CHAPTER II
LITERATURE REVIEW

2.1 Bacterial Cellulose (BC)

Cellulose is the most abundant biopolymer in the nature. It is the main component of all plants and can be produced by metabolism of many strains of bacteria, which was called bacterial cellulose, such as *Acetobacter, Rhizobium, Agrobacterium* and *Sarcina* (Jonas *et al.*, 1998). The most efficient producer is Gram-negative, acetic acid bacteria, *Acetobacter Xylinum*. One of the most important features of bacterial cellulose is its chemical purity, which distinguishes this cellulose from plant cellulose, which is difficult to remove hemicelluloses and lignin.

Because of the unique properties, resulting from the ultrafine structure, bacterial cellulose has found many applications in paper, textile, and food industries, especially a biomaterial in cosmetic and medicine. Wider application is dependent on the scale of production and its cost.

2.1.1 Structure of Bacterial Cellulose

Bacterial cellulose nanofibril is a three-dimensional non-woven network which consist of β-1,4-glucopyranose ring as shown in Figure 2.1. Therefore, the chemical structure is identical to plant cellulose (Czaja *et al.*, 2004), different in its macromolecular structure and properties. Cellulose chains of bacterial cellulose aggregate to form subfibrils, which have a width of approximately 1.5 nm, the thinnest naturally occurring fibers. Bacterial cellulose subfibrils are crystallized into microfibrils, bundles, and the latter into ribbons. Dimensions of bacterial cellulose fibril are in nanoscale. Compare with plant cellulose, the diameter of bacterial cellulose is about 1/100 of that of plant cellulose, the length of these fibril ranges from 1 to 9 μm, form a dense reticulated structure (Yamanaka *et al.*, 2000), stabilized by hydrogen bonding. Bacterial cellulose is also distinguished from plant cellulose by a high crystallinity index (above 60%) and different degree of polymerization (DP).

Macroscopic morphology of bacterial cellulose strongly depends on culture conditions (Watanabe *et al.*, 1998; Yamanaka *et al.*, 2000), which are two common conditions:

2.1.1.1 Static Conditions

Bacteria accumulate cellulose mats on the surface of nutrient broth, at the oxygen-rich air-liquid interface as shown in Figure 2.2. The subfibrils of cellulose are continuously extruded from pores at the surface of the bacterial cell, crystallized into microfibrils, and forced deeper into the growth medium. The product from this condition is the forming parallel but disorganized planes (Jonas and Farah, 1998).

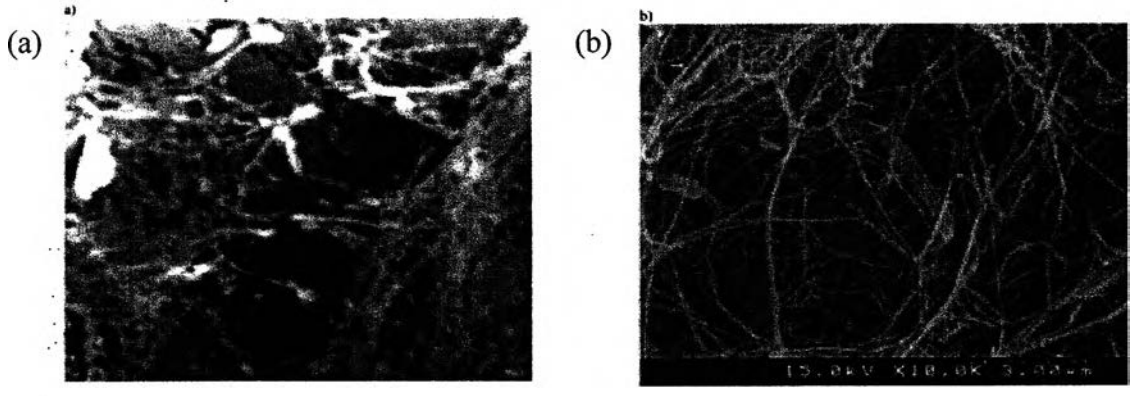

Figure 2.1 Scanning electron microscopy images of (a) bacterial cellulose membrane from static culture of *A. xylinum* and (b) bacterial cell with attached cellulose ribbons.

Figure 2.2 Bacterial cellulose formed in static culture.

2.1.1.2 Agitated Conditions

Bacterial cellulose produced in agitated culture, in a form of irregular granules, stellate and fibrous strands, well-dispersed in culture broth as shown in Figure 2.3 (Vandamme *et al.*, 1998), the strands branch and interconnect of agitated culture more frequently than these produced in static culture, form a grid-like pattern, and have both roughly perpendicular and roughly parallel orientations. Therefore, it has a lower crystallinity index and a smaller crystallite size than the bacterial cellulose that produced in static culture.

Figure 2.3 Bacterial cellulose formed in agitated culture.

Differences in three-dimensional structure, the static culture bacterial cellulose fibrils are more extended and piled above one another in a crossing manner. But strands of agitated culture bacterial cellulose are entangled and curved (Yamanaka *et al.*, 2000), and have a larger cross-sectional width. Beside, morphological differences between bacterial cellulose produced from these two conditions contribute to varying degrees of crystallinity, different crystallite size and I_α cellulose content.

Two common crystalline forms of cellulose is designated as I and II, are distinguishable by X-ray, nuclear magnetic resonance (NMR), Raman spectroscopy, and infrared analysis. The first form, metastable cellulose I, which is synthesized by the majority of plants and also by *A. xylinum* in static culture, parallel β-1,4-glucan chains are arranged uniaxially, whereas β-1,4-glucan chains of cellulose

II are arranged in a random manner. They are mostly antiparallel and linked with a larger number of hydrogen bonds that result in higher thermodynamic stability of the cellulose II. It was also observed that bacterial cellulose synthesized in agitated culture has a significant portion of cellulose II (Watanabe *et al.*, 1998).

2.1.2 Properties of Bacterial Cellulose

Bacterial cellulose has both inter- and intra-fibrilar hydrogen bonding resulting in the ability to maintain the proper moisture level as a hydrogel or the never dried-state and high strength (Czaja *et al.*, 2004). Better properties of the hydrogel which is produced from bacteria over the hydrogel from polymer synthesis are (Klemm *et al.*, 2001):

- High water content (98–99%)
- Good sorption of liquids
- High wet strength
- High chemical purity
- Can be safety sterilized without any change to its structure and properties.

Cellulose which produced from bacteria has an ultrafine structure and Young's modulus of bacterial cellulose is almost equivalent to that of aluminum. Besides, it can be compatible with human cells and has many advantages over plant cellulose such as finer structure, no hemicellulose or lignin need to be removed, longer fiber length, stronger, can be grown to virtually any shape and can be produced on a variety of substrates. It is the only alternative for plant cellulose because bacteria produce this cellulose in a few days, while trees need more than 30 years to grow fully. So it can prevent global warming and preserve the nature. Therefore, bacterial cellulose is expected to be a new biodegradable biopolymer.

2.1.3 Applications of Bacterial cellulose

Due to its unique properties, bacterial cellulose is an interesting material for many applications such as:

- Wound dressing
- Matrix for electronic paper
- Scaffolds for tissue engineering
- Soft tissue replacement
- High strength paper
- Artificial blood vessels
- Diet foods
- Dessert: nata de coco.

In medical applications, it has suitable properties to use as a wound dressing because it provides moist environment to a wound resulting in a better wound healing (Maneerung *et al.*, 2008) and it can maintains the optimum conditions required for the regeneration of broken tissue. In a form of hydrogel, it maintains the proper moisture level and temperature of the wound bed, accelerate healing, activate autolytic debridement of the wound, protect newly formed cells, facilitates angiogenesis and re-epithelisation, alleviate pain, and protect the wound against bacteria and contamination.

2.2 Chitosan

Chitosan is the most important chitin derivative in terms of applications, which is obtains by partial deacetylation of chitin under alkaline conditions. Chitin is generally represented as a linear polysaccharide composed of β (1→4) linked units of *N* -acetyl-2-amino-2-deoxy-d-glucose. Small proportions of these structural units are deacetylated in natural chitin. Structure of chitin is similar to cellulose, different only the hydroxyl group of carbon at C-2 position in cellulose is substituted by an acetamide group in chitin as seen in Figure 4 (Peniche *et al.*, 2008). But both biopolymers are important because they act as structural support and defence materials in living organisms.

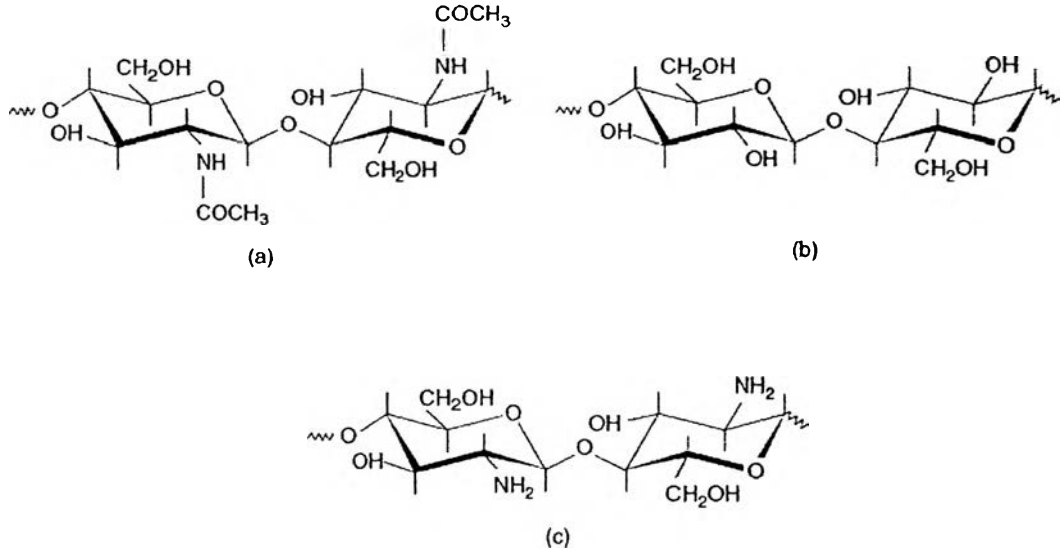

Figure 2.4 Schematic representation of (a) completely acetylated chitin; (b) cellulose and (c) completely deacetylated chitosan.

Chitosan is a linear polysaccharide obtained by extensive deacetylation of chitin. It becomes soluble in aqueous acidic media by protonation of the $-NH_2$ function on the C-2 position of the D-glucosamine repeat unit. Being soluble in aqueous solutions, it is largely used in different applications as solutions, gels, or films and fibers.

2.2.1 Sources of Chitin and Chitosan

Chitin is the second most abundant polysaccharide in nature after cellulose, which is extracted from crustacean. The main chitin sources are the shells of shrimp, crab, lobster, prawn and krill. In animals, chitin occurs associated with other constituents such as lipids, calcium carbonate, proteins and pigments. It is also found as a major polymeric constituent of the cell wall of fungi and algae.

2.2.2 Antimicrobial Properties

Metallic nanoparticle has good antibacterial properties due to their large surface area to volume ratio. Different types of nanomaterials like copper, zinc, titanium, magnesium, gold, alginate and silver have come up (Rai *et al.*, 2009). Among the others, silver nanoparticle is most efficient antimicrobial agents against bacteria, viruses and other eukaryotic micro-organisms. Antimicrobial mechanism occurs by silver ion (Ag^+), very active specie, can rapidly interact with electron

donor group like sulfur-, oxygen- and nitrogen group, which often be in form of thio-, phosphate- and amino groups on the DNA chains of bacteria cells. As a result, the important transport process of bacteria like phosphate and succinate uptake process are obstructed. Therefore, those bacteria are disposed.

In 2008, Maneerung *et al.*, found that "bacterial cellulose itself has no antimicrobial activity to prevent wound infection. To achieve antimicrobial activity, silver nanoparticles were impregnated into bacterial cellulose. The freeze-dried silver nanoparticle-impregnated bacterial cellulose exhibited strong the antimicrobial activity against *Escherichia coli* (Gram-negative) and *Staphylococcus aureus* (Gram-positive)". In 2009, Luiz *et al.*, also studied about the synthesis of colloidal silver (Ag)/biopolymer where Ag submicron particles were prepared in situ on bacterial cellulose produced by *Gluconacetobacter xylinus*. They found that among the reductants used (hydrazine, hydroxylamine or ascorbic acid), the ascorbic acid was the most efficient reductant for Ag^+, and the colloid protector, particularly gelatin, has an important role on avoiding the silver particle coalescence and particle size control on the BC membrane.

Hernane *et al.*, (2008) prepared self-supported silver nanoparticles containing bacterial cellulose (BC) membranes from BC hydrated membranes obtained from *Acetobacter xylinum* cultures, soaked on Ag^+ in triethanolamine (TEA) solutions. They found that "the electron microscopy images and XRD diffraction patterns both lead to the observation of metallic silver particles with mean diameter of 8 nm well adsorbed onto the BC fibriles. The utilization of TEA as stabilizer and reducing agent leads to spherical particles well dispersed on the BC bulk ultrafine reticulated structure, which has the potential use as membranes in antibacterial applications.

Although silver nanoparticle is commonly used as antimicrobial agents, it has some disadvantages as the followings:

- It is metallic substance, can cause irritation to human skin
- The process has to use strong reagents like sodiumborohydride ($NaBH_4$), which compose of boron, hazardous metal that can remain and cause toxic with mammalian cells

- Since silver ion has a small size and very reactive, it can interact with not only DNA of bacteria cells, but also human cells. So it also dangerous for human health.

2.2.2.1 Antimicrobial Properties of Chitosan

In the solid state, chitosan is a semicrystalline polymer. Unlike chitin which is hydrophobic and cannot soluble in water and organic solvents, chitosan can soluble in dilute organic acids such as acetic acid and formic acid. Furthermore, chitosan has an antibacterial property, which is an important property for wound healing applications.

Chitosan has similar antimicrobial properties with silver nanoparticle, but obtains from nature and has larger molecular size, lower reactivity with electron donor resulting in many advantages over silver nanoparticle such as (Dutta *et al.*, 2009):

- Biocompatibility
- Biodegradability
- Higher antimicrobial activity
- Boarder spectrum of activity
- Lower toxicity for mammalian cells
- Large quantity and accessibility
- Versatile chemical and physical properties.

2.2.2.2 Mechanism of Antimicrobial Action of Chitosan

Chitosan is more soluble and has a better antimicrobial activity than chitin result from the positive charge on the C2 of the glucosamine monomer when pH is below 6, (Dutta *et al.*, 2009). Different mechanisms of the antimicrobial action of chitin, chitosan, and their derivatives have been proposed, even though the exact mechanism is still imperfectly known. Antimicrobial mechanism of chitosan occurs from its positively charged amino group which interacts with negatively charged microbial cell membranes, which leading to the leakage of protein and other intracellular constituents of the microorganisms (Shahidi *et al.*, 1999). Chitosan binds with DNA to inhibit RNA synthesis (Rabea *et al.*, 2003). Furthermore, it

known that chitosan acted mainly on the outer surface of bacteria. At a lower concentration (0.2 mg/ml), the polycationic chitosan does probably bind to the negatively charged bacterial surface to cause agglutination, while at higher concentrations, the larger number of positive charges may have imparted a net positive charge to the bacterial surfaces to keep them in suspension (Dutta *et al.*, 2009).

The mechanisms of the antimicrobial activity of chitosan were different for Gram-positive and Gram-negative bacteria (Zheng *et al.*, 2003). In this study they differentiated the effect of chitosan on *S. aureus* (Gram-positive) and on *E. coli* (Gram-negative). For *S. aureus*, the antimicrobial activity increased on increasing the molecular weight of chitosan. But for *E. coli*, the antimicrobial activity increased on decreasing molecular weight. The suggestion of authors for the antimicrobial activity are the following two different mechanisms:

(1) In case of *S. aureus*, the chitosan on the surface of the cell can form a polymer membrane, which inhibits nutrients from entering the cell

(2) In case of *E. coli*, the chitosan of lower molecular weight entered the cell through pervasion.

2.2.2.3 Factors Affecting the Antimicrobial Activity of Chitosan

The effect of the molecular weight on some antibacterial and antifungal activities has been explored (Dutta *et al.*, 2009). Chitosan with a molecular weight ranging from 10 000 to 100 000 have been found to be helpful in restraining the growth of bacteria. In addition, chitosan with an average molecular weight of 9300 was effective in restraining E. coli, whereas that with a molecular weight of 2200 helped in accelerating the growth. Furthermore, the antibacterial activity of chitosan is influenced by its degree of deacetylation, its concentration in solution, and the pH of the medium. Antibacterial activities were also found to be increasing in the order N, O-carboxymethylated chitosan, chitosan, and O-carboxymethylated chitosan.

In 2008, Phisalaphong *et al.*, studied the properties of bacterial cellulose–chitosan film synthesis and characterize cellulose film. They modified bacterial cellulose by the supplement of low-molecular-weight chitosan into the culture medium, and found that "with the addition of 0.75% (w/v) chitosan, the films

of BC-chitosan (BCC) of MW 30,000 and BCC of MW 80,000 were homogeneous with a significantly denser fibril structure, smaller pore diameter and higher surface area in comparison to those of BC films. The pore sizes of the dried films of BC, BCC of MW 30,000 and BCC of MW 80,000 were 224, 151 and 132 Å, respectively. The FTIR spectra indicated the intermolecular interaction between BC and chitosan. The mechanical properties and the water absorption capacity of films were significantly improved. However, the addition of chitosan of low-molecular weight in the dilute concentration as in this study showed no significant influence on some properties of the films such as water vapor transmission rates, average crystallinity index and anti-microbial ability".

Antibacterial activities of six chitosans and six chitosan oligomers with different molecular weights (Mws) were examined against four gram-negative (including *Escherichia coli*) and seven gram-positive bacteria (including *Staphylococcus aureus*) by No *et al.*, (2002). They reported that "chitosans showed higher antibacterial activities than chitosan oligomers and markedly inhibited growth of most bacteria tested although inhibitory effects differed. Chitosan generally showed stronger bactericidal effects with gram-positive bacteria than gramnegative bacteria. The minimum inhibitory concentration (MIC) of chitosans ranged from 0.05% to > 0.1% depending on the bacteria and Mws of chitosan. As a chitosan solvent, 1% acetic acid was effective in inhibiting the growth of most of the bacteria tested. Antibacterial activity of chitosan was inversely affected by pH (pH 4.5–5.9 range tested), with higher activity at lower pH value".

Liu *et al.*, (2006) also studied the effect of MW and concentration of chitosan on antibacterial activity of *Escherichia coli.* From the experiment, they produced chitosans, which different molecular weight (MW) (5.5×10^4 to 15.5×10^4 Da) with the same degree of deacetylation, and found that "the antibacterial activity of low MW chitosan is higher than that of the high MW samples. But the chitosan sample with the middle MW (9.0×10^4 Da) could promote the growth of bacteria. In the different stages of cultivation, the earlier chitosan was added the greater effect it did. And the mechanism of antibacterial activity was that *E. coli* was flocculated".

In 2005, Zhang *et al.*, proposed the new method to determine the degree of deacetylation (DD) of a-chitin and chitosan in the range of 17–94% DD

using X-ray powder diffraction (XRD). The results showed a good linear correlation between the CrI_{020} from XRD and the calibrated DD value. This method is found to be simple, rapid and nondestructive to the sample. From FTIR spectra of chitin (Figure 2.5), they found that "the broad peaks at 3450 cm^{-1} assigned to OH stretching, which became broader and moved to a lower frequency with increasing DD up to 50% (Samples 1, 2 and 3), indicating an increase in the disordered structure. The bands then became narrow and moved back to higher frequency (~3450 cm^{-1}) with the increase of DD up to 94% (Sample 6), indicating a more ordered structure. This implies that there is less intermolecular force within molecules of half-deacetylated chitosan, with the free hydroxyl groups, amino groups and the polymer chain end readily bonding with water".

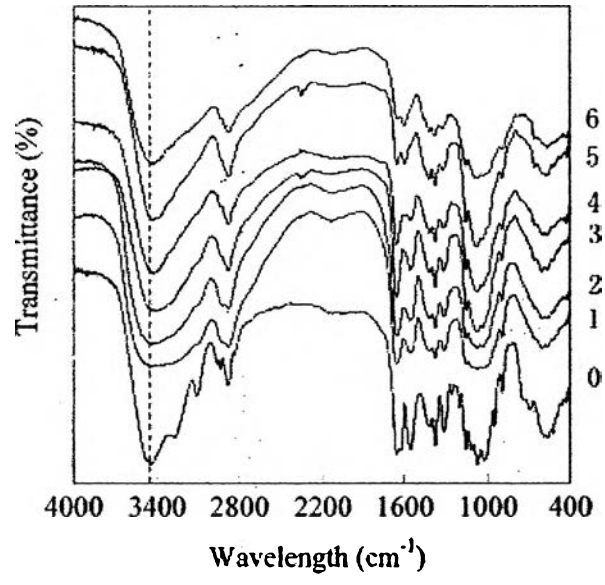

Figure 2.5 Comparison of FTIR spectra of chitin and chitosan with different degrees of deacetylation (DD).

For X-ray diffraction analysis, it is noted that the maximum peak of intensity at 020 reflection decreased with the increase of DD, and moved to a higher angle as shown in Figure 2.6.

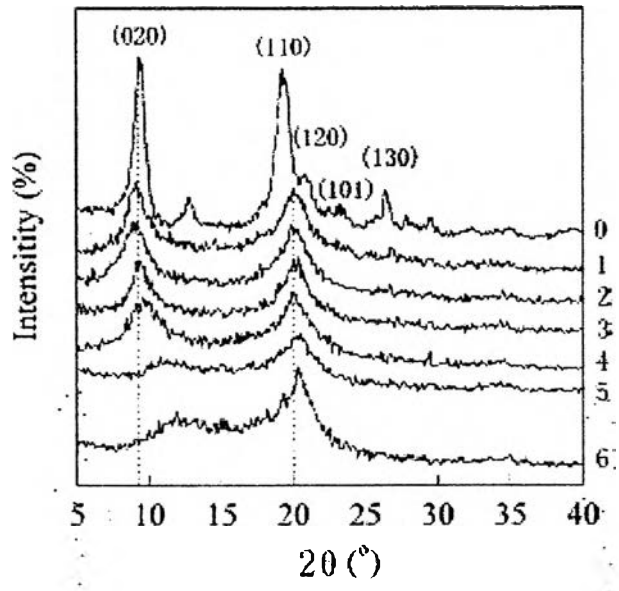

Figure 2.6 Comparison of X-ray powder diffractograms of chitin and chitosan with different degrees of deacetylation (DD).

The effect of degrees of substitution (DS) and weight-average molecular weight (M_w) was also investigated by Peng *et al.*, (2005). They found that "the DS value of water-soluble hydroxypropyl chitosan (HPCS) ranged from 1.5 to 3.1 and the M_w was between 2.1×10^4 and 9.2×10^4". Besides, they also evaluated in vitro antimicrobial activities of the HPCS derivatives by the Kirby–Bauer disc diffusion method and the macrotube dilution broth method, then found that "the HPCS derivatives exhibited no inhibitory effect on two bacterial strains (*Escherichia coli* and *Staphylococcus aureus*); however, some inhibitory effect was found against four of the six pathogenic fruit fungi investigated".

2.2.3 Applications of Chitosan

Chitosan and its derivatives have become interesting biopolymers in a large variety of areas of human activity such as in medicine, pharmacy, agriculture, foods, cosmetics and the others.

2.2.3.1 Medical Applications

Chitosan is very useful for biomedical applications because it has biocompatibility, biodegradability and low toxicity with human cells. Chitin has

also biocompatible and biodegradable properties, but it is less interest compare with chitosan because of its insolubility in water and low reactivity (Peniche *et al.*, 2008).

As a biomaterial, due to its excellent properties when using with the human body like bioactivity, antimicrobial activity, immunostimulation, chemotactic action, enzymatic biodegradability, mucoadhesion and epithelial permeability which supports the adhesion and proliferation of different cell types (Pena *et al.*, 2006). Therefore, chitosan has many applications such as contact lenses, tissue adhesive, preventing bacterial adhesion, sutures and others. Two mains biomedical field which is use chitosan is:

- *Treatment of wounds and burns*

Because of adhesive properties of chitosan, together with its antifungal and antibacterial properties, and permeability to oxygen, are very important properties for the treatment of wounds and burns. Both chitin and chitosan promote granulation and cell organization during wound healing. Furthermore, the reepithelization and tissue regeneration are improved in open wounds, and decrease scarring at the same time.

Wub *et al.*, (2004) prepared the membrane of chitosan and cellulose blends using trifluoroacetic acid as a co-solvent. They suggested that "cellulose/chitosan blends were considerably immiscible. It is believed that the intermolecular hydrogen bonding of cellulose is break down to form cellulose–chitosan hydrogen bonding; however, the intra-molecular and intra-strand hydrogen bonds hold the network flat. The reduced water vapor transpiration rate through the chitosan/cellulose membranes indicates that the membranes used as a wound dressing may prevent wound from excessive dehydration. The chitosan/cellulose blend membranes demonstrate effective antimicrobial capability against *E.coli* and *S. aureus*. " These results indicate that the chitosan/cellulose blend membranes may be suitable to be used as a wound dressing with antibacterial properties.

In 2007, Minagawa *et al.*, studied the effects of molecular weight and deacetylation degree of chitin/chitosan on wound healing. They reported that "Wound break strength and collagenase activity of the chitosan was higher than the chitin. There was no significant change between the concentration of the sample and the break strength and collagenase activity in all samples. As for the

deacetylation degree, the higher the deacetylation degree, the more the stronger the break strength, activated fibroblasts also appeared more (more collagenase activity)".

- *Tissue engineering*

For tissue engineering techniques, the use of three dimensional (3D) supports for initial cell attachment and subsequent tissue formation are required. Chitosan has similar structural characteristics as glycosaminoglycans (GAGs), which is found in extracellular matrix of several human tissues (Peniche *et al.*, 2008), so it widely used in these applications.

2.2.3.2 Food Applications

The antimicrobial properties of chitosan against many strains of bacteria, fungi and viruses resulting in the efficient food preservatives, which can reduce the amount of synthetic food preservatives currently used. Besides, it can be obtained from nature, so it is better for human health and environment. Many important products used chitosan such as packaging wraps or edible coatings for the preservation of fruits, vegetables and meat products.

Recently, Dutta *et al.*, (2009) studied chitosan based antimicrobial films in food applications. They investigated the antibacterial activity of chitosan-starch film using microwave treatment by agar plate diffusion method. The antibacterial activity of the film and their same solution has been evaluated against three different test cultures, which is gram negative bacteria *E. coli*, gram positive bacteria *S. aureus* and gram positive bacteria *Bacillus subtilis*. They found that "the solution of chitosan-starch showed inhibitory effect against the test cultures but film proved to be negative" (Figure 2.7 and Figure 2.8).

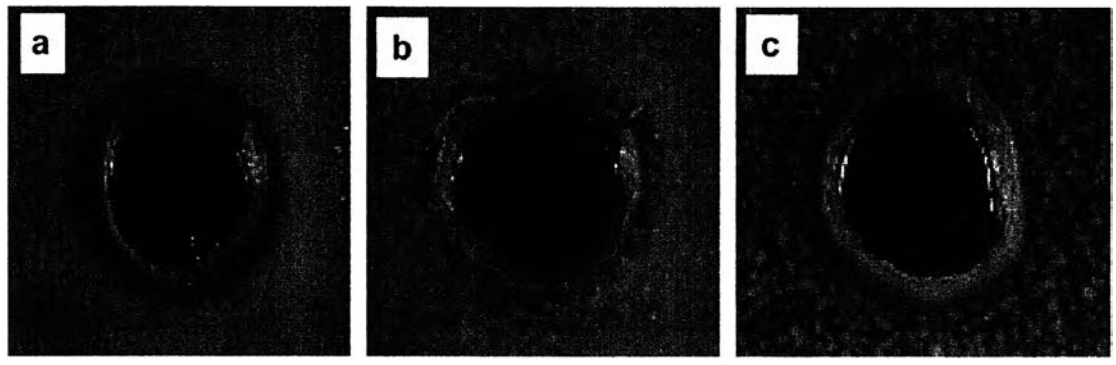

Figure 2.7 Inhibitory effect of chitosan-starch solution against (a) *E. coli* (b) *S. aureus*, and (c) *B. Subtilis*.

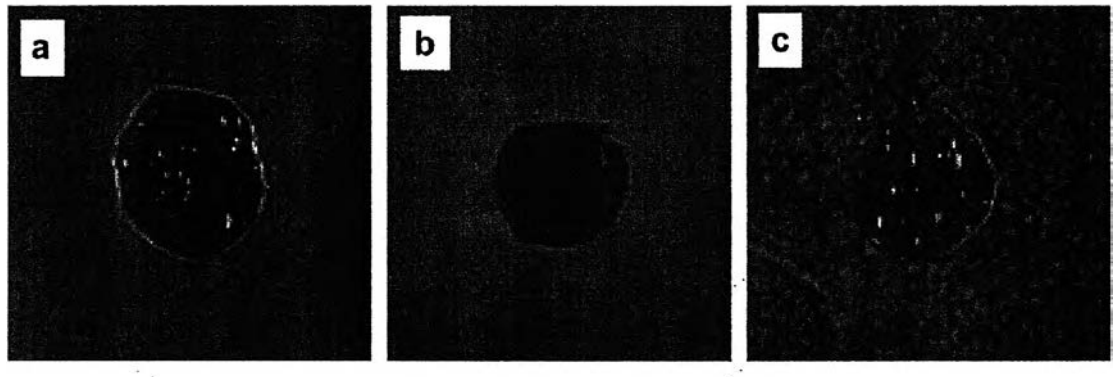

Figure 2.8 Inhibitory effect of chitosan-starch film against (a) *E. coli*, (b) *S. aureus*, and (c) *B. Subtilis*.

2.2.3.3 Cosmetic Applications

This is one of the interesting applications of chitosan. Due to its high molecular weight, water retention and film formation capacity, it can decreases the loss of trans-epidermic water, increasing the humidity of the skin which preserves its softness and flexibility (Peniche *et al.*, 2008). Chitosan is an excellent ingredient for allergic skins, since it was found to reduce skin irritation. As a result of its antibacterial character, chitosan also inhibits inflammatory processes. Furthermore, it can promotes the regeneration of damaged tissues, reduces the electrostatic charges, stables to high humidity. Therefore, it can be used with many

products like sun-protecting emulsions, deodorants, hair-care products, tooth pastes, oral rinsing solutions, chewing gums and others.

2.3 Plasma treatment

Plasma treatment is an efficient, environmentally friendly method of surface preparation prior to bonding, deposition and coating. Plasma treatment provides increased bond strength, wettability, permeability, hydrophobicity, and biocompatibility. It removes organic and inorganic materials that prohibit desired bond strengths without affecting the bulk properties (Borcia *et al.*, 2006). Plasma treatment can add functional groups to a surface at the molecular level, changing surface chemistries for improved lubricity and surface adhesion.

Plasma is ionized gas, which consists of positive and negative ions, electrons, as well as free radicals. The ionization degree can vary from 100% (fully ionized gas) to very low values (partially ionized gas). It occurs naturally as well, lightning and auroras are some classic examples. However, plasmas can be generated artificially at laboratory levels for practical applications. Man-made plasmas are commonly generated and sustained using electrical energy and are often referred to as "discharges".

2.3.1 Plasma Generation

Plasma, the 4th state of matter (Figure 2.9), can be generated by using energy to strip electrons from atoms to make plasma. The energy can be of various origins: thermal, electrical, or light (ultraviolet light or intense visible light from a laser). Without sufficient sustaining power, plasmas can be recombined into neutral gas.

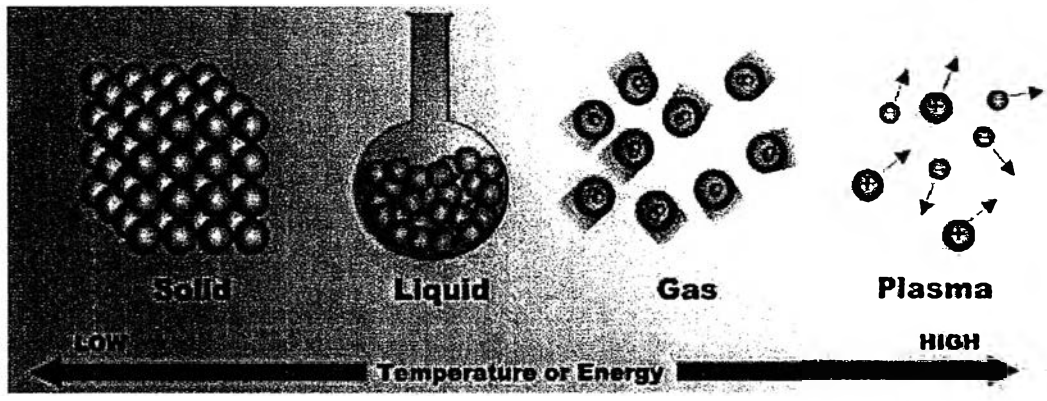

Figure 2.9 Plasma, which usually referred to the 4th state of matter.

The first state is a solid, the coldest state of matter, which molecules are fixed in lattice. As we heat up a solid it becomes liquid, which molecules free to move. As we heat up liquid, it turns to gas. Gas is the third state of matter, which molecules move more freely in larger space. And if we heat up the gas, atoms break apart into charged particles turning the gas into plasma, which ions and electrons move independently.

The separation of electrons and ions produce electric fields. The motion of electrons and ions produce both electric and magnetic fields. The electric fields then tend to accelerate plasmas to very high energies while the magnetic fields tend to guide the electrons. The most common method of generating and sustaining a low-temperature plasma for technological and technical application is by applying an electric field to a neutral gas (Figure 2.10).

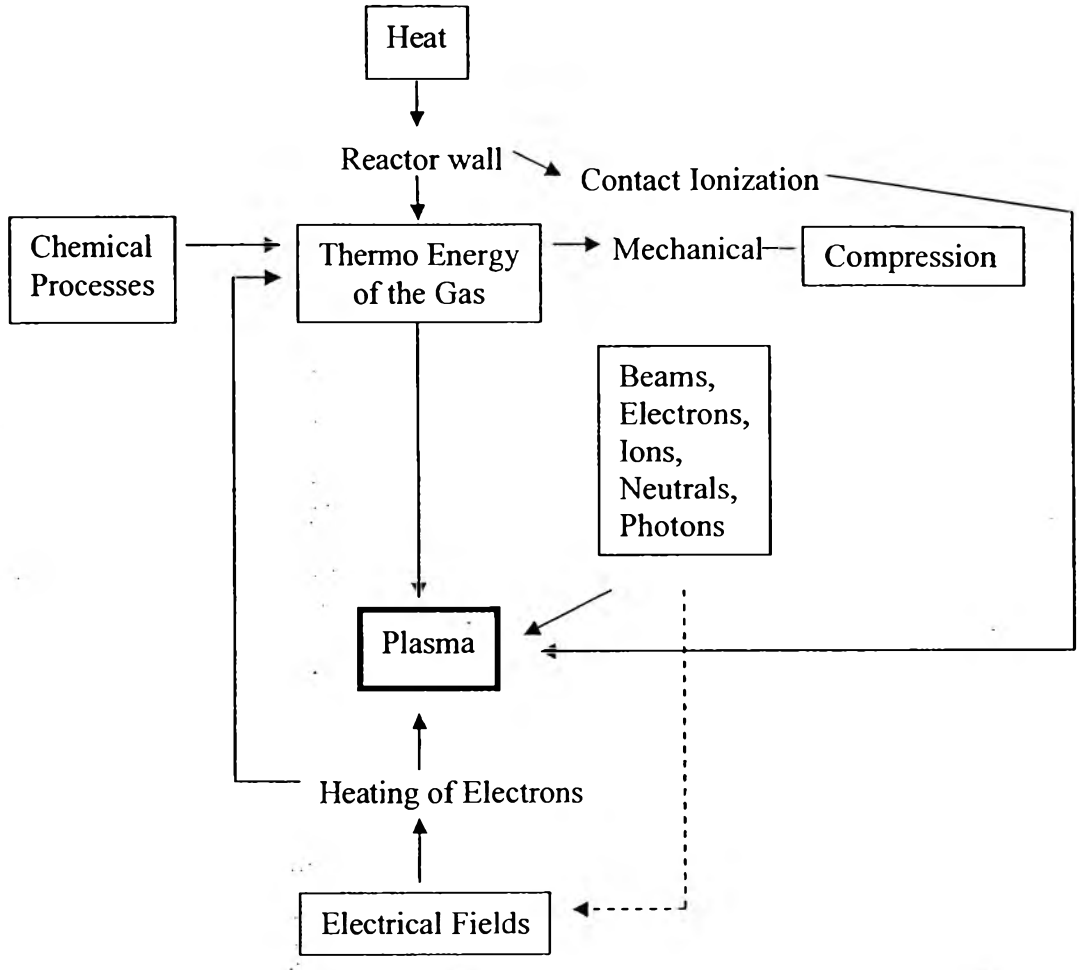

Figure 2.10 Principles of plasma generation.

2.3.2 Type of Plasmas

Plasma state can be divided in two main types: equilibrium plasmas (thermal plasmas) and non-equilibrium plasmas (non-thermal plasmas). The non-thermal plasma is more common, because provides a number of advantages over thermal plasma, which are:

- Lower energy consumption.
- Lower pressure
- Higher selectivity and efficiency.

2.3.2.1 Types of Non-thermal Plasmas

Non-thermal plasmas are divided into many distinctive groups, depending on the mechanism used for their generation, their pressure range,

or the electrode geometry, which are the following types: corona discharge, gliding arc discharge, glow discharge, radio frequency discharge, microwave discharge and dielectric barrier discharge. The latter one, dielectric barrier discharge (DBD), which is shown in Figure 2.11, is the most commonly used technique resulting from its advantages over other kinds of non-thermal plasma such as:

- It is relatively easy to fabricate.
- It is capable of operating at low temperature and atmospheric pressure.
- It has relatively low power consumption.
- Modification is fairly efficient and uniform over the whole surface.
- It produces much less prone that cause surface damage.

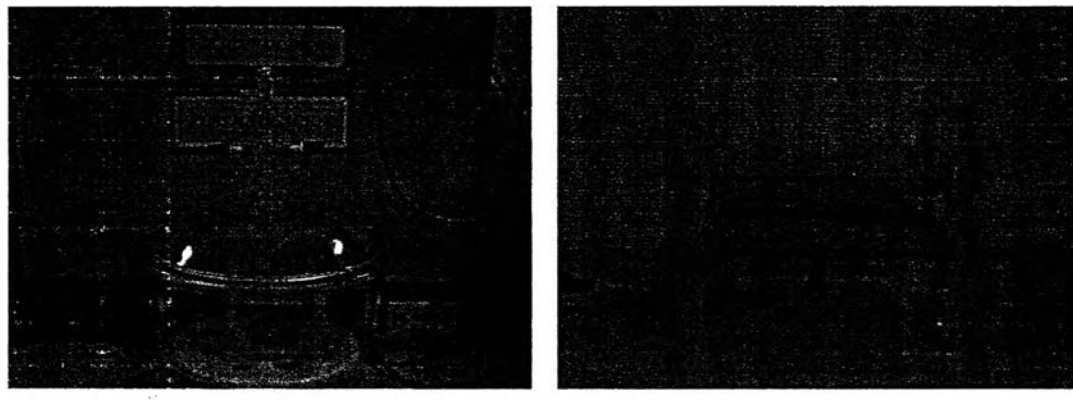

Figure 2.11 Dielectric Barrier Discharge (DBD) Plasma.

Dielectric Barrier Discharge (DBD) or silent discharge is predestined for applications in volume plasma chemistry. First experimental investigations were reported by Siemens (Ulrich *et al.*, 2003) in 1857. They concentrated on the generation of ozone. This was achieved by subjecting a flow of oxygen or air to the influence of a dielectric barrier discharge (DBD) maintained in a narrow annular gap between two coaxial glass tubes by an alternating electric field of sufficient amplitude.

The DBD has inherent advantages over the discharges, which have been treated until now. It combines the large volume excitation of the glow

discharge with the high pressure of the corona discharge. The main elements of a DBD configuration are shown in Figure 2.12.

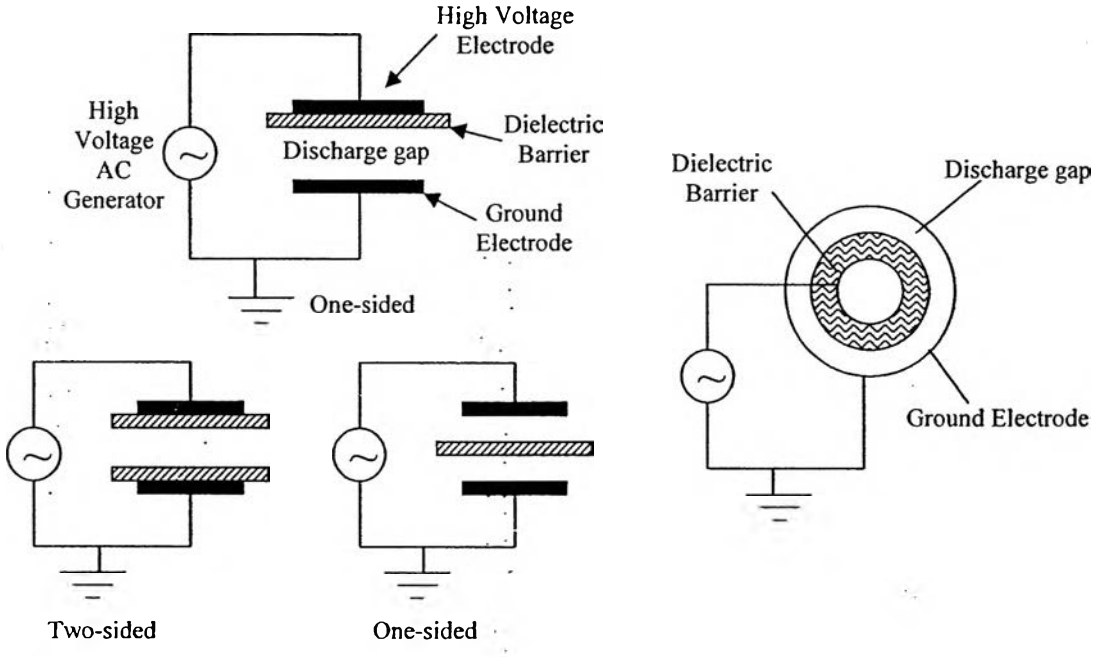

Figure 2.12 Common dielectric barrier discharge configurations with one or two dielectric barriers and micro-discharges are contained in the discharge gap (Conrads H. *et al.*, 2000).

Park *et al.* (2007) investigated the effects of a dielectric barrier discharge (DBD) plasma on surface treatment of polyimide (PI) film in terms of changes in surface wettability and surface chemistry. It was found that "the polymer films modified in N_2 and mixed N_{2+} air gas showed a remarkable increase in the O 1s ratios of the PI films, which is probably due to the increase in the number of nitrogen- and oxygen-containing functional groups on the PI surfaces caused by the DBD plasma treatment, such as C=O and C–O–C species, and the increase in the surface energy of the PI surface following its treatment by the DBD plasma is attributed to the improvement in both the polar and London dispersive components. Also, the roughness of the PI film surfaces were confirmed by AFM observation. The results can be attributed to the increase in the polarity and hydrophilic properties of

the PI surface or the slight increase in the dispersive component and roughness, due to the DBD plasma treatment".

In 2006, Borcia *et al.*, studied the surface treatment of textiles, polyethylene terepthalate (PET) and nylon, using a dielectric barrier discharge, and compared the results of the treatment of fabrics with/without insulating (dielectric) on the electrode. From SEM images show that "if the fabrics are placed during treatment directly on the grounded aluminium cylinder, a localised strong degradation of the fabric takes place for both fabrics (Figure 2.13 and Figure 2.14), with fibres melting at the locations were the fibre or filament cross each other in the weave. The effect is most probably due to nonhomogeneities in the discharge. This phenomenon is readily visible even using very short treatment times, e.g. 0.2 s".

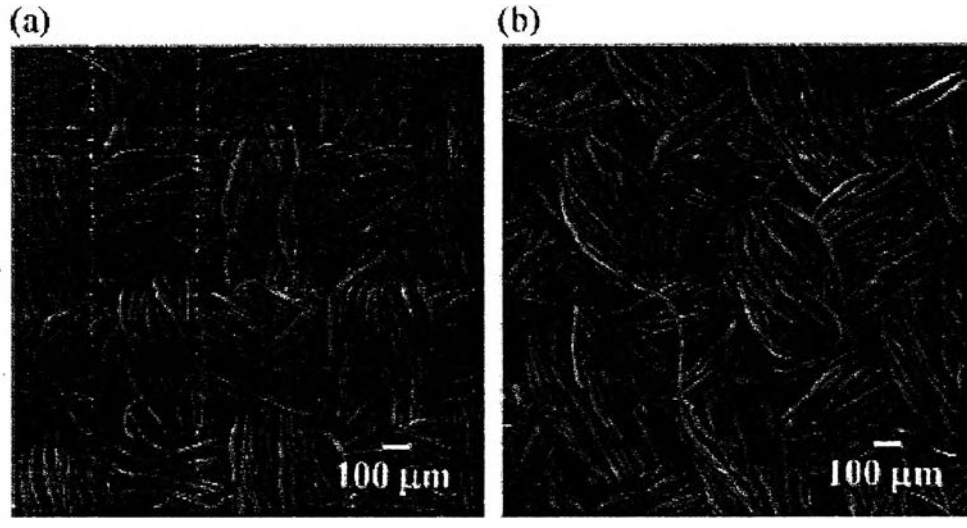

Figure 2.13 SEM images of polyester fabric: (a) untreated, (b) 0.2 s air–DBD treated, placed directly on the grounded aluminium cylinder (Borcia *et al.*, 2006).

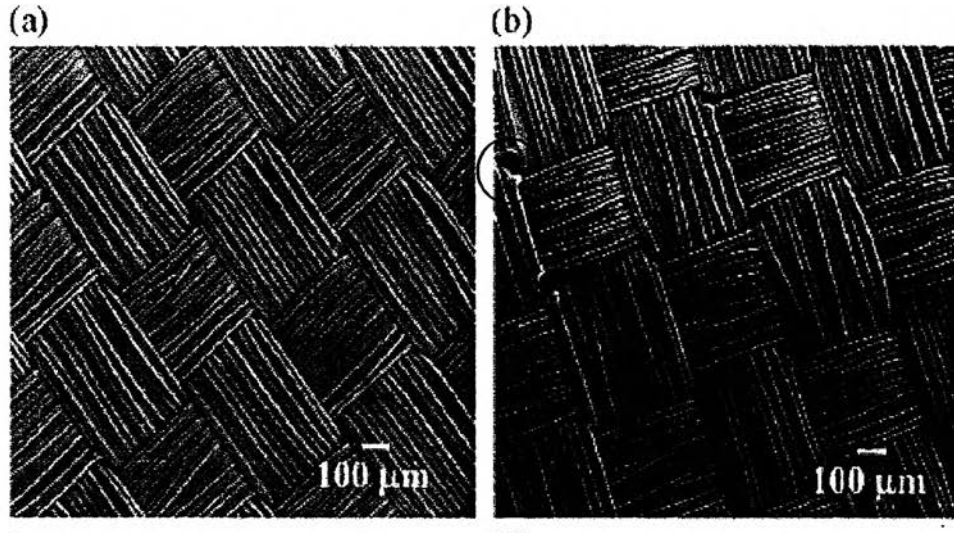

Figure 2.14 SEM images of nylon fabric: (a) untreated, (b) 0.2 s air–DBD treated, placed directly on the grounded aluminium cylinder (Borcia *et al.*, 2006).

Besides the effect of addition of polymer film (dielectric), they also determined the effects of the operating parameters (dielectric layer make-up, discharge energy density, gas flow, gas type and exposure time). From their experiment found that type of gas has no significant effect for the treatment, but surface properties, such as the wickability and the level of oxidation were increased markedly after treatment times of the order of fractions of a second, with minimal change. Due to the basic objectives of any surface treatment are:

- The removal of the inherent loosely-bonded surface contamination.
- The introduction of stable chemical functionalities providing proper nucleation and chemical bonding sites for subsequent over-layer deposition.
- Enhance the hydrophilicity.

In the same year, Weilen *et al.*, (2006) study the surface modification of cellulosic fibers using dielectric-barrier discharge with different treatment intensity. The characterization results indicated that wet-strength and wet-stiffness was improved. Treated fiber surfaces undergo selective oxidation, degradation, and removal of extractives and other contaminants. And also found that "fiber wettability in water increases with low dielectric-barrier discharge treatment

(1.0 kW m^{-2} min), but diminishes with increased treatment intensity (5.0 kW m^{-2} min). This is related to changes in the polar and dispersive components of surface energy. Reductions in surface energy at increased treatment levels occur due to oxidative reactions.

2.3.3 Advantages of Plasma Treatment

In plasma processing technology, plasmas generated in inert gases and/or reactive gases can clean the surface of materials and modify their characteristics, particularly their surface energy. Active species from the plasma react with monolayer on the surface of materials and change their surface properties either temporarily or permanently (Borcia *et al.*, 2006). The surface properties of materials modified using plasma treatment can lead to processes such as polymerization, grafting, cross-linking, etc., with concomitant effects on wetting and wicking, dyeing, printing, surface adhesion, electrical conductivity and other characteristics

This technique is dramatically developed during the past decade, due to its advantages such as it is a rapid process, which can produce higher energetic species, higher temperature and energy density and it can effectively achieve modification of this near-surface region without affecting the bulk properties of the materials of interest. Besides, it is environmental friendly process because no chemical used and no waste released.

In 2009, Wolkenhauer *et al.*, compared sanding and plasma treatment by dielectric barrier discharge (DBD) with respect to their effects on wood surface characteristics (beech, oak, spruce, and Oregon pine). Sanding generates a new and fresh surface by removing the material, whereas plasma treatment affects primarily the chemical composition. They examined the surface energy by contact angle measurement and calculation of work of adhesion and found that "for both methods, an increase in surface energy caused by a heavily increased polar part was found". Plasma treatment turned out to be superior to sanding, but a combination of sanding and plasma treatment would lead to an additional increase in the surface energy.

Surface modification of wool, polyamide 6 and cotton fabrics was investigated with an Ar–CF4 post-discharge plasma to improve hydrophobic and

antimicrobial properties by Canal *et al.*, (2009). It found that "only wool and polyamide 6 fluorinated surfaces become hydrophobic at long treatment times, and show antibacterial properties. The treatment conditions used are mild enough so as not to alter surface topography, as confirmed by scanning electron and atomic force microscopy."

The plasma process parameters such as electrode gap, time of exposure and radio frequency (RF) power have been varied to study their effect in improving the hydrophilicity of the cotton fabric by Vaideki *et al.*, (2008). The neem leaf extract (azadirachtin) was applied on fabric samples to impart antimicrobial activity. They found that "maximum hydrophilicity and hence antimicrobial activity is obtained for a 50 W RF power, air pressure of 0.5 mbar, electrode gap of 3 cm and a time of exposure of 5 min". The antimicrobial activity was analysed by agar diffusion test (SN 195920). The zone of inhibition against bacteria and fungi are shown in Fig. 2.15a and b, respectively. From the figures, it is evident that "the RF air plasma treatment prior to the application of the antimicrobial finish increases the antimicrobial efficacy of the fabric.

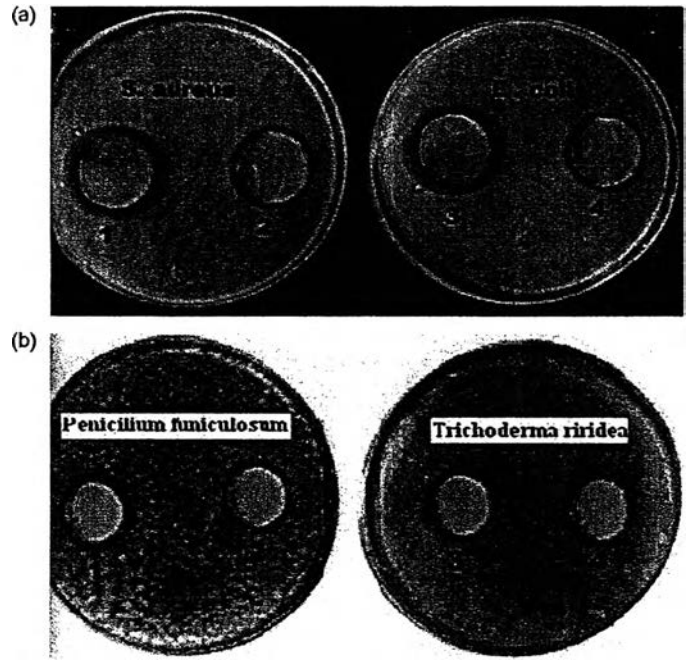

Figure 2.15 Zone of inhibition against (a) bacteria (b) fungi (1 and 3) RF air plasma and azadirachtin treated cotton fabric (2 and 4) azadirachtin treated cotton fabric.