

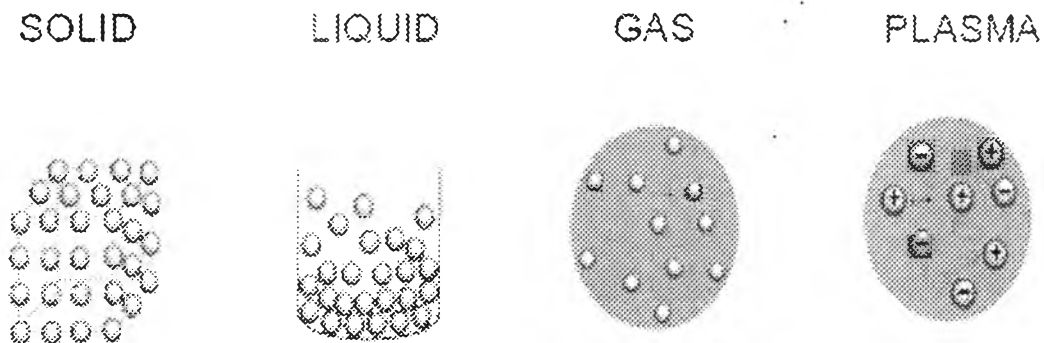


## CHAPTER II LITERATURE REVIEW

### 2.1 Basic Principles of Plasma

The plasma state can be broadly considered to be a gaseous mixture of oppositely-charged and negatively-charged particles with a roughly zero net electrical charge. Ionization processes can occur when for instance, molecules of a gas are subjected to high energy radiation of electric fields. During these processes, the energy levels of particles composing the gas increase significantly, and as a result, electrons are released and charged heavy particles are produced.

Sir William Crooks suggested the concept of the 'fourth state of matter', as shown in Figure 2.1, for electrically discharged matter, and Irving Langmuir first used the term 'plasma' to denote the state of gases in discharge tubes.



**Figure 2.1** Plasma – the 4<sup>th</sup> state of matter.

#### 2.1.1 Classification of plasma

Plasma states can be divided in two main categories: hot plasmas (near-equilibrium plasmas) and cold plasmas (non-equilibrium 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 Hot plasma (Near-equilibrium plasma)*

Hot plasmas have a greatly high energy content, which induces fragmentation of all organic molecules to atomic levels. As an outcome, hot plasma approaches considered for material processing have been initiated with the use of plasma arc heaters, and later on, three distinct application areas emerged: synthesis, melting, and deposition. Progress in thermal plasma processing has been limited by no enough understanding of the greatly complex reaction kinetic, transport properties, and heat transfer during gas-solid, gas-gas, and solid-gas interactions. As a result, thermal plasma processing has only in a few instances promoted beyond laboratory.

#### *2.1.1.2 Cold plasma (Non-equilibrium plasma)*

Plasma may be defined as a partially ionized gas with equal number densities of electron and positives ions, in which the charged particles are “free” and possess collective behavior (Strobel, 2000). Cold plasma occurs at low pressure between 13 and 133 Pa as the heavy particles (gas molecules and ions) and relatively high temperature electrons, and they are combined with low degrees of ionization ( $10^{-4}$ -10%). Accelerated electrons (energetic electrons) induce ionization, excitation, and molecular fragmentation processes, leading to a complex mixture of active species. Chemically reactive species created can partake in homogeneous (gas-phase) or heterogeneous reaction with solid surface in contact with plasma.

### 2.1.2 Generation of plasma

There are several means of generating charged particles to produce plasmas, e.g. collisions between cosmic rays and gases in atmospheric layers. However, in the present study, an externally intense electric field is applied across metal electrodes to cause the reduction in its “potential barrier” and thus the energy

that each electron requires for leaving the metal surface. The most interesting phenomena on the metal surface under an extremely high electric field are that many electrons can leak from the surface despite its less kinetic energy to overcome the potential barriers. This phenomenon is known as “tunnel effect”. And then, the plasma is first generated by the collisions between the electrons emitted from the surface of metal electrodes and the neutral molecules. This process of plasma generation is normally known as the “field” emission process.

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 2.1 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 discharge” 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	$A^* + B_2 \longrightarrow AB + B$

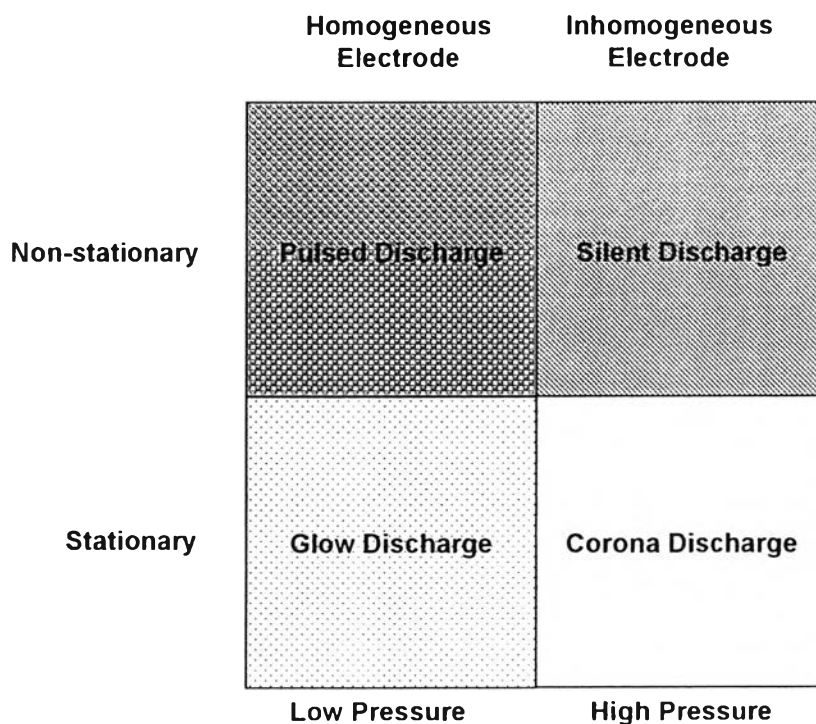
Plasma is divided into two types. The first type is “thermal plasma” or “equilibrium plasma”. In this type, the temperature between gas and electron is approximately equal, which is close to thermodynamic thermal state (Harndumrongsak, 2002). An essential condition for the formation of this plasma is sufficiently high working pressure. An example of this plasma is arc discharge.

The second type is “non-thermal plasma” or “non-equilibrium plasma”, which is characterized by low gas temperature and high electron temperature. Those typical energetic electrons may have energy ranging from 1 to 10 eV, which corresponds to the temperature of about 10,000 to 100,000 K (Rosacha et al., 1993). This plasma can be classified into several types depending upon their generation mechanism, their pressure range, and the electrode geometry (Eliasson et al., 1987). Examples of this plasma are radio frequency discharge, microwave discharge, glow discharge, corona discharge, and dielectric barrier discharge, which the latter was used in this study.

### 2.1.3 Types of non-equilibrium plasmas

When the potential difference is applied across the plasma, the electric field will exert itself the charged particles and impart energy to them. The field does not directly influence the neutral species in the bulk of the plasma. The electrons, due to their light mass, are immediately accelerated to much higher velocities than those of heavier ions in the time available between collisions. Their collision partner takes up the energy they lose through the collisions. If the pressure is small enough or the field strength is high enough, the electron and some of ions will, on average, have a kinetic energy, which is much higher than the energy corresponding to the random motion of the molecules. This plasma type is again called a non-thermal or non-equilibrium plasma and can be classified into several types depending upon their generation mechanisms, their pressure range, and the electrode geometry.

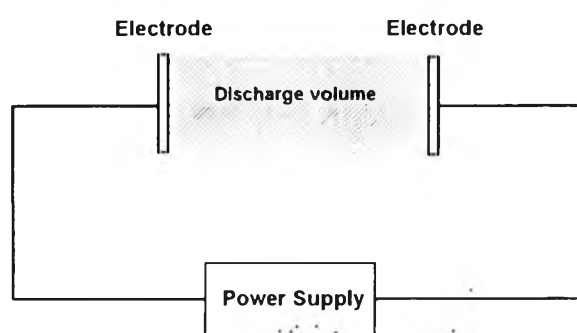
In Figure 2.2, the discharges are grouped according to their temporal behavior, pressure range, and appearance.



**Figure 2.2** Various types of discharge classified according to temporal behavior, pressure, and geometric electrode.

### 2.1.3.1 Glow discharge

The glow discharge is a stationary and low-pressure discharge, usually generated between flat electrodes (Figure 2.3). The glow can be produced by applying a potential difference between two electrodes in a gas. Since the pressure is typically smaller than 10 mbar, the reduced field or the electric field divided by the neutral gas density can therefore be quite high, which is a characteristic of non-thermal plasma.



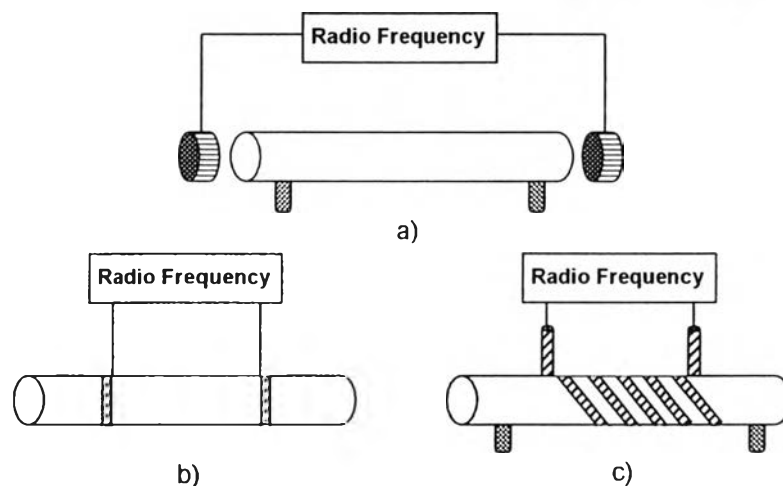
**Figure 2.3** The homogeneous electrode glow discharge can be operated at low pressure.

One reason for the popularity of glow discharges is the comparatively low voltage and current needed to run them. It has become an important laboratory tool for plasma chemical investigations. There are some practical applications of glow discharge in light industry, such as neon tubes (for outdoor advertising) and fluorescent tubes. However, the too low pressure and the resulting too low mass flow of the glow discharge have not been used for industrial production of chemicals.

### 2.1.3.2 Radio frequency discharge

The 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) operating between 2-60 MHz is especially a widespread laboratory tool for spectroscopic analysis. Very common frequency used in the industrial applications is about 13.56 MHz. One advantage of RF discharges 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-thermal conditions can be expected at low pressures, whereas thermal plasmas are generated at about atmospheric pressure. Figure 2.4 shows three typical electrode configurations for RF discharges. While Figure 2.4(a) and (b) use capacitive coupling and are mainly used at low pressure, the configuration shown in Figure 4(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 up to 1 bar.



**Figure 2.4** Schematic of various types of radio frequency discharge: (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.

### 2.1.3.3 *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.

Since at these frequencies only the light electrons can follow the oscillations of the electric field, microwave plasmas are normally far from local thermodynamic thermal state. They can be operated in a wide pressure range, starting from below 1 mbar to about atmospheric pressure. An interesting development is the use of microwaves to induce surface-wave-sustained discharges. They can be operated over a large frequency and pressure range and can produce large-volume non-thermal plasmas of reasonable homogeneity.

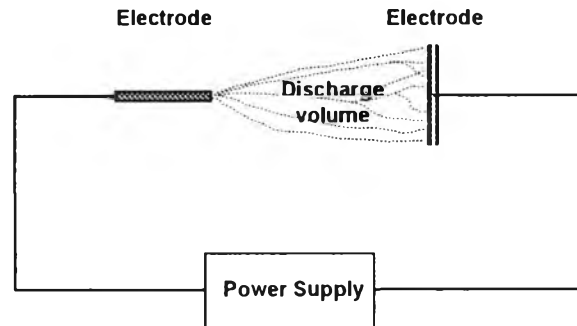
The plasma is contained in a dielectric tube of a few centimeters diameter and is sustained by an electromagnetic wave, which requires only the plasma column and the tube as its propagating media. Plasma columns of up to 4-m length have been thus produced. Due to the large pressure range, under which these discharges can be operated, electron densities between  $10^8$  and  $10^{15}\text{cm}^{-3}$  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 and influencing plasma parameters make these discharges attractive also for plasmachemical investigations.

### 2.1.3.4 *Corona discharge*

The main disadvantage of the glow discharge when it comes to industrial applications is its extremely low pressure. If one increases the pressure, one has to increase the field accordingly. 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



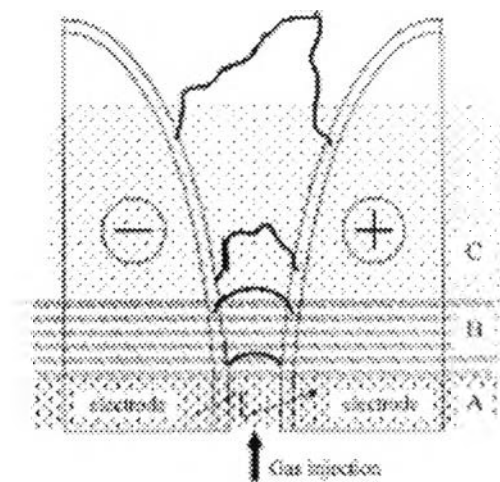
pointed electrode and a plane electrode, such as in Figure 2.5, or a thin wire (Chang, *et al.*, 1991).



**Figure 2.5** The inhomogeneous electrode corona discharge can be operated at high pressure.

#### 2.1.3.5 *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 closest point, spreads along the knife-edges of the electrodes, and disappears. Another discharge immediately reforms at the initial spot. Figure 2.6 is considered to be the simplest case for a better physical understanding of the gliding arc phenomenon (Fridman *et al.*, 1999).



**Figure 2.6** Phase of gliding arc phenomena: (a) reagent gas breakdown; (b) equilibrium heating phase; and (c) non-equilibrium reaction phase.

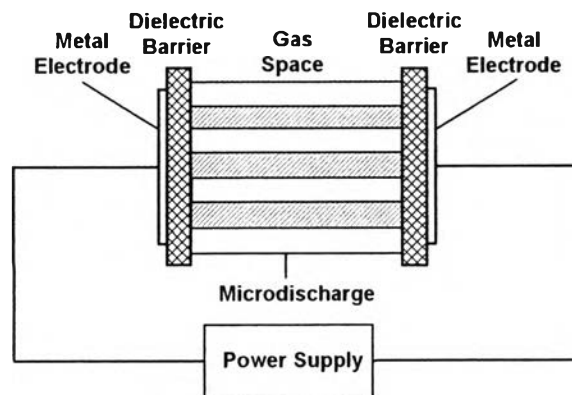
The reagent gas breakdown (a) of the processed gas begins the cycle of the gliding arc evolution. The high voltage generator provides the necessary electric field to break down the gas between the electrodes.

The equilibrium-heating phase (b) takes place after formation of stable plasma channel. The electric discharge spreads along the electrodes, which the velocities 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).

#### 2.1.3.6 Dielectric-barrier discharge (DBD)

The silent discharge is predetermined for applications in volume plasma chemistry. It 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 2.7.



**Figure 2.7** The homogeneous electrode silent discharge. One or both electrode is covered by a dielectric, and micro-discharges are contained in the discharge gap.

A characteristic of the silent discharge is that a dielectric layer covers at least one of the electrodes, sometimes both. For this reason the silent discharge is also referred to as the “dielectric barrier discharge (DBD)” or simply “barrier discharge”. The dielectric is the key for the proper functioning of the discharge. Once ionization occurs at a location in the discharge gap, the transported charge accumulates on the dielectric. The dielectric serves two functions: (1) it limits the amount of charge transported by a single microdischarge and (2) it distributes the microdischarges over the entire electrode area. The silent discharge is an excellent source of filaments containing energetic electrons. In most gases, the reduced field at breakdown corresponds to electron energies of about 1-10 eV. This is the ideal energy range for the excitation of atomic and molecular species and the breaking of chemical bonds. This type of discharge has been mostly used in applications of surface modification.

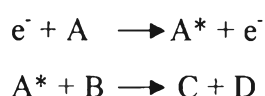
Liu *et al.* (2004) investigated the effects of a dielectric barrier discharge (DBD) plasma on surface treatment of polytetrafluoroethylene (PTFE), polyimide (PI), and poly(lactic acid) (PLA) films in terms of changes in surface wettability and surface chemistry. The purpose was to study the influence of the main operating parameters, i.e. plasma power, treatment period duration (treatment cycles), and electrode gap, on the resultant surface properties. It was experimentally found that the plasma parameters have a selective effect on the changes observed for

the polymers processed. In particular, plasma processing time (treatment cycles) plays an important role in the treatment of PTFE and PI in this study, whereas the size of the electrode gap plays the dominant role in the treatment of PLA.

De Geyter *et al.* (2007) studied 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 an 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.

#### 2.1.4 The Initiation of Chemical Reactions in Non-Thermal Plasma

For initiation of chemical reactions in non-thermal plasma, the energy is very often transferred solely by the electrons. 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 be applied to ions. For example, the reaction schematic is demonstrated below (McQuarrie *et al.*, 1987)



Where A, B are reactant.

C, D are product.

A\* are the excited reactant marked by an asterisk (\*).

Normally, this reaction  $A + B \longrightarrow C + D$  may only take place at 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.

## **2.2 Plasma Technology for Surface Modification of Polymeric Materials**

Plasma treatment is frequently used for the improvement of adhesion and wettability of polymeric materials. The mechanisms of surface functionalization of polymeric substrates are different from the gas-phase processes. While electrons play the most important role in the plasma state, positive ions also play a significant role in the surface chemistry during the interactions of plasma species with polymers. The resulting valence-ionized polymer chains undergo neutralization reactions, leading to sufficiently intense localized internal energy concentrations (electronically excited states), which can induce hemolytic bond cleavages. The development of free radicals and unsaturated bonds can result in cross-linking of polymeric layers. Free radicals can further induce chemical reactions controlled by specific chemical environments (gas-phase or condensed-phase compounds, including, oxygen, monomer molecules, etc.) in the absence of plasma.

Markkula (2002) revealed the expression of adhesion molecules on the surface of human endothelial cells in response to the systematic variation in material properties by the ammonia plasma modification of polyethylene terephthalate (PET) and polytetrafluorethylene (PTFE). The study has shown that the plasma improved the adhesion and growth of endothelial cells and slightly up-regulated the expression of adhesion molecules. This surface modification should promote colonisation of an artificial vascular prosthesis by endothelial cells and make it less vulnerable to immune system cells of the recipient. In addition, it should be considered which passage of cells is used due to the different adhesion features of different passages of human umbilical vein endothelial cells (HUVECs) on untreated PET.

Jaššo *et al.* (2005) reported the modifications of poly(ethylene terephthalate) (PET) by an aborted arc discharge generated at atmospheric pressure. The PET cords were modified by plasma polymerization in a mixture of nitrogen and butadiene. It

was found that the new deposited layer is responsible for the better adhesion of the PET cords to the styrene-butadiene rubber blend.

Almazán-Almazán *et al.* (2006) reported the modifications of PET surface produced by nitrogen and helium cold plasmas. Atomic force microscopy (AFM) showed that both plasmas altered in different extent the surface of PET as they broke the polymer chains and produced low molecular products, which appeared as bumps on the surface. The surface area and the porosity of PET did not change by plasma treatments even after 15 min. The dispersive component of the surface free energy decreased after long treatments with nitrogen plasma whereas it remained almost unchanged after long treatment with helium plasma.

Khorasani *et al.* (2006) investigated the effect of plasma treatment on PVC blood bag samples to improve the hydrophobicity and surface charge and evaluated the effect of these properties on fibroblast cell growth. Water drop contact angle measurement showed that the plasma-treated PVC became more hydrophilic, and wettability increased. Zeta potential and in vitro cell culture measurements noticed that the plasma-treated PVC surface was more negatively charge.

De Geyter *et al.* (2006) 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.

Han *et al.* (2006) studied modifications of the PET-laminated tin free steel plate (TFS) by atmospheric pressure plasma at room temperature in order to enhance the surface adhesive properties. They reported that from the results of XPS and SEM analysis, new functional groups causing the adhesion enhancement were generated due to the carbon cleaning effect and surface oxidation effect by reactive species in the plasma, such as atomic oxygen.

Kotál *et al.* (2006) investigated the effect of Ar plasma treatment on the surface properties of poly(ethylene terephthalate) (PET) in order to examine its possible application for metal-polymer adhesion improvement. The plasma treatment led to an immediate increase of the PET's surface wettability, which however significantly depended on the sample aging, more specifically on the time elapsed after the treatment. It was found that the oxygen concentration in the near surface

layers increased as a result of the treatment, but it also changed with time for the samples in contact with the atmosphere, probably as a result of polar group rearrangements. Plasma-initiated ablation and Au sputtering increased the surface roughness. The nanoindenter measurements revealed that the treatment increased the microhardness of treated PET. On the contrary to the hardness, the elastic modulus decreased. Scratch tests showed that the deformation of samples consisting of Au coatings deposited on both pristine and treated PET was elastic rather than plastic.

### 2.3 Reactions between Plasmas and Polymer Surfaces

In general, reactions of gas plasmas with polymers can be classified as follows (Yasuda *et al.*, 1990).

(a) Surface reactions: Reactions between the gas-phase species and surface species and reactions between the surface species producing functional groups and crosslinking, respectively, at the surface. Examples of these reactions include plasma treatment by argon, ammonia, carbon monoxide, carbon dioxide, fluorine, hydrogen, nitrogen, nitrogen dioxide, oxygen, and water.

(b) Plasma polymerization: The formation of a thin film on the surface of a polymer via polymerization of an organic monomer, such as  $\text{CH}_4$ ,  $\text{C}_2\text{H}_6$ ,  $\text{C}_2\text{F}_4$ , and  $\text{C}_3\text{F}_6$  in a plasma. It involves reactions between gas-phase species, reactions between gas-phase species and surface species, and reactions between surface species.

(c) Cleaning and etching: Materials are removed from a polymer surface by chemical reactions and physical etching at the surface to form volatile products. Oxygen-containing plasmas are used to remove organic contaminants from polymer surfaces, e.g. oligomers, anti-oxidants, anti-block agents, and mold-release agents. Etching differs from cleaning only in the amounts of materials that are removed from the surface. Oxygen plasmas and oxygen- and fluorine-containing plasmas are frequently used for the etching of polymers.

There are several plasma atmospheres used for surface modifications as follows.

### 2.3.1 Inert gas plasmas

Helium, neon, and argon are the three inert gases used in plasma technology. Due to the relatively lower cost, Ar is by far the most common inert gas used. The direct and radiative energy transfer (momentum transfer) processes created by an inert gas plasma can cause physical modification of the surface. In fact, one of the major uses of Ar plasmas is in sputtering processes used in the semiconductor industry. Inert gas plasmas have been used for pretreatment of substrates for cleaning purposes before reactive gases are applied. If a plasma reaction is to be carried out with a high system pressure but a low reactive gas flow rate, an inert gas can serve as a diluent. Treatment of polymer surfaces by exposure to plasmas has been utilized to improve the adhesive characteristics of polymers. Polymers have been subjected to low-power plasmas of noble gases for periods typically from 1 s to several minutes. This exposure is sufficient to abstract hydrogen and to form free radicals at or near the surface, which then interact to form crosslinks and unsaturated groups with chain scission. The plasma also removes low-molecular-weight materials or converts them to a high-molecular-weight by crosslinking reactions. As a result, the weak boundary layer formed by the low-molecular-weight materials is removed; consequently, greater adhesive joint strengths are observed. This treatment has been known as CASING (cross-linking by activated species of inert gases) (Hansen *et al.*, 1966). Sheu *et al.* (1992) used a similar technique to immobilize a coated surfactant on low-density polyethylene substrate by an Ar-plasma treatment in order to produce a wettable and non-fouling (protein resistant) surface. The Pluronic<sup>®</sup> 120 series of poly(ethylene oxide)/poly(propylene oxide)/poly(ethylene oxide) (PEO/PPO/PEO) tri-block copolymer surfactant was first physically adsorbed on the surface via a solvent swelling and evaporation method. The deposited surfactants, acting as the weak boundary layer, were then cross-linked to the surfaces and/or to each other by an Ar-plasma treatment. X-ray photoelectron spectroscopy (XPS) and water contact angle measurements indicated a significant increase in surface hydrophilicity and a decrease in surface energy of the modified substrates. The greatest reduction of



baboon fibrinogen adsorption was observed on the modified surfaces with the highest O/C atomic ratios. A new method was developed by Terlingen *et al.* (1993) to covalently immobilize an adsorbed layer of sodium dodecyl sulfate, a surfactant, onto a polypropylene (PP) surface by applying an Ar-plasma treatment. Using solution concentrations above the critical micelle concentration, plateau levels of sodium dodecyl sulfate adsorption were reached within 10 s. If the PP surfaces with the pre-adsorbed surfactant were dried and plasma-treated with Ar and then immersed in water for 90 min, intact sulfate groups were present at the surface, as shown by ion exchange and XPS measurements.

### 2.3.2 Oxygen-containing plasmas

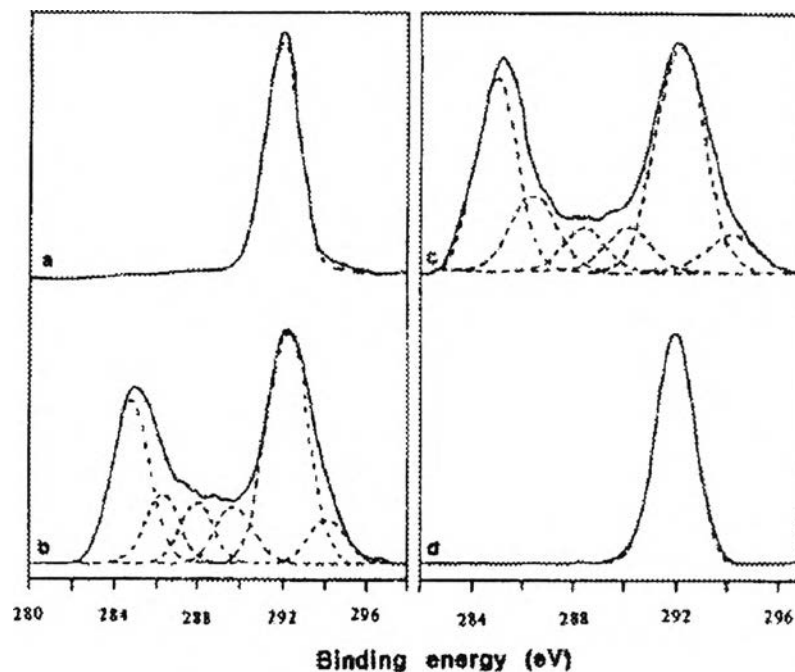
Oxygen and oxygen-containing plasmas are most commonly employed to modify polymer surfaces. It is well known that an oxygen plasma can react with a wide range of polymers to produce a variety of oxygen functional groups, including C-O, C=O, O-C=O, C-O-O, and CO<sub>3</sub>, at the surface. In an oxygen plasma, two processes occur simultaneously: etching of the polymer surface through the reactions of atomic oxygen with the surface carbon atoms, giving volatile reaction products; and the formation of oxygen functional groups at the polymer surface through the reactions between the active species from the plasma and the surface atoms. The balance of these two processes depends on the operation parameters of a given experiment. Oxygen-plasma treatment of PTFE illustrates the competitive nature of these two processes (Morra *et al.*, 1990). The surface chemical composition of oxygen-plasma-treated PTFE as a function of treatment time is shown in Table 2.2. After a short treatment time (0.5-2 min), the fluorine concentration decreased, and the oxygen concentration increased; after a long treatment time, the trend was reversed. This observation was complemented by the change of the C in spectrum as a function of treatment time, as shown in Figure 2.8. After 2 min of treatment, the spectrum revealed features corresponding to hydrocarbon structures and oxygen-containing hydrocarbon structures. At the end of 15 min, the spectrum changed back to be essentially PTFE-like. This peculiar phenomenon was explained by the mechanism that surface modification is dominant at the beginning and then is overwhelmed by surface etching at a later stage of the

process. This explanation is supported by the analysis of optical emission spectra of the discharges, showing a decrease in atomic oxygen and an increase in products formed by interaction with the surface, such as fluorine and  $\text{CO}_2^+$  ions, as the treatment time increased. The increase in the fluorine-ion concentration caused etching of the oxidized polymer surface, and consequently, the oxidized surface became essentially bulk-like.

**Table 2.2** XPS composition of oxygen-plasma-treated PTFE as a function of treatment time.

Treatment time (min)	Chemical composition (%)		
	C	F	O
0	39.8 <sup>a</sup>	60.4 <sup>a</sup>	0.8 <sup>a</sup>
0.5	44.6	48.9	6.4
1.0	42.7	51.1	7.1
2.0	42.6	50.9	6.5
5.0	40.9	57.0	2.1
10.0	38.3	60.5	1.2
15.0	38.3	61.4	0.3

<sup>a</sup> Untreated



**Figure 2.8** Cls spectra of PTFE: (a) untreated; (b) exposed to an oxygen plasma for 0.5 min; (c) exposed to an oxygen plasma for 2 min; and (d) exposed to an oxygen plasma for 15 min (Morra *et al.*, 1990).

The interaction of a microwave plasma of carbon dioxide and polypropylene led to two competitive reactions: modification and degradation (Chappel *et al.*, 1991). Surface modification produced ketone, acid, and ester on the polymer surface, whereas degradation generated volatile products and a layer of oxidized oligomers of polypropylene. The conditions favoring surface modification are low gas pressure, power, and treatment time.

Water plasmas may be used to incorporate hydroxyl functionality onto a material surface. Usually, oxidation rather than reduction reactions are obtained in a H<sub>2</sub>O plasma. Poly(methylmethacrylate) (PMMA) is widely used for its bulk chemical, mechanical, and optical properties in Plexiglass®, contact lenses, biomedical prosthetics, and in electron beam lithography. It is hydrophobic, with a surface energy of 19.2 erg cm<sup>-2</sup>, and does not swell in aqueous solution. Vargo *et al.* (1989) used H<sub>2</sub>O plasma to create a hydrophilic surface on PMMA by the incorporation of hydroxyl and carbonyl functionalities. In a biomedical application,

the interactions of Chinese hamster ovary cells with a number of different polymer surfaces having hydroxyl groups incorporated by H<sub>2</sub>O plasma treatments were investigated by Lee *et al.* (1991). The plasma-treated polymer surfaces all showed increased wettability, and good adhesion, spreading and growth properties for cell attachment.

Hettlich *et al.* (1991) investigated the difference between CO<sub>2</sub> and O<sub>2</sub> in grafting oxygen-containing functional groups to adhere to a poly(dimethyl siloxane) intraocular lens. Although O<sub>2</sub> plasmas induced functional groups onto the intraocular lens at a faster rate than CO<sub>2</sub> plasmas, CO<sub>2</sub> plasmas produced much milder attacks on the substrates than O<sub>2</sub> plasmas, and crack formation was observed on the lens surface after 60 s of O<sub>2</sub>-plasma treatment at 600 W plasma power, 250 ml min<sup>-1</sup> gas flow, and 0.4 bar system pressure. Greater spreading of the larynx carcinoma cell was observed on all plasma-treated samples. The researchers believed that if a macromolecular coating, such as heparin, which is biocompatible with type IV collagen, and laminin on the inner layer of the human lens capsule, is formed via the functional groups produced by plasma treatments, posterior capsule opacifications may be prevented. Ishikawa *et al.* (1985) found that using CO alone or in combination with other gases, such as Ar, N<sub>2</sub>, H<sub>2</sub>O, NH<sub>3</sub>, CO<sub>2</sub>, and SO<sub>2</sub>, to plasma-modify plasticized poly(vinyl chloride) (PVC) blood bags, the surface energies of the modified PVC were increased by 30-45 erg cm<sup>-2</sup>. Of greater importance, the leakage of plasticizer, di-(2-ethylhexyl)phthalate, was prevented; so impairment of platelet functions was suppressed when platelet concentrates were stored in the plasma-treated PVC bags. However, platelet adhesion to the surfaces was increased by the treatments. Plasma modification of low-density polyethylene (LDPE) sheets by CO<sub>2</sub> and acrylic acid (a polymerizable monomer) was studied by Ko *et al.* (1993). Acidic oxygen-containing groups were formed on the surfaces as confirmed by XPS, attenuated total internal-reflection Fourier transform infrared (ATR-FTIR) spectroscopy, and static contact angle measurements. Surface hydrophilicity of both CO<sub>2</sub>-plasma-treated LDPE surfaces and acrylic acid plasma polymer films decreased with time due to the diffusion of hydrophilic oxygen-containing functional groups away from the surfaces of the samples. In assessing the blood compatibility of these two types of plasma-modified surfaces by using platelet

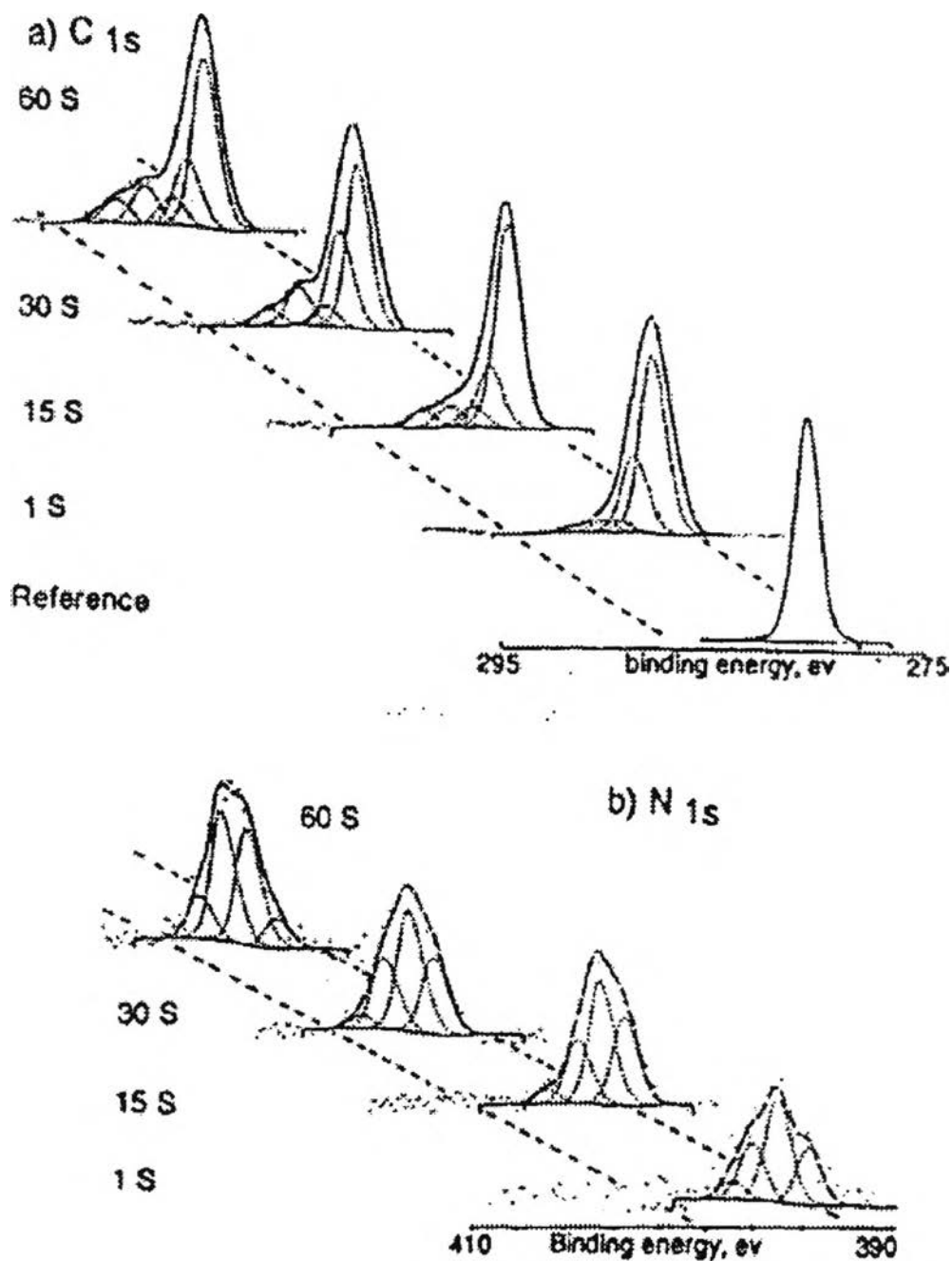
adhesion and spreading tests, the acrylic acid plasma polymers formed at low plasma energies (10 and 30 W) showed an improvement in thromboresistance, but the CO<sub>2</sub>-plasma-treated LDPE surfaces were more thrombogenic than the untreated LDPE-based material. In addition, Ko *et al.* (1994) also investigated the plasma treatments of sulfur dioxide and allyl phenyl sulfone [APS, C<sub>6</sub>H<sub>5</sub>S(O)<sub>2</sub>CH<sub>2</sub>CH=CH<sub>2</sub>] on low-density polyethylene substrates. Hydrophilic sulfur-containing and oxygen-containing functional groups were incorporated onto the substrates in both cases. The APS-plasma-treated LDPE was more thromboresistant than the control samples in terms of canine platelet adhesion and spreading, while SO<sub>2</sub>-plasma-treated LDPE samples were more thrombogenic toward platelets than the untreated LDPE samples. Among the SO<sub>2</sub>-plasma-treated samples, 5 W excitation energy produced the highest sulfur atomic concentration in the samples, which were also the most thromboresistant toward platelet adhesion and spreading in the study. This result illustrates that the power level can be a major factor in determining the surface chemical composition of plasma-treated polymer surfaces.

### 2.3.3 Nitrogen-containing plasmas

Nitrogen-containing plasmas are widely used to improve wettability, printability, bondability, and biocompatibility of polymer surfaces. For example, to improve the interfacial strength between polyethylene fibers and epoxy resins, which are cured by amine cross-linking, amino groups were introduced on the fiber surface to promote covalent bonding. The introduction of amino groups on the surface of polystyrene films with ammonia-plasma treatment was reported to improve cell affinity. Ammonia and nitrogen plasmas have been used to provide surface amino binding sites for immobilization of heparin on a variety of polymer surfaces. Ammonia-plasma treatment was reported to increase the peel strength between polytetrafluoroethylene and nitrile rubber when a phenol-type adhesive was used. Oxygen functionalities are always incorporated in nitrogen-plasma-treated polymer surfaces. It is a common phenomenon that oxygen is incorporated on polymer surfaces after and during non-oxygen plasma treatments. Free radicals that are created on a polymer surface can react with oxygen during a plasma treatment. In addition, free radicals that remain on a polymer surface after a plasma treatment will

react with oxygen when the surface is exposed to the atmosphere. Different nitrogen-containing plasmas have been shown to produce different nitrogen functional groups on a polymer surface (Lub *et al.*, 1989). For example, Benninghoven *et al.* (1990) showed that primary amino groups could be detected at the polystyrene surface after treatment with  $\text{NH}_3$  plasma but not with a  $\text{N}_2$  plasma, with the aid of XPS derivatization technique and secondary ion mass spectrometry (SSIMS). The XPS derivatization is a special technique developed for identifying specific functional groups on polymer surfaces (Chan *et al.*, 1994). Their results revealed that there is a maximum number of primary amino groups that can be formed at the surface. Similar results were reported by Nakayama *et al.* (1988), suggesting that the amount of primary amines comprises 15 to 20% of the total nitrogen and does not depend on treatment time. They used a gas-phase derivatization technique (the sample was exposed to pentafluorobenzaldehyde ( $\text{C}_6\text{F}_5\text{CHO}$ ) gas for 6 h at  $45^\circ\text{C}$ ) and XPS measurements to study  $\text{NH}_3$ -plasma-treated-polystyrene films (Sterilin<sup>®</sup>). All of the plasma-treated samples showed a F1s peak after the chemical modification, indicating existence of primary amine, while there was no F1s peak seen in the control film. Both nitrogen and oxygen were found on the surface after the plasma treatment. Atomic ratios of N/C and O/C increased with longer plasma treatment times. However, the ratio of primary amine, which was believed to affect the cell affinity, for each sample was only 15-20% of the total nitrogen and did not seem to depend on the duration of the plasma treatment, which was in agreement with Lub *et al.* (1989). Nakayama *et al.* (1990) also found a trace amount of carboxylic acids ( $-\text{COOH}$ ) in their  $\text{NH}_3$ -plasma-treated PS films probably due to oxidation in air after plasma exposure. Furthermore, they estimated the relative amounts of non-amino-type nitrogen (i.e. imines and nitriles) by an analysis of the C1s peak of the XPS spectrum of the modified surface. All  $\text{NH}_3$ -plasma-treated samples had better cell affinity (human fetal cell derived from amniotic fluid) than the control PS. The XPS results also revealed that silicon dioxide, which had been sputtered from the glass wall of the plasma treatment vessel onto the PS surface during long plasma treatment times, decreased the cell affinity. From the angle-resolved XPS results, Nakayama *et al.* (1990) found that the plasma treatment was homogeneous within the sampling depth while Lub *et al.* (1989) found that the nitrogen incorporation occurred in the

uppermost layers of the material. Foerch *et al.* (1990) studied the effect of a remote nitrogen plasma on polystyrene and polyethylene. In this study, samples were positioned downstream from the main plasma region. The nitrogen concentration of a nitrogen-plasma-treated polyethylene surface increased as a function of exposure time. It increased very rapidly during the first 20 s of exposure and reached a maximum concentration of approximately 18 at.% after 20 s. An interesting feature observed in the Cls and N1s spectra, as shown in Figure 2.9, is that the chemical nature of the surface continued to change even after the total nitrogen and oxygen concentrations had reached steady state. The exact nature of these nitrogen functional groups is not easy to determine, due to the presence of various oxygen functional groups, but the presence of C-O, C-N, C=N, and C≡N has been suggested. The changes in the XPS spectra were probably caused by surface reactions that converted one type of nitrogen functional group to another. Special functional groups that are not formed during nitrogen-plasma treatment of polyethylene and polystyrene were generated on these polymer surfaces, using a two-step treatment process: nitrogen plasma treatment followed by either corona discharge or ozone treatment (Foerch *et al.*, 1990). The combined nitrogen plasma treatment and corona discharge produced NO<sub>2</sub> groups on the surface of these polymers, indicating that corona discharge oxidation involves both nitrogen and carbon atoms at the polymer surface. Ozone treatment of nitrogen-plasma-treated polyethylene and polystyrene surfaces increased carboxyl and carbonyl concentrations, but did not produce any NO groups.



**Figure 2.9** (a) C1s and (b) N1s spectra of polyethylene as a function of nitrogen-plasma-treatment time.

Amino groups were introduced to the surfaces of polypropylene beads (slightly flattened spheres of 2.5-3.0 mm diameter and 3.5 mm thickness) and polypropylene membranes (Celgard<sup>®</sup>) by exposing them to an anhydrous NH<sub>3</sub> plasma (Sipehia and Chawla, 1982). The optimal plasma conditions for grafting



bovine serum albumin were 30 W energy, 30 min treatment time, and 400 mTorr pressure in a rotatable plasma reactor. ATR-FTIR spectra of the surfaces of Celgard<sup>®</sup> coated with amino groups showed absorption bands at 3460 and 1660  $\text{cm}^{-1}$  representing the asymmetric stretching and in-plane bending of amino groups, respectively. Through these amino groups, bovine serum albumin was attached covalently to the PP membranes or beads at the physiological pH of 7.5. Incorporation of biomolecules-like albumin onto the surfaces of biomaterials could improve their blood compatibility since it is a passivating protein. The beads were then washed with a phosphate buffer solution to remove the loosely bound albumin. After 52 h of washing with saline and human plasma, the concentration of albumin retained by albuminated PP beads ( $125 \mu\text{g cm}^{-2}$ ) was found to be higher than the  $28 \mu\text{g cm}^{-2}$  obtained by covalent binding (Hoffman, 1988). If the attached albumin was further stabilized by crosslinking with 1.5% glutaraldehyde [ $\text{HCO}(\text{CH}_2)_3\text{CHO}$ ] in phosphate buffer, albumin retention was increased to  $170 \mu\text{g cm}^{-2}$  after 52 h of washing. In another study, Sipehia *et al.* (1988) were able to immobilize glucose oxidase and peroxidase onto  $\text{NH}_3$ -plasma-treated PP beads for solid-phase enzyme immunoassays. By using immobilized enzymes, the assay procedures could be improved with respect to selectivity, ease of use, and analytical sensitivity. The enzyme-immobilized beads were then soaked in a 1.5% glutaraldehyde crosslinking solution. After washing with phosphate buffer for 5-6 h, 40-55% of the immobilized enzymes were found to be in the active form. In the case of control beads having no amino groups, no attachment of albumin or enzymes was observed. Nitrogen and ammonia plasmas were applied to modify polypropylene (Duragard<sup>®</sup>), poly(vinylidene fluoride) (Durapore<sup>®</sup>), and polytetrafluoroethylene (Fluoropore<sup>®</sup>) membrane surfaces for immobilization of glucose oxidase using glutaraldehyde as a linking agent for covalent attachment (Kawakami *et al.*, 1988). Enzyme activity was evaluated by the response of a glucose sensor composed of the immobilized enzyme membrane and a dissolved  $\text{O}_2$  electrode. The sensor output indicating the concentration of dissolved  $\text{O}_2$  decreased with increasing glucose concentration, which implied that the enzyme electrode functioned as a glucose sensor. Tran *et al.*, 1989 formed an alkylamine surface on Gore-Tex<sup>®</sup> vascular grafts by exposure to hexane and  $\text{NH}_3$  plasmas for 1 h each. Collagen was attached to the plasma-modified

grafts via glutaraldehyde crosslinkers while no collagen was attached to the control grafts. The adventitial or luminal surfaces of the graft could be modified selectively depending on the initial set-up of the plasma reaction. These collagen-coated grafts may permit better attachment and growth of endothelial cells. Ammonia and allylamine plasmas were used to generate amino-group linkages on low-density polyethylene (LDPE) surfaces for sulfonation and carboxylation by wet chemical grafting reactions with 1,3-propane sultone (3-hydroxy-1-propane sulfonic acid  $\gamma$ -sultone,  $C_3H_6SO_3$ ) and 3-propiolactone (3-hydroxy propionic acid lactone,  $C_3H_4O_2$ ), respectively (Ko Walt *et al.*, 1991). All the sulfonated and carboxylated materials were more platelet reactive than the control LDPE base which suggested that these materials were thrombogenic. However, the acidic surfaces containing sulfonyl or carboxyl groups were comparatively more thromboresistant toward platelet adhesion and spreading than the basic surfaces containing only amino groups incorporated by the plasma reactions.

## 2.4 Silver Nanoparticle

### 2.4.1 Preparation of silver nanoparticle

The most common methods used for the preparation of colloidal suspensions of metals (including silver) are the reduction of corresponding metal cation. In addition to the inorganic or organic reduction agents, the ultrasound, the UV radiation, and the gamma radiation can be used to initiate the reduction.

#### *2.4.1.1 Laser Ablation*

Laser ablation of silver macroscopic material (e.g. silver foil) is a novel and promising physical method for the silver colloid particle preparation. The advantages of this method are an ease of the process, versatility with regard to metal identity or choice of solvent, as well as the absence of additive chemical agent residues. Metal particles prepared by laser ablation are chemically pure.

#### *2.4.1.2 The Reduction by the Action of Ultrasound*

Except for the above-mentioned usage of ultrasound in a dispersion method of colloid particle preparation, it can be also used as a condensation method. The ultrasound is capable of decomposing water into hydrogen and hydroxyl radicals. Subsequent reactions with suitable additives yield organic radicals, which act as reducing agents. By sonification of aqueous silver salt solutions in the presence of surfactants, the silver particles were prepared.

#### *2.4.1.3 The Reduction by the Action of Gamma Radiation*

For the preparation of submicroscopic silver particle, a direct radiolysis of silver salt aqueous solutions can be used. The advantage of this preparation method is that minimum interfering chemical substances are introduced into the reduction mixture, which could possibly absorb onto particles and thus change their specific properties. During the irradiation of silver salt solution under hydrogen gas atmosphere, hydrated electrons and hydrogen atoms are formed, which reduce the silver ions to form silver nanoparticles.

#### *2.4.1.4 The Reduction by the Action of UV Radiation*

Photochemical method of colloid particle preparation using UV radiation yields the particles with properties similar to the particles produced by the above mentioned radiolytic method. Mercury discharge lamp is often used as the

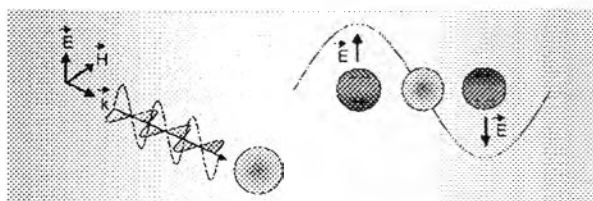
source of UV radiation. In addition to silver salt and eventual stabilizers, the reaction mixture contains suitable organic substance, whose interaction with UV radiation generates radicals to reduce silver ions.

#### 2.4.1.5 *The Reduction by Chemical Agents*

The most commonly used method for the preparation of silver sols is the reduction of silver salt by sodium borohydride ( $\text{NaBH}_4$ ), which generates free electrons and reduces silver ions to form silver particle. By the standard methods of silver salt reduction by  $\text{NaH}_4$ , the particles with units of nanometer sizes and narrow size distribution are prepared.

### 2.4.2 Optical Properties of Silver Nanoparticle

Conduction electrons and ionic cores in metal form a plasma state. When external electric fields (electro-magnetic waves, electron beams, etc.) are applied to a metal, electrons move so as to screen perturbed charge distribution, further move beyond the neutral states, and again return to the neutral states and so on. This collective motion of electrons is called a “Plasma Oscillation”, as shown in Figure 2.10. The surface plasmon resonance is a collective excitation mode of the plasma localized near the surface. Electrons confined in a nanoparticle conform the surface plasmon mode. The resonance frequency of the surface plasmon is different from an ordinary plasma frequency. The surface plasmon mode arises from the electron confinement in the nanoparticle. Since the dielectric function tends to become continuous at the interface (surface), the oscillation mode shifts from the ordinary plasma resonance and exponentially decays along the depth from the surface.



**Figure 2.10** Plasmon oscillation of the free electron on the surface of metal nanoparticle.

### 2.4.3 Antimicrobial Properties of Silver Nanoparticle

Silver metal and silver compound have long been known to have strong inhibitory and bactericidal effects, as well as a broad spectrum of antimicrobial activities. Several proposals have been developed to explain the inhibitor effects of silver ion/silver metal on the both negative and positive bacteria. Silver ions are known to react with nucleophilic amino acid residues in proteins, and attach to sulphhydryl, amino, imidazole, phosphate and carboxyl groups of membrane or enzyme proteins that lead to protein denaturation. Silver is also known to inhibit a number of oxidative enzymes, such as yeast alcohol dehydrogenase, the uptake of succinate by membrane vesicles, and the respiratory chain of *Escherichia coli*, as well as causing metabolite efflux and interfering DNA replication. Recently, microbiological and chemical experiments implied that interaction of silver ion with thiol groups played an essential role in bacterial inactivation. Also, it is revealed that bulk silver in an oxygen-charged aqueous media catalyzes the complete destructive oxidation of microorganisms. However, the antimicrobial effects of silver nanoparticles were not fully investigated. Metal nanoparticles, which have a high specific surface area and a high fraction of surface atoms, have been studied extensively due to their unique physicochemical characteristics, such as catalytic activity, optical properties, electronic properties, antimicrobial activity, and magnetic properties. It can be expected that the high specific surface area and high fraction of surface atoms of Ag-nanoparticles will lead to high antimicrobial activity compared with bulk Ag metal (Kyung- Hwan *et al.*, 2005).