

CHAPTER II

LITERATURE REVIEW

2.1 Conductive Polymer

An organic polymer that possess the electrical, electronic, magnetic and optical properties while retaining the mechanical properties, processibility commonly associated with a conventional polymer is termed an “intrinsically conductive polymer” more commonly known as “synthetic metal”. It was in 1976 that A.G. MacDiarmid, H. Shirakawa, A.J. Heeger and coworkers discovered organic conductive polymers and their ability to dope these polymers over the full range from insulator to metal. The first electrically conductive organic polymer, polyacetylene doped with iodine, was reported. That event heralded the dawn of a new era of conductive polymers. Figure 2.1 shows some of the conjugated polymers, which have been extensively studied, such as Polyacetylene, Polyaniline, Polypyrrole, Polythiophene, Poly(p-phenylene), Poly(phenylene vinylene) etc.

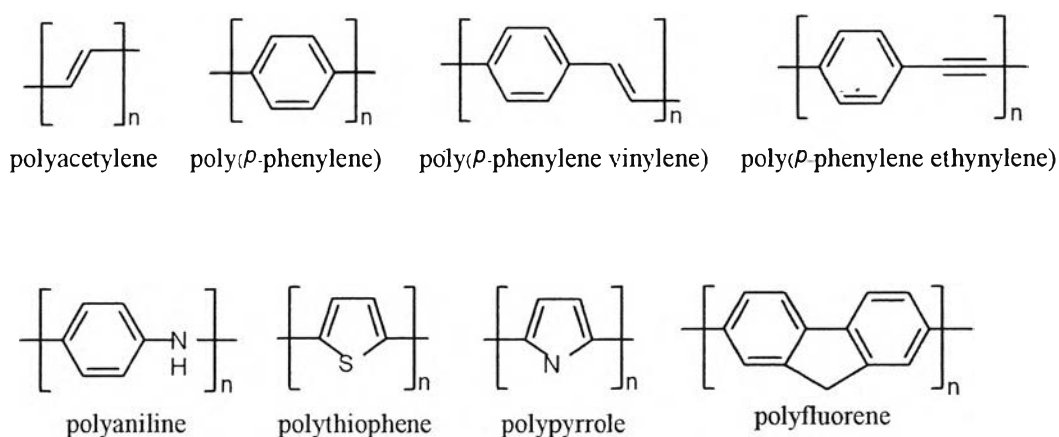


Figure 2.1 Examples of intrinsically conductive polymers.

The electrical properties of conductive polymers depend on the electronic structure and basically on the chemical nature of the repeating unit. The electrical conductivity is proportional to the number of charge carriers of species ‘i’ (n_i), the

charge on each carrier (ϵ_i), and drift mobility of the carriers (μ_i). Conduction in solids is usually explained in the terms of the band theory described by the relation $\sigma = \sum \mu_i n_i \epsilon_i$ where the unit of conductivity is S/cm. It is postulated that when atoms or molecules are formed in the solid state, the outer atomic orbital containing the valence electrons are split into bonding and antibonding orbital, and are mixed to form two series of closely-spaced energy level. These are usually called the valence band and conduction band, respectively. If the valence band is only partly filled by available electrons, or if the two bands overlap so that no energy gap exists between them, the application of an electrical potential will raise some of electrons into empty levels where they will be free to move throughout the solid thereby producing a current. This is the description of a conductor. If, on the other hand, the valence band is full and is separated from the empty conduction band by an external field unless the electron are elevated into the empty band and this process will require a considerable expenditure of energy. Such materials are either semiconductors or insulators, depending on how large energy gap may be. The band model then assumes that the electrons are delocalized and can extend over the lattice. The majority of polymers are insulator.

For the electrical conduction in a polymer, the band theory is not totally suitable because the atoms are covalently bonded to another one, forming polymeric chains that experience weak intermolecular interactions. Thus macroscopic conduction will require electron movements, not only along chains but also from one chain to another.

2.2 Polyaniline

Among several conductive polymers, polyaniline is one of the most promising candidates due to its ease of synthesis, relative high conductivity, environmental stability, and cost economics. Polyaniline is a typical phenylene based polymer having a chemically flexible $-\text{NH}-$ group in the polymer chain flanked by phenyl ring on either side. The general formula of polyaniline containing reduced repeat units and oxidized repeat units is shown in the Figure 2.2.

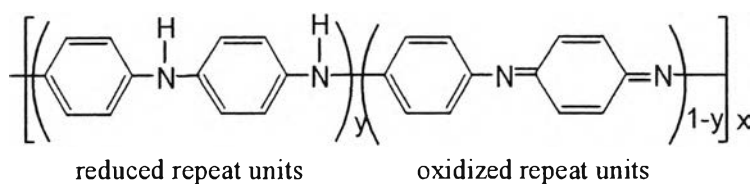


Figure 2.2 The general formula structure of polyaniline.

Polyaniline can exist in three different oxidation states with different colours. The fully reduced form of polyaniline, Leucoemeraldine, corresponds to a value of $y = 1$; the fully oxidized form of polyaniline, Pernigraniline, corresponds to a value of $y = 0$; and the half oxidation form of polyaniline, Emeraldine, corresponds to a value of $y = 0.5$. The different oxidation states of polyaniline are shown in Figure 2.3.

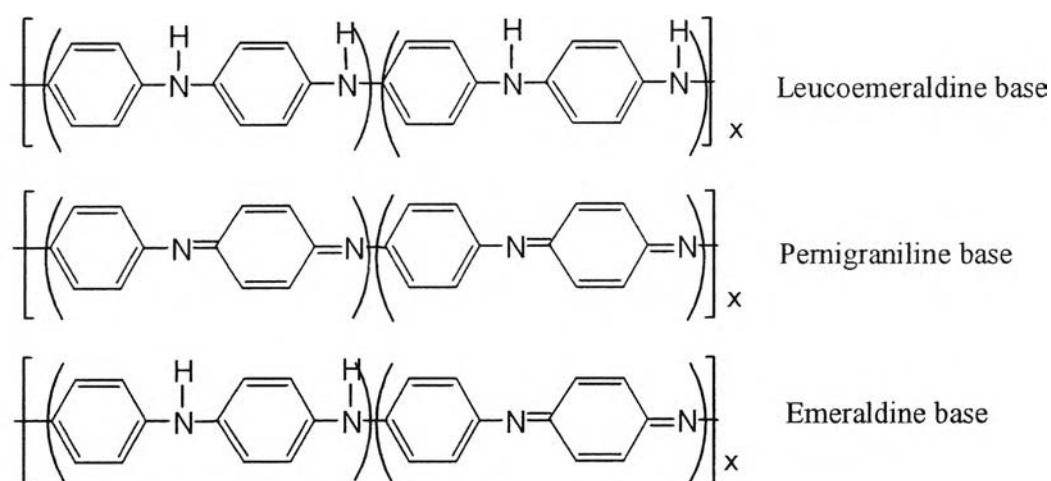


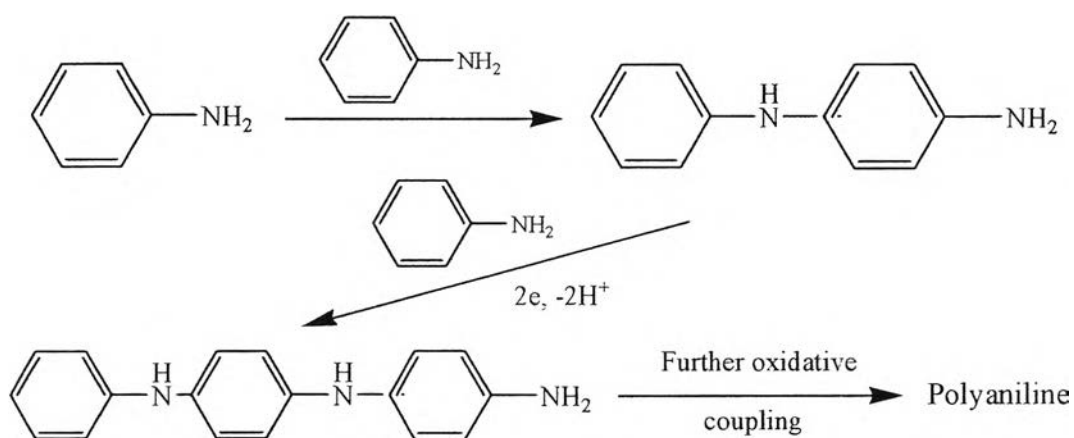
Figure 2.3 The different oxidation states of polyaniline.

2.2.1 Polyaniline Synthesis

Polyaniline can be synthesized mainly by chemical or electrochemical oxidation of aniline monomer under acidic conditions. The chemical method is suitable for bulk production whereas electrochemical method is preferred as for thin films.

2.2.1.1 Chemical Oxidation Polymerization

The conventional method of synthesis of emeraldine salt is the emulsion polymerization of aniline monomer in aqueous media in presence acid like HCl. An oxidant like ammonium persulphate or potassium dichromate was used to initiate the reaction. In general, the aniline salt of protonic acid in the protonic acid medium is mixed with aqueous solution of ammonium per sulphate with a continuous stirring. The polymerization reaction is summarized as shown in Scheme 2.1. The precipitate obtained is then filtered and washed with distilled water so as to obtain emeraldine salt. For dedoping process, the emeraldine salt was treated with basic medium like ammonium hydroxide to convert into its emeraldine base form.



Scheme 2.1 Mechanism of chemical oxidation polymerization of polyaniline.

Cao *et al.* (1989) studied the relationships between the chemical polymerization conditions and the physicochemical properties of polyaniline. The results showed that the reaction yield was not strongly sensitive to most synthesis variables, while the viscosity, or molecular weight, and the electrical conductivity of the as-polymerized and/or post-treated polyaniline salt were found to be markedly affected.

Stejskal *et al.* (1996) studied the oxidative polymerization of aniline. The results indicated that the variety forms of polyaniline have different conductivity and color.

2.2.1.2 Electrochemical Synthesis

Electrochemical polymerization is a radical combination reaction and is diffusion controlled. The anodic oxidative polymerization is the preferable method to obtain a clean and better-ordered polymer as a thin film.

2.2.2 Doping of Polyaniline

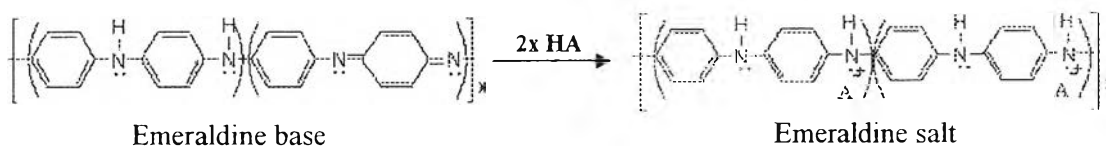
Doping process describe as the method for achieving the high electrical conductivity. The doping of all conductive polymers is accomplished by the redox doping. This involves the partially addition (reduction) or removal (oxidation) of electrons to or from the π -system of the polymer backbone. However, polyaniline holds a special position amongst conductive polymers in that its emeraldine salt form (conducting form) is accessible by two completely different processes namely oxidative doping and protonic acid doping (non-redox).

2.2.2.1 Oxidative Doping

This method by chemical reaction with an appropriate oxidizing agent such as ammonium peroxosulfate and electrochemical charge transfer reaction. The charge transfer reaction causes a change in the total number of π -electron on the conjugate chain. This actually involves the oxidation of the σ/π -system rather than just the π -system of the polymer, as is usually the case of p-doping.

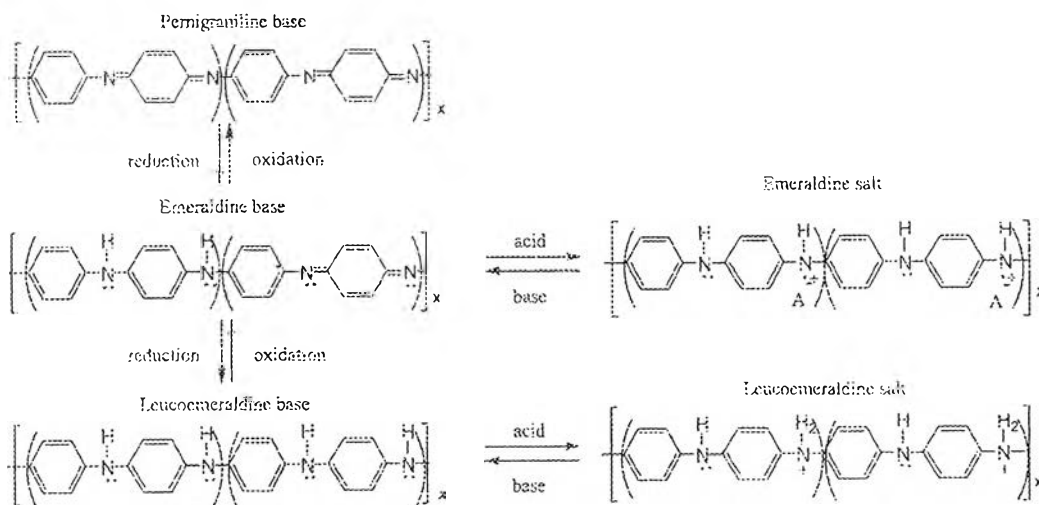
2.2.2.2 Protonic Acid Doping (Non-redox)

This type of doping process, the number of π -electrons associated with the polymer backbone does not change. It is accomplished by treating an emeraldine base with acid-base reaction in the aqueous media to obtain the emeraldine salt, as shown in Scheme 2.2.



Scheme 2.2 Protonic acid doping (non-redox) of polyaniline.

Each oxidation state can exist in the form of its base or its protonated form (salt) by treatment with an acid. The different oxidation states of polyaniline can inter-convert process of polyaniline is shown in Scheme 2.3.



Scheme 2.3 A reaction diagram consistent with the interconversion of different oxidation and protonation states of polyaniline.

2.3 Polyaniline Fiber

Fibers can be made in a variety of processes. Several spinning techniques are used widely to produce fibers, including solution spinning (wet or dry), melt spinning, and emulsion spinning. In solution spinning a viscous solution of polymer is pumped through a filter and then passed through the fine holes of a spinneret into the coagulation baths, the solvent is subsequently removed leaving a fiber that can be stretched to enhance molecular orientation as desired. Wet spinning has been used to produce fibers of conductive polyaniline and its derivatives.

In the literature most of the works, related with fiber actuators, have been done on conductive polymers. One of the more interesting conductive polymers from a processability standpoint is polyaniline due to its solubility in its base form and the environmental stability of the conducting state once the base is doped.

Polyaniline can be dissolved in some solvents, e.g. *N*-methyl-2-pyrrolidone (NMP), *m*-cresol, *N,N'*-dimethyl propylene urea (DMPU), concentrated sulfuric acid ($c\text{-H}_2\text{SO}_4$), 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPSA) in dichloroacetic acid (DCA). Thus, it could be processed into conductive self-standing fibers.

Tzou and Gregory (1995) showed *N,N'*-dimethyl propylene urea (DMPU) is a one candidate for a spin bath solvent for the wet spinning of polyaniline (PANI) fibers in the base form. It is significantly better than the commonly used NMP or NMP/LiCl solvents with regard to solution stability. They have found that solution stability of PANI in DMPU is greatly increased and be able to contained 20% w/w PANI without sensitive to the normal shears encountered in wet spinning and is stable to the gelation process over a much greater length of time than NMP or for that matter NMP/LiCl, a solvent system often used to stabilize wet spin baths. They reported that PANI fibers spun from solution of emeraldine base had tenacity of 2.4 g/d. Conductivity of doped fibers had reached to 350 S/cm.

Mattes *et al.* (1997) reported that adding the gel-inhibitory (GI) agents in concentrated polyaniline emeraldine base (PANI-EB) affects to reduce solution viscosity and increases the gelation time in order to improve spinning processibility. These agents are quite sensitive to the concentration range in GI/PANI-EB molar ratio between 0.5-3. The as-spun fiber had tenacity of ca. 2.8-6.8 cN/tex and elongation at break of ca. 6.0-9.0% and the conductivity was in the range of 1 S/cm (HCl-doping). The conductivity and mechanical properties were further improved by drawing the fiber.

Pomfret *et al.* (2000) developed a new acid-solution processing route for the polyaniline (PANI) fibers in wet-spinning. The fibers achieved from solution of PANI protonated with 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPSA) in dichloroacetic acid (DCA). The fibers were spun into various coagulation solvents i.e. acetone, butyl acetate and 4-methyl-2-pentanone. As-spun fibers have Young's moduli of 40-60 MPa, Ultimate tensile strengths of 20-60 MPa and electrical conductivities of 70-150 S/cm. These fibers may be drawn at elevated temperatures, and then annealed to give fibers with Young's moduli up to 2 GPa and Ultimate tensile strengths up to 97 MPa whilst retaining conductivities of ~600 S/cm.

Wang *et al.* (2000) produced polyaniline-emeraldine base (EB) fibers have been spun from highly concentrated (20% w/w), EB/N-methyl-2-pyrrolidinone (NMP)/ 2-methylazirine (2 MA) solution. These solutions had gelation times, which varied from hours to days depending on the molar ratio of 2 MA to EB tetramer repeating unit in the NMP solvent. To compare the mechanical and electrical properties with dense films, The mechanical properties of the stretched dense films are better and the measured conductivities remain higher than those of stretched fiber because of macro void formation and lower overall material density. Doping the fiber with inorganic acid (HCl) embrittles the fiber, whereas doping with organic acid (acetic acid, benzenephosphinic acid) does not appreciably affect the mechanical strength.

Adams *et al.* (2001) investigated the effect of molecular weight polyaniline (PANI) to mechanical and electrical properties on fiber form. PANI in its emeraldine base was synthesized by polymerizing aniline in acid solution at different sub-zero temperatures to give a range of molecular weights between 100,000 and 300,000 g/mol. PANI fibers were prepared in its electrically conducting form by dissolved in a combination of dichloroacetic acid (DCA) solvent, 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPSA) and formic acid (FA). Fibers were extruded into a butanone bath and were then stretched over a hot pin under tension. The stretched fibers, prepared from high molecular weight of PANI, show higher electrical conductivity (in the range of 590-760 S/cm) and good mechanical properties; tenacity of ca. 4.8-6.9 cN/tex, and elongation at break of ca. 5.0-8.0%, than stretched films resulting from alignment of the polymer chains in fibers compared to films.

Yang *et al.* (2001) studied the effects of polymer concentration, coagulation bath temperature, polymer molecular weight and coagulant on the morphology of wet-spun polyaniline (PANI) fibers. The fibers were spun from concentrated solution of low/medium and medium molecular weight emeraldine base (EB) dissolved in N-methyl-2-pyrrolidinone (NMP) containing heptamethyleneimine as a gel inhibitor. They found that using high EB concentrations, low coagulation bath temperatures, high molecular weight EB and the addition of 20% NMP in the water bath, can minimized the formation of macro voids in the produce fibers. The gained solid EB fibers have a Young's modulus of 1.3 GPa, a peak stress of 30 MPa and a strain at

break up to 6%, which is significantly stronger than the unstretched fiber reported by other researchers. However, all of these fibers are stiff and brittle.

2.4 Natural Rubber Latex

Natural rubber latex (NR latex) collected from *Hevea brasiliensis* rubber trees. Latex can be harvested by gouging the bark with a tapping knife—a diagonal cut through the bark. The latex exudes from the tapping at a rate of about 100-300 ml in 1-3 h, and is collected in a small cup, as shown in Figure 2.14.

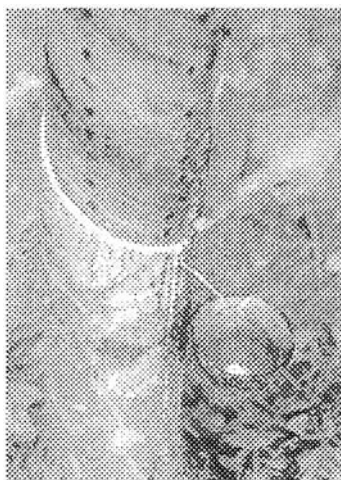


Figure 2.4 Collection of natural rubber latex from *Hevea* tree by tapping.

In general, the latex is a colloidal suspension of rubber particles in an aqueous serum phase. Normally, after tapping latex from the rubber trees, the latex is called as fresh NR latex or fresh field latex.

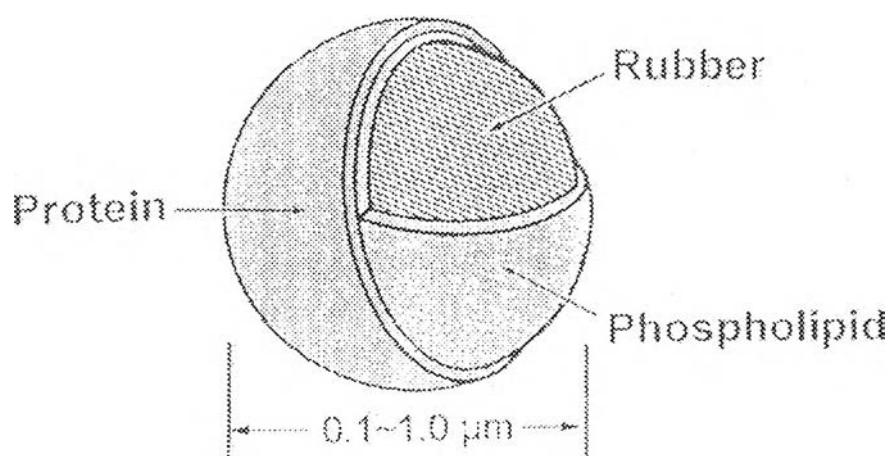
2.4.1 The Composition of Natural Rubber Latex

Fresh field latex exuded from *Hevea* tree naturally composes of about 25-45% dry rubber content (DRC) and 5-10% non-rubber substances. The non-rubber components have been identified as proteins, amino acids, lipids, carbohydrates and inorganic salts as shown in Table 2.1.

Table 2.1 Typical composition of natural rubber latex

Ingredient	% content
Total solids content	41.50
Dry rubber content	36.00
Proteinous substance	1.40
Neutral lipids	1.00
Phospholipids	0.60
Ash	0.50
Inositols and carbohydrates	1.60
Other nitrogen compounds	0.30
Water	58.50

The rubber particles dispersed as white colloidal in water are range in diameter, from 0.01 μm to about 5 μm , with the majority being 0.1-2 μm diameter. Each of rubber particles contains the hydrocarbon surrounded by a surface film of proteins and lipids, including phospholipids, as shown in Figure 2.5.

**Figure 2.5** Representation of rubber particle.

The rubber particles fraction consists of long chains of isoprene monomer (C_5H_8), as shown in Figure 2.6.

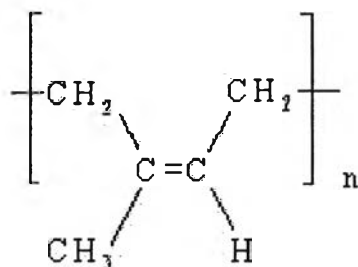


Figure 2.6 The general formula structure of cis-1,4-polyisoprene in natural rubber.

2.4.2 Viscosity of Natural Rubber Latex

In general, fresh latex has density of 0.975-0.986 g/cm³ with pH of 6.5-7.0 and a refractive index of 1.5910. Rubber does not dissolve in water, alcohol, or acetone but it swells and dissolves in benzene, toluene, gasoline, chloroform, carbon tetrachloride, and halogen containing solvents.

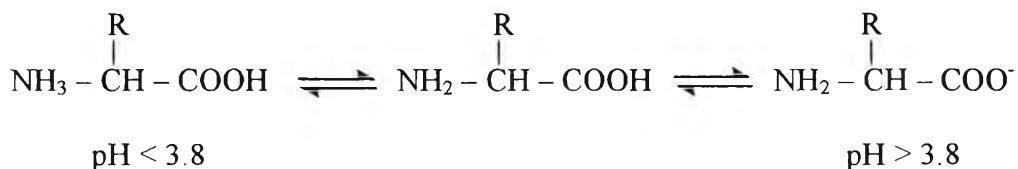
NR latex is a pseudoplastic fluid, and even at rest the rubber particles in it are in random movement. But when sheared, the rubber particles are progressively aligned and offer less resistance to flow. The rheological behavior of latex is considered for manufacturing process such as the count of a latex thread is largely influenced by its viscosity in elastic thread manufacture. The surface-active agents are added to modify the flow behavior of latex to suit the process adopted.

Peethambaran *et al.* (1990) had studied the effect of surface-active agents, casein, polyvinyl alcohol, sodium alginate, and sodium carboxymethylcellulose (NaCMC) were studied at different shear rates and temperatures. The viscosity of the latex lattices can be increased by the addition of surface-active agents, and the effect varies with the type of surface-active agents.

2.4.3 Stability of Natural Rubber Latex

Ho *et al.* (1996) used electrophoresis measurement to characterize the surface of NR particles. They reported that the particles have an amphoteric nature with isoelectric point (pI) at pH 3.8. Above this pH, NR particles possess negative

charges. This was due to the zwitterions of amino acids on latex particles indicated as shown in Scheme 2.4.



Scheme 2.4 The zwitterions of amino acids on natural rubber latex particles.

Moreover, in the ammonia-preserved NR latex, the ammonia promotes hydrolysis of proteins to polypeptides and amino acids and of phospholipids to glycerol, fatty acid anions, phosphate anions and organic bases. The fatty acid anions are also adsorbed on the surface of rubber particles and contribute to colloidal stability of latex. The presence of bound charge on surface of rubber particles in the dispersion medium leads to electrostatic stabilization.

In general, fresh field latex would coagulate within few hours after leaving from the rubber tree. Putrefaction then sets at a later stage, so good preservation is necessary. Preservation of natural rubber latex can be either of short-term or long-term. Short-term implies preservation just sufficient to ensure that the field latex remains liquid for few hours, or even few days. Long-term preservation is intended to preserve during shipment to and storage within the consumer country. Many preservatives have been with NR latex, but the most common and good efficiency is ammonia or systems containing ammonia.

2.4.4 Concentrate Natural Rubber Latex

NR latex exudes, which has rubber content between 25 and 40% by weight depend on the various factors such as type of rubber tree, tapping method, soil conditions and season. The latex is normally called fresh field latex, and its average rubber content is 30% by weight. This material is not utilized in its original form due to the high water content and susceptibility to bacterial attack. It is necessary both to preserve and concentrate it, so the end product is stable and contains 60% minimum rubber content. Extensive blending of the concentrated latex

ensures a consistent high quality material to meet national and international specifications.

Concentrated latex could be differentiated by the method of concentration and type of preservative used. In addition to the general propose type of latex, there are specialty forms such as double centrifuged latex, creamed centrifuged latex (sub-stage latex), and modified types such as prevulcanized latex. Three methods of concentration are employed, centrifugation, evaporation and creaming; centrifugation is one of the most popular method and accounts for 95% of total latex production.

Details of the preservative systems used in the concentrated latex are given in Table 2.2. The predominant lattices are the HA and LA-TZ types. Latex concentrate prepared by evaporation is usually stabilized by potassium hydroxide, whilst creamed latex is normally preserved with 0.7% ammonia.

Table 2.2 Types of preservative system used in centrifuged natural rubber concentrated latex

Designation	Abbreviation	Market Share (%)	Preservative system (% by weight)
High ammonia	HA	66	0.7% ammonia
Low ammonia	LA-TZ	17	0.2% ammonia, 0.025% Zinc oxide, 0.025% tetramethyl thiuram disulphide
Low ammonia pentachlorphenate	LA-SPP	6	0.2% ammonia, 0.2% sodium pentachlorphenate
Low ammonia boric acid	LA-BA	5	0.2% ammonia, 0.24% boric acid

Fresh field latex is collected from the tapping cups and bulked. Preliminary ammoniation to about 0.05-0.2% is carried out to protect fresh field latex from bacterial attack prior to delivery to the latex concentrate factory. On arrival, the latex is tested for properties such as rubber content and volatile fatty acid content. If the test results are satisfactory, the latex is put in the bulking tanks. Then, it supplies to the centrifuges where separation occurs, yielding a concentrate (60% or more rubber content) and a skim latex (3-8% rubber content). The concentrated latex is ammoniated using ammonia gas and treated with the rest of the preservative system, if necessary. It is kept in storage tank for quality tests. The concentrated latex is transferred to the port installation for shipping to the consumer in bulk container or drums. A typical layout of a latex factory is show in Figure 2.7. Gravitational flow is used wherever possible; otherwise air pressure pumps are employed.

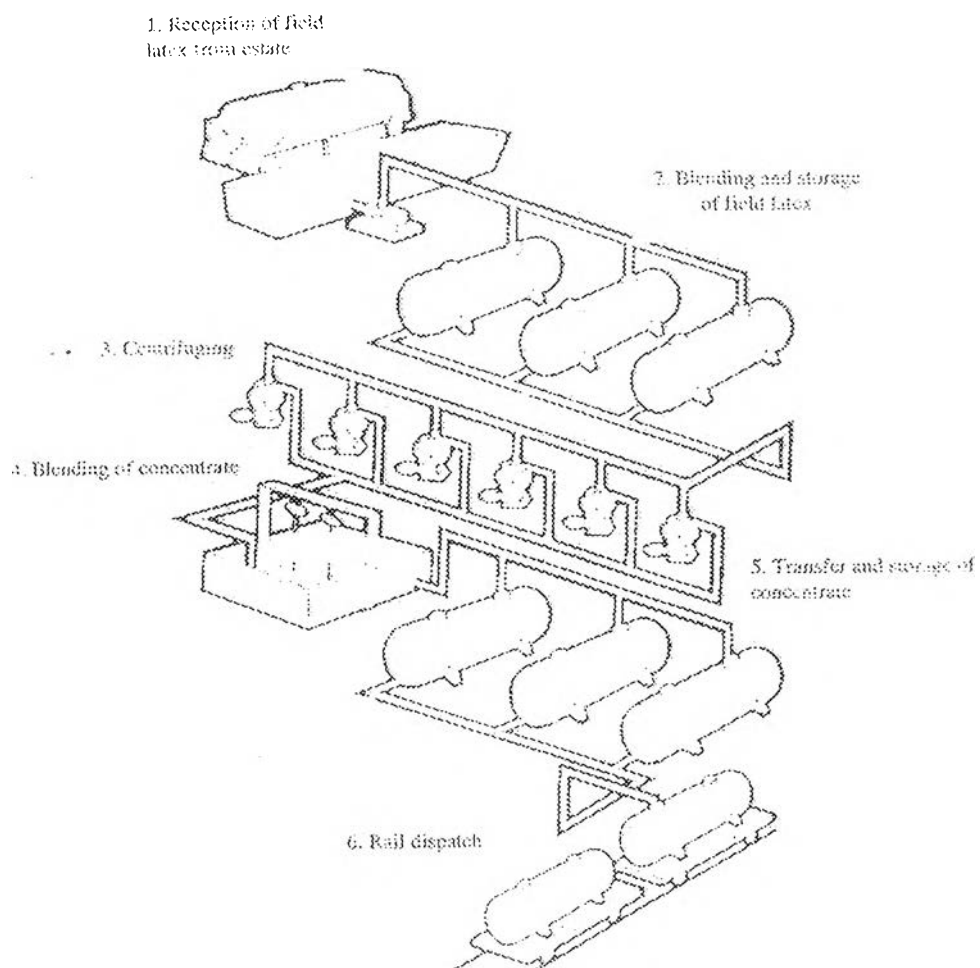


Figure 2.7 A schematic layout of centrifuged latex concentrated plant.

2.5 Electrically Conductive Composites and Blends based on Polyaniline

Composites or blends of two or more polymers are usually prepared to achieve desired properties, which cannot be given by the individual polymers. In order to improve processibility and mechanical properties of conductive polymer, the concept of composites or blends become the most used way to overcome those limitations. Additionally, for technical and economic reasons, it is desirable to minimize the amount of the conductive polymer component in a composite without drastically reducing its electrical conductivity. Therefore, conductive polymer are blended with other highly processible conventional polymers in terms of especially combining between the conductive polymers with elastomers.

Faez *et al.* (1999) prepared vulcanized elastomeric conductive blends of EPDM and polyaniline-TSA (PANI-TSA). Due to the conducting polymer inhibits the crosslinking process in the elastomer. This effect is partially counterbalanced by using a higher concentration of crosslinking agent. In their work, the $[\text{PANI}]/[\text{peroxide}] = 10$ is suitable value. The electrical conductivity of blends is 10^{-9} to 10^{-6} S/cm with 0 to 50 phr of PANI-TSA.

Polyaniline-polyisoprene (PANI-PIP) composite film that used to immobilize glucose oxidase for glucose sensor application was prepared by Xue *et al.* (2001). The PANI-PIP film was synthesized by electropolymerization of aniline onto PIP-coated platinum electrode. The film biosensor has long-term stability and high permselectivity, which can determine H_2O_2 in the presence of electroactive interferent ascorbic acid.

Jeevananda *et al.* (2001) and coworkers prepared ethylene-vinyl acetate copolymer-polyaniline (EVA-PANI) blends with different weight ratios of PANI were obtained by mechanical blending using plasticoder. The results show that tensile strength and % elongation at break decrease with increasing of PANI content whereas their conductivity increases.

Schmidt *et al.* (2004) studied on thermal stability of blends obtained from the mixture of 4-dodecylbenzenesulfonic acid doped polyaniline (PANI-DBSA) and a terpolymer of ethylene-propylene-5-ethylidene-2-norbornene (EPDM) by casting form organic solvents. The TGA results of PANI-DBSA and PANI-DBSA/EPDM

blends showed that there is more than one stage of degradation occurred, it being observed that the second stage was simultaneous degradation of the bound dopant, PANI and elastomer occurred in the case of the blends.

Conductive composites of polyacrylonitrile (PAN) copolymer containing 10% mass ratio methylacrylate and dodecylbenzene sulfonic acid doped polyaniline (PANI-DBSA) were prepared by solution blending that reported by Pan *et al.* (2005). It was found that the electrical conductivity of the composites increases from 10^{-13} S/cm to 10^{-7} S/cm with the increase of PANI-DBSA content up to 5% mass ratio, the conductivity can even reach to 10^{-3} S/cm. The conductivity increases sharply when the mass ratio of PANI-DBSA is less than 4%, after which it will gradually reach to 10^{-1} S/cm when more PANI-DBSA is added. It is shown that the percolation threshold laid around 3.2% mass ratio. They proposed that the formation of the hydrogen bonding between the carbonyl groups in PAN copolymer and the imine groups in PANI-DBSA may be induced good compatibility and an nanolevel dispersion of PANI-DBSA in PAN matrix.

Camillo *et al.* (2005) investigated preparation conditions of polyaniline /natural rubber (PANI-NR) blend films. The blend films containing 20% in volume of PANI in 80% of NR were fabricated by casting in three different ways: (1) adding PANI-EB(emeraldine base) dissolved in N-methyl-2-pyrrolidone (NMP) to the latex, (2) adding PANI-EB dissolved in m-cresol to NR dissolved in xylol, (3) overlaying the surface of a pure NR cast film with a PANI layer grown by in situ polymerization. All films were immersed into HCl solution to achieve the primary doping (protonation) of PANI. The results suggest that the blend films from first method are the most suitable in terms of mechanical and electrical properties due to gain of highest conductivity (10^{-3} S/cm) without losing the elastomeric property of the NR.

The effect of NR on the doping process of PANI-EB with HCl solution was observed by Job *et al.* (2003). The chemical interaction between the NR and PANI were observed by Raman scattering, showing that the NR itself is able to dope the PANI by protonation and also induces changes in the conformation of the PANI chains (secondary doping).

Souza Jr *et al.* (2006) prepared electrically conductive blends based on polyaniline-dodecylbenzene sulphonic acid (PANI-DBSA) and styrene-butadiene-

styrene (SBS) block copolymer by two methods namely melt mixing and in situ polymerization of aniline in the presence of SBS. In the both cases, the presence of PANI-DBSA drastically reduced the ultimate properties (tensile strength and elongation at break), this behavior may be attributed to the interactions between the PANI with the SBS matrix, which contribute for the reduction of physical crosslink strength of polystyrene domains of SBS block copolymer. The blend prepared by in situ polymerization resulted in higher conductivity because of favorable morphology, which is able to form the conducting pathway with lower amount of PANI.

Yoshikawa *et al.* (2006) investigated the electrical conductivity as a function of elongation of blends of polyaniline/polyurethane (PANI/PU), polyaniline/polystyrene-isoprene-copolymer (PANI/SIS). For the PANI/SIS film, the conductivity decreased nearly two orders of magnitude (10^{-6} S/cm to 10^{-10} S/cm) after 100% elongation. This was because the distance between each conductive component increased with the increase of the elongation of the film. For the PANI/PU film, the conductivity did not change (10^{-6} S/cm) with the increase of the elongation may be resulting from the homogeneous structure kept the conductive pathways connected during the elongation.

2.6 Electrically Conductive Composite Fiber

In recent years, electrically conductive composite fiber based on conducting polymers and other substrates have been studied extensively because of their potential in many application. Many researchers proposed that have many methods to achieved, as follow;

Zhang *et al.* (2001) prepared the solution of polyaniline blended with polyamide-11 (poly- ω -aminoundecanoyl) in concentrated sulfuric acid and then spun PANI/PA-11 fibers by wet-spinning. They found that two blend components were incompatible. The morphology of PANI in the fibers was of fibril form, which was valuable for producing conducting channels. The electrical conductivity of the fibers was from 10^{-6} to 10^{-1} S/cm with the different PANI fraction and the percolation threshold was about 5% w/w.

Hirase *et al.* (2003) prepared poly(ethylene terephthalate) (PET) fibers coated with polyaniline (PANI) through electrochemical polymerization of aniline in 0.5 N HCl solution. The content of PANI in composite fibers increased with an increase in both the aniline concentration in the electrolytic solution and the polymerization voltage, although it did not depend on the load applied to the electrodes. They reported the formation processes of PET-PANI composite fibers could be divided into three steps: (1) fine (nano-size) granular PANI was generated from the anode and adsorbed onto the PET fiber surface, (2) the size of the granular PANI increased up to about 90 nm in a short time, and (3) the granular PANI was linked together to form networks. The conductivity of composite fibers increased with an increasing content of PANI networks. The surface resistance of the PET-PANI fabric was about $3 \times 10^5 \Omega/\square$ at a PANI content of approximately 2% w/w.

Jianming *et al.* (2004) produced composite conductive fibers of polyaniline doped with dodecylbenzene sulfonic acid (PANI-DBSA) and polyacrylonitrile containing methylacrylate (Co-PAN) were prepared via a conventional wet spinning process. The influences of PANI-DBSA content on the electrical conductivity, thermal stability and mechanical properties of the composite fibers were investigated. They found that the fiber with 7% w/w PANI-DBSA showed its conductivity of an order of 10^{-3} S/cm up to 10^{-1} S/cm (24% w/w). The tensile strength of the fibers was in the range of 2.5–3.5 cN/dtex. The thermal stability of the composite fiber was superior to both pure Co-PAN and PANI-DBSA.

2.7 Composites for Artificial Muscle or Actuator

Zrínyi *et al.* (2000) developed a new type of electric-field sensitive neutral polymer gels in a non-conductive medium. The main idea was to incorporate finely distributed colloidal particles into a swollen network responding to electric field. Since the particles cannot leave the gel matrix, thus all of the forces acting on the particles are directly transmitted to the polymer chains, resulting in either the locomotion or the deformation of the gel. Structural formation of TiO_2 particles dispersed in silicon oil and bending deformation of weakly crosslinked

poly(dimethyl siloxane) gels containing derives from the interaction of the electric-field-induced charges with the external electric field.

Kyokane *et al.* (2001) prepared polyurethane elastomer (PUE) films that can be applied to moving devices such as mononorph actuator. A doping C₆₀ derivatives (fullerenol) were incorporated into PUE in order to the film actuator could operate under a low voltage. The bends of fullerenol doped PUE actuators were larger than that of non-doped PUE actuators and the working voltage was also small. All of samples were bent in the direction of cathode electrode independent of metal materials and showed polarity effect.