

CHAPTER II

THEORY AND LITERATURE REVIEW

2.1 Natural rubber

Natural rubber is obtained from the tree *Hevea brasiliensis*. Rubber occurs in the trees in the form of particles suspended in a protein-containing serum, the whole constituting latex, which in turn is contained in specific latex vessels in the tree or other plant. Globally, natural rubber consumption is split with tires consuming at around 75%, automotive mechanical goods at 5%, nonautomotive mechanical goods at 10%, and miscellaneous applications such as medical and health-related products consuming the remaining 10%. The majority coming from small holdings in Indonesia, Thailand, Malaysia, India, and West Africa [9].

Natural rubber is a polymer of isoprene (methylbuta-1,3-diene) as shown in Figure 2.1. The repeating unit in natural rubber has the *cis* configuration (with chain extensions on the same side of the ethylene double bond, Figure 2.1, bottom structure), which is essential for elasticity. If the configuration is *trans* (with chain extensions on opposite sides of the ethylene double bond, Figure 2.1, upper structure), the polymer then becomes a hard plastic. The primary source of *cis*-1,4-polyisoprene used in the manufacture of natural rubber product. Natural rubber (NR) contains 93–95% *cis*-1,4-polyisoprene.

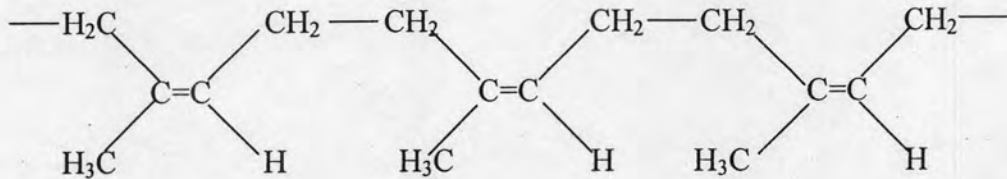
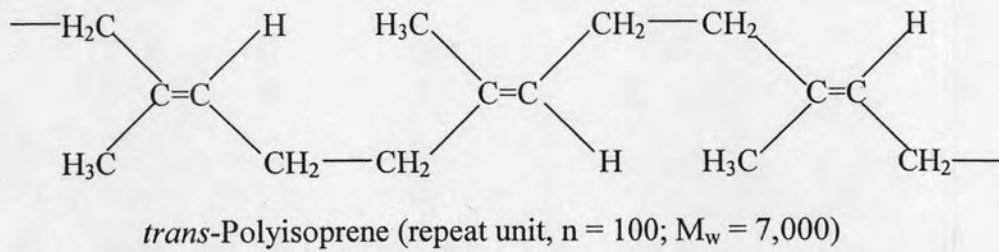


Figure 2.1 *Cis* and *trans* isomers of natural rubber

2.1.1 Natural rubber latex

Natural rubber latex (NRL) is a cloudy white liquid, similar in appearance to cows milk. It is collected by cutting a thin strip of bark from the tree and allowing the latex to exude into a collecting vessel over a period of hours. Fresh *Hevea* latex has a pH of 6.5–7.0 and a density of 0.98 g cm^{-3} . The traditional preservative is ammonia, which in concentrated solution, ammonia is added in small quantities to the latex collected from the cup. The composition of typical field latex is presented in Table 2.1 [9,10].

Table 2.1 Composition of fresh *Hevea* latex

Composition	Content (% by weight)
Total solid content	36
Dry rubber	33
Proteinous substance	1.0-1.5
Resinous substance	1.0-2.5
Carbohydrates	1.0
Inorganic matter	Up to 1.0
Water	60

Natural rubber latex has a dry rubber content (DRC) of about 30 to 40%, the average being about 33%. It is necessary to increase the DRC in the natural rubber latex to 60% or more to reduce the 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, concentrated latex tends 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 [10].

2.1.2 Modification of natural rubber

Natural rubber has been modified in many ways since the establishment of a continuous supply of rubber plantation. Modification highly affects its physical properties. Even thermoplastic or resinous materials can be obtained by a modification of rubber, the most well known types of modification are oxidation, hydrogenation, halogenation, hydrochlorination, chlorosulphonation, and free radical addition grafting [11].

2.2 Polymer grafting on natural rubber

2.2.1 Grafting copolymer

Graft copolymerization has been used as a method for modifying NR in a latex form. Reactions involving free radicals have been the most widely applied in grafting processes, and such reactions have been used with a wide range of polymers and monomers. Free radical initiators may promote grafting in two different ways when added to a monomer/polymer system. These are described below and illustrated in Figure 2.2.

Type I: direct attack by radical initiator



Here, RO^\bullet represents the initiating free radical formed from, e.g. the decomposition of a peroxide, M is the grafting monomer and PH is the polymer chain, containing hydrogen atoms which are sufficiently labile to be abstracted by the radical initiator.

Type II: chain transfer with polymer



Figure 2.2 Graft copolymerization.

In this case, the growing long chain radical ROM_x^\bullet undergoes chain transfer with the polymer, probably by hydrogen abstraction, leading to the initiation of a graft. In both cases, there is also the possibility of formation of homopolymer during the grafting reaction, either by direct initiation of M or via chain transfer with species other than the polymer backbone (e.g. monomer).

Reactions of Type I have been applied in a number of different free radical systems. These include copolymerization and addition or abstraction reactions from small organic molecules. The graft copolymerization would effectively combine the desirable properties of natural rubber with vinyl monomer in order to produce tough, hard, and impact resistant materials with easy processibility [12,13].

2.2.2. Natural rubber-graft-methyl methacrylate

The graft copolymerization of natural rubber latex with methyl methacrylate by *tert*-butylhydroperoxide (TBHPO) initiator, was prepared in the commercial under the trade name, Heveaplus MG. The two main uses for Heveaplus MG rubber are as adhesives and as a means of hard vulcanizates without the disadvantage of poor processing associated with high filler levels [11].

In 1998, Charmondusit et al. [13] studied the grafting of methyl methacrylate and styrene onto natural rubber seed particles by the core-shell emulsion polymerization. The grafted natural rubber properties were strongly influenced by the reaction temperature. The grafted natural rubber prepared using 100 parts by weight

of monomer per 100 parts by weight of natural rubber, 1.5 parts by weight of emulsifier, and 1.5 parts by weight of initiator at 70°C showed a high grafting efficiency and graft ratio. The grafted NR product could be used as an impact modifier for PVC resin to form PVC/grafted NR product blends by mechanical blending and compression molding. The good mechanical properties were obtained at 10 and 15 phr of the grafted NR product.

In 2003, George et al. [14] studied the physical blending of RVNRL and MMA-grafted natural latex, direct radiation grafting crosslinking of MMA onto rubber in natural latex. Physical blending of MMA-grafted NR as latex to RVNRL improved the modulus of the films. Modulus of the films increased with MMA content in the film but tensile strength and ultimate elongation were reduced. Direct grafting crosslinking by irradiation at 15 kGy gave the better physical properties and drying the films at 60°C slightly improved the tensile properties. Irradiating beyond optimum doses reduced the tensile strength. High modulus, without much reduction in tensile strength, could be achieved if the MMA content were 50–60 phr.

In 2006, George et al. [15] studied the graft copolymerization of methyl methacrylate (MMA) onto natural rubber (NR) by emulsion polymerization using cumene hydroperoxide and tetraethylene pentamine as redox initiators in NR latex. The morphology of NR latex seeded graft copolymerization of MMA by emulsion technique depended on the type of surfactant, cross-link density of NR core, and the heterogeneity of rubber particles. Oleic acid produced a large crop of secondary nucleation irrespective of the mode of addition of the monomer. Sodium dodecyl sulfosuccinate and a non-ionic nonyl phenol poly(ethylene oxide) gave the core-shell morphology under semi-batch conditions. Higher cross-link densities of NR core resulted in uniform shell formation. Smaller particles were heavily coated while larger particles were fully coated with PMMA only at a lower NR:MMA ratio.

In 2007, Chumsamrong and Monprasit [16] studied the potential of increasing the weather stability of natural rubber latex for use as a water-based contact adhesive, the natural rubber latex was modified by graft copolymerization with n-butyl acrylate (BA) and methyl methacrylate (MMA) using potassium persulfate as the initiator by varying the monomer mixture ratio. The grafting efficiency of graft-modified natural rubber with a different monomer ratio tended to decrease with an increase of MMA. Characterization of the graft copolymers by $^1\text{H-NMR}$ indicated the occurrence of grafting on the natural rubber backbone in the latex particle. The adhesive performance was characterized by 90° peel strength tests. Only latex GNR-80:20 possessed adhesion properties enough to conduct peel testing. The peel strength values of GNR-80:20 was lower than that of natural rubber latex. However, graft-modified natural rubber latex tends to have higher weather stability than natural rubber latex.

In 2008, Amornchaiyapitak et al. [17] prepared the epoxidised natural rubber (ENR) latex with methyl methacrylate (MMA). The ENR latex film surface was modified by immersing into methyl methacrylate (MMA) emulsion and then alkaline aqueous solution of ferrous ion/fructose for redox-initiated polymerization. The amount of MMA swelled into ENR sheet was proportional to the immersion time of ENR into MMA emulsion. The maximum MMA conversion attained 45% within 4 h of polymerization time. The PMMA contents estimated from ATR-FTIR spectra was in accordance with those calculated from the gravimetric method. The nanoscale indentation of the cross-section of modified ENR sheet indicated that PMMA mainly existed near the rubber surface in the nodular morphology. These nodules increased the surface mean roughness and, hence, reduced friction coefficient of the modified ENR surface.

The grafting of polymer in seed emulsion polymerization occurs on the entry of radicals from the aqueous phase into the polymer particle, where they add to a double bond or abstract hydrogen from the hydrocarbon chain.

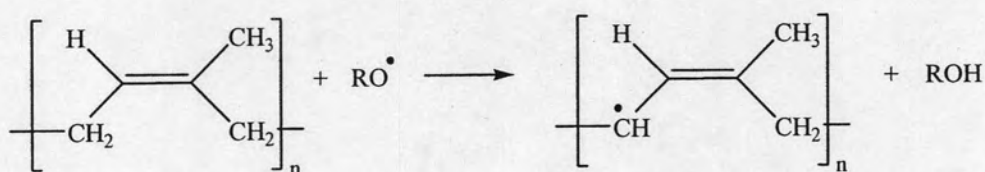
If, in a system containing polymer and growing chains of monomer, chain transfer to polymer (*i.e.*, abstraction of an atom such as hydrogen, or halogen, from

polymer) occurs by the growing chains of monomer units, polymerization of the monomer can take place at these newly formed reactive sites. The product is a graft copolymer. The grafting mechanism is characterized by reaction [18]:

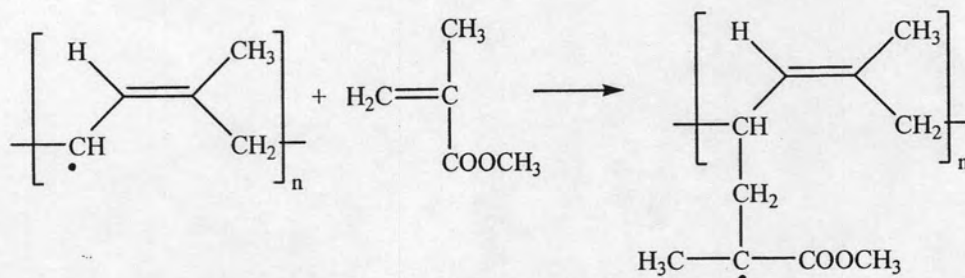
Initiation:



Attacking rubber:

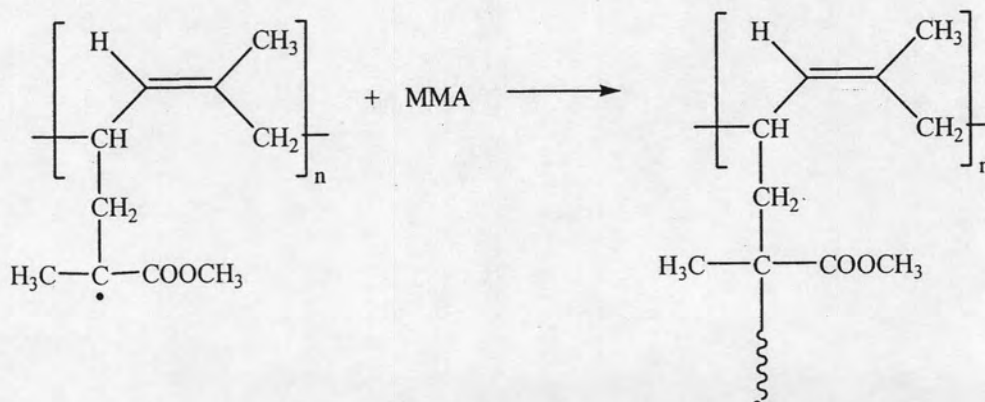


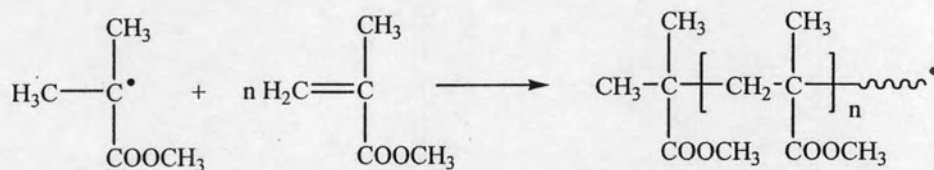
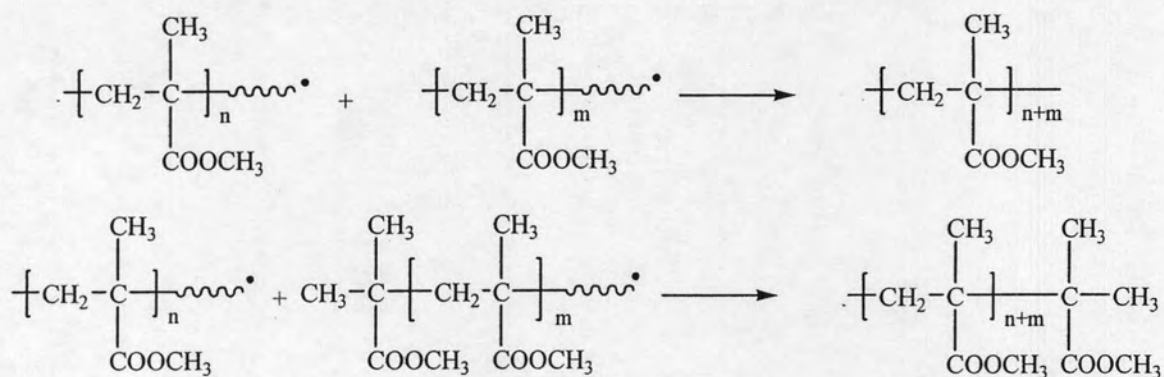
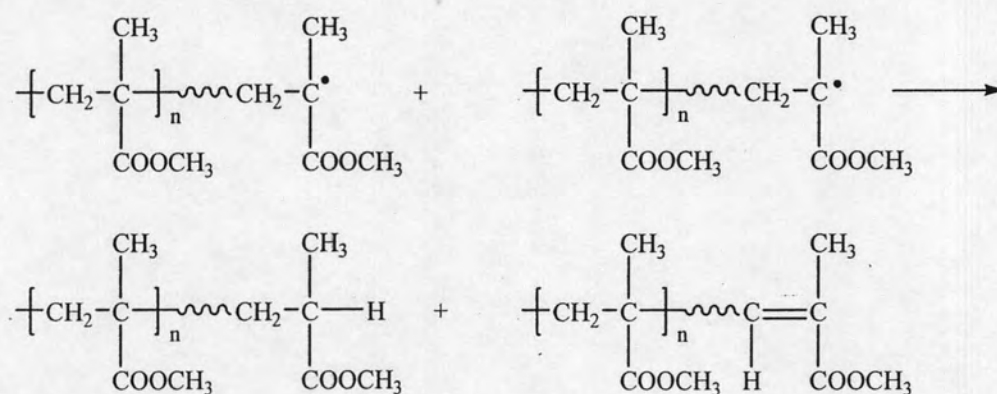
Re-initiation:



Propagation:

Propagation of graft polymerization:



Propagation of free polymerization:**Termination:****Termination by combination:****Termination by disproportionation:****Scheme 2.1** Mechanism of the graft copolymerization of MMA onto NR.

2.2.3 Core-shell mechanism

The core-shell emulsion copolymerization is a well-known process used to control latex particle morphology. According to the polymer particle morphology, there are two main kinds of core-shell copolymers: soft core-hard shell and hard core-soft shell. Polymers with a soft core and a hard shell are used as an impact modifier, for plastics toughening, and as damped oscillation materials, whereas polymers with a hard core and a soft shell are usually applied to the coating and adhesive fields [13].

Oliveira et al. [12] studied grafting copolymers of NR and DMAEMA or MMA prepared using the same amount of a redox couple initiator by seeded emulsion polymerization. Since the peroxide is soluble in both the monomer and the NR particle, whereas the activator TEPA is water soluble, the initiators present in the graft copolymerization of dimethylaminoethylmethacrylate (DMAEMA) or MMA in NR particles seem to be appropriate to create sites of grafting by the abstraction reaction over addition to allylic double bonds acting predominantly at the water/particle interface as shown in Figure 2.3. The cryo-sectioning and chemical fixation techniques were good enough to show the images of the desired core-shell morphologies: hairy-layer for NR grafted with PDMA-EMA, and fruit-cake like for NR grafted with PMMA.

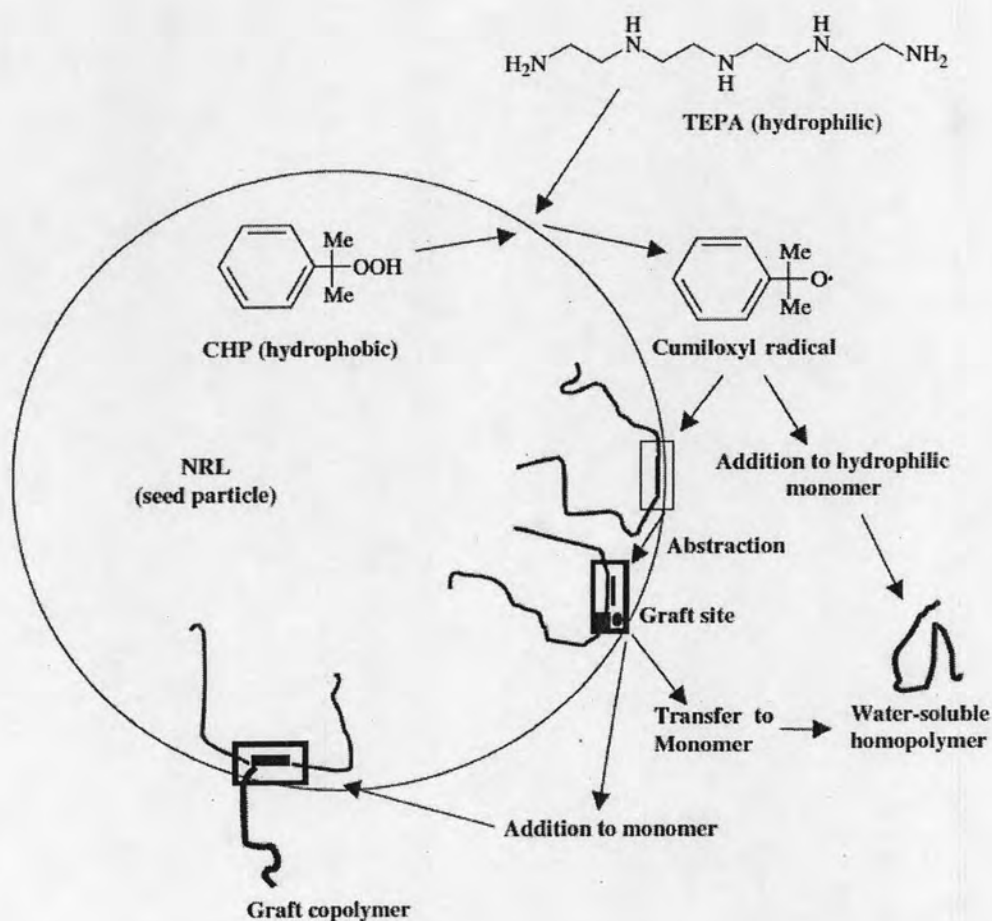


Figure.2.3 Scheme of seeded emulsion polymerization leading to graft copolymer. Water-phase polymerization to form homopolymer of water-soluble monomer and cross-linking of the graftable seed polymer within the particle phase [12].

2.3 Fillers for rubber

The fillers are generally classified into carbon black and white fillers. Non-black fillers such as clays, carbonates, silicates, and precipitated silica are also needed that differ not only in their chemical structure but also in their particle size and shape. Compared to carbon black, these fillers show advantages in cut and flex resistance and heat buildup, they are non conducting, and they are required for colored products, but the reinforcement they provide with regard to modulus and abrasion resistance, is limited.

The principal characteristics of rubber fillers – particle size, shape, surface area and surface activity—are interdependent in improving rubber properties. In considering fillers of adequately small particle size to provide some level of reinforcement, the general influence of each of the other three filler characteristics on rubber properties can be generalized as follows: Increasing surface area (decreasing particle size) gives: higher Mooney viscosity, tensile strength, abrasion resistance, tear resistance, and hysteresis; lower resilience. Increasing surface activity (including surface treatment) gives: higher abrasion resistance, chemical adsorption or reaction, modulus, and hysteresis (except for silane-treated fillers) [19].

2.3.1 Reinforcing fillers

Two types of fillers that are most effective for reinforcing rubber are carbon black and silica. Particulate fillers can increase the strength of an amorphous rubber more than 10-fold. For a filler to cause significant reinforcement, it must possess high specific surface area, *i.e.*, the particles must be small, less than 1 μm in size. Small particles have large surface area to interact with the rubber and close particle-to-particle spacing in the compound. Structure relates to irregularity in shape of filler aggregates (Figure 2.4), determined by the extent and manner of clustering of primary particles. A filler aggregate with high structure has a large void volume within the space it pervades, in which rubber molecules may become "occluded". The combination of occluded rubber and filler then becomes the reinforcing entity, so that the effective volume fraction of filler is increased (Aggregates are not broken down into primary particles upon mixing with rubber). Generally, reinforcement is enhanced by high structure and strong bonding between filler and rubber. Silica fillers are often treated with silane coupling agents to bond them chemically to rubber, or the coupling agents may be added directly to the rubber compound [20].

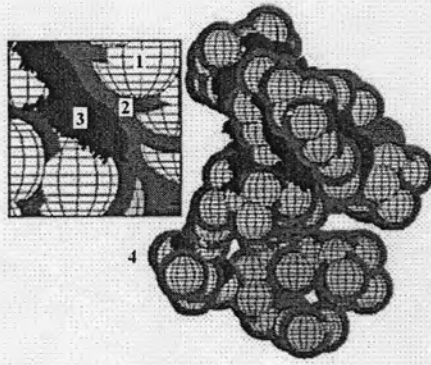


Figure 2.4 Structure of the material: (1) filler, (2) polymer layer around particles, (3) occluded polymer and (4) matrix [21].

2.3.2 Silica

Amorphous silica consists of ultimate particles of the inorganic silicon dioxide (SiO_2)_n, where a silicon atom is covalently bonded in a tetrahedral arrangement to four oxygen atoms. Each of the four oxygen atoms is covalently bonded to either one silicon atom forming a siloxane (-Si-O-Si-) or to a hydrogen forming a silanol (-Si-O-H) functionality [22].

The chemistry of silica can be characterized as follows [23]:

1. Silica, which is amorphous, consists of silicon and oxygen arranged in a tetrahedral structure of a three-dimensional lattice. Particle size ranges from 1 to 30 nm and surface area from 20 to 300 m²/g. There is no long-range crystal order, only short-range ordered domains in a random arrangement with neighboring domains.

2. Surface silanol concentration (silanol groups -Si-O-H) influence the degree of surface hydration.

3. Silanol types fall into three categories—isolated, geminal (two -OH hydroxyl groups on the same silicon atom), and vicinal (on adjacent silicon atoms)—as illustrated in Figure 2.5.

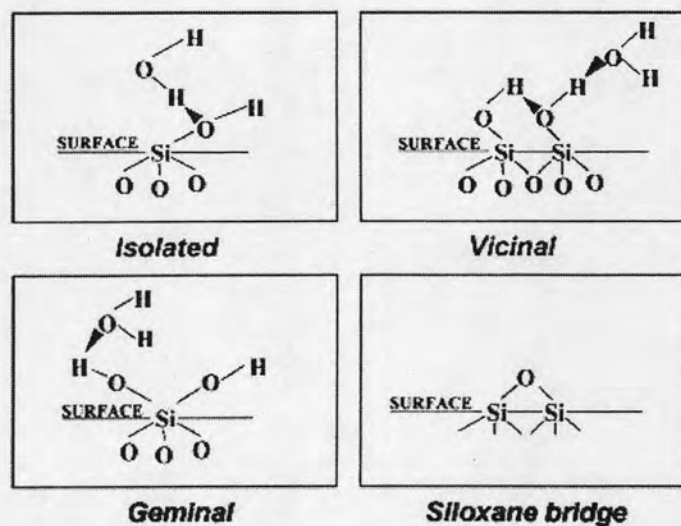


Figure 2.5 Surroundings of Si in silica: geminal, isolated, vicinal, siloxane bridges [9].

During the reaction time, primary particles are first formed in the reactor; later these particles react with each other, accompanied by dehydration, to form aggregates. Within the aggregates, the primary particles are linked together via siloxane bonds. During this process, the aggregates are deposited to form larger units, or agglomerates. In these agglomerates the aggregates are held together by hydrogen bonding or van der Waals interactions that are considerably weaker than siloxane bonds, which are shown in Figure 2.6.

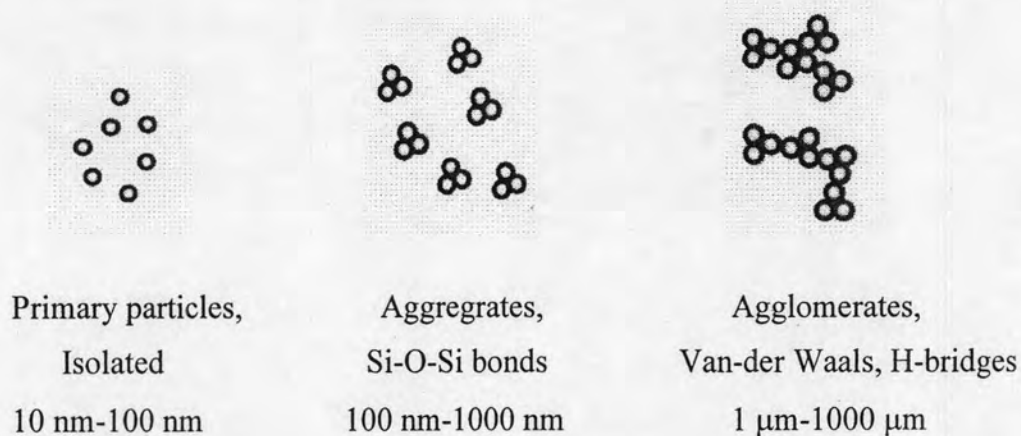
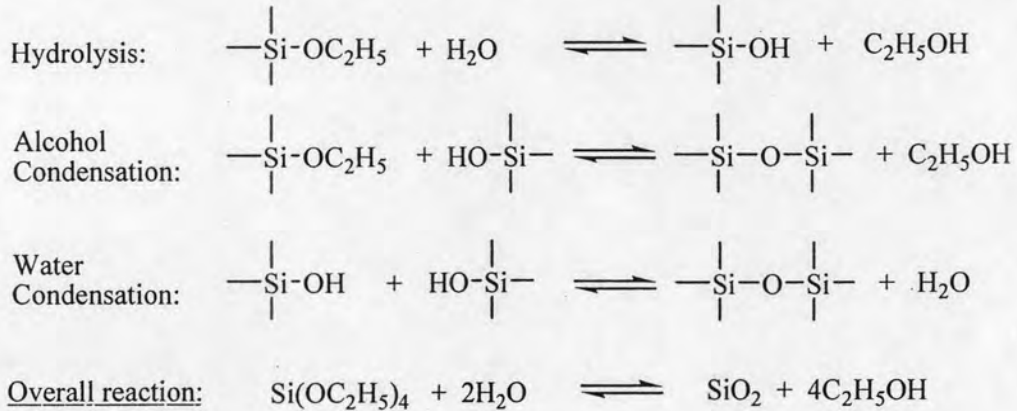


Figure 2.6 Sketches of primary particle, aggregates and agglomerates occurring in silica [9].

2.4 Silica formation by sol-gel process of TEOS

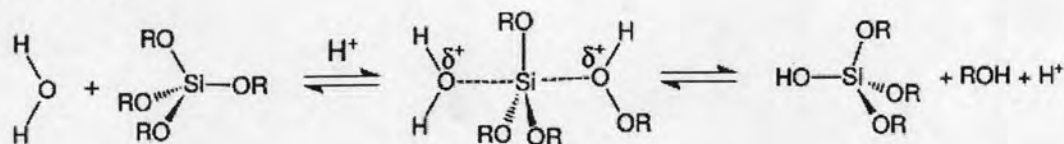
The sol-gel process occurs in liquid solution of metal alkoxide precursors such as tetraethoxysilane or tetraethylorthosilicate, TEOS, which, by means of hydrolysis and condensation reactions, leading to the formation of a new phase-called 'sol'. The sol is made of solid particles of a diameter of few hundreds of nanometer suspended in a liquid phase. Then the particle condense in to a new phase, called 'gel' in which a solid macromolecule is immersed in a liquid phase (solvent). Hydrolysis and condensation reaction of TEOS or other metal alkoxides to form silica is shown in Scheme 2.2. Initially, metal alkoxides react readily with water. The reaction is called hydrolysis, because a hydroxyl ion becomes attached to the metal atom (so that all of the OR groups are replaced by OH). Two partially hydrolyzed molecules can link together in a condensation reaction. By definition, condensation liberates a small molecule, such as water or alcohol. This type of reaction can continue to build larger and larger silicon containing molecules by the process of polymerization [24].



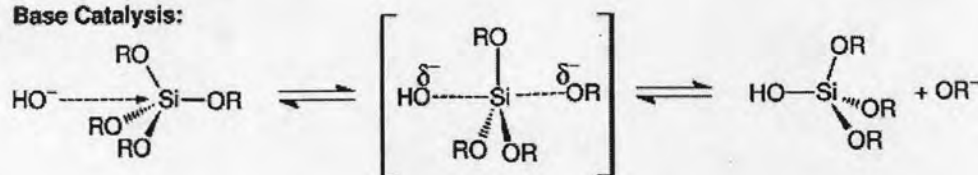
Scheme 2.2 Hydrolysis and condensation reaction of TEOS to form silica.

The mechanisms of acid and base-catalyzed hydrolysis are shown in Scheme 2.3.

Acid Catalysis:



Base Catalysis:



Scheme 2.3 Differences in mechanism depending on the type of catalyst used in the silicon-based sol-gel process [25].

A sol-gel process of TEOS was applied to prepare silica for reinforcement of rubbers.

In 2000, Kohjiya and Ikeda [26] studied *in situ* silica in natural rubber (NR) matrix. Preparation of the silica filled rubber compound was performed by the sol-gel method. The NR sheet was immersed in TEOS for 48 h at room temperature before crosslink by sulfur. The silica-silica interaction of *in situ* silica seemed to be weaker than that of silica-rubber to result in better dispersion compared with the conventional silica. The *in situ* silica particles showed good reinforcement effect on the NR vulcanizate without the silane coupling agent. The *in situ* silica was homogeneously dispersed in the natural rubber matrix.

In 2002, Yoshikai et al. [27] reported a study on silica reinforcement of synthetic diene rubbers by a sol-gel process of TEOS in the latex. The TEOS was mixed directly into the latex of styrene butadiene rubber (SBR) and nitrile rubber (NBR). The sol-gel process of TEOS then proceeded in a mixture of latex. The silica content in the compounds, particle size and reinforcing behavior of silica were found to depend on the amount of TEOS added and the molar ratio of water to TEOS. The average particle size of silica was reported to be smaller than 100 nm. The tensile strength of SBR and NBR were over 25 MPa.

In 2003, Kojiya and Ikeda [28] prepared the *in situ* silica reinforcement of NR by the sol-gel reaction of TEOS using n-butylamine as a catalyst. γ -mercaptopropyl trimethoxysilane was used for modifying the silica surface. The reaction of TEOS in raw NR was conducted before the processing for NR vulcanizates. The *in situ* silica with coupling agent afforded the lowest viscosity compared not only with conventional silica but also with a carbon black. Lower hydrophilicity of the *in situ* silica surface may result in less filler-to-filler interaction in the reason of better performances.

A “green” (eco-friendly) composites were prepared by Ikeda and Kameda. In 2004, Ikeda and Kameda [29] prepared *in situ* silica nano-particles by a sol-gel reaction of tetraethoxysilane (TEOS) in natural rubber (NR), which was prepared by the NR sheets immersing in TEOS. The swelling degree of NR in TEOS was important for controlling the *in situ* silica content in NR. The *in situ* silica was nano-particle, and its particle size became larger with the increase of silica content from ca. 10 nm to ca. 40 nm for 10–40 phr loadings in the NR matrix, respectively. The excellent reinforcement effect of *in situ* silica for the NR vulcanizates was observed with increasing the *in situ* silica content. The *in situ* silica filling in NR is a good method to prepare the rubbery nano-composites with unique characteristics.

In the same year, Nah et al. [30] studied *in situ* silica-filled natural rubber nanocomposites using sol-gel process in terms of friction and abrasion properties. The sol-gel nanocomposite showed a well-dispersed morphology of much finer silica particles of around 40 nm in size. The prepared nanocomposites showed much higher London dispersive component of free energy compared with conventional melt-mixed composites. Also, much lower frictional coefficients were found for the sol-gel nanocomposites. The abrasion resistance of the nanocomposites was proven to be superior to that of melt mixed composites.

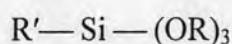
In 2008, Poompradub et al. [31] investigated the parameters of *in situ* silica formation in natural rubber by sol-gel reaction. The NR sheets were immersed in TEOS at room temperature for 3 h. THF was the suitable solvent for the sol-gel

reaction. N-hexylamine was the most efficient base catalyst to produce the high amount of in situ silica in rubbery matrix compared with n-butylamine. It was because the longer chain of n-hexylamine easily penetrated into NR matrix. The higher the mole ratio of TEOS to H₂O, the higher the silica content was obtained. To prevent the phase separation, the mole ratio of TEOS to H₂O should be less than 1:3. This sol-gel method could be applied for the preparation of the new soft nano-composite.

In 2009, Siramanont, et al. [32] studied the sol-gel process of alkyltriethoxysilanes that was dispersed in natural rubber latex was used to generate alkylated silica particles inside the rubber matrix. Three types of alkyltriethoxysilanes were chosen, i.e., vinyltriethoxysilane (VTOS), ethyltriethoxysilane (ETOS), and *i*-butyltriethoxysilane (BTOS). The alkylated silica particles were formed in the rubber matrix by a certain combination of TEOS and alkyltriethoxysilanes. The silane conversion to silica in the NR matrix was almost complete for TEOS, but decreased when the alkyl group of the alkyltriethoxysilanes increased in size. The study on hardness, tensile, and tear properties revealed that the uses of in situ-generated silica and alkylated silicas resulted in a better reinforcement capability to the rubber vulcanizates than did the conventionally added silica powder.

2.5 Silane coupling agent

General formulation of organofunctional silanes is as below:

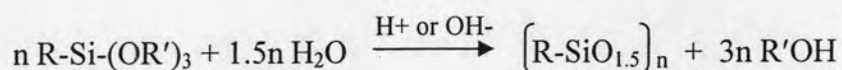


where R' is a functional group and R is a hydrolyzable alkyl group. According to this structure, two different reactions may take place: the alkoxy group which has been hydrolyzed to silanol reacts with the mineral surface, on the other hand the organofunctional group has the capability to react with an appropriate polymer. Each silicone atom has three hydrolyzable sites [33].

Silane coupling agent is a bifunctional compound developed commercially to improve the reinforcing efficiency of silica. It is composed of two functionally active end groups, i.e., the readily hydrolyzable alkoxy group and the organo-functional

group. The former can react chemically with the silanol groups on silica surface to form stable siloxane linkages whereas the latter, which is relatively non-polar, is more compatible with rubbers and also can participate in the sulfur vulcanization to form chemical linkages with rubbers. As a consequence, silane coupling agent could act as a bridge between silica and rubber to enhance the rubber–filler interaction and, thus, give a significant improvement in properties of silica-filled compounds. [34].

Organotrialkoxysilanes are typically co-polymerized with another sol-gel monomer-generally tetramethoxysilane (TMOS) or tetraethoxysilane (TEOS). The sol-gel polymerization of organotrialkoxysilanes involving hydrolysis and condensation usually results in the formation of low molecular weight silica are shown in Scheme 2.4.



Scheme 2.4 Hydrolysis and condensation of trialkoxysilane to give polysilsesquioxane.

The first commercially available coupling agents were the highly reactive 3-mercaptopropyl trimethoxysilane for sulfur-cured compounds and vinyltrimethoxysilane and 3-methacryloxypropyl trimethoxysilane (structure of γ -MPS is shown in Figure 2.7) for peroxide-cross-linked rubber compounds. With the addition of these silanes a marked increase in the reinforcement of white-filled compounds was achieved [9].

γ -methacryloxy propyl trimethoxy silane (γ -MPS) is presented by the formula:

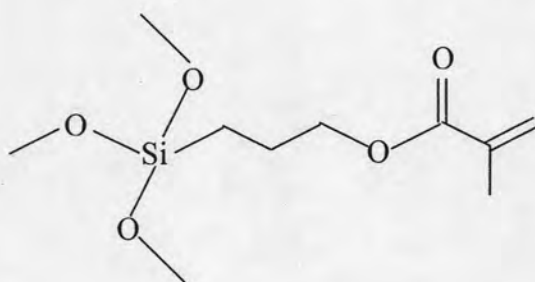


Figure 2.7 Structure of γ -methacryloxypropyl trimethoxysilane (γ -MPS)

Silane–Silane Coupling

A high silica–rubber interaction is achieved by chemical coupling using bifunctional silanes. For the application of the silica–silane filler system, prereacted silica–silane products can be used, but *in situ* modification of the silica with the silane during the mixing process is more common. The silica–silane filler system is needed for industrial rubber goods that require high reinforcement combined with the possibility to manufacture white or colored products such as seals, hoses, and profiles. In some dynamic applications the silica–silane filler system is needed to reduce the heat buildup.

Silane coupling agents that provide a chemical link between the filler and the rubber are needed. The use of silanes allows a modification of the polar silica surface that makes the silica more compatible with the rubber matrix [9].

The γ -MPS, trialkoxysilane act as coupling agents are mainly prepared for coating application. Up to now, there are no literatures reporting the preparation of γ -MPS and couple with TEOS for generated *in situ* silica in the rubber matrix. In this study, γ -MPS is first used to improve compatibility between NR matrix and silica from TEOS.

In 2001, Tissot et al. [35] prepared polystyrene latex particles coated with a silica shell. In a first step, γ -MPS molecules are incorporated into polystyrene latex particles. The pH of the suspension was adjusted to 7 (to slow down γ -MPS hydrolysis and condensation reactions). In a second step, the trimethoxysilyl groups trapped into the organo-mineral seed latexes were reacted with TEOS in water under basic conditions to yield silica-coated latex particles. The structure of the copolymer was characterized by ^{13}C and ^{29}Si solid-state CP-MAS NMR and IR spectroscopy found that the incorporation of γ -MPS units in the copolymer chain by free radical polymerization. The results from TEM showed clearly that the formation of a smooth and regular silica layer on the seed particles is highly dependent on the nature of the latex core. It is presumed that the success of the seeded growth process in this system is due to the unique hybrid structure of the copolymer.

In 2003, Kaynak et al. [36] investigated the effects of using different silane coupling agents, such as methyltrimethoxysilane, vinyltriethoxysilane, 3aminopropyltriethoxysilane, 3(trimethoxysilyl)propylmethacrylate, hexadecyltrimethoxysilane, octadecyltrimethoxysilane, and hexadecyltrichlorosilane to improve the interface between the epoxy resin and recycled rubber particles. The highest tensile strength and modulus values were obtained by methyltrimethoxysilane, 3aminopropyltriethoxysilane and octadecyltrimethoxysilane, but the SCAs was not sufficient to increase the toughness of the system. The decrease in fracture toughness was obtained by 3aminopropyltriethoxysilane treatment.

In 2005, Ni et al. [37] studied the effects of operating conditions on the polystyrene core and hybrid copolymer shell nanoparticles via emulsion polymerization of styrene and γ -MPS. The latex was more stable in neutral conditions while it rapidly turned to a gel after the addition of γ -MPS under acidic conditions. Under basic conditions, although the latex is stable, the particle number significantly decreases, demonstrating the occurrence of agglomeration phenomena. The increase of the γ -MPS concentration accelerates both hydrolysis and condensation, which promotes therefore the formation of a cross-linked network. At low γ -MPS

concentrations, polysiloxane-rich domains are incorporated into the shell which promotes latex particles aggregation.

In the same year (2005), Xu et al. [39] prepared polymethylmethacrylate/SiO₂ nanocomposite particles through microemulsion polymerization by using the silica particles coated with 3-(trimethoxysilyl) propyl methacrylate (MSMA) in both acidic and alkaline conditions. Nanocomposite microemulsion, based on the charge attraction between silanol particles and cation initiators, at low pH values such as pH 2 the surface of silanol precursor has few charges, and as a result, every hybrid particle has only one silica core, while at high pH values such as pH 9, the large negative surface charge causes autocondensation between silanols and thus leads to the formation of cellular structures in the hybrids. The structure of the hybrid is also affected by the amount of silanol and the coupling agent in the system. Increasing either silanol or the coupling agent causes the change of hybrid structures from regular core-shell to cellular structure.

In 2006, Sanchez et al. [38] prepared hybrid SiO₂-PMMA coatings by the sol-gel method and using γ -MPS as bonding agent. The precursor solution was prepared by adding γ -MPS to a pre-polymerized solution of TEOS in ethanol, then water with a diluted solution of HCl (pH=2) was added. On the other hand, the monomer methyl methacrylate was initiated using benzoyl peroxide (BPO). Coatings were deposited on glass substrates by the dip coating method. Infrared spectroscopy measurements clearly showed the formation of the hybrid material. The hardness behavior of the hybrid coatings as a function of the TEOS:PMMA ratio was in a non-linear decrease as the PMMA contents increased.

In the same year (2006), Bonilla et al. [39] studied the thermal and mechanical properties of polyurethane (PU), PMMA and silica generated from TEOS, which were prepared by *in situ* bulk polymerization and using γ -MPS and isocyanatopropyl triethoxysilane (IPTES) as dual coupling agents. The silica network from TEOS, γ -MPS and IPTES was generated within the host PU and then the free radical copolymerization with MMA at room temperature. The surface hardness and storage

modulus at room temperature of PU/PMMA/SiO₂ hybrid materials decreased with increasing silica content, because the condensation reaction of the silanol groups generated during the hydrolysis of the various alkoxy silanes (TEOS, γ -MPS, IPTES) was not fully complete, possibly due to steric hindrances.

In 2007, Lu et al. [40] improved the compatibility of the polystyrene core and the polysiloxane shell, the seed particles were prepared by conventional dispersion polymerization of styrene using γ -MPS as a functional comonomer in an ethanol/water medium. The synthesis of the polysiloxane shell was carried out using a sol-gel process of methyl trimethoxysilane. The addition of silane couple agent, MPS as a comonomer in the preparation of seeds improves the compatibility between the core and the polysiloxane shell effectively. TEM characterization confirmed that the core and the shell were connected tightly to the composite microspheres.

In the same year (2007), Kim et al. [41] studied the optimum conditions for the surface treatment of the silica nanoparticles from TEOS, which were prepared by the Stöber method and using a silane coupling agent (i.e., γ -MPS) to produce dental composite. Monodispersed and spherical silica nanoparticles having various sizes from 5 to 450 nm were produced. The particle size was increased by decreasing the water concentration and by increasing the TEOS and NH₄OH concentrations regardless of solvent used for the synthesis. When surface treatment was performed at optimum reaction conditions, the amount of grafted-MPS per unit area was nearly the same ($6.0 \pm 0.08 \mu\text{mol}/\text{m}^2$) regardless of particle size. Dispersion of the silica particles in the resin matrix and interfacial adhesion between silica particles and resin matrix were enhanced when surface treated silica nanoparticles were used for preparing dental nanocomposites.

In 2008, Brostow et al. [42] synthesized and characterized poly(methyl acrylate) (PMA)+SiO hybrid composites via a sol-gel reaction by co-polymerization of methylacrylate (MA) with γ -MPS and vinyltrimethoxysilane (VTMS). The products were co-condensed with tetraethylorthosilicate (TEOS). Two different methods have been used, the first one was the formation of covalently connected

composites by functionalization of organic polymer backbones with trialkoxysilyl groups. The second method was based on grafting polymeric molecules through covalent bonding to the existing hydroxyl groups; this included silica surface treatment with a silane coupling agent followed by radical grafting polymerization. Silica networks in the PMA/ γ -MPS+SiO₂ hybrids obtained by Method 1 were unstable. In contrast, the samples obtained by Method 2 gave higher degradation temperatures because during the sol-gel process the trimethoxysilyl groups in PMA/ γ -MPS are transformed into a strong silica network. Thus, thermal stability of the hybrids was improved. Thermophysical properties of silica particles in method 2 obtained better than with Method 1.

2.6 Swelling behaviour

A reinforced vulcanized rubber possesses a substantial increase in stiffness (modulus) and a reduction in the extent to which the vulcanizate will swell in a rubber solvent. The amount of rubber which remains associated with the filler when the mixture is subsequently immersed in a rubber solvent (bound rubber) is often used as a measure of this interaction (The quantity of bound rubber normally increases on storage or heating of the rubber-filler mix). Thus, the rubber is adsorbed on the filler surface and this alters the stress-strain properties and reduces the extent of swelling in a solvent. Since equilibrium volume swelling measurements are the principal means of assessing crosslink density, it becomes very difficult to measure crosslink density when a reinforcing filler is present in the rubber because the effects of crosslink cannot be readily distinguished from the effects of rubber-filler interaction.