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# Surface Modification of Dental Polymers by Plasma Treatment: A Review

**ROODABEH KOODARYAN and ALI HAFEZEQORAN***

Department of Prosthodontics, Faculty of Dentistry, University of Medical Sciences, Tabriz, Iran.
*Corresponding author E-mail: Hafezeqoran@gmail.com

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## ABSTRACT

Although the plasma surface modification of polymeric materials has developed enormously for industrial application, but researches are new in the field of dentistry. This paper reviews the physics and chemistry of the plasma and the interaction between the polymer substrate and the plasma which are namely ablation, cross-linking, and activation. The plasma surface modification including sputtering, deposition, and implantation and subsequent effects on surface properties are discussed later.

**Key words**: Plasma, Adhesion, Surface modification, Polymer

## INTRODUCTION

Plasma is the fourth state of matter; other three are solid, liquid and gas. Each state is sequentially converted to the other when enough energy is applied until the gas becomes ionized.[1–3] In general plasma refers to partially ionized gas consisting of positively to negatively charged particles and ultraviolet light.[2–5] Plasma can be generated by intense heat or applying an electric discharge to a gas.[3–7] The latter is frequently called low temperature plasma.[2,3,8] The whole procedure is easily described with the production of highly energetic electrons which are accelerated by electric field and high potential difference between the two electrodes.[2,6,8]

When a direct current is transferred through the gas under low pressure, the gas molecules dissociate into electron and positive ions.[5,6] The bombardment of the cathode with fast positive ions results in secondary electron formation which can gain energy to excite and ionize the gas molecules creating new electrons.[5,8] This process is accompanied with emission of visible light radiation, so is called glow discharge.[2,3,5,8]

In an alternating current glow discharges, both electrodes are made of conductive materials and act as the cathode and anode alternately.[2,6] The mechanism depends on the frequency of the alternation. At higher alternation frequency (>500 kHz) positive ions can no longer traverse the path of field polarity and stay within the inter electrode space.[2,4–6] Electrons collide with the gas molecules, generating even more charged ions and active species within the body of the plasma. Therefore, with no contact between ions and the electrodes, plasma is initiated and sustained in the radiofrequency fields (13.56MHz).[2–6,9]

### Plasma physics and types of collisions

Two main processes, collision and photochemical interactions dissociate gas molecules and generate high density of free radicals.[1,10,11] Electrons comprise the main part of the negative components of the plasma; however other negative ions are also generated.[11,12] The electrons are accelerated when an electric field is administered and depending on the energy they receive, elastic or inelastic types of collisions occur between an electron and atom. Elastic collisions, in which atoms stay in ground state, causes no changes in the structure of atoms; however, in an inelastic collision, an electron jumps to higher energy levels but after a short period of time it releases the received energy and reaches the ground state.[6,9,11,12]

Ionization, excitation and dissociation occur in a glow discharge process. Plasma generation consists of multi-step process in which ionization is the essential step. In the first step, an ionizing electron collides with the atom; the atom is ionized and electron is produced.[4–6,9,11,12] The electrons can gain enough energy for further ionization process. Electrons in the ground state can receive energy and be excited to higher energy levels. Collisional de-excitation occurs mainly with radiative decay.[2] Other than these interactions, electron-ion and ion-ion recombination reactions occur, neutralizing the ionized atoms. [6]

### Atmospheric Plasma Treatment Processes

Surface modification by atmospheric plasma relies on deposition or substitution of specific chemical groups on the substrate. These reactive moieties are responsible in substantial changes of surface energy therefore improving wettabality and adhesion characteristics. [3,6,13–15]

In this treatment process, polymers are exposed to a low-temperature, high density atmospheric glow discharge. The high frequency electric field excites the gas molecules, energizing free electrons. [5,6] Collisions of these high energy electrons with neutral gas atoms lead to the formation of multiple reactive species through energy transfer and dissociation of the molecules.[2,3] Chemical and physical modifications of the polymer surface are the result of complex interaction of these activated species with the substrate exposed to plasma.[2–4,6,15]

The reactions between the substrate and the plasma reactive species define the type of surface modification. However, the Surface treatment is usually performed at lower energies, so the chemical interactions are confined to the surface layer and do not influence the bulk characteristics of the polymer.[1,8,10,12,16]

Surface properties of the treated substrate rely totally on plasma composition and gases utilized for modification procedure. Under the similar conditions N, Ar, O2, He, nitrous oxide, carbon dioxide, ammonia, and others gases generate different plasma compositions leading to various interactions with polymer substrate.[1,3,7,9,10,12,14,15]

### Role of plasma surface treatments on wetting and adhesion

Adhesion is a manifestation of attractive forces among atoms. For a strong polymer to polymer bond, hydrogen and Van der Waals attraction forces are sufficient; however covalent chemical bonding are essential for adhesive bonding of the polymer to metal or ceramics.[1–3,6,10,14]

Recent technologies of atmospheric plasma treatment have replaced traditional chemical and mechanical surface modifications in improving adhesion properties and wettability. Functionalizing the substrate by using a broad range of inert and reactive gases introduces active functional groups onto the surface; moreover, depositing uniform and homogenous plasma at low temperature increases the surface energy and reactivity of the substrate.[1,3,10,14]

The interaction between the plasma and substrate give rise to cleaning, etching, free radical reaction, and cross-linking which will be discussed in the next section.

### Ablation, cross-linking, and activation

The processes that simultaneously alter the surface of substrates are ablation, cross-linking, and activation. In different gas composition, the resulting effect varies. Free radicals, electrons, and ions collide with the polymer surface and break primary chemical bonds generating lower molecular weight fractions by chain cleavage. When the volatile by- products are swept away, ablation occurs. However in the presence of an inert gas (argon and helium) injected into the reaction, no free radical scavengers exists.[1,3,10,15]

Beyond this, the broken bonds can react and crosslink with a nearby free radical of other chains thus chains are linked. Substitution of surface functional groups with other chemical functionalities occurs in activation. The addition of specific functionality to the substrate increases the surface area and enables strong covalent bonding between the substrate and its interface.[1,7,10,12]

Along with activated species, the high energy UV radiation generated in the plasma process creates more unstable free radicals which interact with polymer to form stable chemical bonds on the polymer surface.[1,10]

**Plasma-surface modification techniques**

**Plasma sputtering and etching**

Plasma etching is a surface treatment method based on ablation and simply removes material from a surface. Sputter cleaning of the substrate in inert gas plasma such as neon and argon can lead to the formation of volatile by-products which are sweep away from the surface of the material.[1,2,5,6,10,15] In this process, the accelerated ions of argon plasma collide with the negatively charged substrate and transfer their energy to the surface atoms. Some of the surface layer atoms receive enough energy to leave the surface and get into the streamline.[1,5,10,15] Then the underlying atomic layers are exposed and etched. This process is a surface pretreatment before other procedures such as implantation and deposition.[6]

Modification and degradation are the two main reactions between a polymer surface and plasma. Modification of the substrate is attributed to ion interaction, plasma-graft co-polymerization and, plasma polymerization.[3,15] Also, depending on the nature of the polymer and the energy of the plasma, exposed surfaces of polymer degrade and lose their weight. However, weight loss decreases toward the inner layers of substrate.[2,6] So, the chemical and mechanical properties of the polymer are the same as untreated original polymer.[2,3,6,15]

**Plasma implantation**

Implantation is the introduction of elements into the surface without thermodynamic constraints.[1,10] Ions generated by the high-density plasma surrounding the substrate are accelerated toward the substrate and implanted into the surface of it. In an optimized processing condition, plasma ion implantation excels in uniform surface treatment of sophisticated configurations such as dental implants compared to beam line procedures.[1,7,9,10,12,17]

For polymeric substrates, introduction of functional moieties and cross-linked surface chains are subsequent to the plasma surface treatment. Radicals created at the polymer chains interact with the simple radicals present in the plasma and form active functionalities on the surface of polymer. Hence, the active plasma radicals are mainly involved in implantation process.[2,3,6,15]

Surface modification of polymer by implantation of oxygen functionalities improves the adhesion properties, and renders it hydrophilic characteristics.[2–4,6,15,18,19]

Although oxygen plasma are used to selectively implant oxygen functionalities, other compounds consisting of carbon dioxide, carbon monoxide, nitrogen dioxide, and nitric oxide can increase the adhesion properties.[14]

**Plasma deposition**

A layer with distinct properties is deposited and synthesized using plasma-grafting co-polymerization, plasma polymerization, and plasma spraying techniques.

Plasma deposition consists of physical and reactive sputtering. In physical sputtering, atoms and molecules are released after surface bombardment with positive particles; however, when the process is accompanied with a reactive gas, reactive sputtering occurs.[2,3,13,14] Ions and reactive dissociation compounds of the imposed gas diffuse toward the material and interact with the surface. Those atoms that are absorbed can form stable bonds with the first layer of atoms. Other atoms are absorbed continuously after the initial nucleation process. Then, small islands of atoms coalesce and create a uniform coating. [5,6,15]

In the presence of monomer vapors, polymerization grafting initiates on the surface of the plasma treated substrate.[2,3,5,15] this process alters the surface properties of a polymer without affecting the bulk and renders a hydrophilic character to the polymer surface resulting in higher surface energy; which, in turn, changes the wattability and adhesion properties.[1,5,10,11,15]

**Applications of plasma technology in dentistry**

Surface modification of biomaterials has recently become an interesting topic in dentistry and is now used to improve the adhesion properties of the polymeric materials.[1,10,11]

Polymers utilized in prosthetic materials are mainly composed of polymethacrylate and polydimethylsiloxane which are used as denture base material, autopolymerizing and soft liners. To overcome bonding failures between these polymeric materials, several methods have been evolved with the aim of surface alteration before the application of the other resin materials. [16,17,20] Various mechanical and chemical surface treatments have been applied to improve the bond strength of silicone soft liner to polymethacrylate.[17–19] However, only a few studies are available regarding the effect of plasma surface treatment on adhesion properties.[9,11,16,18–22] According to recent studies, plasma surface treatment can improve the bond strength between two different type of resins.[9,16,18–20,22] Oxygen plasma treatment could enhance the bond strength of autopolymerizing reline resins to heat-cured denture base materials. According to Zhang plasma treatment of an acrylic denture base resin was more effective when the substrate were exposed to air after plasma treatment.[21] Xiaoqing exposed the bonding surfaces of the thermosetting materials to oxygen plasma at atmospheric pressure.[19] The introduction of ester and carbonyl functional groups on the surface of oxygen treated surfaces was verified by x-ray photoelectron spectroscopy. The oxidation process and etching effect of oxygen plasma increases the effective bond strength of silicon soft liners to the heat cured resins. In another study, argon plasma modification of poly methyl methacrylate (PMMA) effectively improved the tensile bond strength of a soft liner to denture base materials.[16] However, emphasis was placed on the effect of short periods of plasma exposure.

## CONCLUSION

Technology of atmospheric plasma treatment can replace the traditional chemical and mechanical surface modifications in improving surface property and wettability of polymers. Ablation removes the contamination without leaving any organic residue. This process combined with cross-linking and activation effects improves the adhesion. Also, functionalizing the substrate by using a broad range of inert and reactive gases introduces surface active groups onto the surface and increases the surface energy and reactivity of the substrate.

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