is given in Table 2.1.

Table 2.1 Typical proportions of composition in natural rubber latex.[5]

Composition	%
Water	55
Rubber hydrocarbon	35
Protein	4.5
Acetone extraction	3.9
Amino acid, etc.	0.2
Quebrachitol	1.0
Inorganic salts	0.4

The total solids of fresh field latex vary typically from 30 to 40 %, depending on the clone, weather stimulation, tapping frequency, and other factors. The non-rubber portion is made up of large number of substances with proteins and the cyclic polyol quebrachitol predominating. The solids, both rubber and non rubber, in freshly latex are distributed though three phases, which are separated by ultracentrifugation. They are the top or rubber phase, the middle or serum phase, and the bottom or lutoid phase.

2.1.2 The Preservation of Natural Rubber Latex

The chemical composition of latex begins to change as soon as it comes in contact with air. Enzymes and bacteria act to lower the pH to a point where the latex coagulates unless preservatives are added. The preservation of field latex used in the production of latex concentrate may begin with the addition of ammonia solution to the cup prior to tapping.[2]

Ammonia is the principal preservation of natural rubber latex. Short-term preservation (0.2% of ammonia) is sufficient to ensure that the latex remains in a liquid condition for a few hours or a few days before being processed into the various forms of dry rubber. Short-term preservative is commonly known as anticoagulants. Long-term preservation (0.7% of ammonia) includes measures that will keep the latex intact and free decay during transportation and storage in country of final use.[2,5,6]

2.1.3 The Concentration of Natural Rubber Latex

Natural rubber latex as it emerges from the tree has dry rubber content (D.R.C.) of about 30 to 40 %, the average being about 33%. Although field latex can be preserved with ammonia or caustic alkali, its low rubber content and high non-rubber solid content severely limit its usefulness. Hence it is necessary to increase the D.R.C. in natural rubber latex to 60% or more to reduce transportation costs and enhance suitability for various latex processes. Concentrated latexes are economically useful as they contain less water to be shipped from the plantations, they are also more efficient in the manufacture of finished products directly from latex. Additionally, latex concentrates tend to more uniform in quality than do field latices. This is due in part to partial removal of non rubber constituents in several concentration processes.

Four methods are used for concentrating natural rubber latex; centrifugation, creaming, evaporation, and electrodecantation. Of these processes, centrifugation is the most widely used. The typical properties of concentrated natural rubber are given in Table 2.2.

Table 2.2 Typical properties of high ammonia type of centrifuged natural rubber
latex.

Properties	Tested results
Total solid content, %	61.54
Dry rubber content, %	60.03
Non rubber solids, %	1.51
Ammonia content (on total weight), %	0.70
Ammonia content (on water phase), %	1.82
pH value	10.92
KOH number	0.5610
Volatile fatty acid number (VFA)	0.0194
Mechanical stability time @ 55% TSC, sec	1,100
Specific gravity at 25^0 C	0.9411
Magnesium content (on solid), ppm	23

Source : Thai Rubber Latex Corporation (Thailand) Public Co., Ltd.
Bangplee Samutprakarn.

2.2.1 Modified Natural Rubber

Natural rubber has been modified in many ways. The term modified rubber can be
referred to any degree of chemical modification form a very small mole percent for the
purposes of introducing bond antioxidant function, crosslinking, bonding, etc., without
introducing any changes to basic physical properties, through the reaction of a significant
number of repeat units, say 20-50 mole%, which does result in changes in the physical

properties of rubber. Higher levels of modification tend to alter the nature of polymer from a rubber to more plasticlike or resinous materials.[7-9]

Liquid or Depolymerized Rubber

Liquid natural rubber is here defined as depolymerized natural rubber that has a sufficiently low viscosity to be able to flow at room temperature. The process is prepared by oxidative scission of natural rubber under controlled conditions. There are commercial grades, which are used for a rubber softener, a lubricating oil additive, a binder in manufacture of grinding wheel, etc., for example.

Cyclized Rubber

Cyclized rubber, the first chemically modified derivative of natural rubber, is the hard, resinous product obtained by treating the rubber with strong acids or Lewis acids. Sulfuric acid and chloride, ferric chloride, stannic chloride, boron trifluoride have been employed. Cyclizations are carried out on solid rubber, solutions, or latex, depending on catalyst.

Cyclized rubber have been used for shoe soles, hard moldings, heavy-duty industrial rollers, adhesives, bonding agents, reinforcing resins, corrosion-resistant surface coatings, and printing inks.

Chlorinated Rubber

Natural rubber readily undergoes both substitution and addition reaction with chlorine. Although it is possible to chlorinate in the rubber latex system, the best

process is the direct chlorinating of a rubber solution in an inert solvent, such as carbon tetrachloride at about 80 $^{\circ}$C. The fine white powder of chlorinated rubber is obtained by steam distillation to remove the solvent.

Fully chlorinated rubber (65% chlorine) has a specific gravity of 1.63-1.66, and readily soluble in aromatic hydrocarbons and chlorinated solvents. Since it is inert, chlorinated rubber is used as a base in chemically resistant paints. It is also useful as adhesive for rubber to metal bonding.

AC Rubber

Better known as anticrystallizing natural rubber, Ac rubber is an equilibrium mixture of cis and trans isomers, which interferes with the orientation, and hence crystallization of rubber when exposed to low temperatures. It is obtained most readily in two ways: (1) addition of thiol acids to the rubber latex at room temperature over night; or (2) treatment of the dry rubber with sulfur dioxide for 10-15 minutes at 170-180 °C.

Deproteinized Rubber

Deproteinized rubber, called DPNR, is a useful rubber where low water absorption is wanted, vulcanizates with low creep are needed, or when more than ordinary reproducibility is required. Normally natural rubber has between 0.25 and 0.50% nitrogen as protein; deproteinized rubber has only about 0.07% nitrogen. One trade-off occurs protein matter in rubber accelerates cure so that deproteinized rubber requires more acceleration.

Treating natural rubber latex with a bioenzyme, by hydrolyzes the protein present into water-soluble forms, makes deproteinized rubber.

Epoxidized Natural Rubber (ENR)

Epoxidized natural rubber is prepared from latex with performic acid. The latex is stabilized with a nonionic stabilizer, and formic acid and hydrogen peroxide are added. The reaction is carried out at 30-65 °C for different periods of time, depending on the degree of epoxidation required. The epoxidized latex is washed and dried. The acid is neutralized with base before or after coagulation.

Commercial production began at the end of 1988, three grades have been available in small tonnage quantities for four years: ENR-10, ENR-25, and ENR-50, corresponding to epoxidation of 10, 25, and 50 mole%, respectively, of epoxides groups. The introduction of epoxide groups progressively increases the glass transition temperature of natural rubber and changes some of its properties markedly. For example, ENR-50 has low air permeability, comparable to butyl rubber and good oil resistance at room temperature, comparable to medium nitrile rubber.

2.3 Emulsion Polymerization

Emulsion polymerization is a means of carrying out this process on the laboratory and industrial scales.[10] The simplest recipe for an emulsion polymerization starts with water, surfactant (soap), monomer, and initiator. The system is agitated to form an emulsion. Heating results in the production of free radicals by thermal decomposition of initiator, and free radical polymerization commences. The end result of the polymerization process is a latex comprising polymer particles, each containing

many polymer chains. The polymer particles constitute a dispersed phase in continuous aqueous phase. These latex particles are typically 200 nm in diameter. They form a colloid, stabilized against coalescence by surfactant, and comprise a new phase that is formed early in the process. Thus the final result of an emulsion polymerization is a latex: a polymer colloid, with water the continuous phase. The latex can be directly (e.g. as an adhesive or surface coating) or, for other applications, the polymer can be extracted.

Emulsion polymerization (including copolymerization) furnishes what in principle is a method for producing a latex and polymer with any desired morphology, composition, sequence distribution, surface end groups, molecular weight distribution, particle size distribution, particle concentration, and so on.

2.3.1 Ingredients and Processes

An overview of the major ingredients and processes in emulsion polymerization is now presented: a list of common monomers and where they are used in commercial products, of surfactants, and initiators, as well as a tiny sample of some of the huge range of products of this process.

a.) Monomers

The major polymerizable component of an emulsion polymerization is a monomer that is of limited solubility in water, and that swells its polymer. The monomers used in emulsion polymerization are thus often of the vinyl type, $CH_2=CHX$. X may be C_6H_5, CN, O_2CCH_3, Cl, and CO_2R. The list of some common monomers is given in Table 2.3.

b.) Initiators

Most initiators used in emulsion polymerization are water-soluble. A commonly used laboratory and industrial initiator is potassium persulfate ($K_2S_2O_8$, properly called potassium peroxydisulfate), or other persulfate salts such as ammonium persulfate. Persulfate produces $SO_4^{..}$ anion free radicals as a result of bond scission; the high energy for this process is quite high, so persulfate is usually employed as the sole initiator at high temperatures (50 °C or higher).
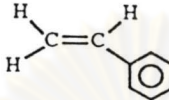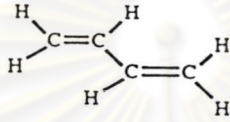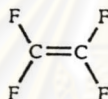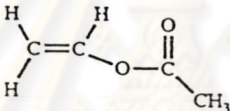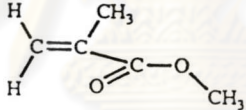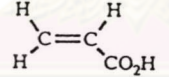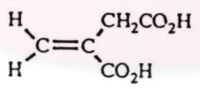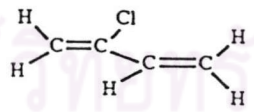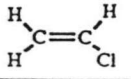
At lower temperature a redox system such as Fe(II) and cumene hydroperoxide, or dimethylhydroperoxide, or persulfate and metabissulfite, is often used. It is common to perform industrial emulsion polymerizations at low temperature: in the case of synthetic rubbers, this reduces the amount of branching of chains, which in turn reduces the time required to incorporate carbon black into the rubber.

Finally, it is possible to employ an organic-phase initiator such as AIBN (azobisisobutyronitrile) in an emulsion polymerization. Oil-soluble initiator can be employed under special circumstances in emulsion polymerization: e.g. in the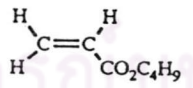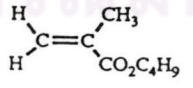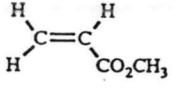 preparation of large-particle size monodisperse polystyrene latexes, using AIBN and water-soluble initiator in seed emulsion polymerization. Oil-soluble initiators also find use in dispersion polymerizations.

c.) Surfactants

Surfactant is used to impart colloidal stability to latex particles, which are the loci of polymerization. There are three basic types of surfactant: (i.) electrostatic stabilizers such as anionic or cationic soaps, which prevent coagulation by electrostatic

Table 2.3 Some monomers used in commonly by commercial emulsion polymerization.[10]

monomer	formula	examples of common usage
styrene	$H_2C=CH-C_6H_5$	ingredient in artificial rubber (SBR — also used in paper coating)
butadiene	$H_2C=CH-CH=CH_2$	(1) ingredient in artificial rubber (SBR — also used in paper coating) (2) impact modifier (toughening of plastics), e.g. HIPS, ABS
tetrafluoroethylene	$F_2C=CF_2$	(1) polytetrafluoroethylene (e.g. Teflon®) (2) ingredient in fluoropolymers, e.g. Viton® rubbers
vinyl acetate	$H_2C=CH-O-CO-CH_3$	(1) polyvinyl acetate (PVA) adhesive (2) ingredient in paint
methyl methacrylate	$H_2C=C(CH_3)-CO-O-CH_3$	ingredient in surface coatings
acrylic acid	$H_2C=CH-CO_2H$	minor ingredient in paint formulation
itaconic acid	$H_2C=C(CH_2CO_2H)-CO_2H$	minor ingredient in paint formulation
2-chloro-1,3-butadiene (chloroprene)	$H_2C=C(Cl)-CH=CH_2$	Neoprene rubber (which has sulfur as co-monomer)
butyl acrylate	$H_2C=CH-CO_2C_4H_9$	rubbery ingredient in surface coatings
butyl methacrylate	$H_2C=C(CH_3)-CO_2C_4H_9$	rubbery ingredient in surface coatings
methyl acrylate	$H_2C=CH-CO_2CH_3$	co-monomer in surface coatings, adhesives
vinyl chloride	$H_2C=CH-Cl$	PVC (usually produced by suspension method, sometimes by emulsion)

repulsion arising from the charges located on the particle surfaces and their associated electric double layer. (ii.) Polymeric stabilizer such as partially hydrolyzed poly(vinyl acetate), which stabilizes *inter alia* through the entropic repulsion caused by trying to pack two chains in the same space, and (iii.) electrostatic stabilizer displays the characteristics of both surfactant types (i.) and (ii.). Some commoner laboratory anionic surfactants are sodium dodecyl sulfate (SDS).

d.) Other Ingredients

It is often to add a modifier in commercial emulsion polymerization: chain transfer agents to control molecular weight. Buffers are another usual additive, their role being control pH. This prevents hydrolysis of surfactants and may also be necessary to ensure reasonable initiator efficiency. Electrolytes may be added. Usually with the aim of including particle size monodispersity; since electrolytes may also have the determental effect of promoting particle coagulation, caution needs to be exercised in using them. It is also common to add a chaser, which is means of reducing residual monomer at the end of the polymerization process (typically a chaser might comprise a shot of redox initiator added late in the batch).

2.4 Graft copolymer

A graft copolymer is a polymer comprising molecules with one or more species of block connected to the main chain as side chains, having constitutional or features that differ from those in the main chain, exclusive of branch points. In a graft copolymer, the distinguishing feature of the side chain is constitutional, i.e., the side chain comprises units derived from at least one species of monomer different from

those that supply the units of the main chain.[11] The general structure of graft copolymer can be indicated as follows:

$$AAAAAAAAAXAAAAAAAAAAAA$$
$$|$$
$$B$$
$$|$$
$$B$$
$$|$$
$$B$$
$$|$$
$$B$$
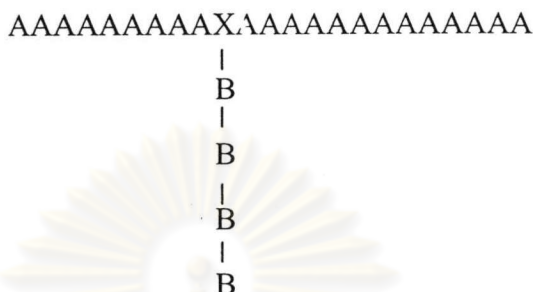
Where a sequence of A monomer unit is referred to as the main chain or backbone, the sequence of B unit is the side chain of graft, and x is the branching point in the backbone to which the graft is attached.

Graft copolymer produced by causing a post polymerization of vinyl monomers such as styrene, acrylonitrile, or methyl methacrylate either independently or as a mixture of a plurality thereof to rubber-like polymer latex have been well known.

2.4.1 Graft Copolymer of Natural Rubber

The idea of graft copolymerization probably first arose as means of modifying naturally occurring polymers, such as cellulose, rubber, or wool. Graft copolymerization, by analogy to the botanical term, refers to the growth of a "branch" of different chemical compositions on the backbone of a linear macromolecule.[7] The importance of these types of polymer structure is basically due to the fact that polymer chains of different chemical structures, which are normally incompatible.

Synthesis of graft copolymer from natural rubber has been investigated in solution, latex and oil state. These graft copolymers were prepared by radical polymerization, metalation with lithium catalyst and living anionic polymerization followed by ene-reaction.[11] Reaction involving free radical has been the most widely applied mechanism in grafting processes, and such reactions have been used with a wide range of polymers and monomers.

In the case of graft copolymerization onto natural rubber, the use of the following basic methods of synthesis have been reported: (i) polymer transfer; (ii) copolymerization via unsaturated groups; (iii) redox polymerization; (iv) photo chemical synthesis; (v) mechanico-chemical reaction; and (vi) high energy irradiation techniques.[13]

(i) Polymer Transfer

In the free radical polymerization, chain transfer is an important reaction. Chain transfer to monomer, mecaptan, solvent, or other growing chain can take place. When a chain transfer reaction to another chain takes place, it creates a radical, which acts as a site for further chain growth and grafting.

$$R_r^{\cdot} + B \longrightarrow P_r + B^{\cdot} \quad \text{(transfer to initiator)} \tag{1}$$

$$R_r^{\cdot} + M \longrightarrow P_r + M^{\cdot} \quad \text{(transfer to monomer)} \tag{2}$$

$$R_r^{\cdot} + RSH \longrightarrow P_r + RS^{\cdot} \quad \text{(transfer to mercaptan)} \tag{3}$$

$$R_r^{\cdot} + S \longrightarrow P_r + S^{\cdot} \quad \text{(transfer to solvent)} \tag{4}$$

$$R_r^{\cdot} + P_s \longrightarrow P_r + P_s^{\cdot} \quad \text{(transfer to polymer)} \tag{5}$$

$$R_r^{\cdot} + R_s^{\cdot} \longrightarrow P_r + R_s^{\cdot} \quad \text{(transfer to polymer radical)} \tag{6}$$
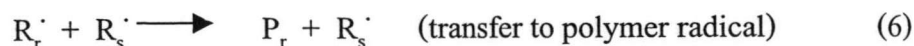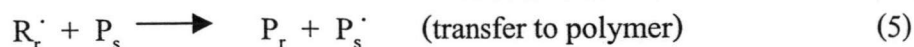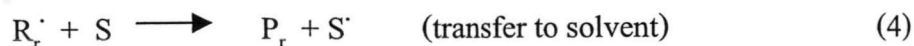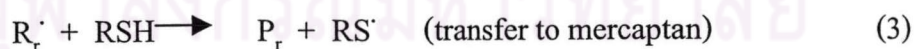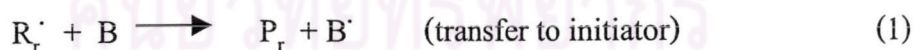
In each of these generalized mechanisms the reaction proceeds by transfer of a hydrogen or halogen atom of the transfer molecule to the growing polymer chain. The growing chain is therefore terminated but the free radical activity is transferred to the molecules donating the hydrogen or halogen atom. In this way a number of polymer chains are formed from each initiator fragment and each chain so formed in the absence of the chain transfer reaction. Although each of those reactions may take place to some extent during graft copolymerization with natural rubber, it is Equation (5), which is of particular importance in the synthesis of copolymer by transfer reactions.

(ii) Copolymerization via Unsaturated Groups

The addition of growing polymer chain to unsaturated groups in natural rubber hydrocarbon has already been referred to as part of the normal grafting process, Equation (8), accompanying the transfer reaction, Equation (7).

$$
\begin{array}{l}
\text{---CH}_2\text{---}\underset{\underset{\text{CH}_3}{|}}{\text{C}}\text{==CH---CH}_2\text{---} + \text{R}'\cdot \longrightarrow \text{---CH}_2\text{---}\underset{\underset{\text{CH}_3}{|}}{\text{C}}\text{==}\overset{\cdot}{\text{C}}\text{---CH}_2\text{---} + \text{R}'\text{H} \qquad (7)
\end{array}
$$

$$
\begin{array}{l}
\text{---CH}_2\text{---}\underset{\underset{\text{CH}_3}{|}}{\text{C}}\text{==CH---CH}_2\text{---} + \text{R}'\cdot \longrightarrow \text{---CH}_2\text{---}\overset{\overset{\text{CH}_3}{|}}{\underset{\underset{\cdot}{|}}{\text{C}}}\text{---}\overset{\overset{\text{H}}{|}}{\underset{\underset{\text{R}'}{|}}{\text{C}}}\text{---CH}_2\text{---} \qquad (8)
\end{array}
$$
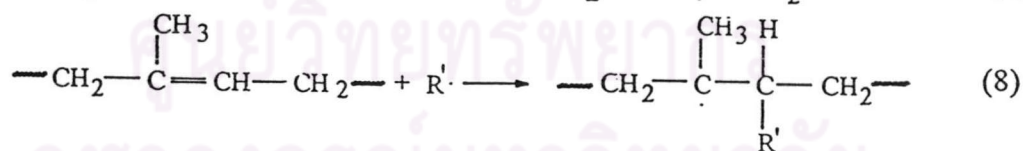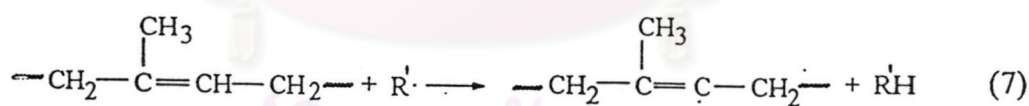
(iii) Redox Polymerization

Redox polymerizations are among the most popular techniques for grafting reaction, and of the possible initiator systems. A prime advantage of redox initiator is that radical production occurs at reasonable rates over a vary wide range of temperatures, depending on the particular redox system, including initiation at moderate temperature.

In redox polymerization, hydroperoxide or similar group is reduced to a free radical plus an anion, which the metal ion or amine are oxidized to a higher valency state, and at the same time a monomer is added. When the reducible group is attached to a polymeric chain, the free radical grafting sites thus formed on the macromolecular backbone, which acts as the initiators for graft copolymerization. This method has been used to graft methyl methacrylate to natural rubber latex (Actually, fresh latex contains a few hydroperoxide groups per macromolecule, which can take part in grafting reactions.). Recentrifuged latex concentrate is mixed with methyl methacrylate and a solution of tetraethylene pentamine is added, followed by a small quantity of ferrous sulfate solution. The homogenized blend is allowed to stand, often overnight. The graft copolymer is isolated by coagulation. Since practically all free radical sites are formed on the rubber backbone, there is very little free poly(methyl methacrylate) in the graft system. On the other hand, some rubber chains are without grafts, since not all chains have hydroperoxy groups. Higher yields of graft copolymer are obtained by allowing the monomers to dissolve in, and equilibrate with, the latex particles before adding the amine and ferrous ion initiator. Passing oxygen (air) through the latex for several hours has been claimed to reduce the free rubber content of polymerization product, but nitrogen purging is then necessary to prevent the dissolved oxygen from acting as a polymerization inhibitor.

2.4.2 Natural Rubber-Graft-Methyl Methacrylate

The chemical modification of natural rubber by grafting with vinyl monomers using various initiator systems has gained considerable importance in modifying the properties of natural rubber. For natural rubber, research has confirmed that methyl methacrylate and styrene are the most suitable monomers when polymerized to give a high level of grafting.

Poly(methyl methacrylate) modified natural rubber has been marketed since the mid-1950s under the trade name "Heveaplus". Heveaplus MM, was a simple mixture of poly(methyl methacrylate) and natural rubber prepared by combining natural rubber latex concentrate with the appropriate amount of poly(methyl mathcrylate) dispersion to give the required rubber/polymer ratio, followed by coagulation, washing, and drying. Heveaplus MG, was grafted by reacting natural rubber latex with the required amount of methyl metacrylate monomer with tert-butyl hydroperoxide as the polymerization initiator. After stirring in tetraethylene pentamine (as the other half of the redox system), the reaction is essentially competed in 2 hr. The product is coagulated by adding boiling water containing 0.1% calcium chloride and then sheeted out and dried. The first of these types never appeared to be of commercial interest, but the grafted type has been proven on several counts and indeed is still in production in Malaysia. Various levels of modification can be achieved according to the proportion of grafted poly(methyl methacrylate), and this alters the modulus of the rubber.

The properties and application of Heveaplus MG have been reviewed, with particular reference to latex preparation procedures and use of the modified latex. The Heveaplus MG materials have been used in two general ways. The first, and probably most importance in terms of current consumption, is as solution or latex-based adhesives or bonding agent to bond rubber to poly(vinyl chloride), leather, textiles, and

metals. The second is in the manufacture of hard rubber products and blends well with natural rubber in all proportions.[15,16]

2.5 Literature Review

The graft copolymerization of methyl methacrylate onto natural rubber using V^{5+} as the initiator was investigated by Lenka et al.[17] It could be seen that as the monomer concentration increased, there was an increase in the percentage of grafting in the lower concentration range. It reached a maximum value at 0.02-0.025 M, and thereafter it decreased. The effect of concentration of V^{5+} ion on grafting of methyl methacrylate onto rubber indicated that increasing $[V^{5+}]$ up to 0.035 M was accompanied by a significant increase in graft yield while further increases in its concentration caused a marked fall in the graft yield. With increasing temperature, the percentage of grafting increased. They also studied the graft copolymerization of methyl methacrylate onto crepper natural rubber using potassium peroxydisulfate catalyzed by silver ion.[18] The graft copolymerization was carried out by varying the concentrations of monomer, initiator, and thiourea over a wide range of polymerization time. The percentage of grafting was maximum at 5 hr, the peroxydisulfate concentration was up to 2.5×10^{-2} M and the thiourea concentration was up to 6.0×10^{-3} M.

Hourston and Romaine [19] studied composite latex particles based on natural rubber latex. It has been synthesized to yield materials, which may be formally regarded as interpenetrating polymer networks, and semi-interpenetrating polymer networks. Methyl methacrylate has been added to carefully stabilize natural rubber latex and polymerize in situ using an amine-activator initiator, tert-butyl hydroperoxide. The

morphology of the materials was determined both by transmission electron microscopy and by dynamic mechanical analysis.

Graft characteristics and solution properties of natural rubber grafted with methyl methacrylate copolymer in MEK/toluene using benzoyl peroxide as initiator were studied by Enyiegbulam and Aluka.[20] An increase in the concentration of methyl methacrylate at a given benzoyl peroxide initiator decreased both the graft level and grating efficiency, but increases the molecular weight of the copolymer. An increase in the concentration decreased the graft level to a constant level when the benzoyl peroxide concentration exceeded 10×10^{-2} M. Dilute solution theory applicable to homopolymers can also be applied to the graft copolymers without any adverse effect in technological application.

Thiraphattaraphun et al. [21] studied the grafting of methyl methacrylate monomer onto natural rubber using potassium persulfate as an initiator. The effects of the initiator concentration, reaction temperature, monomer concentration, and reaction time on the monomer conversion and grafting efficiency were investigated. The grafting efficiency reached a maximum value at initiator concentration of 0.75 phr., reaction temperature 55°C and reaction time 8 hr. The morphology of the grafted natural rubber was determined by transmission electron microscopy and it was confirmed that the graft copolymerization was a surface-controlled process.

Fukushima et al. [12] studied the graft copolymer of highly deproteinised natural rubber latex (HDPNR) with styrene using tert-butyl hydroperoxide/tetraethylene pentamine as an organic redox initiator. The styrene content, grafting efficiency, and molecular weight of grafted polystyrene were significantly increased by deproteinization. The number of graft sites for graft copolymer from HDPNR latex was

about three times larger than that determine for graft copolymer from untreated natural rubber latex. The difference between the behavior of HDPNR and untreated natural rubber was due to the removal of protein and naturally occurring antioxidant present in untreated natural rubber latex.

Schneider et al. [22] studied the graft copolymerization of natural rubber latex with methyl methacrylate using tert-butyl hydroperoxide/tetraethylene pentamine or tert-butyl hydroperoxide/dimethylaniline as an initiator. The morphology of the resulting latex interpenetrating network was characterized by transmission electron microscopy and scanning electron microscopy. Different staining methods increase the contrast between the NR phase and the secondary polymers in the composite latex particles.

The grafting of poly(cis-1,4-isoprene) with methyl methacrylate has been studied using benzoyl peroxide as initiator was studied by Egboh and Fagbule.[23] Graft copolymers were isolated from homopolymers by selective solvent extraction using a soxhlet apparatus. The effects of reaction conditions on the graft yields were investigated. Kinetic study of the graft copolymerization reaction showed that the reactions followed the conventional kinetic behavior of free radical polymerization. The kinetic orders of the grafting with respect to initiator and monomer were 0.5 and 1.0, respectively. The overall activation energy for the graft copolymerization was 24.9 kJ/mol.

Camedon and Qureshi [24] studied the grafting of styrene onto polyisoprene (PIP) in benzene solution at 60°C. The polymerization of styrene at rubber concentration up to 0.5 M shows ideal kinetics with on retardation by PIP. The proportion of polystyrene incorporated as graft is independent of the initiator (benzoyl

peroxide) concentration and was found to be consistent with the kinetic expression. The graft fraction of polystyrene, which is higher than in corresponding styrene-polybutadiene system, reflects the higher reactivity of PIP toward radicals. Azo-bis-isobutyronitrile produces no graft copolymer in this system.

Lee et al. [25] studied the seed emulsion polymerization of natural rubber grafted with poly(methyl methacrylate). The formation of graft sites on the polyisoprene backbone was promoted by adding vinyl neodecanoate(VeoD). Two different redox systems, cumene hydroperoxide(CHPO)/tetraethylene pentamine (TEPA) and tert-butyl hydroperoxide(TBHPO)/TEPA, were used to initiated polymerization. CHPO was observed to be more efficient than TBHPO for grafting of secondary polymers in modified natural rubber; grafting was enhanced considerably in the presence of VneoD.

Lehrle and Willis [1] studied the effect of the presence of small quantities of vinyl acetate (VAc) on the efficiency of grafting methyl methacrylate (MMA) on natural rubber (NR) molecules in latex form. Several VAc concentrations have been examined, and the initiator azo-bis-isobutyronitrile was added to the systems to promote the formation of VAc radicals. There is good evidence for the formation graft copolymer under the conditions used, but it was found that the grafting is not significantly affected by presence of VAc. It is proposed that could be due to the fact of the oil soluble initiator is not accessible to the relatively large amount of VAc.