

CHAPTER 1

Relevance of Plasma Processing on Polymeric Materials and Interfaces

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1.1 INTRODUCTION

With the growing global energy crisis and ecological risks, polymers are playing a vital role in five major areas where the needs of society face huge technological challenges. These are: energy, sustainability, health care, security and informatics, and defence and protection [1]. In order to fulfil the aforesaid diverse societal needs, advanced polymeric materials are developed either by synthesizing new polymers or through the modification of existing polymeric materials. In most of the cases, researchers opt for the modification of existing polymers rather than synthesizing new polymers due to the considerable cost aspects. Polymers are a major class of materials and possess a wide range of mechanical, physical, chemical, and optical properties. Polymers have increasingly replaced metallic components in various applications. These substitutions reflect the advantages of polymers in terms of corrosion resistance, low electrical and thermal conductivity, low density, high strength-weight ratio (particularly when reinforced), noise reduction, wide choice of colors and transparencies, ease of manufacturing and complexity of design possibilities, and relatively low cost.

The interface is defined as the boundary between two layers of materials with different chemistries and/or microstructures. The interphase is described as the volume of material affected by the interaction at the interface. The term interphase is considered as a three-dimensional zone which is different from a two-dimensional interface and it is now widely used in the adhesion community to indicate the presence of a

chemically or mechanically altered zone between adjacent phases. In the interphase zone, one can observe the gradation of properties from one phase to another, rather than the abrupt change necessitated by the acceptance of a two-dimensional interface [2].

Adhesions of polymeric materials have a direct relationship with surface/interfacial properties. The adhesion at the interface/interphases has prime importance when advanced polymeric materials are developed via surface modification techniques. Adhesion problems exist with the bonding of polymers and the adhesion of coatings to polymer surfaces, while interface problems between different phases of melt-blended polymers and polymer composites are recurring and challenging areas in polymer-based industries. With a thorough understanding of the surface and interface phenomenon in polymer multiphase systems, one can control the interfacial properties by engineering the interface/interphase region leading to the development of advanced materials with multifunctional properties.

The first section of this chapter provides a concise introduction to polymeric materials, followed by a description of their structure, properties, and applications. Then it addresses the salient features of polymer surfaces and interfacial problems with a brief overview of surface phenomena and adhesion phenomena in the bonding of polymers. Finally, the major part of this chapter covers the relevance of plasma processing on polymeric materials and interfaces. This part starts with a basic introduction, continues with discussions on the mechanism of plasma surface modification, effects of plasma treatment on specific polymers, various characterization techniques, and applications of plasma in polymeric materials.

1.2 STRUCTURE, PROPERTIES, AND APPLICATIONS OF POLYMERS

Polymers are defined as macromolecules, which are formed by the joining of repeatable structural units. The repeatable structural units are derived from monomers and are linked to each other by covalent bonds. The properties of a polymer depend on the chemical structures of monomeric units, molecular weight, molecular weight distribution, and its architecture. The processes of the formation of polymers from respective monomers is known as polymerization. Two major classifications of polymerization processes are condensation (step-growth or step-reaction polymerization) and

addition polymerization (chain-growth or chain-reaction polymerization). In the former, the bonding takes place by condensation reaction resulting in the loss of small molecules which are often water. In the later, bonding takes place by the reaction of unsaturated monomers without reaction by-products. The final properties of the product made from polymers depends highly on the inherent properties of the polymer/s and the additives used for modification. The influence of molecular weight, structure (linear, branched, cross-linked, or network), degrees of polymerization and crystallinity, glass transition temperature, and additives are briefed below.

The molecular weight and molecular weight distribution of polymers strongly influence the final properties of the end products. The mechanical properties such as the tensile and the impact strength, the resistance to cracking, and rheological measurements such as viscosity (in the molten state) of the polymer etc., increases with increase in molecular weight. Summing up of individual molecular weights of the monomeric units in a given chain gives the molecular weight of the polymer. It is important to keep in mind that the average chain length is proportional to the molecular weight of the given polymer. That is, higher the molecular weight of a given polymer, the greater the average chain length. The size of a polymer chain can be expressed in terms of the degree of polymerization which is defined as the ratio of the molecular weight of the polymer to the molecular weight of the repeating unit. The covalent bonds which link the monomeric units together are called primary bonds and the polymer chains are held together by secondary bonding. In a given polymeric material, the increase in strength and viscosity of the polymer with molecular weight is attributed to the fact that, as the length of the polymer chain increases, the greater is the energy needed to overcome the combined strength of the secondary bonding with primary bonding (covalent). Depending upon the type of chains, the polymers are classified into linear polymers, branched polymers, cross-linked polymers, and network polymers. If the repeating units in a polymer chain are all of the same type, the molecule is called a homopolymer. Copolymers contain two types of polymers and terpolymers contain three types.

Crystallinity plays a critical role in delivering enhanced property to polymeric materials and their products. By controlling the rate of solidification during cooling and the chain structure, it is possible to achieve desired degrees of crystallinity to polymers. The improved hardness, stiffness, and low ductility values of polymeric materials are outcomes of increased crystallinity. The optical properties of polymers are also

influenced by the degree of crystallinity. At low temperatures, the amorphous polymers are hard, rigid, brittle, and glassy while at high temperatures they are rubbery or leathery. The temperature at which a transition occurs is called the glass-transition temperature (T_g). The information on T_g can predict the nature of the polymer at its service temperature—that is, whether it rigid and glassy, or flexible and rubbery.

The two major classes of polymers are thermoplastics and thermosets. When the temperature of a certain polymer is raised above the T_g , or melting point, T_m , they can be easily molded into desired shapes. The increase in temperature weakens the secondary bonding via the thermal vibration of the long molecules which, in turn, enables more free movement of adjacent chains particularly when subjected to external shaping forces. These types of polymers are referred as thermoplastics. If the temperature of a thermoplastic polymer is raised above its T_g , it becomes leathery and on increasing the temperature further, it turns rubbery. At higher temperatures, say above T_m for crystalline thermoplastics, it becomes a molten fluid and its viscosity decreases with increasing temperature. At this stage, it can be molded into different shapes. When thermoplastics are stretched, the long-chain molecules tend to align in the general direction of the elongation. This process is known as orientation. Due to the viscoelastic behavior, thermoplastics are particularly susceptible to creep and stress relaxation. When subjected to tensile or bending stresses, some thermoplastics may develop localized wedge-shaped and/or narrow regions of highly deformed material. This process is known as crazing. It typically contains about 50% voids. With increasing tensile load on the specimen, these voids coalesce to form a crack, which eventually can lead to a fracture of the polymer. The environmental factors such as the presence of solvents, lubricants, or water vapor, residual stresses in the material, radiation, etc., can increase the crazing behavior in certain polymers. An important feature of certain thermoplastics is their ability to absorb water (hygroscopic nature). With increasing moisture absorption, the T_g , the yield stress, and the elastic modulus of the polymer are lowered severely. Compared to metals, plastics generally are characterized by low thermal and electrical conductivity, low specific gravity, and a high coefficient of thermal expansion. Certain polymers can be stretched or compressed to very large strains, and then, when subjected to heat, light, or a chemical environment, they recover their shape. These are known as shape memory polymers [1].

When the long-chain molecules in a polymer are cross-linked in a three-dimensional manner, the structure in effect becomes one giant molecule with strong covalent bonding. These polymers are called thermosetting polymers or thermosets, because the complete network is formed during polymerization and the shape of the part is permanently set. This curing (cross-linking) reaction is irreversible. Thermosetting polymers do not have a sharply defined T_g . Because of the strong covalent bonding, the strength and hardness of a thermoset are not affected by temperature or by rate of deformation. Thermosets generally possess better mechanical, thermal, and chemical properties, as well as electrical resistance and dimensional stability, than thermoplastics.

In order to impart certain specific properties, polymers usually are compounded with additives such as plasticizers (to impart flexibility and softness), fillers (to improve the strength, hardness, toughness, abrasion resistance, dimensional stability, or stiffness of plastics), colorants, flame retardants, and lubricants, etc.

Another important classification of polymers is elastomers which covers a large family of amorphous polymers having a low T_g . They have a characteristic ability to undergo large elastic deformations without rupture. Its soft nature and low elastic modulus make it useful for applications in tires, seals, footwear, hoses, belts, and shock absorbers. Nowadays the two important considerations in polymers are recyclability and biodegradability. Numerous attempts continue to be made to produce fully biodegradable plastics by utilizing various agricultural waste (agro wastes), plant carbohydrates, plant proteins, and vegetable oils. The long-term performance of biodegradable plastics during their life span has not been assessed fully. There is also an increasing concern that the emphasis on biodegradability will divert attention from the issue of the recyclability of plastics and the efforts for conservation of materials and energy [1]. Another significant category of polymers are composites. A composite material is a combination of two or more chemically and physically different phases separated by a distinct interface, in such a manner that its properties and structural performance are superior to those of the constituents acting independently [3]. Composite materials having at least one polymeric phase can be termed polymer composites. Polymer composites with nanoparticles are referred to as polymer nanocomposites. Polymer nanocomposites find suitability in many applications such as biomedical [4,5], optical [5], electronic [6], sensor [7,8], aerospace [9], and nuclear applications [10].

1.3 POLYMER SURFACES AND INTERFACIAL PROBLEMS

To meet specific applications in par with growing demands of polymer industries, the nature of the polymeric material formulations are too complex to allow for the simultaneous optimization of bulk and surface properties. Due to the complexity in polymer formulations, it is also difficult to obtain both bulk and surface properties through a single polymer processing operation. Pre/posttreatment of polymeric surfaces has, therefore, become a common practice in the fabrication of many polymeric materials and its end products. The ultimate aim of polymer surface modification is, either to increase the potential for surface interactions (e.g., adhesion promotion or to obtain a hydrophilic surface) or to decrease the degree to which the surface interacts with a given material (e.g., release or antifouling applications or to obtain a hydrophobic surface). Hydrophilicity, hardness, adhesion, antifouling, antifogging, lubrication, biocompatibility, and conductivity, among others, are considered to be the main properties in demand.

The surfaces and interfaces of polymers are known to have important roles in the final properties and end-use applications of polymeric products. In the case of inhomogeneous polymer blends and composites, the interfaces between different phases are the decisive factor for the final mechanical properties [11]. Not only the strength properties, even the esthetic properties of the polymer product—which might critically influence the decision for the purchase of the product—and its corrosion or scratch resistance, texture, etc., are determined by surface composition and structure.

Hydrophilicity of a solid surface is an important property because controlling the surface wettability is crucial in many practical applications [12]. Surfaces with water contact angles larger than 150 degrees are termed as super hydrophobic surfaces. These type of surfaces have enormous applications in areas such as antisticking, anticontamination [13], and self-cleaning [14], etc. Based on the observations inspired from nature, it can be inferred that, the special functionalities of polymeric surfaces are usually not governed by the intrinsic property of materials, but are more likely related to the unique microstructures or nanostructures. The latest research trend in this domain is to focus on the responsive wettability of surfaces. By combining special topographic structures onto functional surfaces with responsive wettability helps in designing surfaces with responsive switching between superhydrophilicity and super hydrophobicity [15]. A thorough

knowledge of surface phenomenon in polymers as well as the adhesion phenomena in the bonding of polymers is essential to design the surface modification strategies suitable for respective material surfaces with specific properties.

1.3.1 Surface Phenomena in Polymers

The past few years have witnessed dedicated research on surface modification of polymeric materials because of its enormous applications in applied surface science and engineering. This includes applications in biomaterials, coatings, and thin films, demanding smooth, colored, or scratch-resistant surfaces, appearance, durability, and stability which are directly or indirectly linked with external interfaces. Also, the gross behavior (bulk properties) of the material requires properties such as toughness or impact resistance of polymers, which are connected with defect, void, or crack formation which, in turn, involves internal interfaces. The polymer surfaces are different in nature when compared with its bulk, partly due to the difference in molecular weight, addition of functional modifiers such as surfactants, compatibilizers, coupling agents, antioxidants, fire retardants, etc., segregated lower energy components such as lubricants, and migration of additives across the interfaces while contacting with another surfaces. The most accepted method to read the surface characteristics and to measure the surface energy state is the determination of surface tension. This is done by examining the outermost layers of atoms which are typically below 0.2 nm in depth [11]. The work which is required to increase the size of the surface of a phase is referred to as the surface tension. If the phase is a solid, the equivalent term surface free energy is commonly used. If the adjacent phase is a liquid or a solid, reference is made to interfacial tension. Compared with the bulk phase, a molecule at the surface of a material meets fewer molecules with which it can form interactions. Presence at the surface is, therefore, less beneficial from an energy point of view. However, surface tension reflects the strength of bonding within the bulk material. The energy necessary to break these bonds is called the surface energy. In thermodynamics perspective, the surface tension can be defined as the partial differential of the Gibbs free energy (G) of the system with the respect to the area (A), at the constant temperature (T) and pressure (P) [16].

$$\gamma = \left[\frac{\partial G}{\partial A} \right] T, P \quad (1.1)$$

In the thermodynamic consideration of surface energy, the surface free energy (G^S) can be defined as the excess of free energy associated with the surface (A), between the total free energy (G) of the system (G) and the one in the bulk (G^B) [16].

$$G^S = \frac{G - G^B}{A} \quad (1.2)$$

Hard solids are referred as “high energy surfaces” (e.g., metals and their oxides and ceramics, having surface tension $\sim 500\text{--}5000\text{ mJ/m}^2$) due to its very different binding forces (covalent, ionic, metallic). Weak molecular solids and liquids are referred as low energy surfaces (surface tension $<100\text{ mJ/m}^2$) due to van der Waals forces and hydrogen bonding. Most of the polymers are considered as low energy surfaces where the interactions between the chains are dominated by van der Waals forces and hydrogen bonds. Surface and interfacial tensions of polymers significantly affect the wetting and coating processes in the melt blending of polymers and its composites, the behavior of colloidal dispersions, adhesion, friction, and biocompatibility and also in corrosion and adsorption processes. The surface tension of polymers, on the one hand, is determined from the contact angle analysis by positioning a liquid on the sample surface as shown in Fig. 1.1. On the other hand the interfacial tension between different polymers and between a polymer and a substrate is much more difficult to obtain than surface tension. The reason for difficulty in measurement of interfacial tension is due to high viscosities of materials, long time scales for achievement of equilibrium and sample decomposition, etc. However, the interface width and compatibility of polymer materials can be determined on the basis of model assumptions using mean field theory [11].

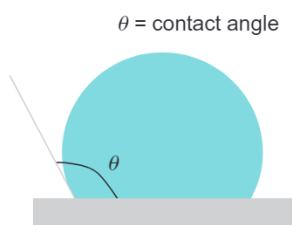


Figure 1.1 Schematic illustration of contact angle measurement.

1.3.2 Adhesion Phenomena in Bonding of Polymers

According to ASTM International, “adhesion” can be defined as a state in which two surfaces are held together by interfacial forces, which may consist of valence forces, interlocking forces, or both [16]. Though adhesion is an interfacial phenomenon, the experimentally measured adhesion depends on many factors in addition to events at the adherend – adherate interface. The material which adheres to the adherent is known as adherate. Thin films, thick films, coatings, and paints, etc., are common examples of adherates. An adhesive is a special type of adherate in which it adheres to two adherends [17]. The materials which are commonly used as adhesives fall under the category of polymeric materials. Only high molecular weight materials having long-chain molecules are expected to possess pronounced adhesive properties [18]. It is important to mention that, rather than relating adhesion to wetting, where it is incorrectly approached the bonding as a thermodynamically reversible phenomenon, the testing of bond strength by analyzing type of failure though determination of the type of separation is a more practical approach for quantifying adhesive bond strength. Adhesion reflects not only fundamental adhesion (which refers to the forces between atoms at the interface) but also the mechanical response of the adhesive, substrate, and interfacial region. (Practical adhesion refers to the results of the various tests of adhesion of the adhesive joint, coating, or composites, such as shear, peel, tensile strength obtained from the related tests). The prime requirement for a successful bond between two phases is to establish contact at a molecular or atomic level. It can be seen that there are no unique mechanisms of adhesion applicable to all adhesion cases and each particular case of adhesive bonding needs to be studied and explained. In order to derive some useful predictions associated with adhesion phenomena at polymer–polymer interfaces, mechanical theory, adsorption theory, chemical theory, diffusion theory, electrostatic theory, rheological theory, and weak boundary layer theory (WBL), etc., are studied by various researchers. The mechanical theory of adhesion relates the interlocking (on a macroscale as well as on a microscale) of the solidified adhesive material with the roughness and irregularities of the surface. However, the attainment of good adhesion with smooth adherends (such as glass, where surface roughness is comparatively low) restricts the general validity of mechanical theory. The adsorption theory proposes that the formation of a strong bond between adhesive and

adherent is attained via intermolecular forces. On the basis of the magnitude of bond energy, the types of bonds are classified into primary bonds (ionic, covalent, metallic) and secondary bonds (van de Waals, etc.). Chemical theory considers molecular bonding as the most widely accepted mechanism for explaining adhesion between two surfaces in close contact. This theory explains that intermolecular forces between adhesive and substrate are due to dipole–dipole interactions, van der Waals forces, and chemical interactions (i.e., ionic, covalent, and metallic bonding). According to diffusion theory, diffusion of polymeric chains across the interface determines the adhesion strength. Appreciable diffusion does not take place in systems involving one or more hard solids (such as metals, glass, oxides, etc.,) under normal conditions of temperature and time scale. According to electrostatic theory, when two dissimilar polymeric materials are brought into contact, a charge transfer takes place which results in the formation of an electrical double layer. According to rheological theory, adhesion occurs due to the interpenetration of substrates across an interface. WBL explains premature adhesive failure due to the existence of WBL's at the surface [19]. The right blend of knowledge of the chemical composition of the polymer surfaces along with adhesion strength tests will uncover the correlations between the chemical bonding mechanism and adhesion. By modifying the surface chemical structures, the adhesion strength can be tailored for specific applications.

1.4 SURFACE MODIFICATION STRATEGIES IN POLYMER MULTIPHASE SYSTEMS

One of the principal focus areas of research in polymer surface science and interfacial engineering has been on improving adhesion at the polymer–polymer interface in order to achieve useful polymer blends and tailored composites. Multiphase polymer blends or composites often have poor physical properties because of low adhesion at the polymer–polymer interface. It is known that, for compatibilization, the favorable enthalpic interactions between the segments of a block copolymer and a homopolymer substrate will enhance adhesion by virtue of interpenetration of the copolymer segments into that phase. As the availability of such preformed copolymers is limited, a potentially viable alternative is to form these copolymers *in situ* by reactive processing during blending, coextrusion, or thermal lamination using functionalized polymers. That is,

the functionally reactive groups can be attached directly to the two immiscible polymers of interest or attached to other polymers which form miscible mixtures with these phases. The chemical reactions at the polymer–polymer interface are also responsible for promoting adhesion. These principles were widely adopted for developing polymer blends/composites which shows toughness characteristics [20]. The surface modification of polymeric materials has been of great research interest in the past few years because of its importance in applications such as biomaterials and coatings [21]. Among the various known techniques, three major surface modification principles which allow the optimization of functional polymer architectures are surface segregation, surface structure, and surface reorganization. These functional polymer architectures can be used for producing adhesive and release surfaces, the suppression of dewetting by the use of functional additives to lower the surface tension of a coating, and the creation of smart polymer surfaces with selective adhesion properties [22]. If the goal of surface modification is to create a hydrophobic surface, then the functional group usually has a lower surface free energy than the polymer backbone, and if adhesion promotion is the objective of surface modification, then the functional group will have higher surface energy than the polymer backbone. In order to design functionalized polymers fundamental knowledge of different facets are required. It includes the appropriate selection of chemistry to introduce specific functional groups, different techniques to incorporate functional groups, processing, rheology, interfacial adhesion, mechanical properties, morphological analysis of blends, and fracture characteristics, etc.

1.5 PLASMA PROCESSING OF POLYMERIC MATERIALS

Plasma-based technologies are emerging to be a proven technology which provides an efficient, economic, and versatile solution to adhesion problems. Plasma technologies find increasing applications in the domain of polymer chemistry in terms of both materials processing and synthesis. Plasma-based technologies can be used to synthesize a new class of polymeric materials with a unique set of properties from an organic or mixed organic – inorganic precursor, for which the structure–property relationships can be varied considerably depending on the final application. Using plasma as a surface modification technique, polymer surfaces can be activated with specific functional groups and thereby design the surfaces for various applications of interest (i.e., for the treatment of

polymer substrates by a reactive or inert gas aiming at a specific surface functionalization).

The plasma is defined as a partially ionized gas containing ions, electrons, various neutral species, and photons at many different levels of excitation. Khelifa et al. proposed a more accurate definition of plasma based on the works of Grill and Bittencourt as “a quasi-neutral gas of charged and neutral particles characterized by a collective behaviour” [23]. When various plasma species interact with a polymer surface, a number of physical and chemical changes occur at the plasma–surface interface. If the objective is to modify the polymer surface using plasma, upon plasma treatment, the free electrons gain energy from an imposed electric field, colliding with neutral gas molecules and transferring energy. These collisions and transfer of energy form free radicals, atoms, and ions, which then interact with the solid surfaces placed in the plasma—that is, the energy and momentum of the plasma-activated species—will be transferred to the lattice atoms at the solid surface. This leads to drastic modifications of the molecular structure at the surface, providing the desired surface properties [24] (Fig. 1.2).

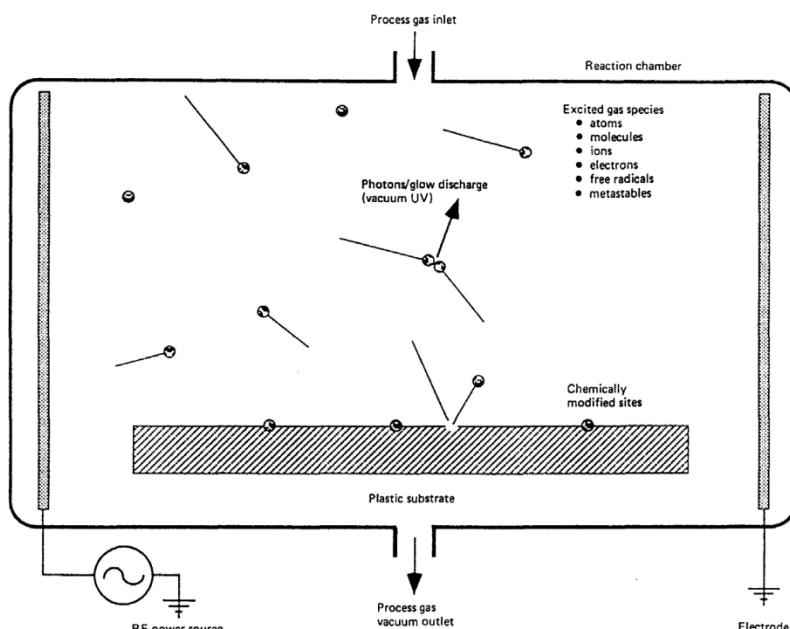


Figure 1.2 Schematic of the surface modification of plastic in a gas plasma reactor. Reproduced with permission from Elsevier.

The plasma process causes changes only to the few molecular layers from the surface of the material subjected to plasma treatment. The plasma treatment also changes the molecular weight of the surface layer by scissioning (reducing the length of molecules), branching, and crosslinking. The type of gas used and the composition of the material surface have a major role in deciding the intended change in the surface of the material. The selection of the process gas determines how the plasma treatment will alter the surface of polymeric material.

Oxygen plasma treatment is regarded as the most commonly used plasma process to enhance adhesion. The oxygen plasma is aggressive and forms numerous components, such as O^+ , O^- , O_2^+ , O_2^- , O, and O_3 , etc. During plasma processing these components recombine and results in release of energy and photons. The photons in the ultra violet region have enough energy to break the polymer's carbon–carbon and carbon–hydrogen bonds. If the energy of the activated species is not sufficient to break the bonds at the surface, it will transfer a part of its energy onto the surface, resulting in localized heating. In addition to this, the incoming high energy ions also result in ion implantation by impinging into the material. When neutral atoms, having very low kinetic energy, are interacting with the material surface, the chemical changes are induced mostly by the recombination of activated species on the surface. The fluorinated plasmas are known to reduce the surface energy and increase chemical inertness, whereas noble gas plasmas induce surface crosslinking. One of the great advantages of plasma treatment in comparison with the chemical method is that “plasma by-products” do not require special handling and are readily removed by a vacuum system. To understand the complex reaction between the plasma and the surface of the polymeric material, the understanding of the plasma parameters and their effect on the surface modification is essential. It is important to consider the effect of all the plasma properties including microscopic plasma parameters like ion energy, ion flux, and degree of ionization, etc., in addition to macroscopic properties, such as excitation source power and time of exposure, to analyze the surface modification of polymers. Optical emission spectroscopy and Langmuir probe analysis are commonly used techniques to characterize plasma and diagnose plasma parameters [25].

The three competing mechanisms which alter polymers upon plasma treatment are ablation, crosslinking and functionalization. The above three mechanisms occur simultaneously to initiate the required change.

The extent of each mechanism depends on the chemistry and the process variables.

1.5.1 Ablation

Ablation results in the evaporation of surface material. Upon treatment, the plasma breaks the covalent bonds of the polymer backbone by bombardment with high-energy particles such as free radicals, electrons, and ions. As a result, long molecules become shorter, their volatile oligomers and monomers boil off (ablate) and are swept away with the exhaust. The bond breaking occurs on the polymer surface usually with the oxygen plasma [24].

1.5.2 Crosslinking

Surface crosslinking is usually carried out with an inert process gas (oxygen-free argon or helium) and/or noble gases. As there are no oxygen by-products in the plasma, the molecule can form a bond with a nearby free radical on a different chain (crosslink) [24].

1.5.3 Functionalization (Activation)

In the activation process, the functional groups present on the surface of polymeric material are replaced with atoms or chemical groups from the plasma. In this process, upon plasma treatment the plasma breaks the polymer's backbone or groups from the backbone, creating free radicals on the surface. The new groups formed on the polymer surface can alter its adhesion characteristics. That is, the type of atoms or groups substituted during plasma treatment determines how the surface will behave [24].

From the engineering point of view, the modified polymer surfaces are very important as they serve as interfaces of blends/composites which are used for high-performance applications [25].

1.6 PLASMA TREATMENT ON SPECIFIC POLYMERS

1.6.1 Engineering Polymers

Engineering polymers belong to a group of polymeric materials referred to as technical thermoplastics which can be used permanently at temperatures between 100°C and 150°C. It possesses good mechanical and thermal characteristics, high dimensional stability, good chemical resistance, and

resistance to wear. Plasma treatment provides an efficient and economical solution to obtain quality adhesive bonds with engineering plastics such as polyamides [26], polyesters [27], polycarbonates [28], polyacetals, aromatic esters, imides [29], and liquid crystal polymers. Upon plasma treatment, it is reported that the mode of failure often changes from adhesive (interfacial) to cohesive in the adherend.

1.6.2 Commodity Polymers

Nowadays plasma-based technologies are used widely for the surface treatment of commodity resins. Hansen et al. reported that plasma treatment of polyethylene and Nylon 6 surfaces greatly improves their bondability, with bond failures occurring in the polymer rather than at the adhesive/polymer interface [30]. Large numbers of studies have been carried out to check the viability of plasma treatment of polyethylene [31–34] and polypropylene [35–39].

1.6.3 Biopolymers/Biodegradable Plastics

Numerous attempts are underway to develop fully biodegradable plastics by the use of various agricultural waste (agrowastes), plant carbohydrates, plant proteins, and vegetable oils. It includes biopolymers made from cereal substitutes, such as rice grains or wheat flour, made almost entirely from starch extracted from potatoes, wheat, rice, or corn, made from coffee beans and rice hulls that are dehydrated and molded under high pressure and temperature, made from potato starch, limestone, and cellulose, etc. Surface modification techniques to improve adhesion and biocompatibility of these polymer surfaces are of paramount importance in the medical field. Selective modification of the near-surface micro-structure and chemical state of biopolymers can be achieved with the radio frequency plasma-enhanced surface modification method provides an effective means for altering the biochemical properties of polymer surfaces without affecting the bulk properties [40–43].

1.6.4 Engineered Composites

Due to their attractive properties, especially high strength-to-weight and stiffness-to-weight ratios, engineered composites are widely used in structural applications where weight savings are a major consideration. A critical factor in engineered composites is the strength of the bond between the reinforcements and matrix. Due to poor chemical compatibility, strong

adhesion at their interface is needed for the effective transfer of stress and bond distribution throughout the interface. Reinforcement fibers derived from high performance polymeric materials provide potential applications in engineered composites. But its structure has limited property development in structural composites. Plasma helps to re-engineer the surface chemistry of any polymer [44–47] to maximize its adhesive qualities which, in turn, makes it possible to use the engineered composites for structural applications.

1.6.5 Fluoropolymers

Fluoropolymers are a group of polymers in which part or all of the hydrogen atom/s has been replaced by fluorine atom/s. Fluoropolymers usually possess outstanding temperature and chemical resistance properties which, in turn, make it difficult to modify for bonding or for surface decoration. Due to handling and disposal problems, the previous option based on metallic sodium etchant has limited usage and paves the way for alternate treatment techniques. The plasma treatment is found to be a reliable option for the treatment of fluoro polymer surfaces. The surface altered by plasma becomes completely wettable. It enables the surface to be apt for printing on, and also bonding by, structural adhesives. The peel strength of adhesive bonded fluoropolymers by plasma treatment is found to be greater than by using a chemical treatment technique [23,48–50].

1.7 OVERVIEW OF CHARACTERIZATION TECHNIQUES FOR THE DIAGNOSIS OF PLASMA PROCESSED SURFACES

The enhanced surface reactivity is characterized in the laboratory by different techniques. It includes wettability analysis, water absorption studies, spectroscopic analysis such as Fourier-transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS), etc., microscopic examination using scanning electron microscopy (SEM) and atomic force microscopy (AFM), etc.

1.7.1 Wettability Analysis

Wettability is the ability of a liquid to spread over a surface. It can be measured by the contact angle between the liquid and the surface. There is a direct relationship between contact angle and surface energy—that is, the contact angle decreases with surface energy. Chapter 10, Wettability Analysis and Water Absorption Studies of Plasma Activated Polymeric

Materials, gives more detailed information about the wettability analysis of plasma activated polymeric materials.

1.7.2 Water Absorption Studies

The water absorption capacity of plasma-treated polymer surfaces can be studied using the water absorbency time test. The water absorptive capacity method provides a measure of the amount of liquid held within a polymer sample after specified times of immersion and drainage [25]. Chapter 10, Wettability Analysis and Water Absorption Studies of Plasma Activated Polymeric Materials, gives more detailed information about the water absorption studies of plasma activated polymeric materials.

1.7.3 Fourier-Transform Infrared Spectroscopy

Plasma surface modifications are confined to a few nanometers below the surface. FTIR spectroscopy in ATR mode (attenuated total reflection) is one of the suitable methods used to bring out the finer surface information of plasma activated surfaces [24]. Chapter 12, Spectroscopic and Mass Spectrometry Analysis of Plasma Activated Polymeric Materials, gives more detailed information about the FTIR analysis of plasma activated polymeric materials.

1.7.4 X-Ray Photoelectron Spectroscopy

XPS analysis is a commonly adopted technique to determine elemental composition of the plasma activated surfaces and O/C ratio, etc. FTIR can only give qualitative information whereas XPS provides quantitative chemical analysis of the plasma activated surfaces. Chapter 12, Spectroscopic and Mass Spectrometry Analysis of Plasma Activated Polymeric Materials, gives more detailed information about the XPS analysis of plasma activated polymeric materials.

1.7.5 Secondary Ion Mass Spectrometry

The secondary ion mass spectrometry (SIMS) analysis is destructive technique (sacrifices the surface particles that are analyzed by the mass spectrometer) for analyzing the mass/charge ratio of ionized particles produced from the sample upon bombardment of an energetic (25 keV) primary ion beam (Bi^+ , Cs^+ , C_60^+). It is a useful technique to evaluate the crosslinking degree of a plasma polymer by means of time-of-flight secondary ion mass spectrometry (ToF-SIMS) analysis. Chapter 12,

Spectroscopic and Mass Spectrometry Analysis of Plasma Activated Polymeric Materials, gives more detailed information about the SIMS analysis of plasma activated polymeric materials.

The morphological features of the plasma activated surfaces can be examined using microscopic techniques. It helps to obtain information about the surface topography and composition in a micrometer scale. Chapter 11, Microscopic Analysis of Plasma Activated Polymeric Materials, deals with the details regarding the sample preparation, analysis, and interpretation of the data from the microscopic analysis of the plasma activated/modified polymeric materials. It includes initial observations of the surface using optical microscope followed by detailed evaluation using a scanning electron microscope, atomic force microscope and transmission electron microscope.

1.8 CONCLUSIONS

Modified polymeric surfaces are gaining wide acceptance especially in biomedical industries. Concurrently the plasma based technologies are also emerging as polymer surface modification technique which allows the surface of a polymer to be modified without affecting its bulk properties. Plasma based technologies can also be used to synthesize a new class of polymeric materials, with a unique set of properties from an organic or mixed organic – inorganic precursor, for which the structure–property relationships can be varied considerably depending on the final application. By controlling the plasma parameters and by understanding the plasma chemistry, it is possible to effectively modify surfaces of polymeric materials.

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