



CHAPTER II LITERATURE REVIEW

2.1 Conductive Polymers (CPs)

Until about 30 years ago all carbon based polymers were rigidly regarded as insulators. The idea that plastics could be made to conduct electricity would have been considered to be absurd. Indeed, plastics have been extensively used by the electronics industry because of this very property. They were utilized as inactive packaging and insulating material. This very narrow perspective is rapidly changing as a new class of polymer known as intrinsically conductive polymer or electroactive polymers are being discovered. In 1958, polyacetylene was first synthesised by Natta *et al.* as a black powder. This was found to be a semi-conductor with conductivity between 7×10^{-11} to $7 \times 10^{-3} \text{ S}\cdot\text{m}^{-1}$, depending upon how the polymer was processed and manipulated. A Logarithmic conductivity ladder of some of these polymers is shown in Figure 2.1.

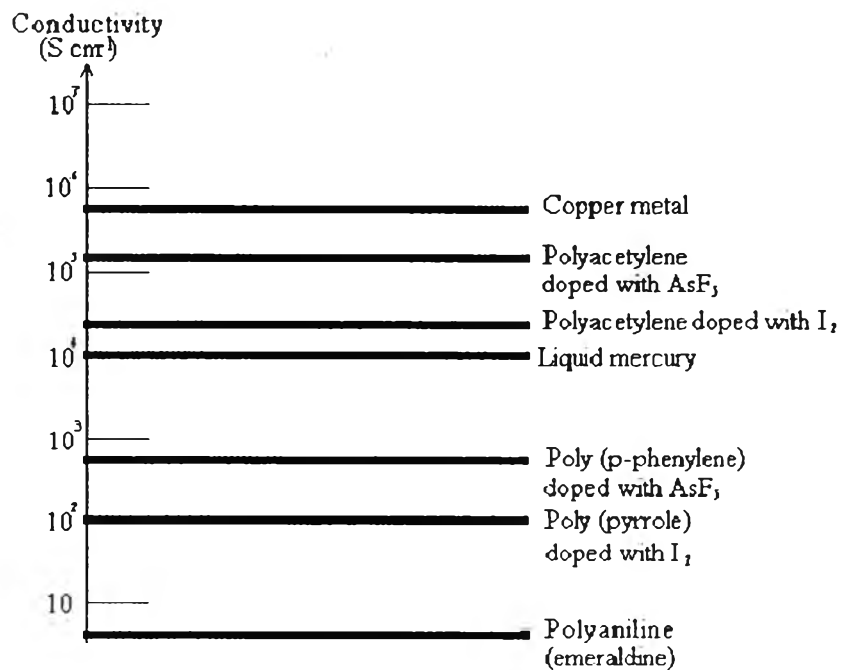


Figure 2.1 A Logarithmic conductivity ladders of some of these polymers.

Since then it has been found that about a dozen different polymers and polymer derivatives undergo this transition when doped with a weak oxidation agent or reducing agent. They are all various conjugated polymers. This also causes the main problems with the use of these systems, that of processability and stability. Most early conjugated polymers were unstable in air and were not capable of being processed. Some of the conjugated polymers, which have been extensively studied today, consist of polyacetylene, polyaniline, polypyrrole, polythiophene, poly(p-phenylene), poly(phenylene vinylene), etc as shown in Figure 2.2. The most recent research in this has been the development of highly conducting polymers with good stability and acceptable processing attributes.

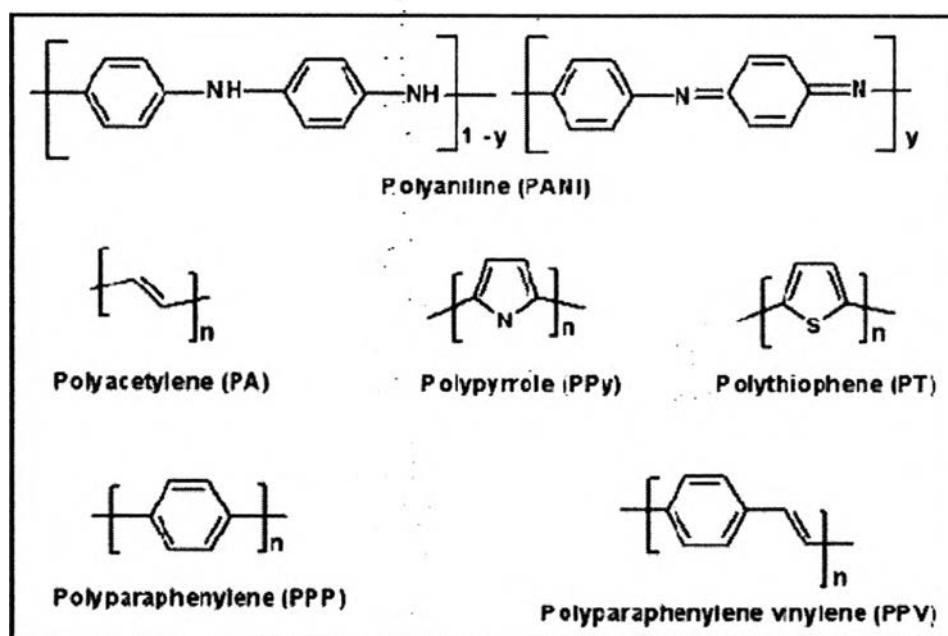


Figure 2.2 Example of intrinsically conductive polymers.

A lot of recent studies concentrated on polypyrrole, polyaniline, and polythiophene because of their superior oxidative stabilities as compared with other inherently conducting polymers. Polypyrrole can be synthesized either by an electrochemical oxidative process or by a chemical oxidation. It is an intractable, brittle solid. Polyaniline, one of the most stable conductive polymers, is also well suited for electrochemical applications because its conductivity can be switched from

low to high to low within the electrochemical potential range of aqueous electrolytes (Wei Pan *et al.*, 2005). The electrical conductivity, environmental stability and processibility of a number of doped conductive polymers are presented in Table 2.1 (Sambhu Bhadra *et al.*, 2009)

Table 2.1 The conductivity, environmental stability and processibility of a number of doped conductive polymers

Polymer	Conductivity(S/cm)	Stability	Processability
Polyacetylene	10^3-10^5	Poor	Limited
Polyphenylene	1000	Poor	Limited
Poly(phenylene vinylene)	1000	Poor	Limited
Poly(phenylene sulphide)	100	Poor	Excellent
Polypyrroles	100	Good	Good
Polythiophenes	100	Good	Excellent
Polyaniline	10	Good	Good

2.1.1 Polyaniline

Among conductive polymers, polyaniline is one of the important conductive polymers due to its ease of synthesis, relative high conductivity, known as having probably the best combination of stability, electrical conductivity, good environmental stability, and cost economics. (Wei Pan *et al.*, 2005). Polyaniline molecule consists of two segments, a flat structure of two imine groups and a quinoid ring, and tetrahedral segments of two amine groups separating three benzenoid rings as shown in Figure 2.3. Because of the presence of aromatic rings, the polyaniline chain should be rigid and mostly turn into an expanded coil conformation. The situation in the polyaniline chain changes upon protonation. This process is accompanied by creation of positive charges on the nitrogen atoms. Their repulsion should cause straightening of the chain, which is extremely beneficial for delocalization of the electrons (charges) along the chain, and creation energetically most favourable polaronic structure. The polymer conformation can be strongly

influenced by a dopant, as well as a solvent used during the sample preparation (Jadwiga Laska 2004).

The general formula of polyaniline consists of two component, one is reduced repeating units and another one is oxidized repeating units as shown in Figure 2.3.

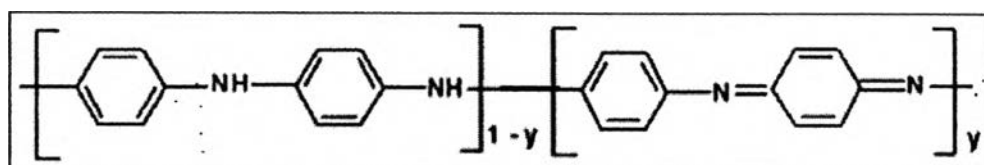


Figure 2.3 The general chemical structure of polyaniline.

Polyaniline can exist in three different oxidation state with different colours as shown in Figure 2.4. The full reduced form of polyaniline, which is called leucoemeraldine, corresponds to a value of y is 1. The full oxidized form of polyaniline, which is called pernigraniline, corresponds to a value of y is 0. And the half oxidation form of polyaniline, which is called emeraldine, corresponds to a value of y is 0.5.

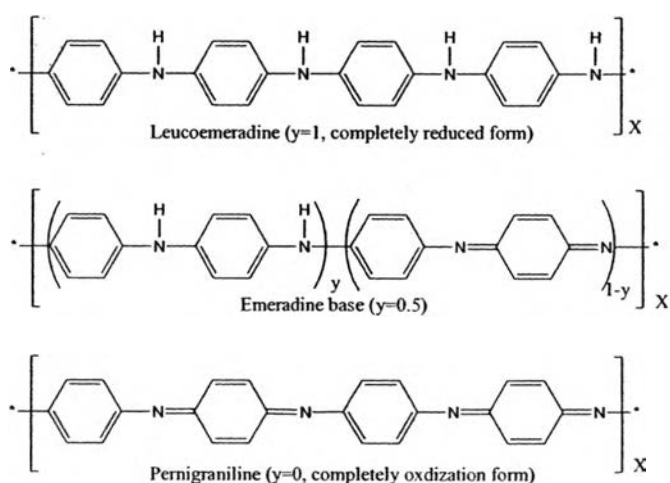


Figure 2.4 The different oxidation states of polyaniline.

2.1.2 Synthetic Methods to Prepare Polyaniline

In the available literature reviewed for this study, different ways to produce Polyaniline have been demonstrated, including chemical, electrochemical, template, enzymatic, plasma, photo, and a number of other special methods.

2.1.2.1 *Chemical Polymerization*

The chemical synthesis of polyaniline is again subdivided into heterophase, solution, interfacial, seeding, metathesis, self-assembling, and sonochemical polymerizations. The different synthesis methods used to produce polyaniline are detailed as following.

2.1.2.1.1 *Heterophase Polymerization*

The heterophase polymerization is used to produce high quality polymers with specially tailored properties from a small to a large scale. The heterophase polymerization technique includes different methods of polymerization such as precipitation, suspension, microsuspension, emulsion, miniemulsion, microemulsion, dispersion, reverse micelle and inverse polymerizations. The detail of different methods is explained in the next.

○ Synthesis of Polyaniline Colloidal Dispersion

Polyaniline is typically produced by the oxidative polymerization of aniline in an acidic aqueous medium and is obtained as a precipitate. Such a process is known as dispersion polymerization. In this process: (a) the monomer is soluble in the reaction medium; (b) the produced polymer is insoluble under the same conditions; and (c) its macroscopic precipitation is prevented by the presence of the so-called steric stabilizer. Hence, such colloids are called dispersions. The colloidal polyaniline particles have a typical average size of a few tens to hundreds of nanometers. The shape of the particles may be spherical, globular, granular.

○ Direct and Inverse Emulsion Polymerization

In the emulsion polymerization the monomer is dispersed in an aqueous phase to form a uniform emulsion. The emulsion is stabilized by a surfactant and the polymerization reaction is carried out. For the synthesis of polyaniline by emulsion polymerization, aniline along with a protonic acid and an oxidant are combined with a mixture of water and a nonpolar or weakly

polar solvent (sparingly soluble or insoluble in water). In some instances to form an emulsion with the above systems, a protonic acid is employed, which has a substantial emulsifying ability in weakly polar solvents. In addition, the product of the above reaction can not be isolated directly, since the polyaniline salt exists in the emulsion along with other by-products. In most cases, the product is isolated by destabilizing the emulsion through the addition of acetone. The polyaniline salt is then collected and subjected to repeated washing to free it from other constituents. The inverse emulsion polymerization process involves the formation of an aqueous solution of the monomer aniline, which is emulsified in a nonpolar organic solvent or in a mixture of solvents. The polymerization is then initiated with an oil-soluble initiator such as ammonium persulfate. The reaction carried out in such a heterogeneous phase has several distinct advantages compared to that of methods discussed earlier. The physical state of the inverse emulsion system makes it easier to control the process. Thermal and viscosity problems are much less significant here than those in bulk polymerization. The product of an emulsion polymerization can be used in many instances directly without further separations. During the polymerization, both a high molecular weight and a high reaction rate can be simultaneously achieved. During the course of the reaction, polyaniline remains as a soluble component in the organic phase. At the end of polymerization the organic phase is separated and washed repeatedly with distilled water. The solution is then treated with anhydrous sodium sulfate or other suitable chemicals to remove the excess water. The viscous organic solution is then added to acetone or other suitable solvent in order to break the emulsion and precipitate the polyaniline salt.

- Direct and Inverse Miniemulsion

Miniemulsion is a relatively stable submicron (50–500 nm) dispersion of oil in water prepared through homogenizing the system containing oil, water, surfactant and a co-surfactant. Miniemulsion is stable for a long period of time and exhibits unique polymerization kinetics. The co-surfactants used (1–5%) in miniemulsions are usually low molecular weight compounds, which have a poor solubility in water but a good solubility in monomer. These co-surfactants retard the outward diffusion of the monomer from droplets and form an intermolecular complex at the oil–water interface, thereby creating a low interfacial

tension and a high resistance to droplet coalescence. For these two reasons, emulsion droplets become quite small and stable.

- Direct and Inverse Microemulsion

A microemulsion is an organized micro-heterogeneous system which provides a large interfacial area and is generally less viscous. Usually, a typical microemulsion system contains water, oil and surfactant, and also often a co-surfactant to stabilize the system. Microemulsion is a molecularly ordered system, and in this system the orientation behavior of the surfactants can be detected. It is well known that the microemulsion polymerization is an effective method in producing polymer particles in the size range of 5–100 nm.

- Reversed micelle polymerization

The polyaniline obtained from reversed micelle polymerization has comparable or even better conductivity, processability, crystallizability, electrochemical activity, solubility, thermal stability and higher molecular weight compared to the products obtained from other processes. The inverse microemulsion polymerization has recently been widely exploited to prepare polymeric nanoparticles, hollow nanospheres and nanotubes. In an inverse microemulsion system, micro-drops of an aqueous phase are trapped within the assembly of surfactant molecules dispersed in a continuous oil phase. The size of the dispersed phase is usually very small (a few nanometers) and various functional reactants can be deliberately introduced into the nanometer sized aqueous phase confined within the inversed micelles.

2.1.2.1.2 Solution Polymerization of Aniline

Polyaniline has also been synthesized by solution polymerization of aniline. Generally the processability of polyaniline is very poor due to its poor solubility in all available solvents. Therefore, the polyaniline prepared through a solution polymerization process has better processability since it is already in a solution.

2.1.2.1.3 Interfacial Polymerization of Aniline

When polymerization reaction is carried out in the interfaces of two immiscible solvents it is known as interfacial polymerization. Polyaniline has been synthesized by an interfacial polymerization technique using a

mixture of two immiscible solvents such as water and chloroform in the presence of different acids acting as dopants. The reaction is initiated by an oxidizing agent at room temperature or at any preferable temperature in the presence or absence of a surfactant. The final product is isolated by centrifugation. Various products ranging from a one-dimensional radially aligned nanofiber to a spherical shaped polyaniline with a narrow size distribution can be obtained using this method, through the correct selection of suitable reaction parameters and reagents.

2.1.2.1.4 Seeding Polymerization of Aniline

The seeding polymerization is a typical template approach where a foreign material is used as the seed and the polymerization reaction is carried out in the presence of this seed. Polyaniline nanofiber has been synthesized from aniline in the presence of some polyaniline powder acting as a “seed” using different acid dopants and different solvents. The polyaniline obtained by this method is similar to a nanofiber with high conductivity. The morphology of this nanofiber depends upon the type of acid used, the acid concentration, type of seed, the solvent used, and the relative amount of seed with respect to solvent. Among these reaction conditions, the influence of monomer concentration and solvent type was found to be pronounced in the morphology of the resultant polyaniline. A higher solubility of the seed polyaniline to the solvent used induces a poorer morphology (fibril structure) of the resultant polyaniline.

2.1.2.2 Electrochemical Synthesis of Polyaniline

At present there is a two fold interest in the electrochemical polymerization process. Firstly, the electrochemical polymerization process reaction provides a better method of polymerization with a fine control of the initiation and termination steps. Secondly, electrochemical polymerization process has a degree of technological potential. The electrochemical reactions are often much cleaner, and the polyaniline obtained is expected to be in a relatively purer form compared to that obtained from chemical polymerization. Furthermore, the use of limited chemicals reduces the problem of pollution.

Electrochemical methods are generally employed for the polymerization of aniline under: (i) a constant current (galvanostatic); (ii) a constant potential (potentiostatic); and (iii) a potential scanning/cycling or sweeping. Fine

nanowires can also be prepared by electrochemical polymerization process using a template. The anodic oxidation of aniline is generally carried out on an inert electrode.

2.1.2.3 *Template Synthesis of Polyaniline*

One of the most effective and simple techniques of nanostructure formation is template synthesis. In this synthesis the desired material with the required shape is synthesized within the pores of a template and the template is then dissolved, leaving the material with the shape of the pores of the template. The template method has been used both for chemical and electrochemical polymerization in order to obtain conducting polymer nanotubes. Template-based methods have attracted great attentions as a viable technology enabling to manipulate a length and a diameter of nanowires. One of the interesting and useful features of this method is its effectiveness in the preparation of one-dimensional microstructured or nanostructured polyaniline with a controllable diameter, length and orientation.

2.1.3 Electrical Conduction in Polyaniline

The electrical conductivity (σ) in any system is proportional to the product of the density of charge carriers (n), the charge carried by each carrier (e) and the mobility of each carrier (μ) as shown in equation 2.1

$$\sigma = e n \mu \quad (2.1)$$

Here e is the unit electronic charge (1.6×10^{-19} C), ' n ' in m^{-3} and μ in $\text{m}^2/(\text{V s})$.

The carrier concentration, its mobility and the type of carrier of semiconductors can be estimated from a Hall's effect measurement. The majority charge carriers in polyaniline are holes, which indicate that the polyaniline is a p -type semiconductor. The delocalized π bonds available in the system are responsible for the semi-conducting properties (Sambhu Bhadra et al., 2009).

2.1.3.1 *Factors Influencing the Electrical Conductivity*

The four most important factors which influence the conductivity of polyaniline are: (i) molecular weight; (ii) percentage of crystallinity and inter-chain separation; (iii) oxidation level and molecular arrangement; and (iv) percentage of doping and type of dopant.

2.1.3.1.1 Molecular weight

This is mainly because long-range delocalization of an electron cloud due to the formation of a conjugated double bond does not occur until the molecule attains a definite size. However, at a very high molecular weight a type of imperfection such as distortion in the chain symmetry may again develop which in turn adversely affects the continuous charge delocalization process in a chain. This may lead to a drop in the conductivity. The bulk conductivity (σ_{bulk}) of the polyaniline is the function of intra-molecular (σ_{intra}), inter-molecular (σ_{inter}) and inter-domain (σ_{domain}) contributions.

2.1.3.1.2 Percentage of Crystallinity

With the increase in crystallinity, the conductivity is increased as the structure becomes more organized. The intra-molecular mobility of the charged species along the chain, and to some extent the intermolecular hopping of charge carriers (due to better packing), is therefore increased. With the decrease in the d -spacing and inter-chain separation the probability of inter-chain hopping of charge carriers is again increased and hence the conductivity increases.

2.1.3.1.3 Oxidation Level and Molecular Arrangement

If there is no emeraldine base structure in polyaniline then other factors as mentioned earlier may not play a significant role towards the achievement of high conductivity as in such case polaron formation will not take place in presence of protonic acid and there will be hardly any charge transport. Therefore, the alternative arrangement of quinoid and benzenoid rings in polyaniline (perfect emeraldine base structure) with 50% doped in the crystalline region seems to be the most important factor required to achieve a high level of conductivity. The suitable way to form this type of structure may be a partial reduction of over oxidized polyaniline.

2.1.3.1.4 Percentage of Doping and Type of Dopant

The doping seems to be the second most important factor in the achievement of a high level of conductivity for polyaniline as shown in Figure 2.5. The protonation of polyaniline helps to form a polaron structure, where a current is carried by the holes. The doping of polyaniline may be carried out by: (i)

chemically mixing emeraldine base and dopant in an aqueous medium or solvent and then simply stirring; (ii) dry mixing of emeraldine base and dopant; (iii) electrochemically; (iv) thermally; and (v) radiation treatment. When the polyaniline is in a perfect emeraldine base form (50% oxidized with alternative quinoid and benzenoid rings), 50% doping will result in the protonation of the entire quinoid ring. This will lead to the formation of perfect polaron leading to a high achievable conductivity. Therefore, from an initial zero level of doping, with the increase in the degree of doping the conductivity is increased due to the formation of increasingly more polaron. The 50% doped perfect emeraldine base shows the highest conductivity achievable. Furthermore, with the increase in the degree of doping beyond 50%, the decreased conductivity may be due to the formation of bipolarons as shown in Figure 2.6.

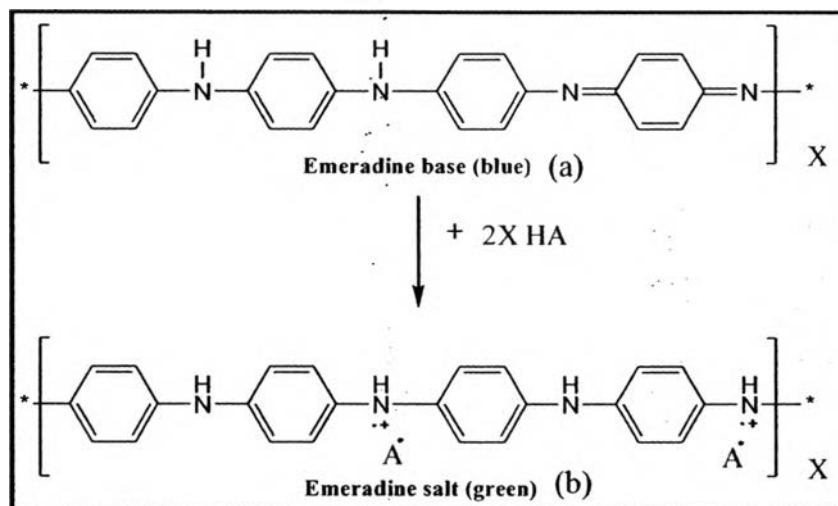


Figure 2.5 Chemical structure of un-doped (a) and doped polyaniline (b).

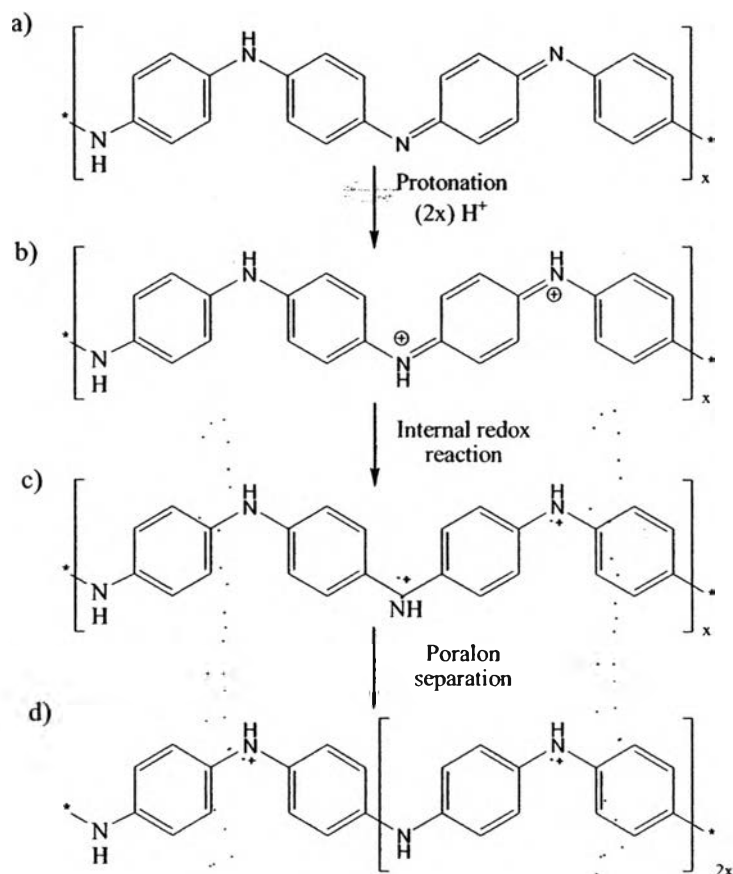


Figure 2.6 Sketch of the geometric structure of polyemeraldine (a) before protonation and (b)-(d) after 50% protonation; (b) formation of bipolarons and (c) of polarons; (d) the polarons separate, which results in a polaron lattice.

2.1.4 Composite of Polyaniline

Among the conductive polymers, polyaniline is one of the most promising candidates for industrial application due to its good conductivity, special doping mechanism, and excellent chemical stability. Its poor solubility in many solvents remains the main disadvantage. One of the advantages of making the composite and blends of conducting polymer is to improve the lower processability and to obtain high performance of the former, which combines the desirable mechanical properties of the insulating host matrix together with the electrical and optical properties of the polyaniline guest (Nicoleta P. *et al* 2006). Known methods to produce composites containing polyaniline may be essentially reduced to two distinct groups: (1) synthetic methods based on aniline polymerization in the

presence of or inside a matrix polymer, and (2) blending methods to mix a previously prepared polyaniline with a matrix polymer. Roughly, these include: (Anand J. *et al.*, 1998)

2.1.4.1 Synthetic Methods

- Dispersion polymerization of aniline in the presence of a matrix polymer in a disperse or continuous phase of a dispersion.
- Chemical in situ polymerization of aniline in a matrix or in a solution with a matrix polymer.
- Electrochemical polymerization of aniline in a matrix.
- Polymer grafting to a polyaniline surface.
- Copolymerization of aniline with other monomers resulting in the formation of soluble aniline copolymers, which can be considered as a composite polymer.

2.1.4.2 Blending Methods

- Solution blending soluble matrix polymers and polyaniline doped by functionalized protonic acids
- Solution blending undoped polyaniline with polymers soluble in amide or acidic solvents.
- Dry blending followed by melt processing (mechanical mixing of doped polyaniline with thermoplastic polymer, then molded in a hot press or extruder).

Naturally, each of these methods has its own advantages and limitations. Specifically, the synthetic direction is probably preferable if it is necessary to produce inexpensive conducting composites, due to use of inexpensive aniline instead of more expensive polyaniline, or when there is a need to form composites which have conductivity only in a thin surface layer. On the other hand, blending methods sometimes seem to be more technological desirable from the standpoint of largescale production, particularly in the case of melt procession techniques.

2.1.5 Application of Conductive Polymers

There are two main groups of applications for these polymers. The first group utilizes their conductivity as its main property. The second group utilizes this electroactivity. They are shown below.

Table 2.2 Application of conductive polymers

Group1	Group2
Electrostatic materials	Molecular electronics
Conducting adhesives	Electrical displays
Electromagnetic shielding	Chemical biochemical and thermal sensors
Printed circuit boards	Rechargeable batteries and solid electrolytes
Artificial nerves	Drug release systems
Antistatic clothing	Optical computers
Piezoceramics	Ion exchange membranes
Active electronics (diodes transistors)	Electromechanical actuators

2.2 Magnetic iron oxide nanoparticles

Magnetic iron oxide nanoparticles have attracted an increasing interest in the fields of nanoscience and nanotechnology because of the unique and novel physiochemical properties. Therefore properties, applications, and syntheses of magnetic iron oxides have been extensively studied today.

2.2.1 Classification of Magnetic Iron Oxide Nanoparticles

Iron oxides exist in many forms in nature, with magnetite (Fe_3O_4), maghemite ($\gamma\text{-Fe}_2\text{O}_3$), and hematite ($\alpha\text{-Fe}_2\text{O}_3$) being probably the most common (R.M. Cornell *et al.*, 2003). These three oxides are also very important technologically. Some of their physical and magnetic properties are summarized in Table 2.3.

Table 2.3 Physical and magnetic properties of iron oxides

Properties	Oxide		
	Hematite	Magnetite	Maghemite
Molecular formula	$\alpha\text{-Fe}_2\text{O}_3$	Fe_3O_4	$\gamma\text{-Fe}_2\text{O}_3$
Density (g/cm^3)	5.26	5.18	4.87
Melting point ($^{\circ}\text{C}$)	1350	1583-1597	-
Hardness	6.5	5.5	5
Type of magnetism	Weakly ferromagnetic or antiferromagnetic	Ferromagnetic	Ferrimagnetic
Curie temperature (K)	956	850	820-986
M_S at 300 K ($\text{A}\cdot\text{m}^2/\text{kg}$)	0.3	92-100	60-80
Standard free energy of formation ΔG_f° (kJ/mol)	-742.7	-1012.6	-711.1
Crystallographic system	Rhombohedral, hexagonal	Cubic	Cubic or tetrahedral
Structural type	Corundum	Inverse spinel	Defect spinel
Space group	R3c (hexagonal)	Fd3m	P4332 (cubic); P41212 (tetragonal)

Hematite is the oldest known of the iron oxides and is widespread in rocks and soils. It is also known as ferric oxide, red ochre, specular iron ore, or martite. Hematite is blood-red in color if finely divided, and black or grey if coarsely crystalline. It is extremely stable at ambient conditions, and often is the end product of the transformation of other iron oxides. And magnetite is also known as black iron oxide, magnetic iron ore, or ferrous ferrite. It exhibits the strongest magnetism of any transition metal oxide (R.M. Cornell *et al.*, 2003, P. Majewski *et al.*, 2008). Maghemite occurs in soils as a weathering product of magnetite, or as a product of heating of other iron oxides. It is metastable with respect to hematite, and forms

continuous solid solutions with magnetite. The crystal structure of the three iron oxides can be described in terms of close-packed planes of oxygen anions with iron cations in octahedral or tetrahedral interstitial sites. In hematite, oxygen ions are in a hexagonal close-packed arrangement, with Fe(III) ions occupying octahedral sites (Figure 2.7 (a)). In magnetite and maghemite, the oxygen ions are in a cubic close-packed arrangement (Figure 2.7 (b)).

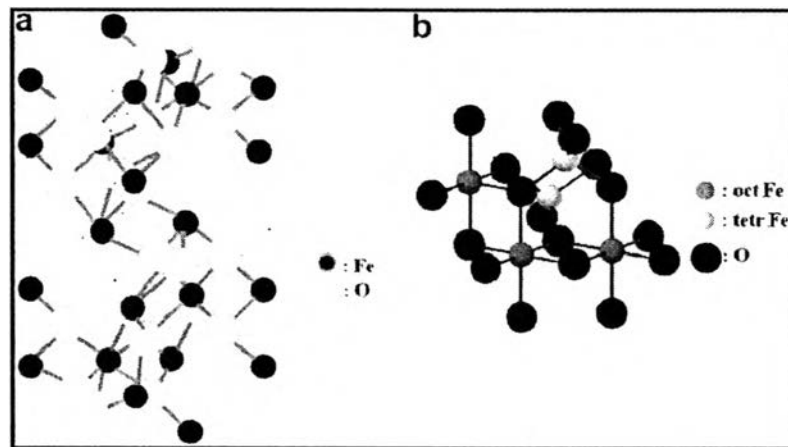


Figure 2.7 Crystal structures of (a) hematite and (b) magnetite.

2.2.2 Magnetic Behavior of Iron Oxides

The iron atom has a strong magnetic moment due to four unpaired electrons in its 3d orbitals. When crystals are formed from iron atoms, different magnetic states can arise as shown in Figure 2.8 (a). The magnetic behavior of materials can be classified into the following four major groups: paramagnetism, ferromagnetism, ferrimagnetism and anti-ferromagnetism.

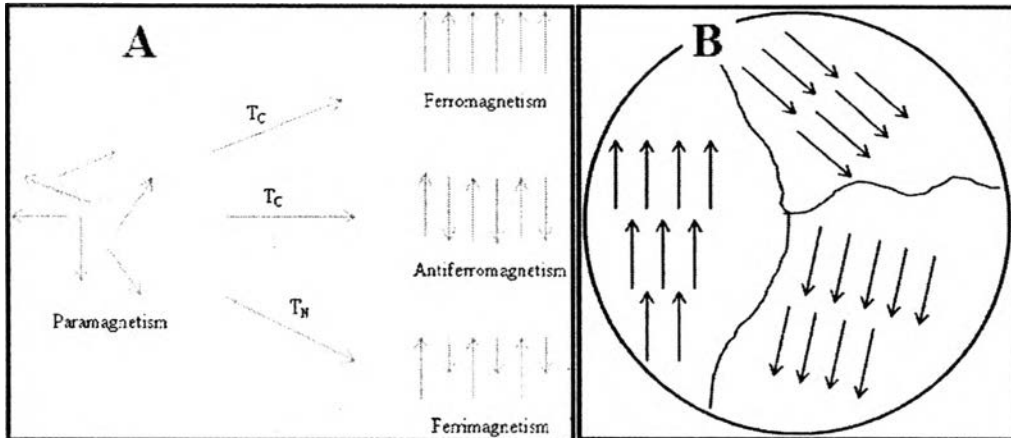


Figure 2.8 (a) Alignment of individual atomic magnetic moments in different types of materials, (b) Magnetic domains in a bulk material.

2.2.2.1 Paramagnetism

In the paramagnetic state, the individual atomic magnetic moments are randomly aligned with respect to each other, and the crystal has a zero net magnetic moment. If this crystal is subjected to an external magnetic field, some of these moments will align, and the crystal will attain a small net magnetic moment.

2.2.2.2 Ferrimagnetism

Ferrimagnetic crystal has a net magnetic moment from two types of atoms with moments of different strengths that are arranged in an antiparallel fashion (see Figure 2.8 (a)). In physics, a ferrimagnetic material is one in which the magnetic moments of the atoms on different sub-lattices are opposed, as in antiferromagnetism; however, in ferrimagnetic materials, the opposing moments are unequal and a spontaneous magnetization remains. This happens when the sublattices consist of different materials or ions (such as Fe^{2+} and Fe^{3+}).

2.2.2.3 Antiferromagnetism

Antiferromagnetic crystal has a no magnetic moment due to antiparallel magnetic moments are of the same magnitude. Generally, antiferromagnetic order may exist at sufficiently low temperatures, vanishing at and above a certain temperature, the Néel temperature. Above the Néel temperature, the material is typically paramagnetic.

2.2.2.4 Ferromagnetism

Ferromagnetism is the basic mechanism by which certain materials (such as iron) form permanent magnets and/or exhibit strong interactions with magnets; it is responsible for most phenomena of magnetism encountered in everyday life (for example, refrigerator magnets). All permanent magnets (materials that can be magnetized by an external magnetic field and which *remain* magnetized after the external field is removed) are either ferromagnetic or ferrimagnetic, as are other materials that are noticeably attracted to them.

In a bulk ferromagnetic material, the magnetization, M , is the vector sum of all the magnetic moments of the atoms in the material per unit volume of the material. The magnitude of M is generally less than its value when all atomic moments are perfectly aligned, because the bulk material consists of domains (Figure 2.8 (b)) with each domain having its own magnetization vector arising from an alignment of atomic magnetic moments within the domain. The magnetization vectors of all the domains in the material may not be aligned, leading to a decrease in the overall magnetization (Figure 2.8 (b)).

If an external magnetic field of strength H is applied to a ferromagnet of magnetic strength M , the magnetization curve of Figure 2.9 is obtained showing that M increases with H until a saturation value, M_S , is reached. The magnetization curve displays a hysteresis loop, because all domains do not return to their original orientations when H is decreased after the saturation magnetization value is attained. Thus, when H returns to zero, there is a remnant magnetization, M_R , which can only be removed by applying a coercive field H_C in the opposite direction to the initially applied field. A single domain magnetic material has no hysteresis loop and is said to be superparamagnetic. Iron oxide nanoparticles smaller than about 20 nm often display superparamagnetic behavior at room temperature (R.M. Cornell *et al.*, 2003).

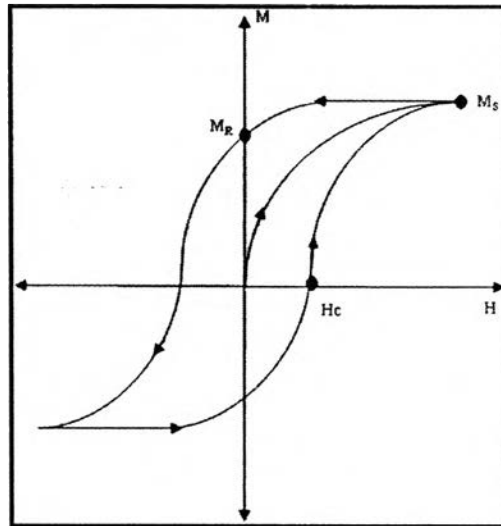


Figure 2.9 Magnetization M as a function of an applied magnetic field H .

The ordered arrangement of magnetic moments decreases with increasing temperature due to thermal fluctuations of the individual moments. Beyond the Neel or Curie temperature, the material becomes disordered and loses its magnetization. The transition temperature is termed the Curie temperature T_C for ferromagnetic and ferrimagnetic substances, and the Neel temperature T_N for antiferromagnetic substances. Superparamagnetic particles are usually ordered below a blocking temperature, T_B (P. Majewski *et al.*, 2008).

2.2.3 Magnetism in Nanoparticles: Superparamagnetism

When the diameter of magnetic nanoparticles is small enough, each particle is a single magnetic domain. Consequently, the alignment of spins under applied field is no longer impeded by domain walls. Further reduction in particle size allows for thermal vibrations to randomly fluctuate the net spins and the domains are considered unstable. Since the particles' net spins are randomly oriented, they cancel one another and the net moment of the collective particles is zero. If a magnetic field is applied, the particles will align producing a net moment. This behavior is characteristic of paramagnetic materials, but the difference is that each molecule has a large net moment, e.g. $4 \mu_B$ per molecule of Fe_3O_4 . Thus, it's called in the term of superparamagnetism. Superparamagnetic magnetite nanoparticles are useful for the applications. As fillers in composites, they can improve the modulus of the matrix

and provide additional functionality such as electromagnetic interference (EMI) shielding. There are two characteristic behaviors of superparamagnetism (Amin S. *et al.*, 2008): 1) magnetization curves, i.e. magnetization vs. applied field, do not change with temperature and 2) no hysteresis is observed, i.e. coercivity, $H_c = 0$.

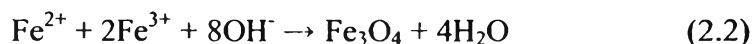
2.2.4 Synthesis of Magnetite Nanoparticles

Many of the useful attributes of iron oxides depend on the preparation method for the nanomaterials. The preparation method plays a key role in determining the particle size and shape, size distribution, surface chemistry, crystallinity and therefore the applications of the material. In addition, the preparation method also determines the degree of structural defects or impurities present in the particles, and the distribution of such defects. Many synthesis routes have been developed to achieve proper control of particle size, polydispersity, shape, crystallinity, and the magnetic properties. Currently there are three main methods for synthesizing metal oxide (e.g. magnetite and other ferrites) nanoparticles in solution: chemical coprecipitation (Ajay Kumar Gupta *et al.*, 2005), microemulsion (A. Tavakoli *et al.*, 2007; V. Chhabra *et al.*, 1996), and decomposition of metal organic salts (Dairong C. *et al.*, 1997). Coprecipitation is the least expensive and the simplest approach for making nanoparticles. For example, inexpensive iron salts may be mixed with a precipitating agent such as NaOH to form nanoparticles of iron oxides.

2.2.4.1 *Synthesis of Fe₃O₄ (Magnetite) Nanoparticles by Chemical Co-Precipitation Method*

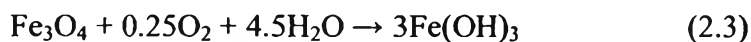
Chemical co-precipitation can produce nanoparticles in large quantities (order of grams) in a relatively short amount of time and utilizes inexpensive and readily available chemicals as precursors. The versatility and simplicity of co-precipitation has made it one of the preferred techniques to produce nanoparticles. Nanoparticles produced by coprecipitation are usually polydisperse, but generally spherical in shape.

The coprecipitation reaction to form magnetite is described simply by the following Equation 2.2 (Ajay Kumar Gupta *et al.*, 2005):



Ferrous ions are easily oxidized, and the products may deviate from the desired stoichiometric ratio of ferric to ferrous ions. Therefore precipitation is performed

under inert atmosphere to avoid side products, which will affect the purity of the final product. Examples of side reactions and their products are shown in Equation 2.3 and 2.4 (D. Maity *et al.*, 2007):



In coprecipitation, ferric and ferrous salts are dissolved in an aqueous solution and undergo accelerated hydrolysis to produce particles of iron oxides with single domain structures. A number of studies have been conducted over the years on the hydrolysis of ferric and ferrous ions to form different phases of iron oxides/hydroxides.

There are many different phases of iron oxides and oxyhydroxides that are possible and the final phases are highly dependent on the process variables such as temperature (Jun Hua Wu *et al.*, 2007, 2008), pH (D.K. Kim *et al.*, 2001), ionic strength of the media (Sjogren CE *et al.*, 1994), concentration of precursors (Aaron C. *et al.*, 2008), precipitation rate (Jorge A. *et al.*, 1997), and type of ions used in the reaction (M. Răcuciu. *et al.*, 2008).

2.3 Bacterial Cellulose

2.3.1 Introduction of Cellulose

Cellulose has been used daily for centuries in several applications. It is the major constituent of paper and cardboard and textiles, which are made from cotton, linen, and other plant fibers. Cellulose is the most abundant form of living terrestrial biomass. The cellulose molecule is derived from D-glucose units, which condense through $\beta(1\rightarrow4)$ -glycosidic bonds. Cellulose is a straight chain polymer: unlike starch, no coiling or branching occurs, and the molecule adopts an extended and rather stiff rod-like conformation, aided by the equatorial conformation of the glucose residues as shown in Figure 2.10 (a). The multiple hydroxyl groups on the glucose residues from one chain form hydrogen bonds with oxygen molecules on the same or on a neighbor chain, holding the chains firmly together side-by-side and forming micro-fibrils with high tensile strength as shown in Figure 2.10 (b).

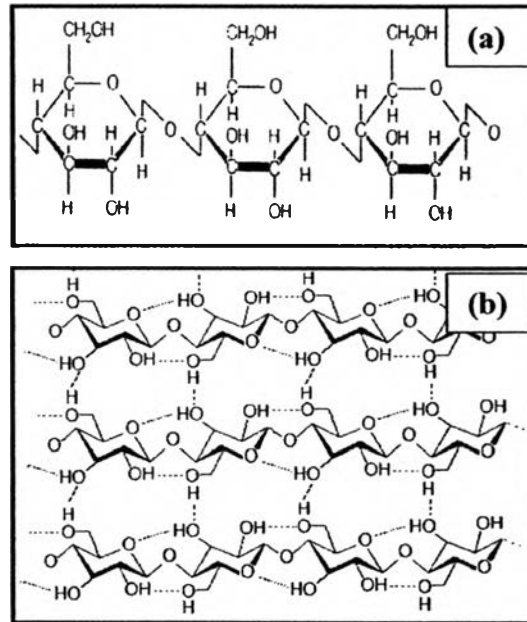


Figure 2.10 (a) Chemical structure of cellulose unit and (b) the hydrogen bonds within and between cellulose molecules.

2.3.2 Principal Pathways to Cellulose

Up to now there are four different pathways to from the biopolymer cellulose the first one is the most popular and industrial impotent isolation of cellulose of plants including separation processes to remove lignin and hemicelluloses (Tarchevsky *et al.*, 1991). The second way consists in the biosynthesis of the cellulose by different types of microorganisms as shown in Figure 2.11. In recently a considerable amount of interest in the source of cellulose is from the structurally strong framework in the cell walls of wood pulp (called plant cellulose) and micro-organisms (called bacterial cellulose).

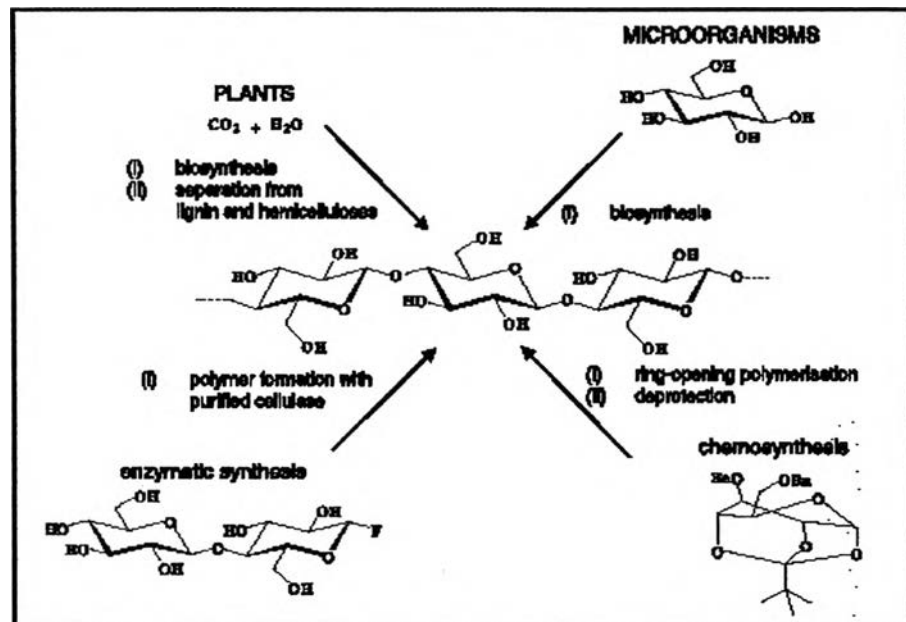


Figure 2.11 The pathways to from the biopolymer cellulose.

2.3.2.1 Plant Cellulose

Plant fibers are generally comprised mainly of cellulose: examples include cotton, flax, and hemp. This fiber can be further categorized into the following; seed fiber, leaf fiber, fruit fiber and stalk fiber. Fibers are actually the stalks of the plant e.g. straws of wheat, rice, and other crops. Tree wood is also such a fiber. Wood is one of the most abundant resources in the bio-based industry and it is also one of the most complex materials, composed of polymers of cellulose, lignin and hemi-cellulose that are physically and chemically bound together. Considerable amounts of energy are required to separate the polymers from each other. Wood fiber is composed of layers of crystalline cellulose (fibrils) wrapped in a cylindrical shape with an open center, or "lumen" as shown in Figure 2.12.

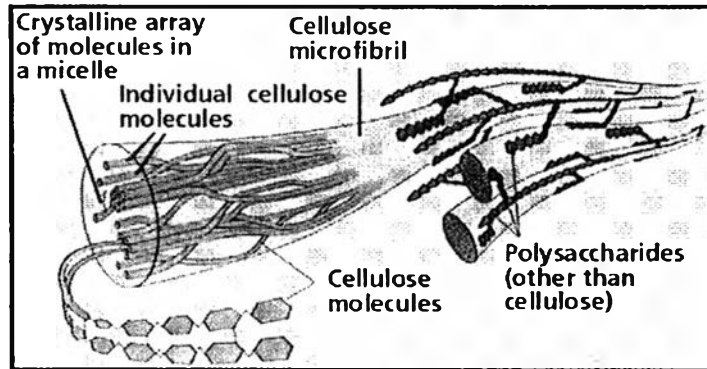


Figure 2.12 Plant cellulose structure.

2.3.2.2 Bacterial Cellulose

Bacterial cellulose belongs to specific products of primary metabolism and is mainly a protective coating, whereas plant cellulose plays a structural role. Cellulose is synthesized by bacteria belonging to the genera; *Acetobacter*, *Rhizobium*, *Agrobacterium*, and *Sarcina* (Jonas et al., 1998). Its most efficient producers are Gram-negative, acetic acid bacteria *Acetobacter xylinum* (Yamanaka et al., 2000). Moreover, several bacteria are able to synthesize the cellulose. An overview of bacterial cellulose producers is presented in Table 2.4 (Jonas et al., 1998).

Table 2.4 Bacterial cellulose producers and feature of their product

Genus	Cellulose structure
Acetobacter	Extracellular pellicle
Achromobacter	Fibrils
Aerobacter	Fibrils
Agrobacterium	Short fibrils
Alcaligenes	Fibrils
Pseudomonas	No distinct fibrils
Rhizobium	Short fibrils
Sarcina	Amorphous cellulose
Zoogloea	Not well defined

One of the most important features of bacterial cellulose is its chemical purity, which distinguishes this cellulose from plant cellulose, usually associated with hemicelluloses and lignin, removal of which is inherently difficult. Because of the unique properties, resulting from the ultrafine reticulated structure, bacterial cellulose has found a multitude of applications in paper, textile, and food industries, and as a biomaterial in cosmetics and medicine (Vandamme E. J *et al.*, 1997).

2.3.3 Structure and Properties Bacterial Cellulose

Cellulose is an unbranched polymer of β -1,4- linked glucopyranose residues. Bacterial cellulose is chemically identical to plant cellulose, but its macromolecular structure and properties differ from the latter in shown in Figure 2.13.

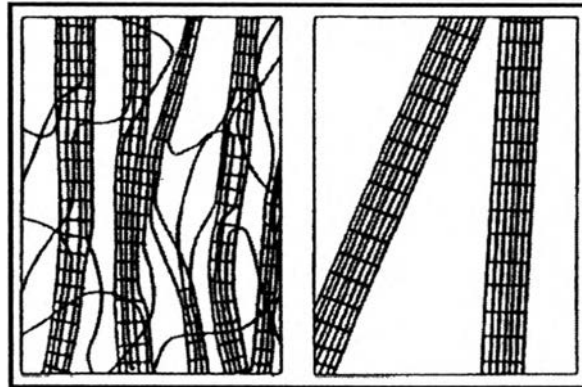


Figure 2.13 Schematic models of bacterial cellulose microfibrils (right) drawn in comparison with the 'fringed micelles'; of plant cellulose fibrils (left).

Nascent chains of bacterial cellulose aggregate to form sub-fibrils. Bacterial cellulose sub-fibrils are crystallized into microfibrils (Jonas *et al.*, 1998), these into bundles, and the latter into ribbons (Yamanaka *et al.*, 2000). Dimensions of the ribbons are 3 ± 4 (thickness) \times 70 ± 80 nm (width) whereas the width of cellulose fibers produced by pulping of birch or pines wood is two orders of magnitude larger. The ultrafine ribbons of microbial cellulose form a dense reticulated structure (Figure 2.14), stabilized by extensive hydrogen bonding.

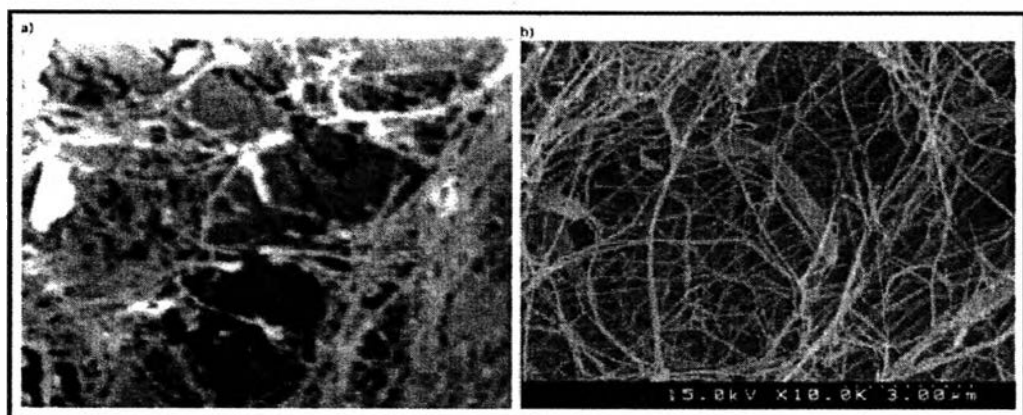


Figure 2.14 Scanning electron microscopy images of bacterial cellulose membrane from static culture of *A. xylinum* (a) and bacterial cell with attached cellulose ribbons (b).

Bacterial cellulose is also distinguished from its plant counterpart by a high crystallinity index and different degree of polymerization. Moreover, the properties of bacterial cellulose are also different from properties of cellulose produced from plant. The distinguishing properties are concluded in Table 2.5.

Table 2.5 Distinguishing features of microbial cellulose

Property	Description
Purity	Cellulose is the only biopolymer synthesized Absence of lignin or hemicelluloses Completely biodegradable and recyclable a renewable resource
Great mechanical strength	High strength crystalline cellulose I _α Consistent dimensional stability High tensile strength Light weight Remarkable durability
Extraordinary absorbency in the hydrated state	Remarkable capacity to hold water Selective porosity High wet strength High surface-to-volume carrier capacity
Direct membrane assembly during biosynthesis	Intermediate steps of textile assembly from yarn unnecessary Extremely thin, submicron, optical clear membranes can be assembled
Cellulose orientation during synthesis	Dynamic fiber-forming capabilities
Direct modification of cellulose during assembly	Control of physical properties of the cellulose during assembly (molecular weight and crystallinity)

2.3.4 Macroscopic Morphology of Bacterial Cellulose

Macroscopic morphology of bacterial cellulose strictly depends on culture conditions (Yoshinaga *et al.*, 1997; Watanabe *et al.*, 1998; Yamanaka *et al.*, 2000). In static conditions (Figure 2.15 (A)), bacteria accumulate cellulose mats (S-BC) on the surface of nutrient broth, at the oxygen-rich air-liquid interface. The subfibrils of cellulose are continuously extruded from linearly ordered pores at the surface of the bacterial cell, crystallized into microfibrils, and forced deeper into the growth medium. Therefore, the leather-like pellicle, supporting the population of *A. xylinum* cells, consists of overlapping and intertwined cellulose ribbons, forming parallel but disorganized planes (Jonas *et al.*, 1998). The adjacent S-BC strands branch and interconnect less frequently than these in bacterial cellulose produced in agitated culture (A-BC), in a form of irregular granules, fibrous strands, well-dispersed in culture broth (Figure 2.15 (B)) (Vandamme *et al.*, 1998).

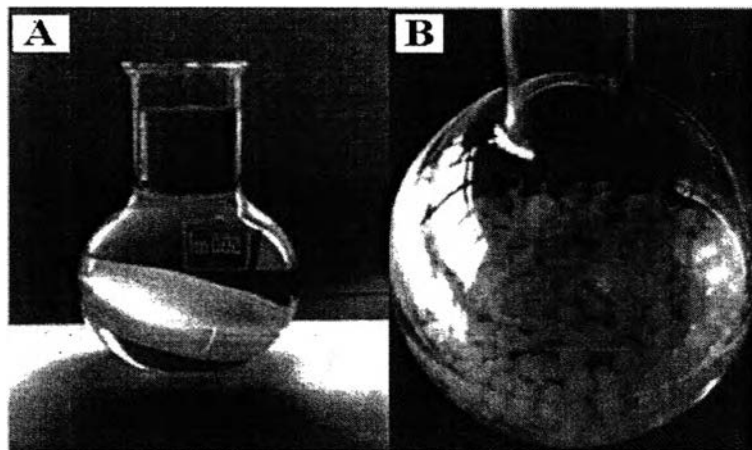


Figure 2.15 Bacterial cellulose pellicle formed (A) in static culture and (B) formed in agitated culture.

The strands of reticulated A-BC interconnect to form a grid-like pattern, and have both roughly perpendicular and roughly parallel orientations (Watanabe *et al.*, 1998). The S-BC fibrils are more extended and piled above one another in a criss-crossing manner. Strands of A-BC are entangled and curved.