

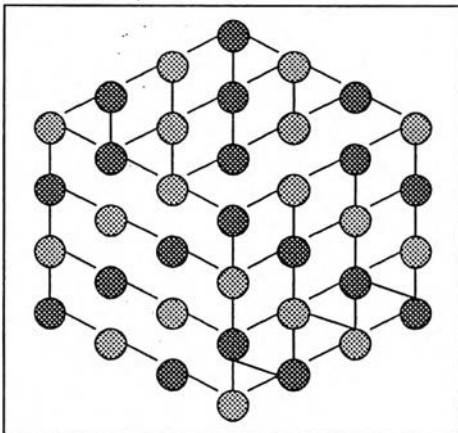


CHAPTER II

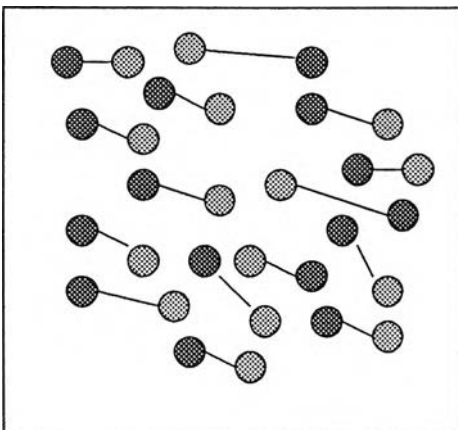
LITERATURE REVIEW

2.1 Plasma

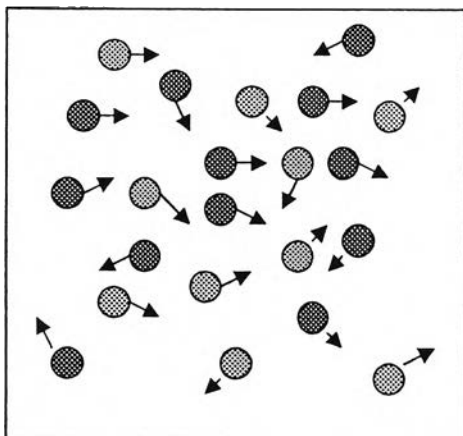
Plasma is ionized gas. It consists of positive and negative ions, electrons, as well as free radicals. The ionization degree can vary from 100% (fully ionized gas) to very low values (partially ionized gas). The plasma state is often referred to as the fourth state of matter. Much of the visible matter in the universe is in the plasma state. Stars, as well as visible interstellar matter, are also in the plasma state. Besides the astro-plasmas, which are omnipresent in the universe, laboratory plasma can be also divided into two main groups, i.e. the high temperature or fusion plasma, and so called low-temperature plasmas or gas discharges (Lieberman *et al.*, 1994).



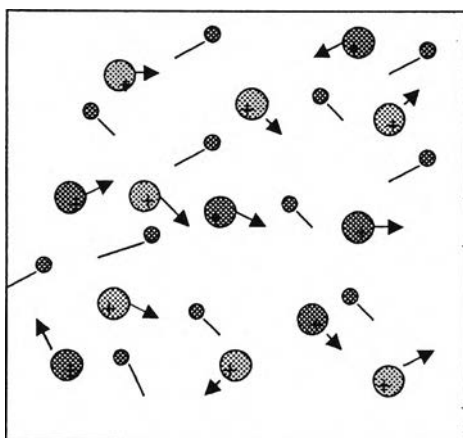
At very low temperatures, matter is in a solid state with the atoms arranged in well-organized grids.



When temperature increases above a critical value, solids melt and become a liquid. The grid of atom is broken, but molecular bonds are maintained.



A liquid heated above a second critical temperature turns into a gas.



If we keep raising the temperature, the electrons and the nucleus that constitute an atom no longer can stay together, the atoms are stripped of their electrons, and plasma is formed.

Just like other states of matter, plasmas occur naturally as well. Lightning and Auroras are some classic examples. However, plasmas can be generated artificially at laboratory levels for practical applications. It is understood that a continuous source of energy is required to generate and sustain a state of matter. Man-made plasmas are commonly generated and sustained using electrical energy and are often referred to as 'discharges'.

In general, plasmas are realized by the generation of free electrons that make the gas conductive. These electrons obtain energy from the electric field and further ionize, excite, and dissociate gas molecules via energy transfer during collisions. This makes plasmas very reactive. Also, plasmas possess higher temperatures and energy densities in comparison with most other chemical processes, which make them interesting and efficient for various applications. They can be generated over a wide range of pressures with different electron temperatures and densities. Most applied plasmas have electron temperatures between 1 – 20 eV (1 eV

$\approx 1.6 \times 10^{-19}$ Joule ≈ 11600 K) and densities between $10^6 - 10^{18}$ (electrons/cm³) (Fridman and Kennedy, 2004).

The applicability of artificially generated plasma varies based on its nature. Hence, it is necessary to identify and classify the nature of plasma generated in order to evaluate its candidature for a given application. This classification is discussed in the next section.

2.1.1 Types of Plasma

Plasma state can be divided in two main categories: equilibrium plasmas (thermal plasmas) and non-equilibrium plasmas (non-thermal plasmas) (Denes *et al.*, 2002). Hot plasmas include electrical arcs, plasma focus, plasma jets of rocket engines, thermonuclear reaction generated plasmas, etc., while cold plasmas include low-pressure direct current (DC) and radio frequency (RF) discharges (silent discharges), and discharges from fluorescent (neon) illuminating tubes. Corona discharges are also identified as cold plasmas. Corona treatment is one of the most interesting techniques for surface oxidation activation. This process changes the surface energy of the fibers. Electrical discharge (corona and plasma) methods are known to be very effective for non-active polymer substrates, such as PS, PE, and PP.

2.1.1.1 *Equilibrium Plasma or Thermal Plasma*

As the name suggested, thermal plasmas are ‘hot’. They have high gas temperatures (usually $> 10,000$ K). Due to equilibrium distribution of energy between electrons and gas molecules, the average electron temperature (T_e) is approximately equal to average gas temperature (T_g). Hence, thermal plasmas are characterized by low electric fields and high pressures. These plasmas are usually sustained at high power densities (power input per unit volume) and have low chemical selectivity. Also, the number density (number per unit volume) of electrons (n_e) is comparable to that of the gas (n), i.e. ionization degree, $n_e/n \geq 10^{-3}$. Lightning and thermal arc discharges (shown in Figure 1) are examples of naturally occurring and artificially generated thermal plasmas, respectively.

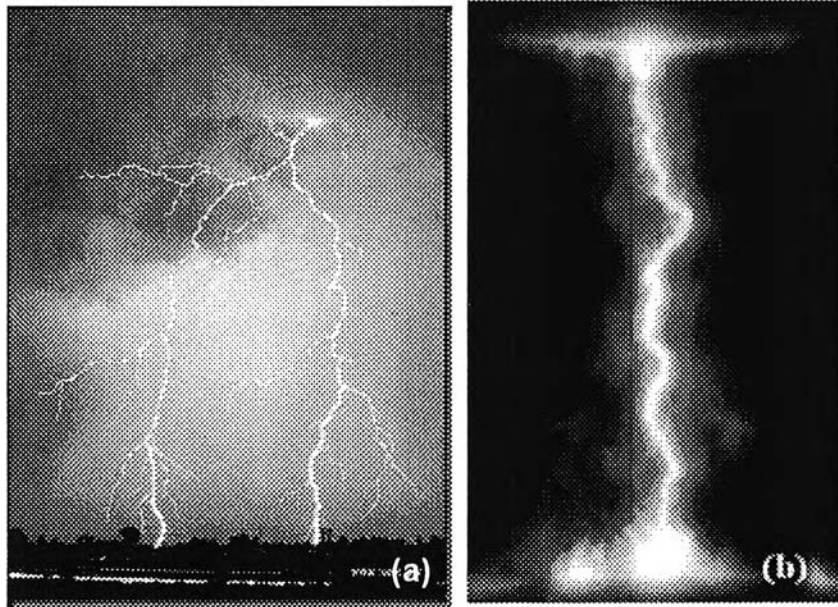


Figure 2.1 Examples of naturally occurring and artificially generated thermal plasmas: (a) lightning and (b) arc discharge.

2.1.1.2 Non-equilibrium or Non-thermal Plasma

On the other hand, non-thermal plasmas are characterized by high electric fields and low pressures. This implies that the average electron and gas temperatures significantly differ from each other, hence the name being ‘non-equilibrium’ plasma. Here, electron temperature (T_e) is extremely higher than gas temperature (T_g). The gas temperatures in non-thermal plasmas can vary from 300 – 3000 K. They operate at low power densities, but have very good chemical selectivity. Also, the ionization degree is usually $n_e/n \leq 10^{-5}$ in these plasmas. Auroras and low pressure glow discharges (shown in Figure 2) are examples of naturally occurring and artificially generated non-thermal plasmas, respectively.

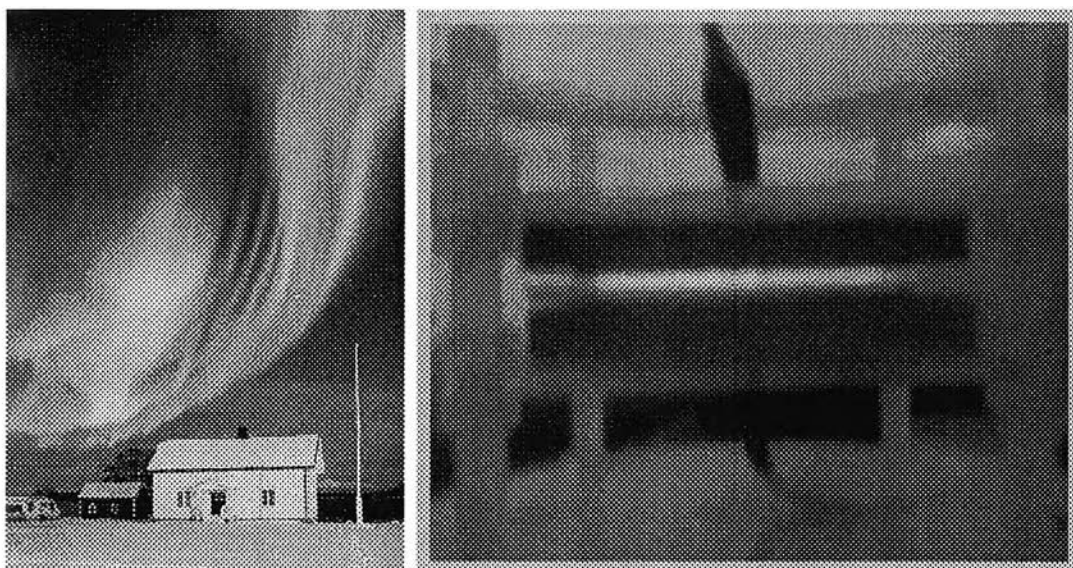


Figure 2.2 Examples of naturally occurring and artificially generated non-thermal plasmas: (a) aurora and (b) dielectric barrier discharge.

2.2 Plasma Generation

Plasmas are generated by supplying energy to a neutral gas, causing the formation of charge carriers (Figure 3). Electrons and ions are produced in the gas phase when electrons or photons with sufficient energy collide with the neutral atoms and molecules in the feed gas (electron-impact ionization or photo ionization).

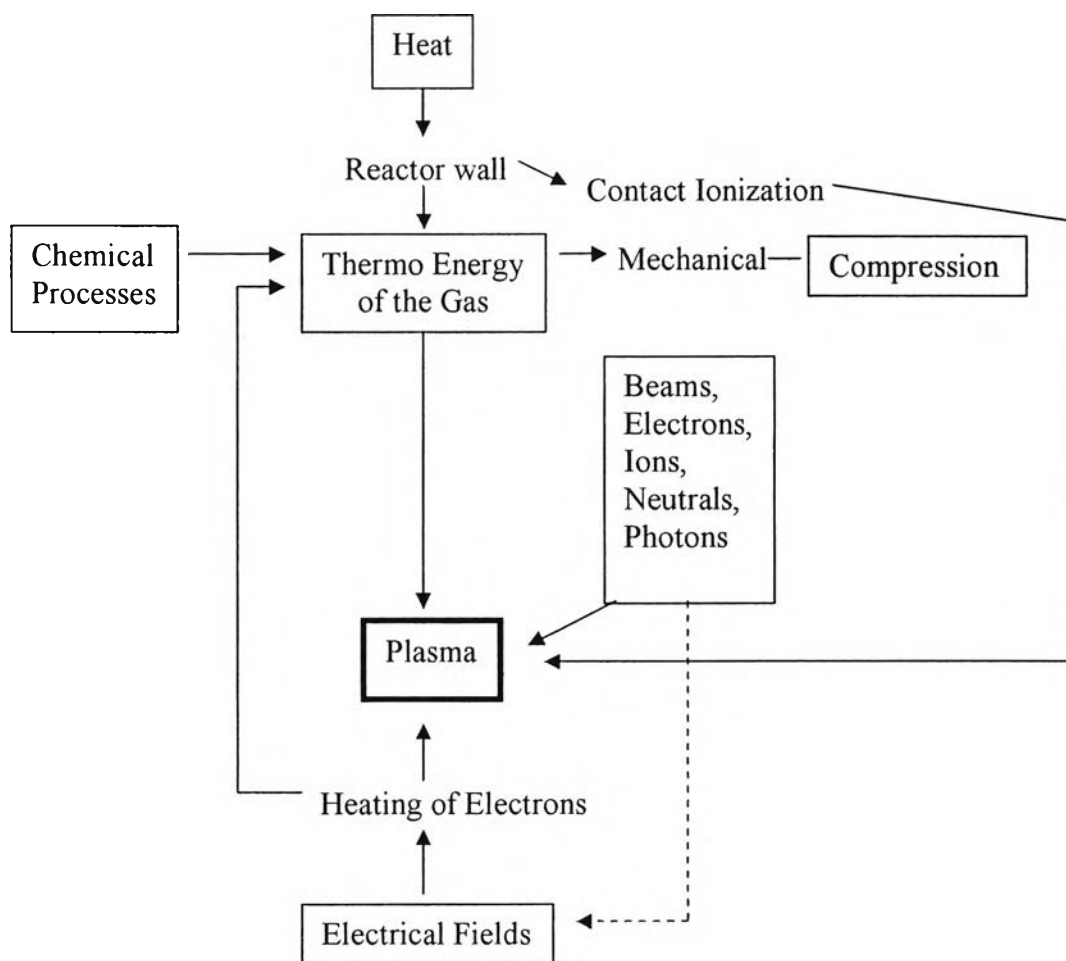


Figure 2.3 Principles of plasma generation.

There are various ways to supply the necessary energy for plasma generation to a neutral gas. However, the most commonly used method of generating and sustaining a low-temperature plasma for technological and technical application is by applying an electric field to a neutral gas. Any volume of a neutral gas always contains a few electrons and ions that are formed, for example, as the result of the interaction of cosmic rays or radioactive radiation with the gas. These free charge carriers are accelerated by the electric field, and new charged particles may be created when these charge carriers collide with atoms and molecules in the gas or with the metal surfaces of the electrodes.

The electrons liberated from the metal surface will immediately be accelerated to move corresponding to the direction of the electric field, and then can

collide with any neutral gaseous particles in their vicinity to form the ionized gases with an additional set of electrons. Accordingly, these electrons can further move and collide with other species. As a result, a large quantity of electrons, including the excited atoms and molecules, ions, and radicals, can be formed in the bulk of the gases within a very short period of time after the application of electric field has been started. Many active species can initiate the chemical reactions, leading to the production and destruction of the chemical species (Kruapong, 2000). Table 1 shows some important collision mechanisms. The combined steps of the field emission process among these plasma species and the collisions between the species and the electrode surfaces are referred to as “electric discharges” phenomena.

Table 2.1 Collision mechanisms in the plasma (Nasser, 1971)

Collision	Reaction
Elastic Collision	$e^- + A \longrightarrow e^- + A$
Excitation	$e^- + A \longrightarrow e^- + A^*$
Ionization	$e^- + A \longrightarrow 2e^- + A^+$
Attachment	$e^- + A \longrightarrow A^-$
Dissociative Attachment	$e^- + B_2 \longrightarrow B^- + B$
Recombination	$e^- + B_2^+ \longrightarrow B_2$
Detachment	$e^- + B_2^- \longrightarrow 2e^- + B_2$
Ion Recombination	$A^- + B^+ \longrightarrow AB$
Charge Transfer	$A^\pm + B \longrightarrow A + B^\pm$
Electronic Decomposition	$e^- + AB \longrightarrow e^- + A + B$
Atomic Decomposition	$A^* + B_2 \longrightarrow AB + B$

2.3 Types of Non-equilibrium Plasmas

It is customary to divide non-equilibrium plasmas into distinctive groups, depending on the mechanism used for their generation, their pressure range, or the

electrode geometry. In this section, the most notable characteristics of the following five non-equilibrium discharges are briefly listed:

2.3.1 Glow discharge

2.3.2 Corona discharge

2.3.3 Microwave discharge

2.3.4 Radio Frequency discharge

2.3.5 Gliding arc discharge

2.3.6 Silent discharge (dielectric barrier discharge), which the latter will be used in this study.

In figure 2.4, the discharges are grouped according to their temporal behavior, pressure range, and appearance.

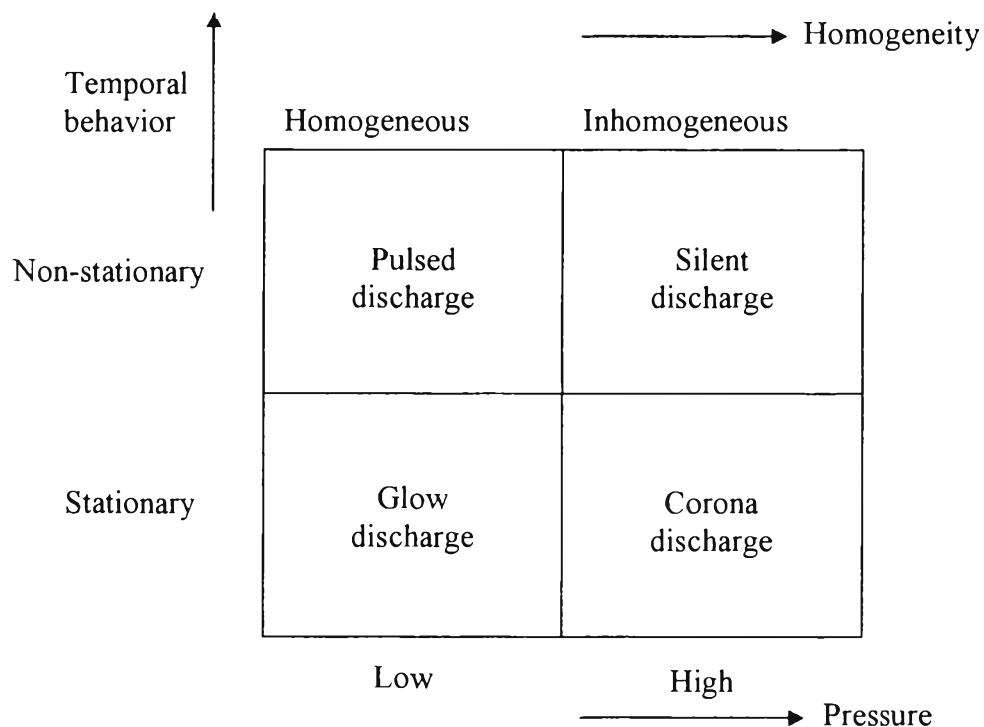


Figure 2.4 Various discharge types arranged according to temporal behavior, pressure, and appearance.

2.3.1 Glow Discharge

The stationary glow discharge is a low-pressure discharge, usually between flat electrodes encapsulated in a tube (Figure 5). Since the pressure is typically smaller than 10 mbar, the reduced field can therefore be quite high. Due to the high energy of the electrons, they excite the neutral atoms and molecules, easily producing for each gas a typical glow (therefore the name). This is the discharge of the fluorescent tube. Typical parameters of glow discharges are summarized as follows:

Pressure	< 10 mbar
Electric field	10 V/cm
Reduced field	50 Td
Electron energy	0.5-2 eV or 5000-20000 K
Electron density	$10^8 - 10^{11} \text{ cm}^{-3}$
Degree of ionization	$10^{-6} - 10^{-3}$

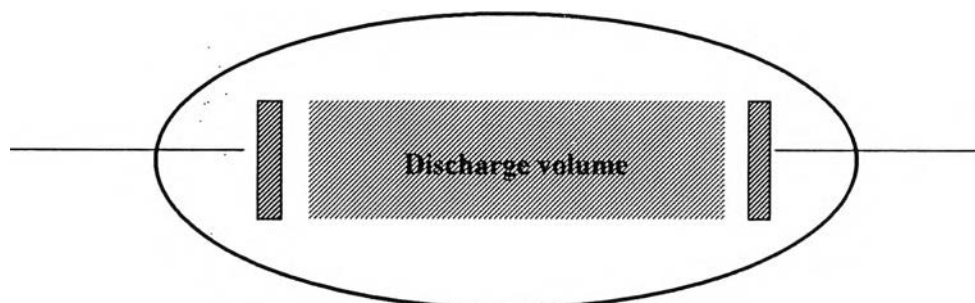


Figure 2.5 The glow discharge-homogeneous discharge at low pressure.

Because of the low pressure and the resulting low mass flow, the glow discharge has not been used for industrial production of chemicals. In the lighting industry, however, the neon tubes used for outdoor advertising and the fluorescent tubes are examples of practical applications of glow discharges. Miniature glow discharges can also be found in the new energy-efficient light bulbs.

2.3.2 Corona Discharge

At higher pressures and fields, one normally finds that the discharge becomes highly unstable and turns into a high-current arc discharge if the power

supply provides enough current. One way of stabilizing the discharge at high pressure is the use of inhomogeneous electrode geometries; e.g. a pointed electrode and a plane, such as in Figure 6.



Figure 2.6 The corona discharge-inhomogeneous discharge at atmospheric pressure.

2.3.3 Microwave Discharge

In the microwave region (0.3-10 GHz), the wavelength of the electromagnetic field becomes comparable to the dimensions of the discharge vessel, which necessitates other coupling mechanisms. Most microwave-induced plasmas are produced in a waveguide structure or resonant cavity. As the dimensions of the cavities diminish when the frequency increases, the maximum microwave frequencies used for discharge applications are usually below 3 GHz. A very common frequency is 2.45 GHz, which is also used in microwave ovens.

An interesting development is the use of microwaves to induce surface-wave-sustained discharges (Chaker M. *et al.*, 1986). They can operate over a large frequency and pressure range and can produce large-volume non-equilibrium plasmas of reasonable homogeneity. The plasma is contained in a dielectric tube of a few centimeters diameter and is sustained by an electromagnetic wave, which uses only the plasma column and the tube as its propagating media. Plasma columns of up to 4-m length have been thus produced. Due to the large pressure range, under which these discharges can be operated, electron densities between 10^8 and 10^{15} cm^{-3} have been reported. These surface wave plasmas have many similarities with the positive column of a glow discharge. Applications so far have been limited to elemental analysis and lasing media. The ease of operation and the possibility of imposing a gas flow make these discharges attractive also for plasma chemical investigations.

2.3.4 Radio Frequency Discharge

Radio frequency (RF) discharges are used extensively in the laboratory to produce plasmas for optical emission spectroscopy and for plasma chemical investigations. The inductively coupled plasma (ICP) operation is that the electrodes can be kept outside of the discharge volume, thus avoiding electrode erosion and contamination of the plasma with metal vapor. Since the wavelength of the electric field is much larger than the vessel dimensions, reasonably homogeneous plasmas can be generated. RF discharges work well at low pressure, but are used also at atmospheric pressure. Low-pressure RF discharges for etching purposes have found widespread applications in semiconductor manufacturing. As long as the collision frequency is higher than the frequency of the applied field, the discharge behaves very much like a dc discharge. This implies that non-equilibrium conditions can be expected at low pressures, whereas thermal plasmas are generated at about atmospheric pressure. Figure 2.7 shows three typical electrode configurations for RF discharges. While Figure 2.7(a) and (b) use capacitive coupling and are mainly used at low pressure, the configuration shown in Figure 2.7(c) uses inductive coupling by placing the discharge in the magnetic field of an induction coil. This arrangement is typical for RF torches and is used at pressures of up to 1 bar.

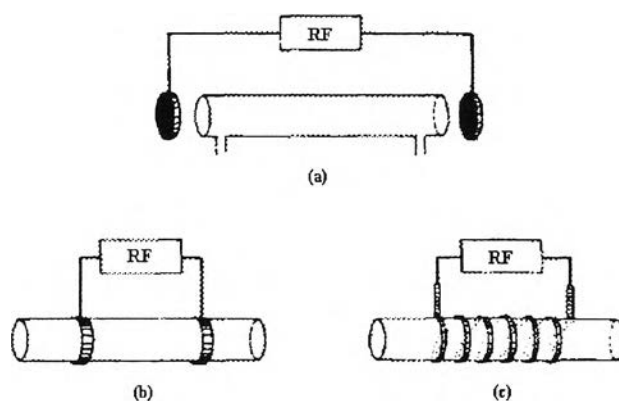


Figure 2.7 Typical arrangements for radio frequency discharges: (a) and (b) contain capacitive coupling, normally used at low pressure, (c) use inductive coupling instead of capacitive coupling, which can be operated at pressure up to 1 bar.

2.3.5 Gliding Arc Discharge

The gliding arc discharge is a cold plasma technique, which has at least two diverging knife-shaped electrodes. These electrodes are immersed in a fast flow of feed gas. A high voltage and relatively low current discharge are generated across the fast gas flow between the electrodes. The electric discharge forms at the closet point, spreads along the knife-edges of the electrodes, and disappears. Another discharge immediately reforms at the initial spot. Figure 2.8 is considered to be the simplest case for a better physical understanding of the gliding arc phenomenon (Fridman *et al.*, 1999).

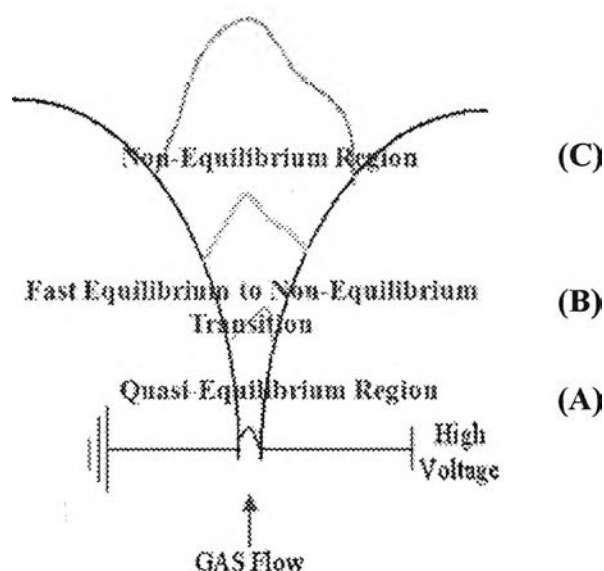


Figure 2.8 Phase of gliding arc phenomena: (A) reagent gas break-down; (B) equilibrium heating phase; and (C) non-equilibrium reaction phase.

The reagent gas break-down (A) of the processed gas begins the cycle of the gliding arc evolution. The high voltage generator provides the necessary electric field to break down the gas between the electrodes.

The equilibrium-heating phase (B) takes place after formation of stable plasma channel. The electric discharge spreads along the electrodes, which the velocity of the gas flow and the gliding arc are very close.

The non-equilibrium reaction phase (C) begins heat loss from the plasma to exceed the energy supplied by the source, and it is not possible to sustain the plasma in the state of thermodynamic equilibrium. As a result, the discharge plasma rapidly cools to the gas temperature. After the decay of the non-equilibrium discharge, there is new break-down at the shortest distance between the electrodes, and the cycle repeats (Fridman *et al.*, 1999).

2.3.6 Silent discharge (Dielectric Barrier Discharge)

The silent discharge is predestined for applications in volume plasma chemistry. First experimental investigations were reported by Siemens (Ulrich, 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 silent discharge 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 silent discharge configuration are shown in Figure 2.9.

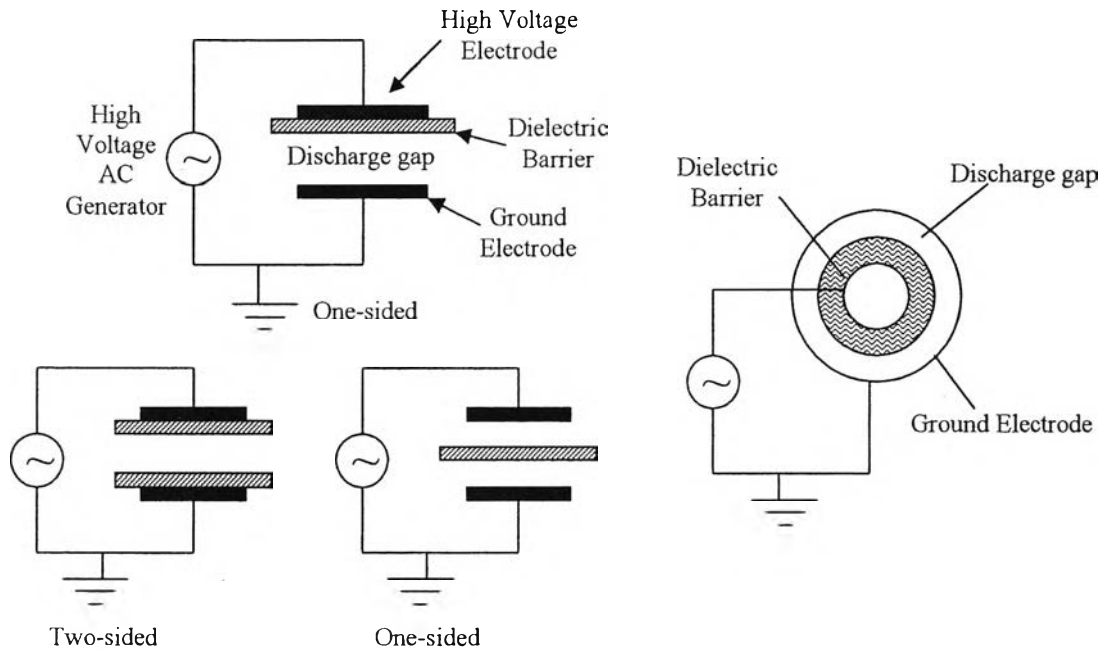


Figure 2.9 Common dielectric barrier discharge configurations with one or two dielectric barriers and micro-discharges are contained in the discharge gap (Conrads H. *et al.*, 2000).

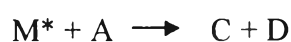
As a consequence of the presence of at least one dielectric barrier, these discharges require alternating voltages for their operation. The dielectric, being an insulator, cannot pass a DC current. To transport current (other than capacitive) in the discharge gap, the electric field has to be high enough to cause breakdown in the gas. In most applications, the dielectric limits the average current density in the gas space. It thus acts as ballast, which, in the ideal case, does not consume energy. Preferred materials for the dielectric barrier are glass or silica glass, in special cases also ceramic materials, and thin enamel or polymer layers. In some applications, additional protective or functional coatings are applied.

Also in figure 2.9, annular discharge gaps between cylindrical electrodes and dielectrics are used in many technical applications. The discharge gap itself has a typical width ranging from less than 0.1 mm to several centimeters, depending on the application. To initiate a discharge in such a discharge gap filled with a gas at about atmospheric pressure, voltages in the range of a few hundred V to several kV are required.

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 N₂ and mixed N₂ + 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 roughnesses 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.

2.4 The Chemistry of Non-equilibrium Discharge

It is mainly the fast electrons created by the discharge that initiate the chemistry, which takes place in the plasma. Firstly, the accelerated electrons are created by discharge mechanism. Secondly, such electrons collide with neutral gas and excite them to higher energy state. Finally, the excited gas molecules can either dissociate or initiate to the new chemical species because of their high energy level. The same can also applied to ions. For example, the reaction schematic might look like this (McQuarrie *et al.*, 1987):



Where M, A are reactants.

C, D are products.

M* is the excited reactant marked by an asterisk (*).

As the reaction $A + M \rightarrow C + D$ might only take place at very high temperatures, but in this case the product C and D can be obtained at the lower temperature induced by non-thermal plasma.

Besides transferring energy to gas molecules via fast electrons and ions, photon can also involve with initiating the new chemical species if it is energetic enough. The photon is taken place by emitting energy of excited molecules to lower state. The characteristics of electron and photon are therefore quite different.

2.5 Interaction of Plasmas with Polymer Surfaces

In the plasma treatment of polymers, energetic particles and photons generated in the plasma interact strongly with the polymer surface, usually via free radical chemistry. In plasma which does not give rise to thin film deposition, four major effects on surfaces are normally observed. Each is always present to some degree, but one may be favored over the others, depending on the substrate and the gas chemistry, the reactor design, and the operating parameters. The four major effects are (Mittal, 1994):

(a) Surface cleaning: This is one of the major reasons for improved bonding to plasma-treated surfaces. Most other cleaning procedures leave a layer of organic contamination that interferes with adhesion processes; of course, any clean surface rapidly requires a layer of contamination when exposed to ambient atmosphere. Oxygen-containing plasmas are capable of removing organic contamination from inorganic and polymeric surfaces, but it is critically important to plasma-clean a polymer for a sufficiently long time to remove all of the surface contamination. Almost all commercial polymer films, and most moulded parts, contain additives or contaminants, such as oligomers, anti-oxidants, mould release agents, solvents, or anti-block agents, which are oily or wax-like. Most of these are deliberately incorporated into polymer formulation to improve its properties or manufacturability, and they are designed to 'bloom' to the surface and to coat that surface.

(b) Ablation or etching: Ablation is distinguished from cleaning only by the amount of material that is removed. Ablation is important for the cleaning of badly

contaminated surface, for the removal of weak boundary layers formed during the fabrication of a part, and for the treatment of filled or semi-crystalline materials. This change in surface morphology can improve mechanical interlocking, and it can increase the area available for chemical interactions.

(c) Cross linking or branching: CASING (Crosslinking via Activated Species of Inert Gas) is one of the earliest-recognized plasma treatment effects on polymer surface. As suggested by the acronym, CASING occurs in polymer surfaces exposed to noble gas plasmas (e.g. He or Ar), which are effective at creating free radicals but do not add new chemical functionalities from the gas phase. Ion bombardment can break C-C or C-H bonds, and the free radicals resulting under these conditions can only react with other surface radicals or with other chains in chain-transfer reactions; therefore, they tend to be very stable. If the polymer chain is flexible, or if the radical can migrate along it, this can give rise to recombination, unsaturation, branching, or crosslinking. The latter may improve the heat resistance and bond strength of the surface by forming a very cohesive skin.

(d) Modification of surface-chemical structure: The most dramatic and widely reported effect of plasma is the deliberate alteration of the surface region with new chemical functionalities capable of interacting with adhesives or other materials deposited on the polymer, which can occur during plasma treatment itself, and upon re-exposure of the treated part to air, at which time residual free radicals can react with atmospheric oxygen or water vapor.

2.6 Literature Survey on Surface Modification of Polymers by Plasma Treatment

In 2003, Simor *et al.* reported that the atmospheric-pressure nitrogen plasma treatment of polyester nonwoven fabrics for electroless plating. The plasma was produced in a surface barrier discharge generating a thin plasma layer in good contact with the fabric fibers. The optimum quality nickel coating was obtained for a 1 s treatment time. Treatment times longer than 1 s resulted in a reduction of the nickel plating deposition rate, uniformity, and adhesion values. The plasma-induced

surface changes were characterized by liquid strike-through time measurements, X-ray photoelectron spectroscopy, and scanning electron microscopy. Because of atmospheric-pressure operation, very short treatment times, and its robustness, the method has the potential to be used in line with standard metal plating lines.

Borcia *et al.* (2003) studied on 80 kHz dielectric barrier discharge (DBD) in air for the treatment of PET and nylon fabrics, and recently a DBD in air, nitrogen, or argon for the treatment of natural, synthetic, and mixed fabrics (Borcia, et al., 2006). The enhanced wettability and wickability appeared to be strongly increased within the first 0.1–0.2 s of treatment. Any subsequent surface modification following longer treatment (>1.0 s) was less important. The increased wettability could be attributed to the increased level of oxidation, where supplementary polar functionalities are created on the fabric fibre surface, as observed by X-ray photoelectron spectroscopy (XPS).

In 2004, Yang and Gupta demonstrated that an atmospheric-pressure plasma source could be used to modify PET surfaces using a gas mixture of helium and oxygen. It was found that contact angle could be reduced from 70 to 28° in less than 1 s of exposure time, and analysis on ion energy suggested that ions have no direct contribution to the surface modification. The absorption spectroscopy measurements indicated the presence of ozone and oxygen atoms that are responsible for the surface modification.

After that, in 2005, Esena *et al.* reported the surface modification of polyethylene terephthalate film (PET) after the exposure to an atmospheric pressure air dielectric barrier discharge (DBD). The treated surface has been analyzed using atomic force microscopy (AFM) and contact angle measurement. The AFM analysis showed that the surface roughness increases with the duration of exposure to air-plasma, and the modification of the shape of surface features is evident, as shown in Figure 2.10.

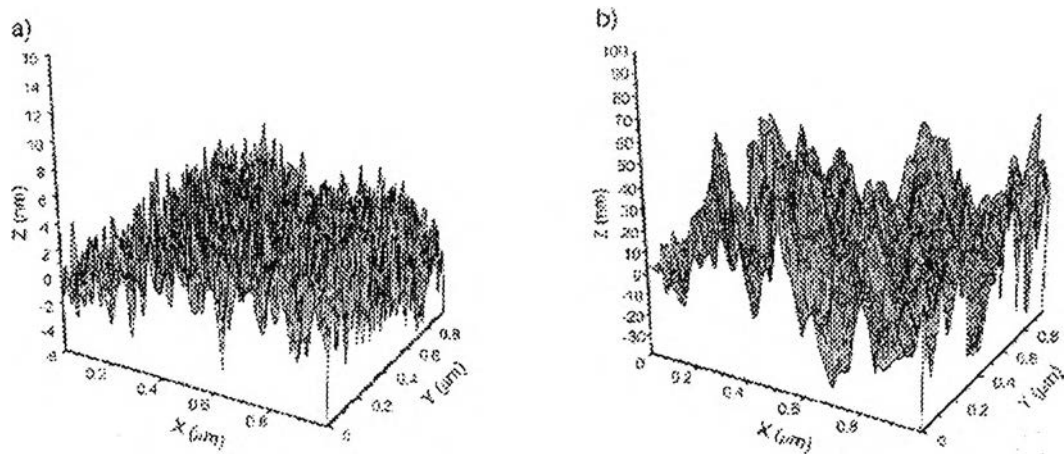


Figure 2.10 Three-dimensional views obtained with AFM scans of the PET sample (scan area $1 \times 1 \mu\text{m}^2$), where (a) is the untreated surface and, (b) represents the 17 s treated surface.

Roughness changes in both amplitude and peak spacing, and surface modifications cause both optical properties changes and enhancement of adhesive to coatings and depositions. The applications of these results can regard, for example, the increase in wettability and printability (as the decrease in contact angle values), the increase in adhesion, and the change in the optical properties, such as the increase in reflectivity in the UV and visible wavelength range.

Recently, Esena *et al.* (2008) studied the optical surface effects on PET films after dielectric barrier discharge (DBD) treatment operating at atmospheric pressure. The increase in reflectivity versus wavelength is linear in PET samples treated by atmospheric pressure plasma due to the interaction of light with surface roughness, which depends on wavelength. The increase is larger for smaller wavelengths. These results support the idea that the effects of air-plasma treatment on the PET are due to plasma bombardment of the surface and scission of the polymeric chains, as well as due to oxidation processes. In fact, ozone and oxygen-based highly reactive radical species produced by internal microdischarges can cause oxidation, resulting in the production of carbonylic, hydroxylic, and carboxylic groups originated by breaking of C-H and C-C bonds. This result agrees with the increase in reflectivity.

In 2006, De Geyter et al. reported the modifications of non-woven polyester by plasma treated with a dielectric barrier discharge (DBD) in air at medium pressure (5.0 kPa) and at different discharge powers. Results showed that an increasing power leads to a better plasma treatment of the sample.

Also in 2007, De Geyter et al. studied the modification of polyester (PET) and polypropylene (PP) films by a dielectric barrier discharge in air, helium, and argon atmospheres at medium pressure (5.0 kPa). It was found that the polymer films modified in air, helium, and argon showed a remarkable increase in hydrophilicity due to the implantation of oxygen-containing groups, such as C–O, O–C=O, and C=O. In the formation of oxygen-containing functionalities on the polymer surfaces, it is shown that air plasma is more efficient in implanting oxygen functionalities than an argon plasma, which is more efficient than a helium plasma. In an air plasma, most of the created radicals at the polymer surface will quickly react with an oxygen particle, resulting in an efficient implantation of oxygen functionalities.

Plasma-surface modification (PSM) is an effective and economical surface treatment technique for many materials, also with growing interests in medical application.

In 1997, Latkany et al. modified artificial corneas for optimal epithelialization by using argon RF plasma. It was found that cells become confluent on the argon-plasma-treated surfaces and turn multilayered after incubation for 2 weeks. At the same time, adhered proteins are present only when the surface is treated with argon RF plasma. The acetone- and ammonia-treated surfaces do not yield the desired results. The organ culture experiments further demonstrate the efficacy of the argon plasma technique. In addition, intact keratoprosthesis devices with modified hydrogel surfaces have been implanted into rabbit corneas, and it was found that the limbal epithelial cells can migrate to a synthetic cornea containing a modified hydrogel-treated surface and form a confluent surface of epithelium. The treated artificial corneas possess better biocompatibility.

In 2006, Chu worked on plasma modification of orthopedic materials, including titanium and nickel–titanium shape memory alloys, as well as diamond-like carbon (DLC) as cardiovascular materials. NiTi alloys that possess shape

memory and super-elastic properties are of interest in spinal deformity correction. Shape recovery inside the human body allows for less traumatic gradual correction while obviating the needs for multiple surgeries. However, leaching of harmful nickel ions from the materials causes health hazards. To reduce leaching of harmful Ni ions from the NiTi alloy, the researcher performed plasma immersion ion implantation (PIII) to form a barrier layer consisting of TiC, TiN, or TiO to impede Ni out-diffusion by taking advantage of the preferential formation of Ti–O, Ti–C, or Ti–N bonds, thereby depleting Ni from the implanted surfaces. Plasma surface modification enhanced the surface bioactivity of Ti by conducting Ca plasma implantation into Ti, and enhanced bone bioactivity was observed. And, the properties of DLC can be enhanced by doping with adventitious elements, such as nitrogen and phosphorus. The doped DLC films were synthesized by operating a carbon filtered cathodic arc source in concert with a nitrogen/argon plasma in an immersion configuration, and doping and film fabrication were carried out in the same vacuum chamber without breaking vacuum. The blood compatibility of the materials was evaluated utilizing *in vitro* platelet adhesion tests. It was found that the P-doped DLC coating surface significantly minimizes the interactions with blood plasma proteins. Further analysis showed that the surface of P-doped DLC has excellent wettability

2.7 Chitosan

2.7.1 Basic Principles of Chitosan

Chitosan is the deacetylated derivative of chitin that is the second most abundant polysaccharide found on earth next to cellulose. There is not a sharp boundary in the nomenclature distinguishing chitosan from chitin. When chitin is deacetylated over about 60%, it becomes soluble in dilute aqueous acids and is referred to as chitosan. Chitin is the main component in the shells of crustaceans, such as shrimp, crab, and lobster. It is also found in exoskeletons of mollusks and insects, and in the cell walls of some fungi (Muzzarelli, 1977, Roberts, 1992). Chitosan is found in some fungi, but its quantity is so limited that it is mainly produced commercially by alkaline deacetylation of chitin (Roberts, 1992).

Huge amounts of crab and shrimp shells have been abandoned as wastes by worldwide seafood companies. This has led to considerable scientific and technological interest in chitin and chitosan as an attempt to utilize these renewable wastes (Hudson *et al.*, 1998). Chitosan has become the preferred commercial form of these materials, as it is more tractable to solution processes than chitin. In the past thirty years, it has been demonstrated by a number of researchers that chitosan has a great potential for a wide range of uses due to its biodegradability, biocompatibility, antimicrobial activity, nontoxicity, and versatile chemical and physical properties. The applications of chitosan include uses in a variety of areas, such as pharmaceutical and medical applications, paper production, textile dyeing and finishing, fiber formation, wastewater treatment, biotechnology, cosmetics, food processing, and agriculture (Dunn *et al.*, 1997).

2.7.2 Chemical and Physical Properties of Chitosan

Chitin and chitosan are naturally occurring as β -1,4-linked linear polysaccharides similar to cellulose, as shown in Figure 11. Chitin has the same backbone as cellulose, but it has an acetamide group on the C-2 position instead of a hydroxy group, and its molecular weight, purity, and crystal morphology are dependent on their sources (Salmon *et al.*, 1997)

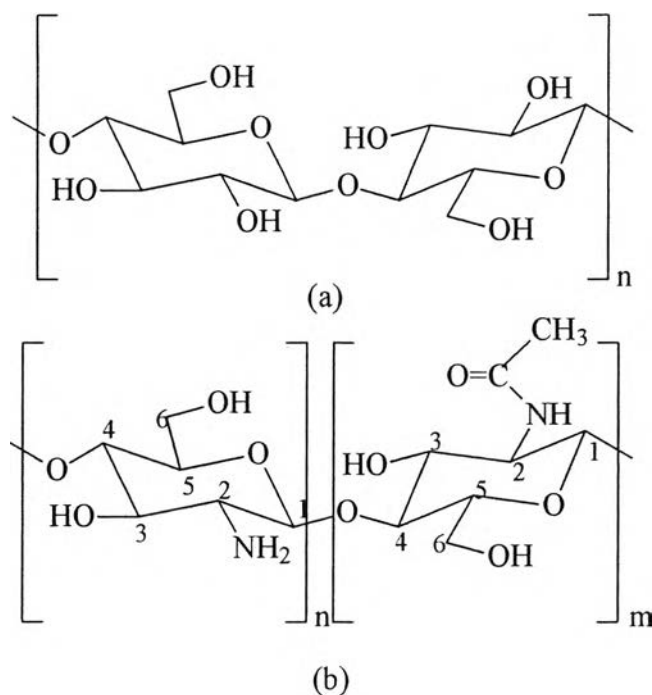


Figure 2.11 Chemical structures of (a) cellulose and (b) chitin and chitosan (chitin occurs as mostly the “m” or *N*-acetyl form and chitosan occurs as the “n” or amino form).

Chitin is essentially a homopolymer of 2-acetamido-2-deoxy- β -D-glucopyranose, although some of the glucopyranose residues exist as 2-amino-2-deoxy- β -D-glucopyranose. Chitosan is the *N*-deacetylated derivative of chitin, and the majority of its glucopyranose residues is 2-amino-2-deoxy- β -D-glucopyranose.

2.7.3 Antimicrobial Activity of Chitosan

The antimicrobial activity of chitosan against various bacteria and fungi is well known, and it has been reported by a number of authors. This unique property, due to the polycationic nature of chitosan, facilitates its application in a variety of fields, including food science, agriculture, medicine, pharmaceuticals, and textiles. In this section, the mechanisms of this action and factors affecting antimicrobial activity are described.

Several different mechanisms for microbial inhibition by chitosan have been proposed, but the exact mechanism is still not known. The most accepted one is the interaction of the positively charged chitosan with the negatively charged

residues at the cell surface of many fungi (Fang *et al.*, 1994) and bacteria (Sudardshan *et al.*, 1992), which causes extensive cell surface alterations and alters cell permeability. This results in the leakage of intracellular substances, such as electrolytes, UV-absorbing material, proteins, amino acids, glucose, and lactate dehydrogenase. As a result, chitosan inhibits the normal metabolism of microorganisms and finally leads to the death of these cells.

For example, Fang *et al.* (1994) reported that the growth of *Aspergillus niger* was inhibited by chitosan. Chitosan at the concentration of 5.0 mg/mL induced considerable leakage of UV-absorbing and proteinaceous materials from *A. niger* at pH 4.8. In contrast, chitosan at pH 7.6 and chitin at pH 4.8 did not induce the leakage, which suggests that the antifungal activity of chitosan is related to the polycationic nature of chitosan and is directly affected by the pH value. The leakage of nucleic acid and protein from *Escherichia coli* was observed by Hwang *et al.* (1998) in their study on the bactericidal activity of chitosan on *E. coli*. Transmission electron microscopy (TEM) revealed that the outer cell wall of *E. coli* was greatly distorted and frayed, and the cytoplasmic membrane was detached from the inner part of the cell wall after chitosan treatment. Tsai and Su (1999) observed the chitosan-induced leakage of glucose and lactate dehydrogenase from *E. coli* cells and suggested that the death of cells resulted from the interaction between chitosan and the *E. coli* cell, which changed the membrane permeability and consequently resulted in the leakage of intracellular components, such as glucose and lactate dehydrogenase.

And in 2004, Liu *et al.* (2004) studied the bactericidal activity of chitosan acetate solution against *Escherichia coli* and *Staphylococcus aureus*. The results from transmission electron microscopy (TEM) showed that chitosan-treated *E. coli* altered outer membranes, which were disrupted and covered by an additional tooth-like layer (Figure 2.12).

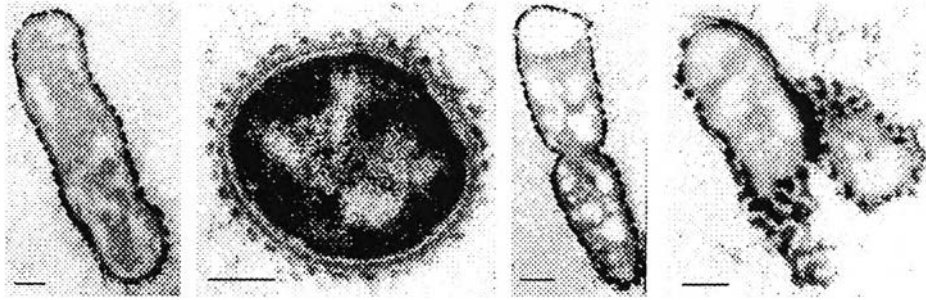


Figure 2.12 Transmission electron microphotographs of *E. coli* cells after treatment with the 0.5% chitosan acetate solution for 20 min.

In electron micrographs of chitosan-treated *S. aureus*, the membrane of dividing cells was disrupted in the constricting region with the loss of cell contents (Figure 2.13). Newly formed cells were irregularly shaped and were without membranes or cell wall on one side. Cell contents were lacking from some. Thus, membrane damage is at least one mechanism, by which both *E. coli* and *S. aureus* are destroyed by chitosan.

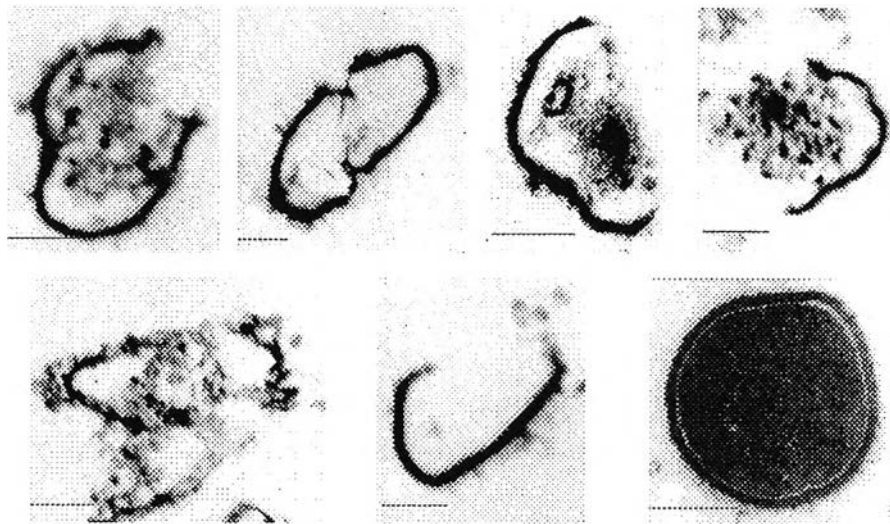


Figure 2.13 Transmission electron microphotographs of *S. aureus* cells after treatment with the 0.5% chitosan acetate solution for 20 min.

Another mechanism is that the positively charged chitosan interacts with cellular DNA of some fungi (Hadwiger *et al.*, 1986) and bacteria (Liu *et al.*, 2001), which consequently inhibits the RNA and protein synthesis.