

CHAPTER II

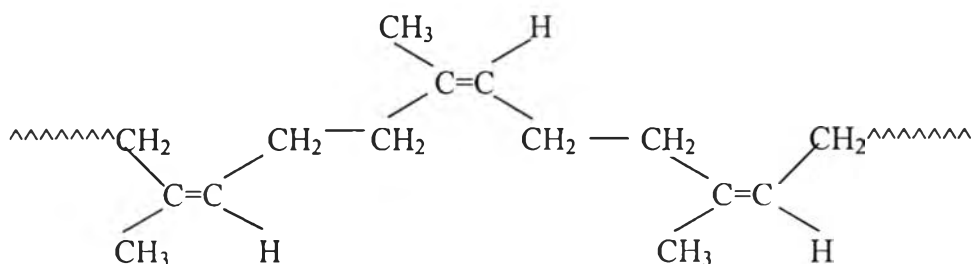
THEORY AND LITERATURE REVIEW

2.1 Natural Rubber

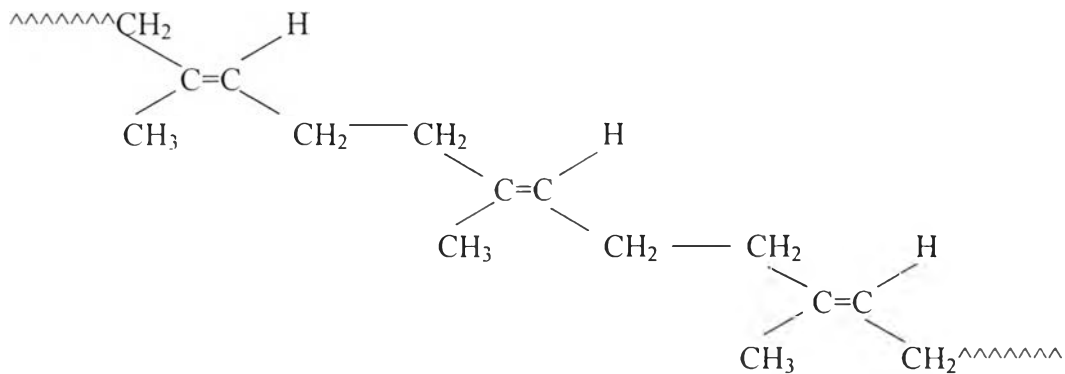
Natural Rubber (NR) is found in about 2000 plant species all over the world. Only Para rubber tree, *Hevea brasiliensis* is the rubber producing plant of commercial significance for over 99% of the world's natural rubber production. Other plants that contain rubber is guayule, balata and gutta percha tree [6,7].

It has already been noted that natural rubber has the chemical name of polyisoprene. The rubber from *Hevea brasiliensis* and guayule is *cis*-1,4-polyisoprene, while the rubber from balata and gutta percha is *trans*-1,4-polyisoprene. The molecular structures of polyisoprene are as follows [8,9]:

(a) *cis*-1,4- polyisoprene



(b) *trans*-1,4- polyisoprene



II

There is a great deal to be said the use of the term “natural rubber” known as *hevea rubber* comes from the rubber tree *Hevea brasiliensis*.

2.1.1 Natural Rubber Latex

Natural rubber latex is the form in which rubber is extruded from the *Hevea brasiliensis* tree as an aqueous emulsion, as rubber and non rubber particles dispersed in an aqueous serum phase, as a milk- like liquid.

Latex is harvested from the tree by a process called tapping. Freshly tapped latex (field latex) has a pH of 6.5-7.0, a density of 0.98 g/cm³, and a surface energy of 4.0-4.5 μJ/cm² (0.96-1.10 μcal/cm²) [10-12]. The proportions of composition in natural rubber latex varied between wide limits are given in Table 2.1. The following composition is typical:

Table 2.1 Typical proportions of composition in natural rubber latex [12].

Composition	%
Water	55
Rubber hydrocarbon	35
Proteins	4.5
Acetone extract	3.9
Lipins, aminoacids, etc.	0.2
Quebrachitol	1.0
Inorganic salts	0.4

The total solid of fresh field latex varies typically from 30 to 40%. The latex has a rubber content varies between the limits of 25 and 35%, depending on factors such as type of tree, tapping method, soil conditions, and season. The difference between the total solids and dry rubber contents of fresh latex is of the order of 3%.

Both rubber and non rubber, in freshly tapped latex are distributed between three principal phases, which can be separated by ultracentrifugation. They are the top or rubber phases, which account for some 35% of the latex by weight; the middle or serum phases, which is approximately 55% by weight of the whole; and the bottom or lutoid phases, which accounts for most of the remaining 10%.

(i) The Rubber Phase

The rubber particles are usually spherical in shape with a diameter ranging from about 0.01 μm to 5 μm . The particle in latex as comprising a sphere of mainly rubber hydrocarbon, surrounded by concentric spherical shells, first of phospholipid and then of protein. The probable structure of natural rubber latex particle is shown in Figure 2.1

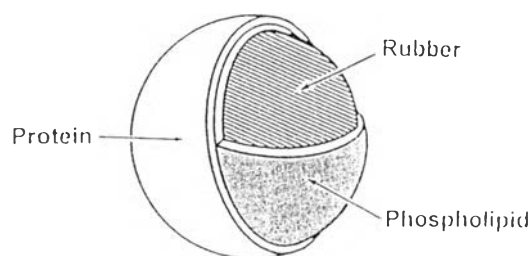


Figure 2.1 Diagrammatic representation of probable structure of natural rubber latex particle [10].

A typical composition for the rubber phase of natural rubber latex is shown in Table 2.2.

Table 2.2 Typical composition of the rubber phase [10].

Composition	%
Rubber hydrocarbon	86
Water (dispersed in the rubber hydrocarbon)	10
Proteinous substances	1
Lipid substances	3

Trace amounts of metals, notably magnesium, potassium, and copper are also associated with the rubber particles to an aggregate extent of approximately 0.05%.

(ii) The Serum Phase

The serum phase, sometimes referred to as the C-serum or aqueous phase, is a dilute aqueous of density slightly over 1.0 g.ml^{-1} . The serum contains many different chemical species, including carbohydrates, proteins, amino acids, enzymes, and nitrogenous bases.

(iii) The lutoid phase

The lutoid phase or bottom fraction consists mainly of lutoid particles. Lutoid particles contain 20 wt% of water-soluble protein, of which 70 wt% is hevein. The yellow color of the lutoid phase is caused by Frey Wyssling particles, which are spherical, non-rubber particles, whose color is due to the presence of carotenoid pigments [7].

2.1.2 The Preservation of Natural Rubber Latex

Natural rubber latex coagulates within a few hours of leaving the tree. The actual time required for coagulation to occur depends very much upon the ambient temperature and upon the stability of the latex itself. But always the result is a separation into clots of rubber and a clear serum. At a later stage, putrefaction sets in, with the development of bad odours. It is to prevent both of these processes that preservation is necessary [10].

The preservative protects the latex against spontaneous coagulation and putrefaction by suppressing the activity and growth of microorganisms, enhancing colloid stability, and deactivating trace metals by sequestration in solution or precipitation as insoluble salts.

The most widely used preservative for natural rubber latex is ammonia. 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 of decay during transportation and storage in the country of final use [7,10,12].

2.1.3 The Concentration of Natural Rubber Latex

Natural rubber latex as it emerges from the tree (field latex) has a 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 fixed 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 [10]. 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 be more uniform in quality than do field latices. This is due in part to the partial removal of non-rubber constituents in several concentration processes [12,13].

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 latex are given in Table 2.3.

2.2 Graft Copolymers of Natural Rubber

By the term “graft copolymer” is meant a special type of block copolymer in which the blocks of the one monomer are grafted on to a backbone polymer which consists exclusively of units derived from the other monomer. The general structure of graft copolymer can be indicated as follows [10,14]:

AAAAAAAAAAAAAAAAAAAAAAAAAAAA

B
B
B
B
B
B
B

III

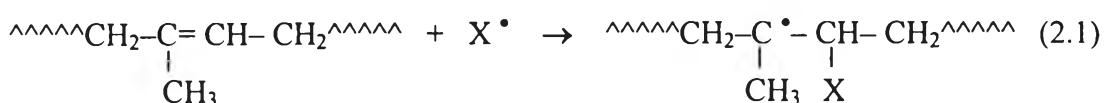
Table 2.3 Typical properties of once-concentrated natural rubber latex [10].

Properties	Evaporated		Creamed	Centrifuged	Electro-decanted
	KOH Preserved	NH ₃ Preserved			
Total solid content (%)	72-75	61-63	61-62	61-62	61-62
Dry rubber content (%)	65-68	55-57	59.5-60.5	59.5-60.5	59.5-60.5
Alkalinity (g alkali per 100g latex)	0.8-0.9	0.6-0.7	0.6-0.7	0.6-0.7	0.6-0.7
Ash (%)	> 1	> 0.5	0.6	0.5	0.5
Nitrogen (%)	0.50	0.40	0.20	0.20	0.20
Approximate viscosity (poise)	10-30	0.8-1.5	0.10-0.3	0.10-0.30	0.10-0.30

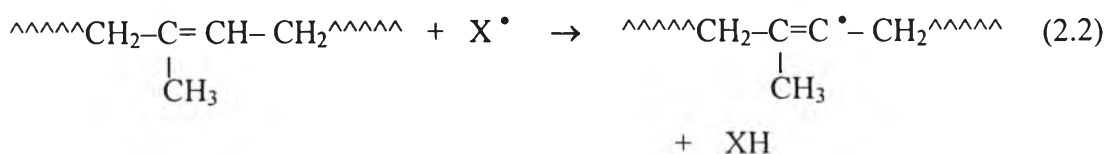
Graft copolymerization has been used as a method for modifying natural rubber in both latex form and in solution. Reaction involving free radicals has been the most widely applied mechanism in grafting processes, and such reactions have been used with a wide range of polymers and monomers [15]. The principal reaction responsible for the formation of graft copolymers seems to be the reaction of radical transfer to polymer. This reaction was originally thought most likely to occur by transfer from a growing polymer chain, but in some cases, grafting results chiefly from the direct attack of the polymer by an initiator radical. It is not thought that termination reactions contribute significantly to the formation of graft copolymers.

In the case of graft copolymerization onto unsaturated polymers, such as natural rubber, the interaction between a radical (whether polymeric or initiator) and the polymer may take place in at least two ways: by addition across a carbon-carbon double bond, or by abstraction of a labile hydrogen atom, notably methylene hydrogen atom. These interactions may be represented respectively as follows [10,16]:

(a) addition :



(b) hydrogen abstraction :



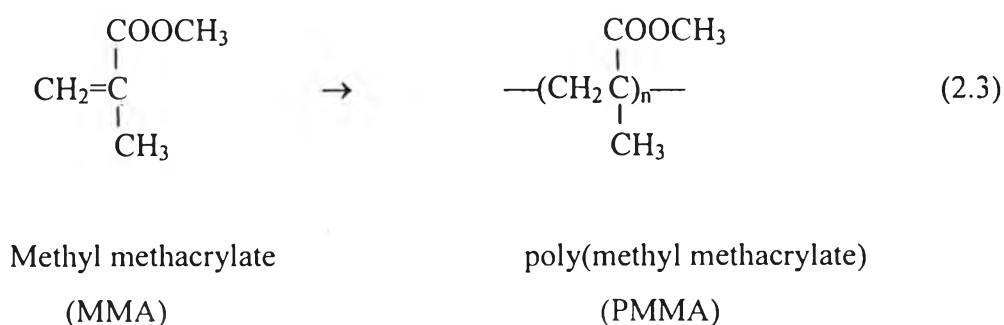
X^{\bullet} is the primary radical derived from the initiator. It is evident that an addition reaction which involves a polymeric radical formed by the polymerization of the added monomer will lead to the formation of a graft copolymer.

2.2.1 Natural Rubber-graft-Methyl Methacrylate

The graft copolymer of natural rubber with methyl methacrylate has been commercialized as 'Heveaplus MG'. The properties and applications of these materials 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 [7,17].

2.3 Poly(methyl methacrylate) (PMMA) [14,18,19,20]

PMMA is polymerized by solution, suspension, and emulsion processes. PMMA is completely amorphous but has high strength and excellent dimensional stability due to the rigid polymer chains ($T_g=105^{\circ}\text{C}$).



The best known and remarkable property of PMMA is probably its excellent transparency. PMMA is the most resistant of all transparent plastics to ultraviolet radiation, and moisture. The outstanding transparency, light piping qualities, colorability, and dimensional stability of PMMA coupled with the retention of these properties in outdoor applications over long periods of time make this resin useful in many industries. The chemical resistance of PMMA example of the effect of various environments upon the acrylics in general. It is essentially unaffected by weak solutions of oxidizing acids, but deteriorates rapidly in highly concentrated solutions of oxidizing acids. Aliphatic hydrocarbons, amines, and esters containing more than 10 carbon atoms in the molecule are completely acceptable. Aromatic hydrocarbons, phenols, chlorinated aromatics, ethers, ketones, and low-molecular-weight esters and aliphatic acids have adverse solvent effect upon the acrylics.

PMMA is used for aviation parts, including pilot's canopies and windows on commercial aircraft, because it is free from optical distortion, resistance to light and weathering, resistance to shattering, and able to withstand sharp pressure and temperature differentials. Other uses include safety glass interlaying, glazing, dentures, contact lenses, and various coatings and finishes.

2.4 Polymer Blend

The term polymer blend is used in two ways. First, it involves all multicomponent polymer materials composed primarily of two or more polymers. Second, it is used specifically to describe combinations of two or more polymers that are not bonded chemically to each other. Important combinations of two or more polymers bonded together include graft copolymers, block copolymers, AB-crosslinked polymers, and interpenetrating polymer networks (IPNs) [21].

The blending of polymers has become an important industrial technique which is an economic and versatile way to produce materials having a wide range of properties. The first category involves homogeneous polymer alloys, which exhibit

properties intermediate between those of the individual components following a simple monotonic function that depends on the ratio of the two polymers in the blend. The other category involves heterogeneous polymer blends, wherein one polymer (Polymer A) is dispersed within the other polymer, a continuous phase (Polymer B, Figure 2.2), and they are immiscible. This type of blend has an important potential advantage in that it provides the additivity of the phase properties along with new features derived from a unique and particular morphology.

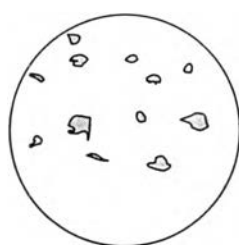


Figure 2.2 Polymer A (dispersed phase) blended with Polymer B (continuous phase) [22].

For such engineered properties, they dispersed in finely divided domains throughout the continuous phase. Such properties are generally achieved by suitable modifiers, which can interlink the phases as depicted in Figure 2.3.

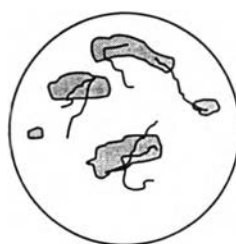


Figure 2.3 Compatibilization of Polymer A with Polymer B [22].

Development of a new heterogeneous blend usually starts with the search for a compatibilizer. It may be a polymer that is soluble in the individual homopolymers or prepared by functionalizing one or more of the component polymers with complimentary properties are the keys to novel polymer blend materials [22].

2.5 Thermoplastic Elastomers (TPEs)

Thermoplastic elastomers (TPEs) prepared from blends of rubber and plastic have created very much interest in the industrial sector. TPEs are a relatively new class of materials which have the excellent processing characteristics of the thermoplastics and the elastic characteristics of the rubbers. TPEs capable of being moulded like plastics at suitable processing temperatures but also have a measure of the resilience, recovery, and flexibility associated with rubber at the normal temperature of use [23]. This rapidly growing field thus brings together the conventional commercial and technical disciplines of rubber and thermoplastics. The thermoplastics are commonly produced by a continuous process that is readily controlled and yields elastomer of high uniformity. In many cases no additional compounding is required. If additives are needed or desired to improve ozone resistance, add color, modify electrical properties, and so on, they can be incorporated in the melt with relative ease and uniformity, and without concern that base polymer is being affected [1].

2.6 Mixing of Rubber [24]

As a very sweeping statement, the equipment used for mixing the compounds may be broken down into two categories:

- (a) Open mill mixer
- (b) Internal mixer

2.6.1 Open Mill Mixing

An open mill consists of two parallel rollers, adjustable for nip distance setting. Sizes range from approximately 12 inches long for use in laboratories to as long as 84 inches. Common mill sizes are 60 inches and 84 inches, particular factory concern. Roller speeds vary from an even speed to ratios as high as 1:1.2 for grinding purposes. Common speeds for general purpose work are approximately 1:1.05.

The open mill mixing process is to masticate the polymers until an even and smooth band is formed around the front roller. The fillers and oils are added alternately by any small additions and finally followed by the vulcanizing materials. During the whole operation, cutting and blending by hard rolling are carried out. With those compounds containing mixed polymers, the best dispersion and blending them together should be while they are still hot. The addition of the fillers and other component can then carry out subsequently in a usual way.

2.6.2 Internal Mixing

Two types of the internal mixer most widely used, worldwide, are the Banbury mixer and the Intermix machines. Banbury and Intermix machines work on two entirely different principles, whilst achieving the same objective, i.e. adequate mixing and dispersion of the ingredients at satisfactory mixing speeds.

Internal mixers, the 'ideal' set-up is to have two mills in the chain. The first is used to remove the heat from the compound rapidly, prior to the addition of the vulcanizing ingredients on the second mill. This also has the advantage of keeping the internal mixer free from curing materials, with far less tendency to scorch problems. It could be claimed that such a system is expensive from the point of view of initial capital cost of plant, but on balance the ease of processing of the resultant compound during subsequent operations more than justifies its high investment..

Many factories are indeed installed in this manner. As with open mill mixing cycles, the general rule is to masticate in the mixers, and when the polymer has reached the desired state, the powders and other ingredients are then added for mixing and dispersion to take place. The batch is now dropped, passed through the first mill several times, and the curatives are added on the second mill as stated above. It cannot, however, be over-emphasised that the exact mixing procedure used, whether it be an open mill or an internal mixer, depends on local conditions peculiar to the particular factory, and indeed upon the wishes and experience of the factory compounder.

2.7 Literature Review

Sundardi and Kadariah [25] studied a method of radiation grafting of methyl methacrylate monomer on natural rubber latex. The irradiation dose for radiation grafting of MMA monomer on latex was around 300 krad to obtain a 75% degree of conversion. Radiation grafting of MMA monomer on NR latex does not influence the pH of the latex, but influences the viscosity significantly. The viscosity of the NR latex increased with an increase in irradiation dose, due to the increase of the total solid content in the latex.

Lenka et al. [26] studied the kinetics and mechanism of graft copolymerization of methyl methacrylate onto rubber using acetylacetonate complex of Mn (III). It has been predicted that the initiation process is essentially the scission of a ligand to generate a free radical and the reduction of the metal to a lower oxidation state. The free radicals might interact with the rubber molecules producing rubber macroradicals, which initiates grafting.

Lenka et al. [27] studied the graft copolymerization of methyl methacrylate onto natural rubber using V^{5+} as the initiator. 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 MMA onto rubber indicated that increasing $[V^{5+}]$ up to 0.035 M was accompanied by a significant increase in graft yield while further increase in its concentration caused a marked fall in the graft yield. With increasing temperature, the percentage of grafting increased.

Lenka et al. [28] studied the graft copolymerization of methyl methacrylate onto crepper natural rubber using potassium peroxydisulfate catalyzed by silver ion. The graft copolymerization was carried out varying the concentration of monomer, initiator, thiourea, and polymerization time over a wide range. The percentage of grafting was maximum at 5 hr, the peroxydisulfate concentration was up to 2.5×10^{-2} mol/l and the thiourea concentration was up to 6×10^{-3} mol/l.

Hourston and Romaine [29] studied composite latex particles based on natural rubber latex. Methyl methacrylate was added to natural rubber latex and polymerized using an amine-activated initiator, tert-butyl hydroperoxide. The resulting materials were casted to yield solid sheets. The morphology of the materials was determined both by transmission electron microscopy and by dynamic mechanical analysis.

Enyiegulam and Aloka [30] studied graft characteristics and solution properties of natural rubber-g-methyl methacrylate copolymer in MEK/ toluene using benzoyl peroxide as initiator. An increase in the concentration of methyl methacrylate at a given benzoyl peroxide initiator decreased both the graft level and grafting efficiency but increases the molecular weight of the copolymer. An increase in the concentration of the benzoyl peroxide initiator at a given monomer concentration decreased the graft level to a constant level when the benzoyl peroxide

concentration exceeded 10×10^{-2} mol/cm³. Dilute solution theory applicable to homopolymers can also be applied to the graft copolymers without any adverse effect in technological application.

Shaw and Singh [31] studied impact modification of polystyrene by ethylene-propylene-diene (EPDM). Polystyrene (PS) is incompatible with EPDM. In the present system, it was shown that the PS/EPDM-g-Styrene blends shown higher improved impact strength behavior than that of the products based upon a simple dispersion of EPDM in polystyrene. High impact polystyrene containing EPDM rubber might show improved weathering resistance.

Razzak et al. [32] studied the preparation of thermoplastic elastomer (TPE) by radiation-induced grafting of methyl methacrylate onto radiation vulcanized natural rubber latex (RVNRL). Processability of this TPE has been evaluated thoroughly using a kneader and hot roll mill. The processability was found to be strongly affected by the mixing time and the revolution rate of the kneader. It was also found that blending of RVNRL-g-PMMA and NRL-g-PMMA results in TPE with a good processability that can be achieved within a shorter mixing time such as 20 min and a lower revolution rate such as 20 rpm while keeping considerable mechanical properties. The RVNRL-g-PMMA TPE had an almost similar tensile strength with commercially available olefin- and styrene-type thermoplastic elastomers.

Oommen and Thomas [3,4] studied the natural rubber/poly(methyl methacrylate) blends. The mechanical properties and failure behavior varied with the blend ratio, graft copolymer concentration, and mixing conditions. Improvements in mechanical properties were noted with the addition of graft copolymer. The fracture surfaces of the compatibilized blend showed improved interfacial interaction between the phases.

Asaletha and Thomas [33] studied the blends of natural rubber and polystyrene. Compatibility of natural rubber/polystyrene blend is poor and could be enhanced by addition of a graft copolymer of natural rubber and polystyrene. The addition of the graft copolymer improved the mechanical properties of the blend. The mechanical properties were in agreement with the morphological changes. It was found that the tensile strength and modulus increased upon the addition of the compatibilizer and finally leveled off at higher concentrations.

Abdullah et al. [34] studied the blending of natural rubber with linear low-density polyethylene (LLDPE). The blends were prepared by melt blending of the materials in a plasticorder mixer. The optimum processing conditions were a temperature of about 135°C and a mixing rate of 55 rpm. The tensile properties, stress and strain of the blend had been improved significantly with the addition of liquid natural rubber (LNR) into the blend. For blends with compositions around 50% NR, about 10-15% LNR produced the most significant improvement in the physical properties. Interfacial linking between the NR and LLDPE phases was attributed to the presence of active groups on the polyisoprene chains of LNR, which induced the interphase reaction between the NR and LLDPE phases.