

CHAPTER II

LITERATURE REVIEW

2.1 Wound Healing Process

Wound healing is continuous and complex process, involving the interaction of biological system an immunological with coordinated interaction. It is divided into four phases : (1) Homeostasis, (2) Inflammatory, (3) Proliferation and (4) Remodeling (Velnar T. *et al.*, 2009)

2.1.1 Homeostasis

This phase occur immediately after injury. The aim of this phase is to limit blood loss by platelet aggregation and clot formation. The blood clot formation consists of fibronectin, fibrin, vitronectin and thrombospondin. The important of clot formation is also in term of providing as matrix for cell migration in the subsequent phases of the homeostasis and inflammatory phases

2.1.2 Inflammatory

This inflammatory phase, produced immune barrier against invading of microorganisms. Neutrophil infiltrate in the wound site to prevent infection by phagocytosis. The function of phagocytosis activity is to destroy and remove bacteria, foreign particles and damaged tissue by releasing proteolytic enzymes and oxygen derived from free radicals species. The excess of ROS cause the harmful on cells and tissue from oxidative damage by involving NADPH mechanism which generate from neutrophil accumulation in wound area Moreover, the inflammatory response regulate cells and provide an abundant reservoir of potent tissue growth factors, particularly TGF- β , as well as other mediators (TGF- α , heparin binding epidermal growth factor, fibroblast growth factor (FGF), collagenase), activating keratonocytes, fibroblasts and endothelial cells (Velnar T. *et al.*, 2009)

2.1.3 Proliferation

The proliferative phase involves the fibroblast migration and deposition of newly synthesized extracellular matrix to replace the loss tissue. First, the formation of granulation occurs in this stage. Fibroblast synthesized collagen, act

as foundation for intracellular matrix formation in the wound and many new capillaries are formed. After that, the open wound was closed by wound contracture. Myofibroblasts composed of actin and myosin which generate contractile force resulting in smaller wound size (Stojadinovic A. *et al.*, 2008). Next, migration of epithelial cells from wound edge, cells meet resulting in migration stops and the basement membrane starts to form (Velnar T. *et al.*, 2009)

2.1.4 Remodeling

This phase is final step of wound healing process. This phase is responsible for controlling the equilibrium of synthesis and breakdown collagen. The tensile strength of wound derives from collagen collection. Collagen fibers contribute to the approximately 80 % of the original strength compared with unwound tissue (Velnar T. *et al.*, 2009)

2.2 Bacterial Cellulose

2.2.1 Cellulose

Cellulose is an organic compound with the formula $(C_6H_{10}O_5)_n$, a polysaccharide consisting of a linear chain of several hundred to over ten thousand $\beta(1\rightarrow4)$ linked D-glucose units, as shown in Figure 2.1. Cellulose is the most abundant biopolymer in the earth with an estimated output of over 10^{11} tons per year. Most of its biosynthesis takes place in the cellular walls of plants, but four sources are known, animal, bacterial, chemical and enzymatic.

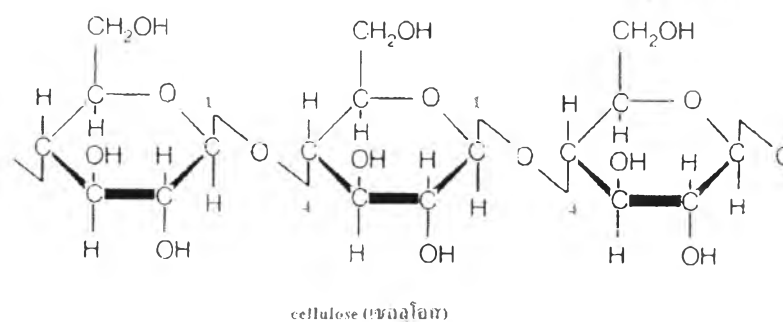


Figure 2.1 The structural of cellulose.

2.2.2 Principal Pathways to Cellulose

There are four different pathways to synthesize the biopolymer cellulose that are described schematically in Figure 2.2. The first one is the most popular and industrial important isolation of cellulose of plants including separation processes to remove lignin and hemicelluloses. The second way is biosynthesis of cellulose by different types of microorganisms such as algae (*Vallonia*), fungi (*Saprolegnia*, *Dictyostelium*, *Discoideum*) and bacteria (*Acetobacter*, *Achromobacter*, *Aerobacter*, *Rhizobium*). The third way is enzymatic in vitro synthesis starting from cellobiosyl fluoride. The last way is the first chemosynthesis from glucose by ring-opening polymerization of benzylated and pivaloylated derivatives (Klemm D. *et al.*, 2001).

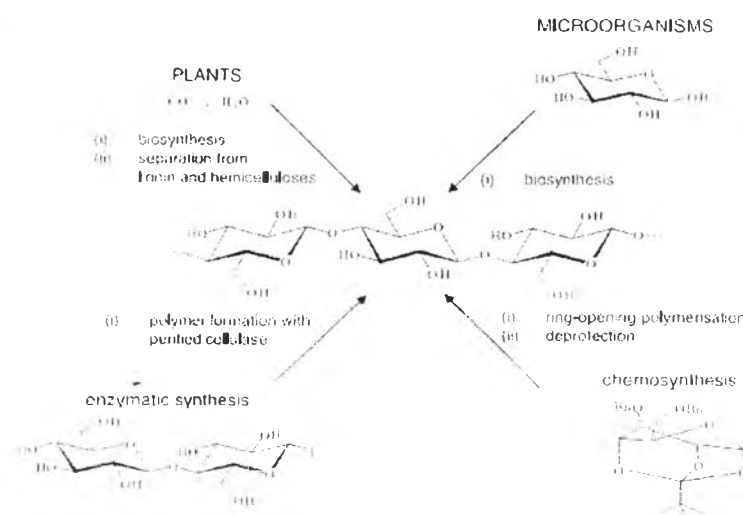


Figure 2.2 Pathways to the cellulose.

In this research, we investigated on cellulose that can be synthesized by bacteria, it was called bacterial cellulose (BC). Bacteria which used in this research is *Acetobacter xylinum* genus because it is the most efficient producer of cellulose. There are many bacterial cellulose producers that can be used for biosynthesis of bacterial cellulose but the structures of bacterial cellulose are different depend on the type of bacterial cellulose producers. All of these bacterial cellulose producers shown in Table 1.1. (Jonas & Farah, 1998).

Table 2.1 Bacterial cellulose producers (Jonas & Farah, 1998)

Genus	Cellulose Structure
Acetobacter	extracellular pellicle composed of ribbons
Achromobacter	fibrils
Aerobacter	fibrils
Agrobacterium	short fibrils
Alcaligenes	fibrils
Pseudomonas	no distinct fibrils
Rhizobium	short fibrils
Sarcina	amorphous cellulose

2.2.3 Bacterial Cellulose Synthesis using *Acetobacter Xylinum*

For the first time, the bacterium *A. xylinum* was described in 1886 by Brown. He identified a gelatinous mat formed in the course of vinegar fermentation on the surface of the broth as chemically equivalent to cell-wall cellulose. *Acetobacter xylinum* is a gram negative, rod-shaped, non-pathogenic and aerobic bacterium which is interested for many studies due to the large quantity of cellulose product. The cellulose synthesized by *A. xylinum* is identical to that made by plants in the respect to molecular structure. However, the secreted polysaccharide is free of lignin, pectin and hemicelluloses as well as other biogenic products, which are associated with plant cellulose. Additionally, extracellularly synthesized microbial cellulose differs from plant cellulose with respect to its high crystallinity, high water absorption capacity and mechanical strength in the wet state, ultrafine network structure, mold ability in situ and in an initial wet state. (Dieter K. *et al.*, 2001). Figure 2.3., SEM images shown difference between the structure of bacterial cellulose and the structure of plant cellulose.

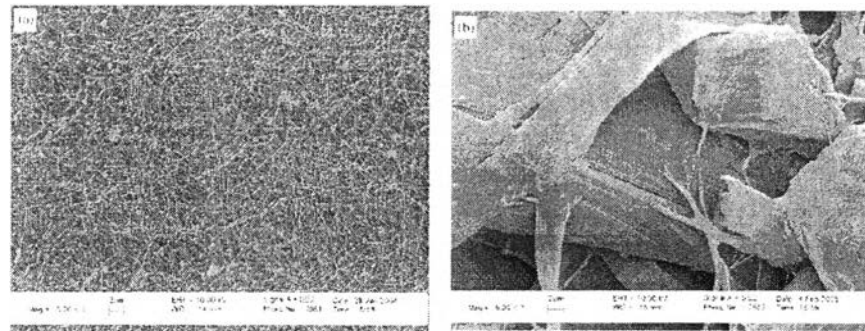


Figure 2.3 SEM image (a) plant cellulose and (b) bacteria cellulose (Czaja M. *et al.*, 2006).

The cellulose formation includes five fundamental enzyme mediated steps: the transformation of glucose to UDP-glucose-6-phosphate and glucose-1-phosphate and finally the addition of UPD-glucose to the end of growing polymer chain by cellulose synthase a shown in Figure 2.4. Cellulose synthase (UPD-glucose: 1,4- β -D-glycosyltransferase) is regarded as the essential enzyme in the synthesis process. It is subjected to a complicated regulation mechanism, which controls activation and inactivation of the enzyme (Klemm D. *et al.*, 2001).

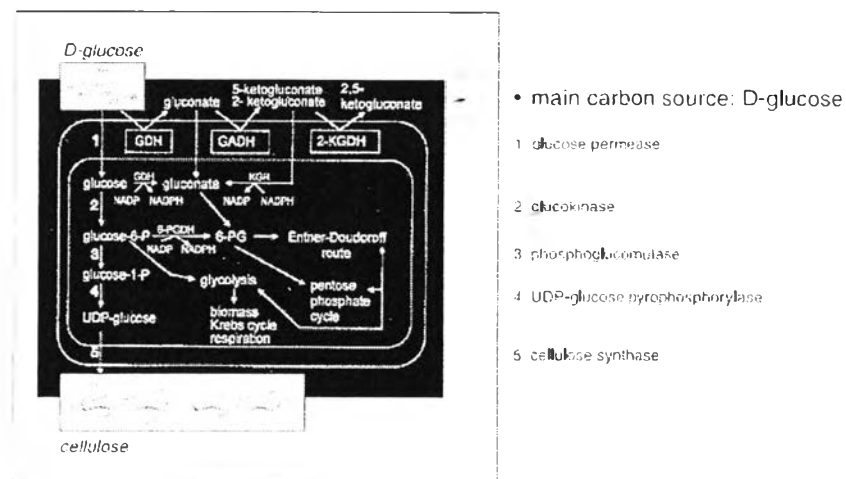


Figure 2.4 Pathways of carbon metabolism in *Acetobacter xylinum*.(Klemm D. *et al.*, 2001).

A. xylinum forms the cellulose between the outer and the cytoplasmic membrane. The cellulose-synthesizing complexes or terminal complexes (TC) are linearly arranged, and in association with pores at the surface of the bacterium. In the first step of cellulose formation glucan chain aggregates consisting of approximately 6-8 glucan chains are elongated from the complex. These subelementary fibrils are assembled in the second step to form microfibrils followed by their tight assembly to form a ribbon as the third step that presented in Figure 2.5. The Matrix of the interwoven ribbons constitutes the bacterial cellulose membrane or pellicle. Bacteria cellulose ribbon produced by one bacterial cell as shown in Figure 2.6 and Figure 2.7 demonstrate that *A. xylinum* cells are distributed throughout the network of the cellulose ribbons.

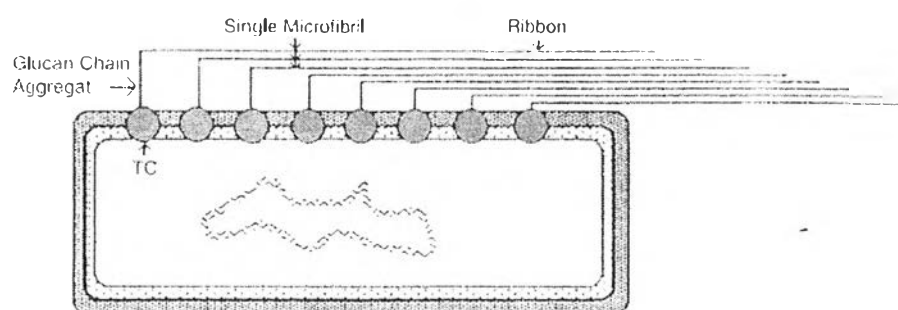


Figure 2.5 Formation of bacterial cellulose. (Klemm D. *et al.*, 2001).



Figure 2.6 TEM image of bacterial cellulose ribbon produced by a bacterial cell. (Klemm D. *et al.*, 2001).

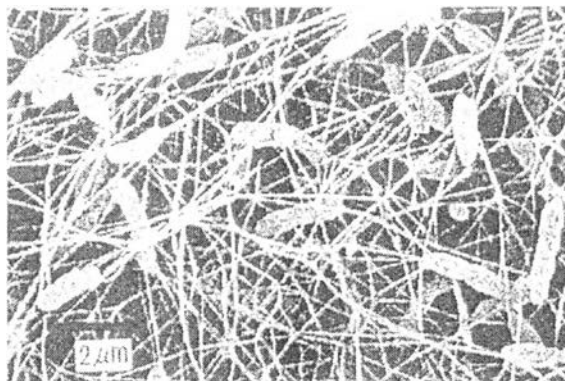


Figure 2.7 SEM image of a bacterial cellulose network including the bacterial cells. (Klemm D. *et al.*, 2001).

2.2.4 Structure of Bacterial Cellulose

Cellulose is an unbranched polymer of $\beta(1\rightarrow4)$ linked glucopyranose residues. Extensive research on BC revealed that it is chemically identical to plant cellulose (PC), but its macromolecular structure and properties differ from the latter (Figure 2.8). In table 2.2 shown the difference between bacterial cellulose and plant cellulose.

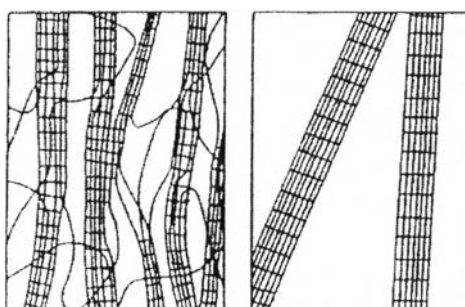


Figure 2.8 Schematic model of BC microfibrils (right) drawn in comparison with the 'fringed micelles'; of PC fibrils (left) (Iguchi M. *et al.*, 2000).

Table 2.2 Comparison between bacterial cellulose (BC) and plant cellulose (PC) (Edison P. *et al.*, 2008)

Properties	PC	BC
Fibre width	$1.4-4.0 \times 10^{-2}$ mm	70-80 nm
Crystallinity	56-65%	65-79%
Degree of polymerization	13 000-14 000	2 000-6 000
Young's modulus	5.5-12.6 GPa	15-30 GPa
Water content	60%	98.5%

In the bacterial cellulose biosynthesis, the cellulose chains (formed by glucose units linked through $\beta(1 \rightarrow 4)$ glucosidics bonds) interact through hydrogen bonds, assuming a parallel orientation among them. The structure and rigidity of bacterial celluloses is provided by the OH intra and intermolecular hydrogen bonds as shown in Figure 2.9.

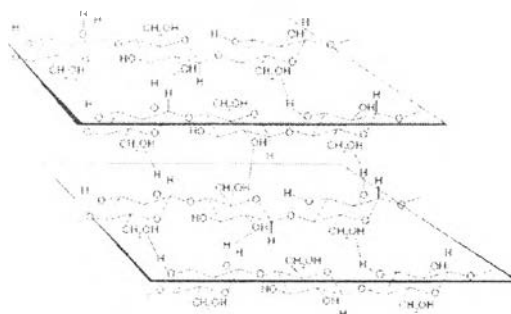


Figure 2.9 Outline of intra and intermolecular hydrogen bonds among cellulose chains. (Edison P. *et al.*, 2008).

The physical and mechanical properties of bacterial cellulose arise from the unique 3-D ultrafine network structure. Preliminary study has measured the Young's modulus of bacterial cellulose as high as (>15 GPa), in any direction across the plane of sheet. It is considered that the high mechanical strength arise from the high density of interfibrillar hydrogen-bonds, due to the very fine fibrils and large

contact area. In addition, there is no significant effect of varying cultivation time and amount of cellulose content on mechanical properties. Furthermore, the pulp derived from bacterial cellulose can enhance reinforcement to the ordinary cotton lint pulp (Yamanaka S. *et al.*, 1989).

This unique structure can also enhance to absorb a large amount of water (up to 200 times of its dry mass) because of the large surface area. Moreover, bacterial cellulose in wet state show great elasticity, high wet strength, high conformability and transparency (Klemm D. *et al.*, 2001; Czaja W. *et al.*, 2006).

The production of bacterial cellulose has quite successfully in static culture that resulted in pellicle formed on the surface of static culture as shown in Figure 2.10. But there are low productivity and labor intensive. In case of, bacterial cellulose in agitated culture produced in well-dispersed slurry as irregular mass as shown in Figure 2.10. (Hestrin&Schram, 1954). The agitated culture has not been successful in bacterial cellulose production due to its low yield (Byrom D. 1991). Another problem for agitated culture is associated with the culture instability that resulted in loss of cellulose producing cells because of non-producing mutants (Valla &Kjosbakken, 1982). However, some researchers suggested that the agitated culture might be suitable for economical scale production (Yoshinaga F. *et al.*, 1997).

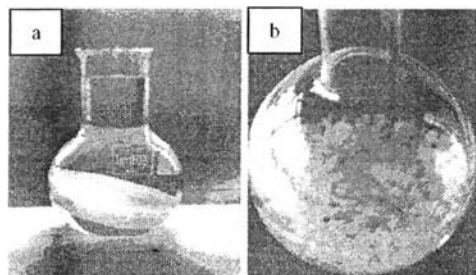


Figure 2.10 BC pellicle formed (a) in static culture and (b) in agitated culture (Bielecki *et al.*, 2002).

2.2.5 Bacterial Cellulose in Wound Dressing Applications

The physical and mechanical properties of bacterial cellulose membranes arise from their unique structure, which differs significantly from the structure. Basically, well-separated nano and micro fibrils of bacterial cellulose create an extensive surface area which allows it to hold a large amount of water while maintaining a high degree of conformability. The hydrogen bonds between these fibrillar units stabilize the whole structure and give it a great deal of mechanical strength. Even though plant cellulose is composed of microfibrils which are similar to those found within bacterial cellulose, the plant cellulose microfibrils are part of a larger aggregation of the cell wall. Thus, bacterial cellulose can absorb much higher volumes of liquid than plant cellulose. BC can be considered an ideal material for high quality wound dressing. Table 2.3 summarizes most of the physical and mechanical properties of bacterial cellulose which characterize it as an ideal wound dressing material. Wound repair is a dynamic process that associates with a complex interaction of various cell types, extracellular matrix (ECM) molecules, soluble compounds. Typically, the process of wound healing has been divided into four phases: homeostasis, inflammation, granulation tissue and remodeling (Eming S.A. *et al.*, 2002).

Wound dressings can be classified into traditional and advance wound dressings (moist wound dressings such as hydrocolloid, alginate and hydrogel). Advance wound dressings have been developed because it provide moist environment which facilitate for wound healing process (Boateng J.S. *et al.*, 2008). In 1962, George Winter found that the re-epithelization was accelerated if the wound was kept moist. Since then, almost effective wound dressing are designed to maintain a moist environment within the affected region. Moist dressing are permeable to water, and this property has advantages for wound healing. For example, high water vapor permeable dressing show enhanced healing, probably due to an increased concentration of growth-promoting factors within the exudates and to the creation of a more extensive ECM of fibrinogen and fibronectin. The highly water vapor permeable wound dressing (PEU) can promote a high amount of fibrinogen and fibronectin which associated with accelerated epithelization during wound healing

process (Jonkman M.F. *et al.*, 1990). In addition, the moist wound environment can enhance eschar and clot removal, re-epithelialization and collagen synthesis which promote proteolytic environment and the growth factor over the dry wound (Chen W.Y.J. *et al.*, 1992). Thus, moist wound dressings have been developed as an improvement on the traditional wound dressings.

Due to its unique properties, bacterial cellulose has shown great potential for using as wound dressing material as shown in table 2.3. Bacterial cellulose actually performed better than conventional wound dressings in 1. conforming to the wound surface (excellent molding to all facial contours and a high degree of adherence even to the contoured parts such as nose, mouth, etc., 2. Maintaining a moist environment within the wound. 3. Significantly reducing pain. 4. Accelerating re-epithelialization and the formation of granulation tissue, and 5. Reducing scar formation (Czaja W. *et al.*, 2007). These BC membranes can be created in any shape and size, which is beneficial for the treatment of large and difficult to cover areas of the body.

Many studies have reported on the successful of bacterial cellulose as wound dressing. The product called Biofill has been used for temporary skin substitutes. It can help to promote healing of many skin injuries treatments such as basal cell carcinoma, skin graft, severe body burns, facial peeling, sutures, dermabrasions, skin lesions, chronic ulcers and both donor and receptor sites in graft (Fontana J.D. *et al.*, 1990). Farah, *et al.*, (1990) described many advantages of Biofill product on the lesion region such as close adhesion to body location, enhancing the absorption of exudates, reduced pain (isolated nerve ending), reducing scar formation, no allergic reaction and easily stored.

Another bacterial cellulose product is Xcell. Unlike other wound dressing products in the market, Xcell product has ability to manage the moisture balance by absorbing excess exudates and donating moisture in wound area. Alvarez O.M. *et al.* (2004) reported that Xcell success with the chronic venous ulceration treatment. The combination of bacterial cellulose wound dressing and compression bandage resulted in less wound pain, improved autolytic debridement and developed of granulation tissue as compared with standard wound care. Moreover, Heasley D.

et. al. (2003) proved that Xcell can be effectively used to treat on the diabetic foot ulcers.

Another interesting and important advantage of the bacterial cellulose dressing includes its transparency, which facilitate for observation in the healing progress.

Table 2.3 Properties of bacterial cellulose and how they relate to the properties of an ideal wound dressing material. (Czaja W. *et. al.*, 2007)

Properties of ideal wound care dressing	Properties of bacterial cellulose
Maintain a moist environment at the wound/dressing surface	High water holding capacity (typical membrane can hold up to 200 g of its dry mass in water); high water vapor transmission rate
Provide physical barrier against bacterial infections	Nanoporous structure does not allow any external bacteria to penetrate into wound bed
Highly absorbable	Partially dehydrated membrane is able to absorb fluid up to its original capacity
Sterile, easy to use, and inexpensive	Membranes are easy to sterilize (by steam or γ -radiation) and package. The cost of production of 1 cm ² is \$0.02
Available in various shapes and sizes	Ability to be molded in situ
Provide easy and close wound coverage, but allow easy and painless removal	High elasticity and conformability

Table 2.3 (Cont.) Properties of bacterial cellulose and how they relate to the properties of an ideal wound dressing material. (Czaja W. *et. al.*, 2007)

Properties of ideal wound care dressing	Properties of bacterial cellulose
Significantly reduce pain during treatment	The unique BC nanomorphology of never-dried membrane promotes specific interaction with nerve endings
Provide porosity for gaseous and fluid exchange	Highly porous material with pore sizes ranging from several nanometers to micrometers
Nontoxic, nonpyrogenic, and biocompatible	Biocompatible, nonpyrogenic, nontoxic
Provide high conformability and elasticity	High elasticity and conformability
Provide mechanical stability	High mechanical strength (Young's modulus value of several GPa)

2.3 Plasma Technology

2.3.1 Basic Principle

Plasma, a quasi-neutral gas, is considered to be the fourth state of matter, following the more familiar states of solid, liquid & gas and constitutes more than 99% matter of the universe. It is more or less an electrified gas with a chemically reactive media that consists of a large number of different species such as electrons, positive and negative ions, free radicals, gas atoms and molecules in the ground or any higher state of any form of excited species (figure 2.11). It can exist over an extremely wide range of temperature and pressure. It can be produced at low-pressure or atmospheric pressure by coupling energy to a gaseous medium by several means such as mechanical, thermal, chemical, radiant, nuclear, or by applying a voltage, or by injecting electromagnetic waves and also by a combination of these to dissociate the gaseous component molecules into a collection of ions, electrons,

charge-neutral gas molecules, and other species. It is thus an energetic chemical environment that combines particles and radiations of a diverse nature, an incredibly diverse source of chemistry that is normally not available in other states of matter. Parallel to the generation of plasma species, loss processes also take place in the plasma. In fact, all energy ends up as heat with a small fraction invested in surface chemistry.

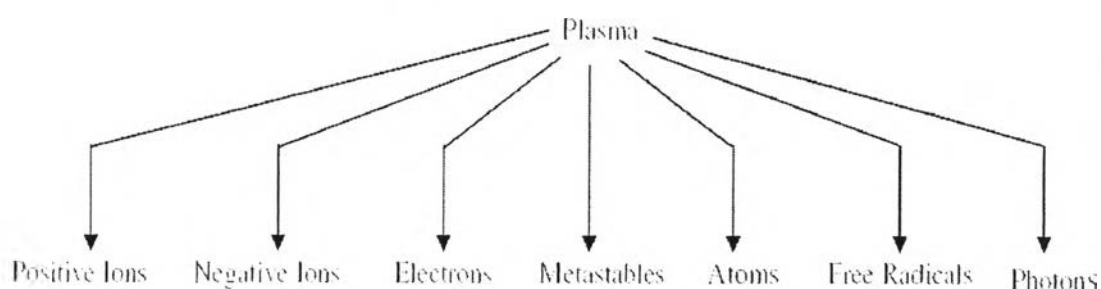


Figure 2.11 Constituents of plasma.

Plasma principle is a mixture of gases consisted of charged particles with a roughly zero net electrical charge. When apply a high energy source, like electric field, to a high voltage (HV) electrode, an ionization process occurs, thus generating a number of ionized species. The plasma has been used to modify the surfaces of both organic and inorganic substrates. This technique is a dry process and is operated under a wide range of pressure. Moreover, the surface modification by the plasma treatment occurs at the outermost surface, so it does not change the bulk properties of materials. Due to its several advantages over the conventional chemistry methods, the plasma becomes more interested.

2.3.2 Classification of Plasma

Plasmas can be distinguished into two main groups i.e., the high temperature or fusion plasmas and the so called low temperatures or gas discharges. High temperature plasma implies that all species (electrons, ions and neutral species) are in a thermal equilibrium state. Low temperature plasma is further subdivided into thermal plasma, also called quasi-equilibrium plasma, which is in a local thermal

equilibrium (LTE) state, and non thermal plasma (NTP), also called non equilibrium plasma or cold plasma.

Thermal plasmas (TP) are characterized by an equilibrium or near equality between electrons, ions and neutrals. Commonly employed thermal plasma generating devices are those produced by plasma torches, and microwave devices. These sources produce a high flux of heat and are mainly used in areas such as in plasma material processing and plasma treatment of waste materials. High temperature of TPs can process even the most recalcitrant wastes including municipal solids, toxic, medical, biohazard, industrial and nuclear waste into elemental form, ultimately reducing environmental pollution caused due to them. But for several technological applications, the high temperature characteristic of TPs is neither required nor desired, and in some cases it even becomes prohibitive. In such application areas, cold plasmas become more suited.

Cold plasmas refer to the plasmas where most of the coupled electrical energy is primarily channeled to the electron component of the plasma, thereby producing energetic electrons instead of heating the entire gas stream; while the plasma ions and neutral components remain at or near room temperature. Because the ions and the neutrals remain relatively cold, this characteristic provides the possibility of using cold plasmas for low temperature plasma chemistry and for the treatment of heat sensitive materials including polymers and biological tissues. The remarkable characteristic features of cold plasma that include a strong thermodynamic non-equilibrium nature, low gas temperature, presence of reactive chemical species and high selectivity offer a tremendous potential to utilize these cold plasma sources in a wide range of applications.

2.3.3 Dielectric Barrier Discharge (DBD) Plasma

Dielectric barrier discharge, also referred to as barrier discharge or silent discharge is a specific type of AC discharge, which provides a strong thermodynamic, non-equilibrium plasma at atmospheric pressure, and at moderate gas temperature. It is produced in an arrangement consisting of two electrodes, at least one of which is covered with a dielectric layer placed in their current path between the metal electrodes. The presence of one or more insulating layer on/or

between the two powered electrodes is one of the easiest ways to form non-equilibrium atmospheric pressure discharge. Due to the presence of capacitive coupling, time varying voltages are needed to drive the DBD. One of the major difference between the classical and a DBD discharge is that in a classical discharge, the electrodes are directly in contact with the discharge gas and plasmas, and therefore during the discharge process, electrode etching and corrosion occurs. On the contrary, in DBDs the electrode and discharge are separated by a dielectric barrier, which eliminates electrode etching and corrosion. Another fundamental difference is that the DBDs cannot be operated with DC voltage because the capacitive coupling of dielectric requires an alternating voltage to drive a displacement current. An AC voltage with amplitude of 1-100 kV and a frequency from line frequency to several megahertz is applied to DBD configurations. DBD cold plasma can be produced in various working mediums through ionization by high frequency and high voltage electric discharge. The DBDs unique combination of non-equilibrium and quasi-continuous behavior has motivated a wide range of applications and fundamental studies.

The DBD plasma was invent by Siemens in 1857. The discharged plasma are generated by a number of individual filaments. The breakdown channel (micro-discharge) is controlled and the DBD process is optimized for appropriate application. The DBD plasma system is composed of DBD reactor, energy source, metallic electrode (such as aluminum, copper, etc.), and dielectric material (such as glass, quartz, ceramic, etc.).

Generally, dielectric material is cover either at one side of electrode or both of them. To initiate and sustain the generated electron in the DBD system, the energy sources are important. The energy source in DBD system can be alternative current (AC), DC, RF, and MW. After applying the energy to HV electrode, the electrons from metallic electrode strike the dielectric material before emitting the electron in the system. These electron are subsequently at the bond of gas molecules, so the high energetic species are generated. These species are used to modify the substrate surfaces. The lower electrode is ground electrode which is connected to the resistor.

Dielectric barrier discharge (DBD) plasma is widely used to modify the surface properties of polymer in many application such as improving the adhesion of coating to polymers, printing and biomedical application. The interactions of plasma with polymer surface are physical bombardment and chemical reaction. Leading to increase surface roughness and hydrophilicity by etching polymer surface and incorporated new polar functional groups, respectively. The major advantages of DBD plasma treatment over other techniques include modification on the top layer of substrates, minimization of thermal degradation, rapid treatment time and DBD plasma treatment does not require a vacuum system and can be operate at atmospheric pressure.

2.3.4 DBD Structure

The discharge burning between two electrodes, at least one electrode insulated with a dielectric layer can be operated in a wide range of geometrical configurations such as the classical volume discharge, surface discharge, and coplanar discharge.

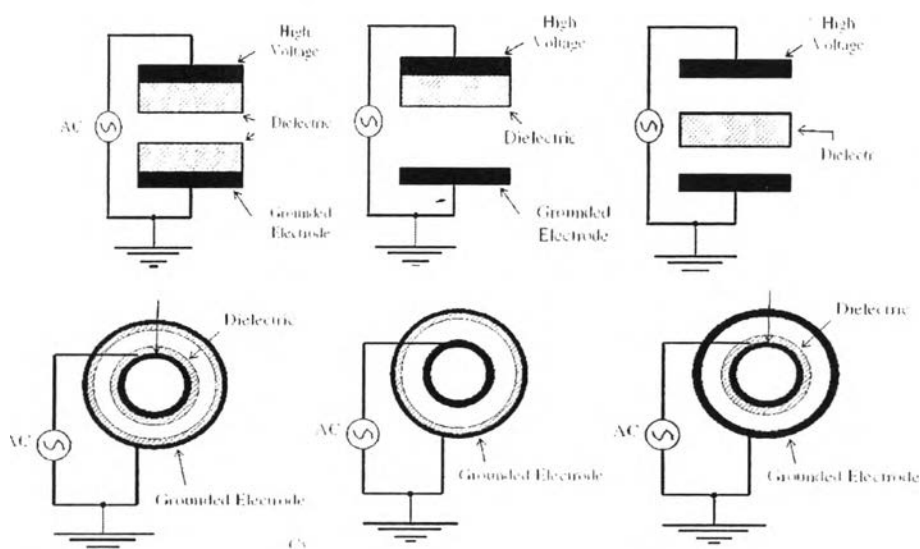


Figure 2.12 Typical DBD electrode arrangements.

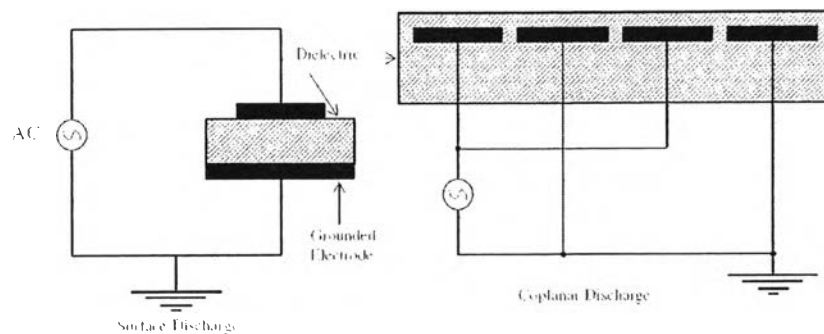


Figure 2.12 (Cont.) Typical DBD electrode arrangements.

Volume discharges can also have either planar or coaxial arrangements. In planar electrode arrangements, the two electrodes are parallel to each other, and one or two dielectric barriers are always located either (1) on the powered or the ground electrode, or (2) on both the electrodes, or (3) in between the two metal electrodes. The electrodes in DBD can also be arranged in a coaxial manner having one electrode inside the other with at least one or two dielectric barriers located either (1) on the outer side of the inner electrode/on the inner side of the outer electrode, or (2) on both the electrodes facing each other, or (3) in between the two cylindrical electrodes. Besides the volume discharges, other designs also exist that use either surface or coplanar discharge geometry. Surface discharge devices have a thin and long electrode on a dielectric surface and an extended counter-electrode on the reverse side of the dielectric. In this configuration, the discharge gap is not clearly defined and so the discharge propagates along the dielectric surface. There also exist combinations of both volume and surface discharge configuration such as the coplanar arrangement used in plasma display panel. The coplanar discharge device is characterized by pairs of long parallel electrodes with opposite polarity, which are embedded within a dielectric bulk nearby a surface. In addition to these configurations, other variants of DBD are also used in various applications. The typical arrangements of DBD are shown in figure 2.12. DBD can exhibit two major discharge modes either filamentary mode, which is the common form of discharge composed of many micro discharges that are randomly distributed over the electrode surface; or homogenous glow discharge

mode, also known as atmospheric pressure glow discharge mode due to similarity with dc glow discharges.

2.3.5 Plasma-Substrate Interaction

In the plasma bulk, reactive species (positive and negative ions, atoms, neutrals, metastables and free radicals) are generated by ionization, fragmentation, and excitation. These species lead to chemical and physical interactions between plasma and the substrate surface depending on plasma conditions such as gas, power, pressure, frequency, and exposure time. Plasma-substrate interaction can be classified as :

1. Plasma etching is the key process for the removal of surface material from a given substrate. This process relies on the chemical combination of the solid surface being etched and the active gaseous species produced in the discharge. The resulting etched material will have a lower molecular weight and the topmost layer will be stripped. In previous methods, such as chemical wet processing, plasma has shown much more controllability and a much finer resolution. Due to the etching mechanism on polymer surfaces, morphological and topographical changes will occur. These changes are visible through atomic force microscopy (AFM) or scanning electron microscopy (SEM). Since most polymers are semi-crystalline, that is, they contain both crystalline and amorphous regions, they produce very distinctive morphology changes due to selective etching. Plasma etching led to increase surface roughness and surface degradation.

2. Chain-scission is defined as any event that results in the breakage of one polymer molecule into two or more parts. This can occur through a direct rearrangement of the backbone into two separate entities, or by the loss of side groups and consequent rearrangement, which inherently results in molecular division (Clough and Shalaby, 1996). Both processes can occur as a result of etching via plasma exposure. The first interaction involves ion bombardment, in which ion energy is transferred to the polymer molecules comprising the substrate. Bond scission and radical formation then occur, causing weight loss and a reduction in molecular weight (Inagaki, 1996). In addition to physical modifications, plasma

exposure leads to changes in the elemental composition of the polymer surface. This includes the formation of free radicals. These radicals enable reactions such as cross-linking by activated species of inert gas, surface graft polymerization, as well as the incorporation of functional groups.

2.3.6 Literature Review on DBD Plasma Surface Treatment

Dumitrascu N. *et al.*, 2006 developed dielectric barrier discharge (DBD) plasma to modify surface of polyamide-6 surface at atmospheric pressure. The result from AFM shown a new structure of surface is observed in nanoscale, with an increase roughness and a large surface area. DBD plasma can improve adhesion properties of polymer surface.

Geyter N.D. *et al.*, 2006 developed dielectric barrier discharge (DBD) plasma to modify surface of polyester non-woven fabric. The results shown that DBD plasma can improve hydrophilicity of polyester non-woven fabric compare with non-treated DBD plasma. The increasing of the hydrophilicity of the polyester non-woven after DBD treatment is caused by creation of oxygen-containing polar groups (O-C=O groups and C=O groups) on the surface.

Hyun N.L. *et al.*, 2009 developed dielectric barrier discharge (DBD) plasma to modify polycaprolactone (PCL) films. The rearrangement of PCL films by DBD treatment was attributed to surface oxidation which produced hydrophilic groups, such as oxygen and carbon onto the PCL film surface. Therefore, the hydrophilic properties of DBD treated PCL films might be improve, which would improve the adhesion properties. The results found that the level of cell attachment and proliferation of human prostate epithelial cells was ten times better than that observed on the untreated PCL films.

Seyed A.M. *et al.*, 2012 found that hydrophilicity, wettability and roughness of polyhydroxybutyrate (PHB) film was remarkably improve after plasma treatment. To study biocompatibility of the untreated and plasma-treated PHB samples cell proliferation method has been used. The attachment and growth of L929 fibroblast cells onto the untreated PHB surface was negligible, yet improved attachment and growth of L929 fibroblast cells were observed on plasma-treated

PHB surfaces. It can be concluded that plasma treated PHB film will provide an environment for better cell attachment and growth.

Borcia G. *et al.*, 2005 developed dielectric barrier discharge (DBD) plasma to modify polyamide-6 surface in helium atmospheric pressure. The results from AFM shown that the surface roughness of polyamide-6 films increased depend on treatment time. DBD plasma treatment time was 10s, 30s and 60s. Using long treatment time, the surface roughness was increased.

Wang C.X. *et al.*, 2008 developed dielectric barrier discharge (DBD) plasma to treat polyester fabric surface. Significant changes in morphology of fabric surface were observed after plasma treatment. As shown in figure 2.13, untreated sample shown the smooth surface while for the plasma treated sample, micro pits were formed on the fabric surface. The formation of micro pits on the treated fabric surfaces were caused by the etching reactions, in which some degradation reaction occurred due to the bombardment of the ions and the electrons as well as the oxidative reactions with atomic oxygen. Therefore the surfaces of plasma treated polyester fabric were roughed resulting in change of the fabric surface properties.

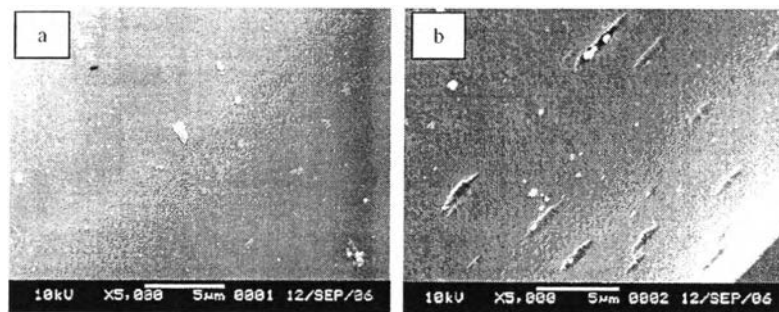


Figure 2.13 Surface morphology of polyester fabric (a) untreated and (b) treated DBD plasma 2 s.