Chapter 1

Introduction

Abstract

In this chapter the fundamentals of thermoplastic polymers used are explained. An overview of the most important surface treatment and surface modification techniques used. A brief overview of surface forces and surface energies is given before explaining the adhesion mechanism. A detailed literature survey and motivation for the present work is emphasized at the end of the chapter.

1.1 Polymers and its classification

Polymer is a substance composed of molecules which consist of a long chain of one or more species of atoms or groups of atoms linked to each other by usually covalent bonds. The word polymer is derived from the Greek words poly meaning "many" and mers meaning "parts". Polymers are classified as homopolymer and copolymer. If a polymer is consists of one type of monomer, it is called homopolymer and more than one monomer is called copolymer. The covalent bonds are characterized by high binding energy (146 – 628 kJ/mole) and short bond lengths (0.11 – 0.16 nm) and relatively constant angles between successive bonds. [1]

Polymers are further classified into thermoplastics, elastomers and thermosets. Thermoplastics are linear or weakly branched polymers with negligible entanglement. They can be crystalline or amorphous. Those which crystallize do not form perfect crystalline materials but instead are semi-crystalline with both amorphous and crystalline regions. The crystalline phases of such polymers are characterized by their melting temperature (T_m). Many thermoplastics are completely amorphous polymers which exist as glassy solids. These polymers are characterized by their glass transition temperature (T_g), the temperature at which they transform from glassy state (hard) to the rubbery state (soft). Elastomers are cross-linked rubbery polymers that can be stretched easily to high extensions and which rapidly recover their original dimensions when the applied stress is released. Thermosets are rigid network polymers in which chain motion is greatly restricted by a high degree of cross-linking.

Generally polymer chains are very flexible coiled with free volume in between. The simplest chains are of linear skeletal structure which may be represented by a chain with two ends. Branched polymers have side chains, or branches of significant length which are bonded to the main chain at the junction points. They are characterized in terms of the number and size of the branches. Network polymers have three dimensional structures in which each chain is connected to all others by a sequence of junction points and other chains. Such polymers are known as cross linked polymers.

Polymers are being used successfully in many industrial applications such as packaging, adhesion, thin films, biomaterials and coating etc. Polymers are inexpensive and easy to process and have excellent bulk physical and chemical properties.

1.2 Need for polymer surface modification

Polymer surfaces typically have low surface tension and high chemical inertness and hence they usually have poor wetting and adhesion properties. The surface properties can be altered by modifying the molecular structure using low energy plasma treatment. Plasma treatment converts the polymeric surface from hydrophobic to hydrophilic. Plasma polymer interactions for purpose of improving wetting and adhesion of metal-polymer laminate are being studied. Polymers have wide-ranging applications in food packaging and decorative products, and as insulation for electronic devices. For these applications, the adhesion of materials deposited onto polymer substrates is of primary importance. Not all polymer surfaces possess the required physical and/or chemical properties for good adhesion. Plasma treatment is one means of modifying polymer surfaces to improve adhesion while maintaining the desirable properties of the bulk material.

Depending on the gas composition and plasma conditions, ions, electrons, fast neutrals, radicals and VUV radiation contribute to the polymer treatment, resulting in etching, activation and/or cross-linking [2, 3]. Plasma treatment of polymer surfaces causes not only a modification during the plasma exposure, but also leaves active sites at the surfaces which are subjected to post-reactions; this is also called aging [4]. Aging effects depend on external influences like adsorption or oxidation, and on the internal tendency to attain an energetically favourable state (thermodynamic equilibrium) by restructuring processes and diffusion. Especially, a high-energy surface is prone to adsorb contaminants from the atmosphere in order to lower its surface energy [5].

Although the mechanisms of adhesion enhancement after plasma or ion beam pre-treatment have been discussed thoroughly in the last two decades, there is still only little known about the reason for loss in adhesion above some "critical level" of pre-treatment [6]. Therefore, a lack of understanding about the processes that occur in a near-surface polymer layer during ion bombardment still remains, as well as about the kinetics of post-bombardment chemical processes. Therefore, much efforts have been made to control the microstructure and thermal stability of metal-polymer interfaces, with the aim to prevent their degradation and to improve adhesion [7].

In order to increase adhesion property of the polymeric surfaces by means of plasma treatment, it is necessary to characterize the plasma treated surfaces and relate the alterations in optical, chemical and structural properties caused by the plasma treatment at the surfaces.

1.3 Polymer Surface modification techniques

Surface modification techniques enable the alteration of chemical and physical properties of polymer surfaces without affecting their bulk properties. The surface treatments help in improving adhesion characteristics, increasing hydrophobicity, introducing special functional groups at the surface, or modifying the surface morphology. Following are the techniques used for surface modification and are explained briefly in the next paragraphs.

(i) Flame treatment

Flame treatments have been used commonly in the polymer industry to improve adhesive characteristics of surfaces. The high flame temperature (1000-2000°C) and reaction with excited species in the flame, basically leads to an increased of oxygen concentration at the treated surface. [8] Flame treatment oxidises a thin layer of substrate surface. Several studies in literature concern the effects of flame treatment on surface of polymers. Evidently, formation of functional groups, cross-linking, chain scission, breaking of the long chain molecules and micro roughening occurs in the surface of polymer. It is agreed that flame treatment increases polarity and oxidation of the surfaces which leads to improve printability and adhesion. [9 - 12].

(ii) Corona discharge

Corona discharge is widely used in surface modification of polymers for printing and adhesion [13]. A corona discharge (atmospheric pressure plasma) is produced when air is ionized by a high electric field. Often a corona discharge is used for continuous treatment of films. Advantages of corona and flame treatments are that these processes can be used in continuous operation. The disadvantages arise from the fact that both treatments are carried out in open air, which often makes it difficult to control uniformity or chemical nature of the modification, due to variations in ambient conditions such as temperature and humidity or contaminations. [14]

In the corona discharge process, the surface substrate is bombarded with high speed electrons. The energy level of these electrons is high enough to break the molecule bonds of the most substrate surfaces. These oxidants present in corona i.e. ozone, atomic oxygen and oxygen free radicals create oxidised groups with free radicals present on the surface. [15-16] Even small amount of these reactive functional groups incorporated into polymers can be highly beneficial for improving surface characteristics and wettability.

Several researchers have verified that the corona treatment effect decays over time along with the adhesion properties of the surface. [17- 19] The main reason for this decay is that during the aging in air, the oxygen concentration at the surface is reduced, either because the functional groups migrate to the bulk or since the surface active additives or LMW (low-molecular-weight) fragments migrate from the bulk to the surface. [20]

(iii) Chemical treatments

In industry, chemical etchants like chromic or sulfuric acid can be used to convert smooth hydrophobic surfaces to rough hydrophilic surfaces by dissolution of amorphous regions and surface oxidation. [14] Chemical treatment of the fibre can stop the moisture absorption process, clean the fibre surface, chemically modify the surface or increase the surface roughness. The coupling agents were found to be effective to improve the surface properties of flax fibre and form a mechanically interlocked coating on its surface. Therefore, physical microstructure changes occurred to the fibre surface by chemical treatment.

The most important factor for obtaining good fibre reinforcement in the composite is the strength of adhesion between matrix polymer and fibre. Due to the presence of hydroxy and other polar groups in various constituents of jute, the moisture absorption is high which leads to poor wettability and weak interfacial bonding between fibres and the more hydrophobic matrices. Therefore, in order to develop composites with better mechanical properties, it is necessary to impart hydrophobicity to the fibres by suitable chemical treatments. Such surface modification of jute would not only decrease the moisture absorption, but would concomitantly increase the wettability of fibres with matrix polymer and the interfacial bond strength, both critical factors for obtaining better mechanical properties of the composites. [21] The surface modification of polyacrylonitrile membrane was studied using ethanolamine, triethylamine, sodium hydroxide, and potassium hydroxide solutions. [22] At lower NaOH concentration, morphological changes became evident with increased hydrophilicity. [23] This was due to the change of surface morphology.

(iv) Photon irradiation

Ultraviolet (UV) and infrared (IR) lasers can be used to treat very small and localized surface areas. UV irradiation includes surface photo-oxidation, increase of hydrophilicity, and photocuring of paintings. Pulsed UV-lasers are used in surface modification in many areas. Pulsed UV-laser irradiation can produce submicron periodic linear and dot patterns on polymer surfaces without photomask. These interference patterns can be used to increase surface roughness of inert polymers for improved adhesion. These images can also be transferred to silicon surfaces by reactive ion etching. [24] Pulsed laser beams can be applied to inert polymer surfaces for increased hydrophilicity and wettability. Polymer surfaces treated by pulsed UV-laser irradiation can be positively or negatively charged to enhance chemical reactivity and processability. Pulsed UV-laser exposures with high fluence give rise to photoablation. Other application of laser photoablation is diamond-film deposition. [24]

(v) Plasma treatment

Plasma treatment will be referred to as the modification of a surface with a non-polymerizable gas such as argon, oxygen, nitrogen or fluorine, in a vacuum system. Functional groups and cross-links are introduced at the surface of the polymer by reaction of gas-phase species and surface species.

Advantages of plasma processes:

1. The modification is limited to the top surface layer and does not affect the bulk properties of the polymer.
2. The modification by plasma processes is largely independent on the structure or chemical reactivity of the substrate.

3. A broad range of functional groups can be introduced at the surface, by variation of the gas that is used.
4. In general, the modification is fairly uniform over the whole substrate.
5. The plasma treatment or polymerization is a simple one step procedure, and is an all dry process.

Disadvantages of plasma processes:

1. A vacuum system is required for plasma treatments. This demand increases the cost of the operation.
2. Due to the complexity of plasma processes, it is not easy to achieve a good control over the chemical composition of the surface after modification. The influence of process parameters such as reactor geometry, input power, and gas flow on the chemical composition of the modified material should be investigated separately to find the optimal treatment conditions for each gas.

(vi) Ion-beam modification:

Ion beam modification has been used to texturize polymer surfaces, to increase adhesion. [25] The bombardment of polymer surfaces with ions has been shown to lead the reduction, oxidation, cross-linking, ion implantation, loss of heteroatoms and loss of aromatic via ring opening, depending on the polymer, ion, ion beam energy and dose. [14] Ion bombardment, polymers are related to the energy deposition from the incoming ions to the target. The basic quantity characterizing ion to target energy transfer is the projectile's energy loss per unit length, dE/dx. Another important parameter is the ion penetration depth and therefore the damage distribution. The ion impact may also cause some structural rearrangements in the surface of a target material like the formation of vacancies and interstitials, changes in the stoichiometry etc.

In present work, we have used argon plasma treatment for the surface modification of thermoplastic polymers. In plasma treatment, the substrate holder on which the polymer is kept is biased using bipolar pulse. The pulse duration, pulse amplitude and repetition rates will be varied and plasma properties changes because of polymer surface charging. The plasma property will be tailored using different characterization techniques. Plasma application is a good way of surface modification. Surfaces of selected thermoplastic polymers were modified by plasma technique and mainly the hydrophilicities and the surface free energy of the surface changed. Surface free energy and hydrophilicity mainly studied by increasing the treatment time using same set-up. XPS and ATR-FTIR have been used to analyse oxidation and the surface chemical composition. Surface morphology results of plasma treated and untreated samples, as measured by AFM are presented.

1.4 What is plasma?

Plasma is referred to as a partially ionized gas that contains roughly equal number of positively and negatively charged particles. The plasma state is more highly activated than the solid, liquid or gas state, and is often called the fourth state of materials.

For example, the transition of ice to an aqueous vapor. The thermal motion of the H_2O molecules is restricted in ice (solid state), but they still vibrate with a small amplitude around a given mean position. As the temperature of the ice increases, the vibration of the H_2O molecules also increases, until at 0 °C they leave the position determined by the free energy, and transition from ice to water occurs. As the temperature of water is raised further, the kinetic energy of the H_2O molecules increases. At 100 °C, the kinetic energy of the molecules becomes larger than their potential energy, and the molecules escape from the liquid state into the gas phase (vaporization). In the gas state, the H_2O molecules move around freely, until they collide with other particles. At temperatures of more than a few thousand degrees Celsius, the kinetic energy of the H_2O molecules becomes so high that collisions with other molecules lead to the dissociation of H_2O, and ionization of the atoms. The whole transition process is visualized schematically in **Figure 1.1**. [26]

Two types of plasma exist – high temperature and low temperature. High temperature plasma is found at atmospheric pressure in its manmade form as a plasma torch such as that used in stainless steel deposition, or occurring naturally as lightning. Low temperature plasmas, used in surface modification and organic cleaning, are ionized gases generated at pressures between 0.1 and 2 torr.

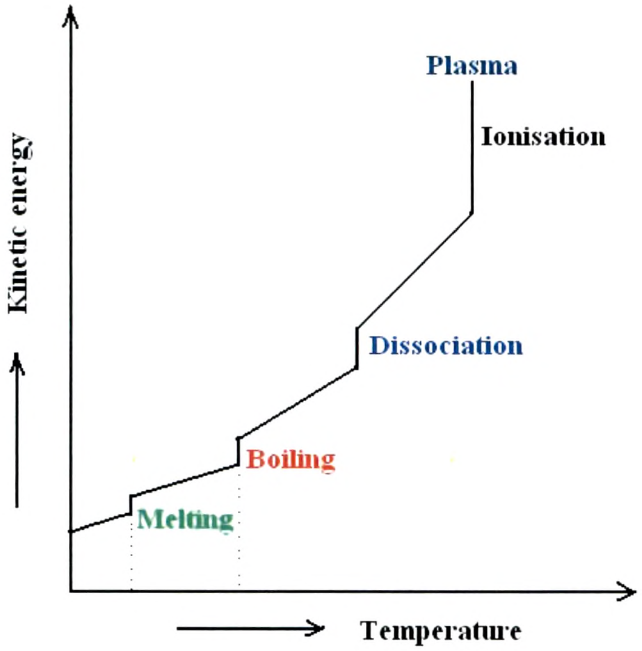

Figure 1.1: *Schematic diagram of the state transition processes*

The basic concepts of plasma physics, different collision processes and surface modification processes are explained briefly in the next sub-sections.

(i) Fundamental aspects of plasma physics

Some of the basic concepts of plasma physics are useful for the understanding of plasma polymerization. First of all, the negative particles in glow discharge plasma are mostly electrons, however negative ions are also formed. When an electric field is applied, the electrons gain energy according to Newton's law,

$$a = \frac{q}{m_e} E \quad \text{--------} \quad (1.1)$$

where, 'a' is the acceleration of the electron, q is its electric charge, m_e is its mass, and E is the electric field. [27] Three different types of collisions can occur between an electron and an atom, depending on the energy K that is transferred to an electron in the atom:

1. $K = 0$. The electrons in the atom remain in the ground state. The collision is elastic and causes no change in the structure of the atom.

2. $0 < K < qV_i$, where V_i is the ionization potential of the atom. An electron in the atom is excited to a higher energy level, but returns to the ground state in a short time, releasing the gained energy again. The collision is inelastic.

3. $K > qV_i$. The atom is ionized by inelastic collision and becomes positive with charge $+q$.

Between the energy level of the ground state and that of the ionized state, a number of other energy levels can exist. An electron in an atom that receives energy from a primary electron can jump to a higher energy level, but after a short period of time (of the order of 10^{-8} s) it falls back to lower energy levels or to the ground state. In this process, the electron's excess energy is released e.g. by emission of a photon. When an electron falls back from energy level E_m to E_n, the frequency ν of this photon is given by:

$$h\nu = E_m - E_n \quad \text{--------} \quad (1.2)$$

where h is Planck's constant.

The temperature of colliding species plays an important role on the collision processes occurring in a glow discharge. The electron temperature T_e in a plasma is given by,

$$T_e = (e/k)(E\lambda_e/2\sqrt{2})(m_m/m_e)^{1/2}(\pi/6)^{1/4} \quad \text{--------} \quad (1.3)$$

where k is the Bolzmann constant, λ_e is the mean free path of electrons, and m_m *is* the mass of particles (neutral atoms and molecules). [28] Since the ratio of m_m/m_e is very high, the electron temperature in a low pressure plasma is extremely high (e.g. on the order of 10^4 K). Because ions have roughly the same mass as the corresponding neutral atoms and molecules, they lose most of their kinetic energy in collisions with molecules. The ion temperature T_i is therefore much lower than T_e (in the range of 300-1000 K), and it is only slightly higher than the temperature of molecules T_m (~ 300 K). [27]

(ii) Types of collisions:

A number of different collision processes occur in a glow discharge, including ionization, excitation, dissociation and attachment. [14] Ionization is the essential step in creating and sustaining a plasma, but is not necessarily the primary step in initiating plasma polymerization. [27] For example, the ionization of a helium atom can be visualized as follows:

$$\mathrm{He} + e^- \rightarrow \mathrm{He}^+ + 2e^- \qquad \text{(ionization)}$$

A positive ion and two electrons are produced in this reaction. The two electrons are accelerated by the electric field and can produce further ionization. It was mentioned that electrons in the ground state can jump to higher energy levels (excitation), without resulting in ionization:

$$\mathrm{He} + e^- \rightarrow \mathrm{He}^* + e^- \qquad \text{(excitation)}$$

After a very short period of time the electron falls to a lower energy level, or returns to the ground state by radiative decay (deexcitation):

$He^* \rightarrow He + h\upsilon$ (de-excitation)

Some excited states however have much higher stability than others, and have lifetimes of 1 ms or longer. Such a state is called a metastable state. [29] Penning discovered in 1937 that the voltage necessary to initiate a neon glow discharge was reduced dramatically by the addition of only 0.1 % of argon to the gas. [30] The reason behind this behavior is that the excitation energy of the metastable state of neon is higher than the ionization energy of argon. The metastable neon atom returns to the ground state upon collision, but transfers the excess energy to the colliding argon atom. The neon gas acts as a catalyst in the gas ionization of argon:

$Ne^* + Ar \rightarrow Ne + Ar^+ + e^-$ (Penning ionization)

A metastable atom can also be ionized by electron impact directly. Negative ions such as F^-, Cl^-, Br^-, I^-, O^- and O_2^- can also be produced in a glow discharge, if a free electron is captured by a molecule, for example:

$Cl_2 + e^- \rightarrow Cl^- + Cl$ or $O_2 + e^- \rightarrow O_2^-$ (formation of negative ions)

Collisions between charged species take place in ionized gas as well, but do not play an important role overall, simply due to the fact that most plasmas are only partially ionized, and contain for more neutral than charged species. An example of such a collision is recombination:

$Ar^+ + e^- \rightarrow Ar$ (electron-ion recombination)

$O^- + Ar^+ \rightarrow O + Ar$ (ion-ion recombination)

Recombination also occurs at the surface of the reactor. Collisions of electrons with the reactor wall charge the surface (depicted as S) negatively, which then attracts positive ions that neutralize the charge:

$S + e^- \rightarrow S^-$ and $S^- + Ar^+ \rightarrow S + Ar$ (surface recombination)

In this reaction the energy gained in the ionization process is released, and absorbed by the surface in the form of thermal energy. [27]

(iii) Plasma surface modifications

Plasma surface modification involves the interaction of the plasma generated excited species with a solid interface. The plasma process results in a physical and/ or chemical modification of the first few molecular layers of the surface, while maintaining the properties of the bulk.

Materials used in microelectronics and optoelectronics industries include ceramics, glass, polymers and metals – such as gold, copper, aluminium, nickel, palladium, tungsten, and silver. The effectiveness of the plasma on these complex interfaces is determined by the plasma source gases, the configuration of the plasma system and the plasma operating parameters.

Surface modification processes can be classified into four categories:

a) Contamination removal

Contamination may exist in the form of residues, mold release agents, anti-oxidants, carbon residues or other organic compounds, which prevents adequate adhesion. Oxygen plasma is commonly used excellent process for removing organics. [31] Oxygen plasma causes a chemical reaction with surface contaminants resulting in their volatilization and removal from the plasma chamber.

Sufficient care must be taken while choosing cleaning process parameters to ensure that only organics are completely removed. It is possible that the surface may modify instead of removing contamination. Whether or not organic removal is complete can be assessed through the use of contact angle measurement.

b) Surface activation

When plasma is brought into contact with polymers, this will induce chemical and physical modifications of the surface, producing more reactive sites, or changes in cross-linking or molecular weight. [32] Surface activation by oxygen, nitrogen, hydrogen, and ammonia plasma, dissociate and react with the surface, creating different chemical functional groups on the surface. These functional groups have strong bonds with the bulk material and have the capability to further bond with adhesives to promote better adhesion. In microelectronics applications, plasma surface activation prior to die attach provides better contact, improved heat transfer and minimal voiding.

c) Etching

Roughening of the surface can play a significant role in adhesion by increasing the total contact area between the adhesive and the subsurface. Plasma etching can be used to remove material from a surface. [33] Etching can be accomplished with either active or inert gases and can cause extremely porous surfaces by long exposure to the plasma. The semiconductor manufacturing industry has been using plasma etching as primary treatment. Similarly, circuit board industry using plasma as a means of etching polymers smeared in the drilling process.

d) Cross Linking

Cross-linking employs inert gases such as argon or helium to remove some atomic species from the surface, and generates reactive surface radicals. These free radicals in turn recombine on the surface causing a stable cross-linking of the surface structure. Argon plasma effectively sputters nanometers of material from the sample surface, by roughening the surface on the nanometer scale. The cross-linking improves the adhesion of metal layers to the plasma treated polymer laminate. [34]

1.5 Polymer surface properties relevance to adhesion

Adhesion is the most important surface property subjected to many applications of polymers. The necessary condition for the adhesion is the tight contact between the two parts. It is important to form strong and stable adhesive joint between the interfacial surfaces. The next stage includes the generation of adhesion forces across the interface. In this section, a brief overview of surface forces and surface energies is given before explaining the adhesion mechanism. [35]

(i) Surface forces:

When a material interacts with the surrounding environment, it is the nature of the surface forces that determines the kind of interaction. Van der Waals' and electrostatic are long range forces, whereas hydrogen, acid-base and covalent are short range forces. Van der Waal's forces are always present during the interaction. Electrostatic ones occur at the same time in some cases. These forces arise from the interaction between charged bodies, described by the charge and the potential. The combination of van der Waals' and electrostatic effects in water (or a high dielectric constant solvent) is described by the so-called DLVO (Derjaguin, Landau, Vervey and Overbeek) theory of colloid stability.[36] Van der Waals' forces are a set of forces characterized by the same power dependence on distance. The important parameters in such a kind of interaction are the dipole moment, which arises from an uneven charge distribution in molecule, and the atomic polarizability, which indicates the tendency to redistribute the charge when the molecule is subjected to an electrical field. Owing to the process of charge redistribution, a molecule becomes a dipole and gives rise to an electrical field. An important contribution to the van der Waals' forces is the interaction between the instantaneous dipole moment arising from the instantaneous position of electrons with respect to the nucleus. The van der Waals' forces are always involved in the interaction between bodies, unlike other kinds of forces that require a particular feature.

The van der Waals' contribution to the free energy of interaction between two molecules is given by

$$w_{vdw} = - C / r^6 \quad \text{--------} \quad (1.4)$$

where r is the distance.

The free energy of interaction between macroscopic bodies, W, of different geometries can be described by a relationship of the kind:

$$W(D) \infty UA / D^n \quad \text{--------} \quad (1.5)$$

where U is a factor which contains numerical constants and the relevant dimensions of bodies involved, D is the distance between the bodies, and $A = \pi^2 C \rho_1 \rho_2$ is the Hamaker constant (ρ is the number density of molecules in the solid).

The above equation shows that the free energy of interaction between macroscopic bodies depends on the dimensions of the bodies (factor U). Van der Waal's forces between large bodies are more long-ranged than between molecules. Finally, the effect of the chemical and physical nature of the materials involved in the interaction on the interaction itself, is described by the Hamaker constant, which contains the relevant atomic or molecular parameters in the constant C. Even if Van der Waal's bonds are always present, the energy of such bonds is the lowest compared to other bond types. Therefore, they are only of significance in cases where other kind of bonding is not possible.

In addition to the long-range forces, short-range forces are also present in the interactions. These are usually strong covalent, hydrogen, or acid-base forces. The structural feature required to form hydrogen bonds is a hydrogen atom covalently bonded to a highly electronegative element, such as O, N, F, etc. It is expected that hydrogen bonding plays an important role in the interaction between polymer surfaces bearing hydroxyl, carboxyl, amino or similar groups. When surface atoms and molecules come very close together, very strong forces arise from the overlap of electronic clouds and sharing of valence electrons. The process when intervening atoms lose their identity and create a new species is known as covalent bonding. The details of covalent bonding depend on the chemistry and the electronic and geometrical configuration of the species involved. Most synthetic polymers do not bear surface functional groups suited for covalent bonding, as chemical inertness is a desired property for many applications. When it is necessary to join the polymer covalently with another molecule, surface activation is applied by means of surface modification introducing special functional groups suitable for covalent bonding.

(ii) Surface energy and surface tension:

The atoms and molecules at the surface are in different environment as compared to their inner counterparts. The inner molecules are equally attracted in all the directions by the neighbouring counterparts, while the surface molecules are attracted from one side only. The surface energy of the material can be understood by one to one summation between the atoms of one medium with all the atoms of other medium.

The surface energy can be determined as:

$$W = -\text{constant} + \frac{A}{12\pi D_0^2} \qquad \text{--------} \quad (1.6)$$

Where constant is the bulk or cohesive energy of the atoms of a given phase in their equilibrium position. The second term is for two isolated surfaces.

The free energy for two isolated surfaces is given by

$$W = \frac{A}{12\pi D_0^2} = 2\gamma$$

$$\text{Or} \quad \gamma = \frac{A}{24\pi D_0^2} \quad \text{--------} \quad (1.7)$$

Where γ is the surface tension. Interfacial contact separation $D_0 = 0.165$ nm (universal cut off distance)

The surface tension can be measured by using contact angle measurements. If a liquid drop placed on the solid surface, three interfacial tensions exists between liquid-solid (γ_{sl}), liquid-vapour (γ_{lv}) and solid-vapour (γ_{sv}). The contact angle θ of liquid with solid is given by Young's equation:

$$\gamma_{sv} = \gamma_{sl} + \gamma_{lv} \cos\theta \quad \text{--------} \quad (1.8)$$

It is possible to measure the surface tension of a polymer using various liquids. [37]

(iii) Mechanism of adhesion:

Mechanism of adhesion can be explained with the following four theories. These theories are mechanical interlocking, diffusion theory, electrostatic attraction and adsorption theory. [38-40]

The mechanical interlocking theory originates from rough empirical observations. The adhesion is more successful on rough and irregular surfaces. It was observed that good adhesion is possible between two perfectly smooth surfaces. [36]

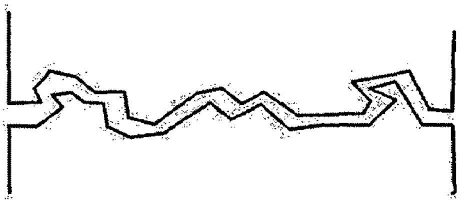

Figure 1.2 : *Mechanism of adhesion : Mechanical interlocking*

The diffusion theory explains the adhesion between two identical polymer surfaces. This model explains how two macromolecules in intimate contact results from diffusion of the molecules of the superficial layers.

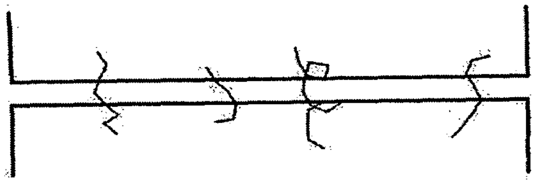

Figure 1.3 : *Mechanism of adhesion : Interdiffusion of chains*

This model has limited applications due to mobility of macromolecules above glass transition temperature and mutual solubility. The model is doubtful to describe the behaviour of polymers which are not or only slightly soluble in one another, or if the polymer surface is crystalline or highly crosslinked. [40]

The electrostatic attraction theory explains the occurrence of electrical double layer at the interface between two solids. However, the observation is that any electrical double layer does not contribute to the adhesion. [39, 36]

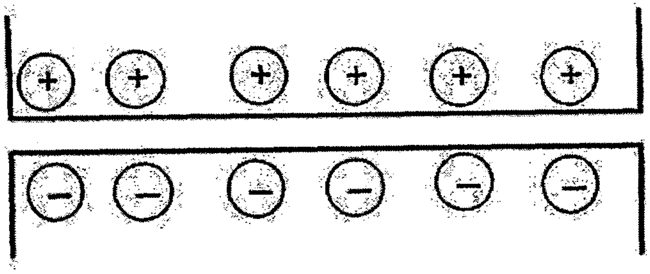

Figure 1.4 : *Mechanism of adhesion : Electrical interactions*

The adsorption theory is the most widely applicable theory. The adsorption theory explains the interatomic and intermolecular forces which are established between adhesive and the substrate, when sufficiently intimate molecular contact is achieved at the interface. [39, 40]

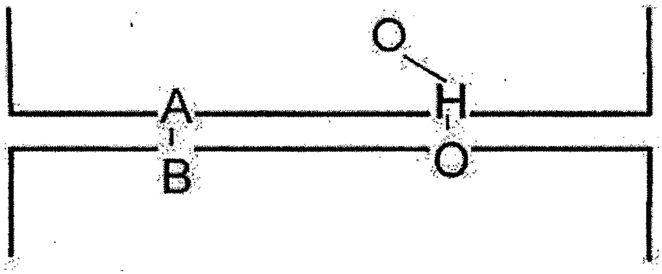

Figure 1.5 : *Mechanism of adhesion : Chemical interactions (adsorption theory)*

Most surface treatments are used to enhance adhesion by introducing functional groups or creation of a heavily cross-linked layer. Adsorption theory has wide applications as it is based on chemical interactions. Mechanical interlocking, Electrostatic and diffusion theories are important in some specific applications or systems. An essential condition required for adhesion model is a close and intimate contact between the substrate and the adhesive. Hence, the adhesive must wet the substrate surface. Qualitatively, higher the surface energy of the solid, the better is the wettability of the solid and the smaller is the contact angle and the greater is the adhesion between two materials.

The adhesion assumes that only secondary bonds act at the interface which have a much lower bond energy compared to primary chemical bonds (covalent, ionic, metallic) or acid-base interactions. Adhesion by chemical bonding takes place rather frequently in the case of polymer-metal interfaces [38]. The formation of such bonds is based on a charge transfer from the metal to the polymer. An increase in adhesion through the connection by primary bonds is obtained when special side or functional groups are introduced along the polymer chain or new adsorption sites containing radicals, unsaturation etc. are created.

The examination of various theories made on the basis of adhesion specifically referred to polymers, has shown that only those based on chemical interactions have a general character and a wide application. Electrostatic and interdiffusion theories are important in some specific systems and mechanical interlocking may cause other mechanisms to take part in the adhesion phenomenon. The theories were referred to the adhesion enhancement at the interface of the adherent and the substrate. However, the cohesive failure suggests the formation of some weak boundary layer in one of the solids. [35]

1.6 Review of plasma-polymer interaction

In present study, we have been using four thermoplastic polymers such as polycarbonate (PC), polyethyleneterephthalate (PET), polytetrafluoroethylene (PTFE), and polyethersulfone (PES) for surface modification using low energy argon plasma treatment. We have done an extensive literature survey, and found that lot of work yet to be done on surface modification to meet the desired surface characteristics.

Polymers have been applied successfully in fields such as adhesion [41-43], biomaterials [44-45], protective coatings, friction and wear-resistant composites, microelectronic devices [46] and thin film technology. PCs can be used for plastic vessels, machine parts and optical grades can be used for compact discs (CDs, CDROMs and DVDs), optical fibres, etc. Many applications in industry, biology and medicine require improvement in surface properties without altering the bulk properties. Some of the techniques have been developed to modify the polymer surfaces for improved adhesion, wettability, printability and many other technologically important characteristics. The common methods of surface modification include mechanical or chemical treatment and exposure to flames, photons, ion beams, and other types of radiation. Among all the methods of modifying polymer surfaces to improve wettability and adhesion, low pressure plasma treatment has proved to be one of the most effective, ensuring uniformity, as well as being non-polluting. [47]

Over the years treatment of PC was performed by many research groups to modify polymer surfaces for improved wettability, adhesion, etc. Cho et. al [48] investigated the effect of oxygen gas on polycarbonate surface irradiated with keV energy Ar^+ ions and found that the hydrophilic group formed by chemical reaction between unstable chain generated by ion irradiated and oxygen. Koh et. al [49] studied the surface modification of polymers (PC, PET, and PMMA) by ion assisted reaction in reactive gases environment. The comparison between the conventional surface treatments and the ion assisted reaction are described in terms of physical bombardment, surface damage, functional group, and chain mobility in the polymer. Seidel et. al [50] studied the adhesion property of Ar plasma treated Al-metallized polycarbonate. Hofrichter et.al [51] studied the influence of N_2, H_2, and O_2 plasma treatment on pure and commercial grade polycarbonate in order to enhance the adhesion of plasma deposited silica films. Hegemann et. al [52] studied the plasma treatment on PC for the improvement of wettability and adhesion as well as for the reduction of friction of polymer surfaces. Boldyryeva et. al [53] investigated the possibility of nano particle formation in PC implanted with Ag^- and Cu^- ions and reported optical property and structure of PC. Kitova et. al [54] studied the RF plasma treatment of polycarbonate substrates and found that all RF plasma treatments led to an increase in the polar component of PC due to an increased hydrogen bonding ability. Sira et. al [55] investigated the surface modification of polycarbonate in homogeneous atmospheric pressure discharge burning in nitrogen and in the mixture of nitrogen and hydrogen.

They found that the treatment of polymers in the homogeneous discharge is spatially homogeneous and the surface roughness of the treated samples is smaller in comparison to that of filamentary discharge.

Extensive works have been carried out on PET using different plasma species. Koh et. al [49] studied surface modification of polymer by ion assisted reactions in reactive gases environment. Surface analysis showed formation of hydrophilic functional groups such as C=O, (C=O)-O, C-O etc. without surface damage after ion assisted reaction treatment. Lee et. al [56] found substantial improvements in the hardness and wear resistance after a treatment with low energy ions on number of polymers. Nishino et. al [57] studied the in-situ observation of surface deformation of polymer films by atomic force microscopy. To improve the adhesion between the Cu layer and PET film for high-quality electromagnetic interference (EMI) shielding materials, Pd chemisorption was employed to establish strong chemical bonds between the nonconductive substrate and the copper layer and the effect of plasma treatment with various gases, argon (Ar at 50 W), oxygen (O_2 at 75 W), ammonia (NH_3 at 100 W)) prior to Cu plating was investigated by Kyung Wha Oh et. al [58]. Inagaki et. al [59] modified the surfaces of PET by pulsed plasma and observed that the pulsed Ar plasma is advantageous in formation of hydroxyl groups on the PET film surfaces. Yoshida et. al [60] investigated the characteristics of carbon films formed on PET by plasma source ion implantation using CH_4 and C_2H_2. They found that surface modification with CH_4 is a viable alternative method for reducing the oxygen transmission rates. Ueda et. al [61] studied the treatment of PET by aluminum plasma for oxidation protection. Sakudo et. al [62] developed a new technique to enhance the barrier characteristics of PET film against CO_2 and O_2 gases. Plasma based ion implantation of nitrogen was found to be able to change a polymer surface into diamond like carbon. Wang et. al [63] studied the C_2H_2

plasma immersion ion implantation deposition on PET to improve its blood compatibility. Later on Inagaki et. al [64] studied that the surface modification of poly (ethylene terephthalate) (PET) film by average etching rate using argon (Ar) (0.79 nm/s), oxygen (O_2) (2.3 nm/s), hydrogen (H_2) (1.15 nm/s), nitrogen (N_2) (0.93 nm/s), and ammonia (NH_3) (0.58 nm/s) plasmas of rf power at 50 W. The surface roughness was in the order of NH_3 plasma > N_2 plasma > H_2 plasma > Ar plasma > O_2 plasma. The O_2, Ar, H_2, and N_2 plasmas modified mainly CH_2 or phenyl rings rather than ester groups in the PET polymer chains to form C-O groups. On the other hand, the NH_3 plasma modified ester groups to form C-O groups. Singh et. al [65] studied Vickers' microhardness, surface roughness and melting properties of nitrogen plasma treated PET films. Rusu et. al [66] and Rory Wolf [67] analysed the role of plasma and its use in increasing the surface energy to achieve Wettability.

Polytetrafluoroethylene (PTFE) is a polymer used as insulator in cables, connector assemblies and for printed circuit boards because of its good dielectric properties. [68] The polymeric devices are meeting the requirements of biocompatibility between the physiological environment and the biomaterial surface. Mostly PTFE is used as vascular grafts in cardiovascular applications. The main drawback of plasma treatment for activation of polymers is ageing. The various functional groups formed during plasma treatment are not stable with time. The surface tends to approach to its untreated state. Hence, the surface keeps loosing its hydrophilic character spontaneously. [69] Wilson et. al modified PTFE by RF plasma with 50 W argon ions and found that their process significantly increased the wettability of the PTFE surface. Initial contact angle of water was 108° and after plasma processing a contact angle became 62°. [70] Clark and Hutton also found that hydrogen plasma leads to rapid defluorination of PTFE to a depth of 20 A°. [71] Ryan et.al verified by X-ray photoelectron spectroscopy (XPS) that plasma treatment leads to defluorination, the production of hydrocarbons, cross-linking, chain scission and the grafting of oxygen and nitrogen containing groups. [72, 73] The incorporation of polar groups and oxidation grafted to polymer radicals are a commonly cited phenomenon. This occurs both during plasma treatment and the subsequent exposure to ambient air after processing. Typical polar groups found via X-ray photoelectron spectroscopy (XPS) studies are oxygen groups, such as carbonyls, hydroxyls and nitrogen groups such as nitriles and amides. [71, 74-76] Chen et. al found that XPS results indicated the presence of oxygen and nitrogen containing groups on the plasma treated surfaces. [77]

Polyethersulfone is a high temperature and high performance engineering thermoplastic. [78] This polymer has good oxidative, thermal, mechanical and film-forming properties. PES has been applied in a wide range of areas such as electrical, automotive, aerospace, medical, consumer products, and separation processes. Hydrophilic, hydrophobic and ionic species are always used as modifiers in terms of specific application. The reconstructable surfaces change their wettability and permeability, as well as their adhesive, adsorptive, mechanical and optical properties. [79] Graft-polymerization can be initiated without a photoinitiator, thus, UV-light is particularly useful for chemically attaching hydrophilic monomers to PES membranes for antifouling. Malaisamy et. al [80] used, a hydrophilic, positively charged, quaternary ammonium derivative of a vinyl monomer, [2-(acryloyloxy)ethyl] trimethyl ammonium chloride (AETMA) to modify a commercially available polyethersulfone (PES) microfiltration membrane.

Lee et. al [81] reported a novel method for producing a selective protein adhesion pattern on a PES film surface using atmospheric pressure plasma using reactive gases. Zhu et. al [82] modified surface of PES membrane by graft polymerization of acrylic acid by using corona discharge treatment, which helps to improve hydrophilicity and anti-fouling properties at the surface. Vatuna et. al [83] found that the modification of PES fabric by RF plasma seems to be more effective than that of the MW plasma. Bruggen [84] found that the plasma treatment introduces functional groups on the membrane surface due to variation of plasma treatment parameters, surfaces with different properties can be obtained. Possible gases include CH_4, Ar, O_2, H_2, He, Ne, N_2 and CO_2 in addition to H_2O. He et. al [85] introduced a concept of composite membrane with a coating layer of sulfonated polyetherssulfone (SPES) onto a polysulfone (PSf) support. The sulfonated polymer itself will be investigated interms of mechanical properties as well as adhesion onto the PSf support. Steen et. al [86] studied H_2O plasma treatment to PES membrane to investigate the role of membrane material (chemical composition) and structure (i.e. degree of asymmetry) in hydrophilic modification. Wavhal et. al [87] studied the surface and permeation properties of membranes and compared results before and after plasma treatment and subsequent grafting with acrylic acid (AA). Kull et. al [88] examined the influence of nitrogen containing plasmas, specially N_2, NH_3, Ar/NH_3, and O_2/NH_3 on PES membranes. Kroll et. al [89] developed a strategy for modifying hollow fibre surface with a wide variety of different reactive ligands. Such membranes find applications in high speed separations of amino acid and protein mixtures. Vesel et. al [69] studied the surface modification of various polymers by oxygen plasma. On all polymer surfaces increased concentration of oxygen was detected by observing groups like C-O, C=O and O=C-O on the surface. The concentration of these groups depends on the type of polymer. Hegazy et. al [90] studied the membrane obtained by radiation grafting for separation process and waste water treatment from heavy and toxic metals, low level nuclear waste management and separation of Zr from uranium in their wastes and enzyme immobilization.

In context of the above mentioned review it is observed that plasma treatment is the unique technology of polymer surface modification. Thus an attempt has been made to study the plasma induced surface modification in four commercial thermoplastic polymers. Polycarbonate bisphenol-A (PC), poly-ethylene-terephthalate (PET), polytetrafluoroethylene (PTFE), and polyethersulfone (PES) have been selected in the present investigation. In order to have better understanding of basic concepts and systematic correlation between optical, chemical and structural changes with plasma treatment. PC, PET, PTFE and PES were treated with low energy argon plasma (600 eV). The treatment time was varied for 5 min, 10 min and 50 min. The pristine as well as argon plasma treated samples were characterized by means of different techniques viz: contact angle measurements, X-ray Photoelectron Spectroscopy (XPS), Attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy, Atomic force microscopy, and Vicker's microhardness indentation.

1.7 Concept of this thesis

The basic motivation of this work is based on the remarkable change in the physical and chemical properties of thermoplastic polymers associated with plasma treatment. The low energy argon plasma was chosen in order to induce changes only in the polymer surfaces.

The objective of the thesis is to increase adhesion property of the polymeric surfaces by means of plasma treatment.

This will be monitored / studied by

1. An increased polymer surface free energy (contact angle measurement) with increasing fluence or treatment time indirectly shows the improvement of polymer surface adhesion.
2. The degree of hydrophobicity of insulating materials is depending on the surface roughness. Therefore, the roughness has to be taken into account if insulating materials shall be compared to each other.
3. Polymer chains undergo chain scissions with plasma treatment creating sputtering, and free radicals creating cross link networks, branching and double bonds. X-ray Photoelectron Spectroscopy (XPS) and Attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy are used to determine created functionalities at surface.
4. The microhardness study on untreated and argon plasma treated samples of PC, PET, PTFE and PES helps to understand the modification in properties due to inter and intra molecular interactions.

The whole work is divided into following chapters, Chapter 1 deals with the introduction about polymers, their classification, plasma interaction, polymer surface properties, review of latest work, and the motivation for present work. Chapter 2 deals the details for selected thermoplastic polymers, plasma irradiation and characterization techniques. Chapter 3 includes results of spectroscopic studies using XPS and ATR-FTIR. Chapter 4 presents results of surface free energy, morphology and hardness studies. The results part is divided into two separate chapters (Chapter 3 & Chapter 4) that present the most important obtained results of the goal mentioned above. Finally Chapter 5 contains a short summary of the results and conclusions obtained by bipolar argon plasma treatment including the future plan of work.