Plasma Modification of Polymer Surfaces

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ABSTRACT

Coated polymers have many and diverse applications such as manufacturing of electronic devices, packaging of foods, and fabrication of decorative products. Understandably, adhesion of deposited films to polymer substrates is of primary importance. Not all polymer surfaces possess the requisite physical and/or chemical properties for good adhesion. Plasma surface treatment is one means of improving adhesion between polymers and vapor deposited materials while maintaining the desirable properties of the bulk. Each of the components of a plasma, including reactive neutral species, ions, electrons and photons, can contribute to surface modification leading to improved adhesion. Plasma system configuration, gas composition and plasma parameters each play major roles in determining the extent and type of modification. Characteristics of the modified surfaces include changes to surface chemical composition, increased degree of crosslinking and roughening.

INTRODUCTION

Plasmas are collections of charged particles. Although they can exist in liquids and solids, they most commonly occur in the gaseous state, with stars, fluorescent lights and neon signs among the more familiar examples. This paper focuses on the types of gaseous plasmas used for surface modification of organic polymers for improving adhesion to vacuum-deposited materials (especially metals). Plasmas used for these applications, although not fully ionized, are collections of ions, electrons, photons, neutral atoms and molecules in ground and excited electronic states. Each of these components have the potential of interaction with surfaces with which they come in contact. Plasmas can be employed to modify surface properties of a material without affecting the characteristics of the bulk.

As a result of extensive research and development, polymers have become the fastest growing segment of materials since World War II, with hundreds of polymers being used in an increasing number of applications [1-3] including films for food packaging electrical insulation, resins for photoresists, and advanced composites for superior mechanical properties. Table I lists a series of common commercial polymers and some of their typical applications.

Polymers are selected for a given application based on their physical, electrical and chemical properties, e.g., thermal stability, coefficient of thermal expansion, toughness, dielectric constant and dissipation factor, solvent absorption and chemical resistance. However, seldom, if ever, is adhesion a criterion for polymer material selection.

Plasma treatment for modification of polymer surfaces has been used for a variety of applications. For example, treatment of poly(methylmethacrylate) (PMMA) intraocular lenses, used to replace the natural lens of the eye during cataract surgery, imparts hydrophobic properties and minimizes adverse interactions [4]. Treatment of organic fibers used as reinforcement in polymer composites enhances interlaminar adhesion to organic matrices to improve structural stability [5]. Nitrogen plasmas have been used to improve the adhesion between poly(ethylene terephthalate) (PET) or Nylon-6 tire cord and

TABLE I. Some commercial polymers and their applications.

POLYMER	APPLICATIONS
Polyethylene	Films, flexible molded parts, high modulus fibers, food packaging
Polypropylene	Films, carpet yarns, bottles
Polystyrene	Sheet stock, cellular foam
Polymethyl methacrylate	Lenses, signs, skylights, optical fibers
Polyamides	Fibers, bearings, gas tanks
Polycarbonates	Lenses, windshields, housings
Polyimides	Flexible circuits, cable insulation, passivation layers
Polyetherether ketone	Wire coverings, composites
Fluoropolymers	Coatings, release agents, seals
Epoxy resins	Adhesives, encapsulants, coatings
Polyurethanes	Foams, fibers, elastomers
Polyethylene-terephthalate	Films, tire cord

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rubber [6,7]. Corona discharge improves the adhesion of paint to polypropylene auto bumpers [8] and increases the laundry shrink resistance and color depth in printing of wool fabrics [9]. Golf balls can be plasma treated to prevent paint from chipping [10].

Early investigations of plasma-polymer interactions for purposes of improving wetting and adhesion of metal-polymer laminate systems included studies, in 1967, by Schonhorn and Hansen [11] using helium plasmas. These researchers attributed polymer modification to crosslinking by activated species of inert gases (CASING). In 1969, Hollahan, et al. [12], found that low temperature gaseous plasmas of ammonia or nitrogen-hydrogen mixtures produced attachment of amino groups and qualitative improvements in wettability for a variety of polymers, including poly(tetrafluoroethylene) (PTFE). They suggested that this might have implications with respect to adhesion. That same year, Hall and coworkers [13] used low temperature discharges of oxygen, helium, and nitrogen to increase joint strength of metal-polymer adhesive bonds.

Other means of modifying polymer surfaces to improve adhesion include mechanical abrasion, treatment with solvents [13], acid etching [14], caustic treatment like NaOH [15], graft polymerization of polar monomers from reactive sites generated on the surface (by wet or plasma techniques) [16,17], adsorption of a polymer from solution [18], or plasma-induced polymer deposition [7]. Sodium/naphthalene treatment of fluoropolymers results in a defluorinated, unsaturated, partially oxidized surface a few hundred nanometers deep [19], two to three orders of magnitude deeper than typical plasma treatments. In part, because plasma processing eliminates the need for undesirable wet chemical etching and the associated waste disposal problems, plasma modification of polymer surfaces is becoming more widespread and utilized on a wide range of part sizes and shapes [10].

PLASMAS AND PLASMA SYSTEM CONFIGURATIONS

Plasmas can be generated by several techniques. For example, as energy is added to a material, it undergoes various phase transitions. As the temperature is increased, melting, vaporization and ionization can occur. As an illustration, to achieve a level of ionization comparable to that found in typical processing plasmas for argon gas at a pressure of 1 Torr would require a temperature on the order of 7000 °K (iron boils at around 3000 °K). Obviously, other means of sustaining a plasma are desirable for materials processing.

The major components of most plasma processing systems include a vacuum chamber (to house the plasma and the substrates), a means of evacuating the chamber (pumping system), a gas introduction system, and a means of initiating and sustaining the plasma, namely an excitation source (to supply energy to the free electrons). Size and shape of vacuum chambers are largely determined by the size and shape of the material being processed. Materials of construction in the vacuum chamber should not interact with the processing gases and their dissociative products. Such interaction could result in contamination of the surfaces being processed.

To initiate and sustain a plasma, energy must be supplied to the free electrons. The electrons interact with atoms and molecules in the gas, leading to fragmentation (dissociation) and ionization. These fragments are highly reactive. A sample distribution of electron energies in the glow discharge is given in Figure 1.

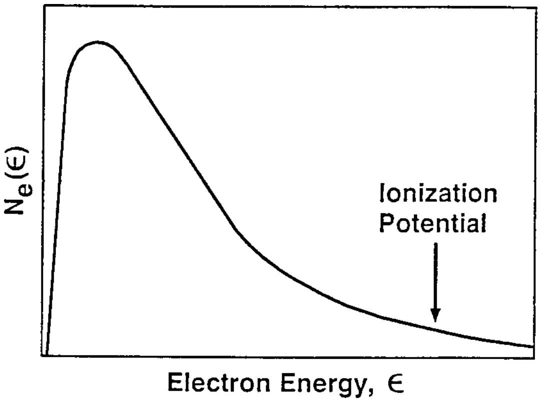

Figure 1. Sample electron energy distribution function.

Although the probability that an an electron-molecule collision will result in dissociation does not increase linearly (and can even decrease) with electron energy, it is generally true in most processing plasmas that higher electron energies will result in greater dissociation efficiencies and, subsequently, higher processing speeds.

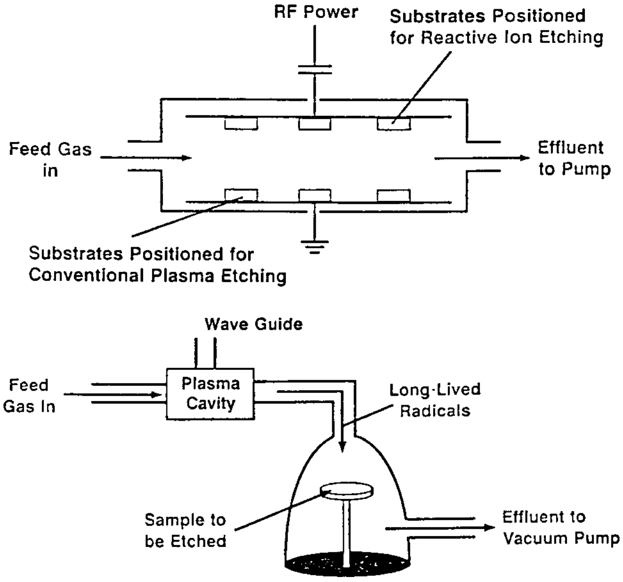

Figure 2. Planar diode plasma system configuration (a) and downstream configuration (b).

In certain plasma etching system configurations, substrates reside directly in the chamber housing the plasma. These typically operate using direct current (DC) or radio-frequency (RF, often at 13.56 MHz) sources. Since the plasma exists at a greater electrical potential than any surface with which it is in contact, positive ions from the plasma are accelerated toward the substrate surface through this potential difference (space charge sheath), typically in a direction normal to that surface. The average energy of ions striking the surface can be varied from several electron volts (eV) to greater that 1.0 KeV. Ion bombardment can enhance processing speeds (ion-assisted gas-surface chemistry). These systems are often configured such that the electrodes, powered and grounded, are parallel, with substrates positioned on either electrode for processing (Figure 2a). In another configuration, samples reside downstream from the plasma and, hence, are not subjected to energetic ion bombardment. Microwave (MW) frequencies are common (but not exclusive) as excitation sources in these systems (Figure 2b). MW frequencies can be relatively more efficient in terms of dissociation, possibly due to an enhanced density of higher energy electrons [20,21] in the plasma, i.e., electrons in the high energy tail of the distribution shown in Figure 1. Corona discharges are highly-localized plasmas generated by applying a very high voltage, commonly at atmospheric pressure, sometimes in air. For surface modification, electrodes can be configured as point-to-plane, parallel plane, or using special electrodes that are shaped to conform to the object being treated.

A list of vendors providing equipment and services for plasma modification of polymer surfaces is given in reference [10].

PLASMA CHARACTERISTICS

Among the characteristics of the plasma which need to be understood and monitored for development and control of processes are (a) electrical potentials between the plasma and any surface with which it is in contact and (b) gas phase species concentrations.

Electrical Potentials

In the configuration of Figure 2a, substrates may be positioned on either electrode, or remain electrically insulated from the electrodes and reside in the region between them. In all cases, the plasma possesses a more positive potential than any surface with which it is in contact. Positive ions that drift from the plasma into the space charge sheath are accelerated toward the opposing surface along electrical field lines which run perpendicular to that surface.

For such a configuration, Koenig and Maissel [22] showed that the potential drops across the sheaths adjacent to the two electrodes depends on the ratio of the surface areas of these electrodes according to $V_1/V_2 = (A_2/A_1)^4$ where V_1 and V_2 are the potential differences between the plasma and the electrodes of surface areas A_1 and A_2, respectively. A sheath also exists at surfaces that are insulated from the electrodes. The associated voltage drop across this sheath is referred to as the floating potential.

Gas Phase Species

Gas phase species include electrons, ions, dissociation products of the parent feed gas (or gases), and products of gas/surface interactions. Several diagnostics techniques can be employed to measure either absolute or relative concentrations of these species. Electrostatic probes can be used to monitor electron and ion densities, average energies of these species and electron energy distribution functions (the number of electrons as a function of their energy) [23,24]. A common technique used to measure relative number densities of neutral and ionized gas species in the plasma is optical emission spectroscopy. Ground state number densities, n(B), of particle B are related to the intensity of light, $I(B^*)$, emitted from electronically excited states of B following decay with photon emission. Since a correlation between the number density of particles in electronically excited states, $n(B^*)$, and those in the ground state is not simple, optical emission intensities yield relative number densities.

Adjustable Process Parameters

Plasma parameters such as ion and electron densities, energy distributions, sheath potentials and gas phase species concentrations can be controlled by adjustment of a number of processing parameters. The excitation source can vary in frequency and power level. Typically, higher power results in greater electron densities and energies and therefore a greater degree of dissociation. Chamber pressure and gas flow rates determine the gas flow regime, gas flow velocities and, hence, residence times of gases in the plasma.

POLYMERS AND POLYMER SURFACES

Polymers are high-molecular-weight substances that contain repeating units of one or more low-molecular-weight monomers [1]. They can be either linear, branched, or have crosslinked networks. Their origin may be either natural (e.g., proteins and cellulose) or synthetic (e.g., polyimides and polyethylene). Recent advances in biotechnology have made it feasible to modify and produce many important biopolymers [2]. The four synthetic polymers produced in the highest volume are polyethylene, polypropylene, polystyrene, and polyvinyl chloride.

Chemical Structure and Composition

Chemical structure and composition are important in determining the degree and mechanisms of interaction that a given polymer has with a plasma environment. To a large extent, they determine the wetting and adhesion properties of the polymer. Several of these characteristics are defined below.

Saturation. For a saturated polymer, only single bonds are present within the molecule. Two examples are PTFE and poly(ethylene). Polymers with moieties having higher bond orders (double or triple bonds) possess some degree of unsaturation. Unsaturated groups tend to be more highly reactive than saturated groups.

Functionality. Functional groups are discrete portions of molecules. Some examples of particular interest for polymer wetting and adhesion are carbonyl groups (-C = O), hydroxyl groups (-OH), acid groups (-COOH) and amino groups ($-NHR_2$ or $-NH_2R$, where R is another organic group). Functional groups are a convenient means of dissecting complicated polymer structures into more manageable portions, especially for purposes of describing chemical reactions.

Aromaticity. Aromatic polymers incorporate benzene rings into the molecule. Polyimides and PET are examples of polymers having aromatic backbones. Poly(styrene) possesses aromatic side chains. Although unsaturated, aromatic groups are quite stable. Aromatic groups are good absorbers of ultraviolet radiation.

Radical. A radical is a neutral fragment possessing unpaired electrons. Radicals are very reactive. They are usually formed as intermediates during a chemical reaction.

Crosslinking. Intermolecular crosslinking occurs when two polymer molecules react to form a linkage. Intramolecular crosslinking occurs when one portion of a polymer molecule interacts (forms a linkage) with another portion of the same molecule. As a result, the mobility of the polymer network becomes more restricted, diffusion processes become slower, and the mechanical characteristics related to adhesion can be improved [25]. Branching is a form of crosslinking that involves attachment of the end of a fragment from one chain to form a side group onto another main chain.

Chain scission. If a chemical reaction is somewhat selective, polymers subjected to surface reactions break down at their weakest links. This process is known as chain scission. The ends of the segments can react such that the chain is terminated, resulting in low molecular weight fragments, or they can react with neighboring molecules (crosslinking). The former process may degrade mechanical performance.

Polymer Classifications

Polymeric materials are generally grouped as thermoplastics, thermosets and elastomers. Thermoplastic polymers are fully polymerized and deform with heat and pressure in order to produce a desired shape. Thermosetting polymers, on the other hand, form a polymeric network by polymerization from lower molecular weight components during the curing stage. Elastomers may be grouped within the class of thermosetting polymers. They are characterized by long molecular chains with low mobility, promoting “rubber-like” properties; that is, they quickly regain their shape after removal of force that induced distortion.

Commercial films may differ from those films prepared in the lab and the properties of the finished product are a consequence of the fabrication process selected. In general, molecular segregation, molecular orientation, thermal degradation and crosslink density are properties that can vary from the surface to the bulk of the same film depending on the fabrication method chosen to produce a material.

For example, opposite sides of a drum-cast polyimide film can differ in properties that affect film characteristics, e.g., surface roughness and solvent diffusion [26]. In addition, care must be taken in processing polymers to account for the effects of impurities in the films, some intentional (e.g., silicon containing slip additives) and some unintentional e.g., hydrogen in fluorocarbon polymers [27,28].

Surface Analytical Techniques

Those techniques which have been reported to be particularly useful in the analysis of polymers are briefly discussed in Table II. These techniques are x-ray photoelectron spectroscopy (XPS), Rutherford backscattering spectroscopy (RBS), static secondary ion mass spectroscopy (SSIMS), and Fourier transform infrared spectroscopy (FTIR). The interested reader can find a more detailed discussion of these techniques as they apply to plasma processing and surface modification in references [29] and [30].

Measurement of the contact angle of a liquid drop on a solid surface is a technique that may be more accessible to the plasma engineer than those listed in the table. This technique provides monolayer sensitivity to surface modification. A liquid drop is placed on the surface to be analyzed and allowed to spread. Wettability of the surface can be gauged by the degree of spread of the liquid (advancing contact angle). Water is a common liquid used for contact angle measurements. Besides the obvious convenience which it imparts to the method, its relatively high surface tension (about 73 dynes/cm in air) provides for measurable angles over a wide range of polymer surface energies.

Often, water is withdrawn from the drop in a manner which causes the drop to recede over the previously “wetted” surface (receding contact angle). Differences between advancing and receding contact angles can be indicative of surface contamination, surface roughness or surface immobility (substrate drag), e.g., for some anistropic polymers [31].

RELATIONSHIP BETWEEN SURFACE COMPOSITION, WETTABILITY AND ADHESION

From the earliest studies dealing with plasma removal of polymers, it was clear that even brief plasma treatments changed the nature of polymer surfaces. Figure 3 shows the reduction in DI water contact angle which results from treatment of

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Kapton® films downstream from oxygen microwave plasmas. A high resolution XPS spectrum in the C 1s region is shown for a treated film in Figure 4. Peak 1 represents the contribution from C-C and C-H bonds, peak 2 that of C-N and C-O, and peak 3 arises from C = O. Peak 4 has been attributed to formation of carboxylates [32] and peak 5 to polycarbonate or peroxy groups [33,34]. Similar contact angle and XPS results have been obtained using RF, DC and MW-generated oxygen plasmas [34]. However, these techniques do not yield any information at depths greater than 10 nm nor do they infer information about crosslinking or molecular weight.

The adhesion, or bondability, between polymer surfaces and other materials deposited onto them can often be related to the wettability as determined from contact angle measurements. Katnani, et al. [35], have shown a correlation between the intensity of the C 1s XPS peak attributed to C = O groups, the water contact angle, and the peel strength of chromium films deposited onto polyimide treated for various durations using an oxygen plasma.

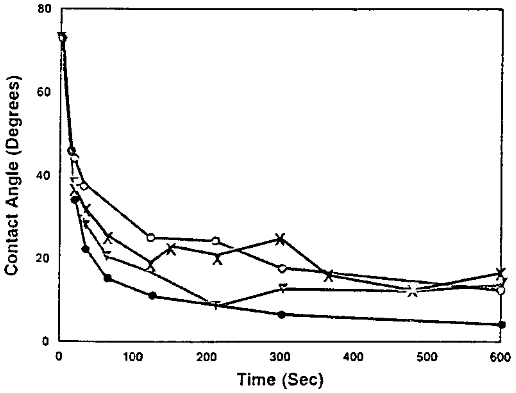


Figure 3. Change in advancing DI water contact angle with treatment duration for Kapton films downstream from oxygen microwave plasmas at 30 watts (o), 60 watts (x), and 120 watts (∇), and for an 85/15 mixture of oxygen and nitrogen at 60 watts (·).

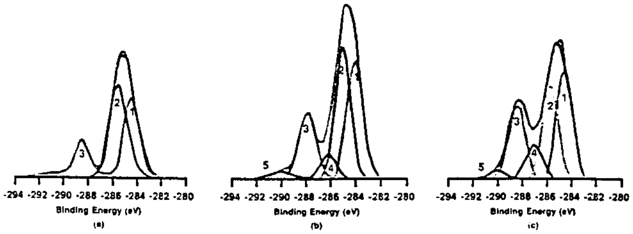


Figure 4. High resolution C 1s XPS spectra for Kapton films with no treatment (a), and treated downstream from oxygen plasmas for 10 seconds at 30 watts (b) and 600 seconds at 120 watts (c).

Liston [19] suggested that wetting, enhanced by an increase in polar groups from plasma treatment, can result in spreading of adhesives to fill voids in the polymer surface for better bonding. Upon curing, these adhesives can react with surface oxygen for covalent bonding. These plasma-induced polar groups that increase wetting may also react with vacuum deposited materials to improve chemical bonding by virtue of electronic interaction. In this case, a correlation will exist between wetting and adhesion. However, the presence of a highly wettable weak boundary layer will lead to a low value of practical adhesion. Such weak boundary layers can result from lack of crosslinking at the surface [25] or surface contamination.

Adhesion between two surfaces results from a combination of mechanical and chemical contributions. Surface micro-roughness can induce mechanical interlocking as well as produce a greater surface area for chemical interactions between the components of the interface. Roughening of polymer surfaces can be induced by ion or photon treatments (see below). Chemical interactions include acid-base and dipolar effects. The former view can be considered to include the latter.

Table II. Some useful analytical techniques for polymer surface analysis.

TECHNIQUE	SAMPLING PROBE (Energy)	DETECTED SPECIES	SAMPLING DEPTH	INFORMATION DERIVED
XPS	X-rays (1.2-1.5 KeV)	photoelectrons	3-5 nm	elemental composition, chemical environment, molecular orientation
RBS	He ions (2 MeV)	backscattered He ions	0.02 to 10 microns	elemental composition, depth profiles
SSIMS	Ions (3-5 KeV)	sputtered ions	< 0.5 nm	fragmentation pattern, relative mol. wt. and crosslinking density
FTIR	IR radiation (5000 to 400 cm^{-1})	bond vibrations	1 nm to bulk	chemical groups, molecular orientation

Acid-base interactions have been shown to play an important role in adhesion [35]. However, the definitions of acid and base need not include only the classical concept of the Bronsted-Lowry theory, i.e., acids as hydrogen (proton) donors and bases as hydrogen (proton) acceptors. A broader definition is given by the Lewis criterion that considers acids as electron acceptors and bases as electron donors. In a Lewis sense, polymers can be classified as acidic, basic, or neutral. Incorporation of carboxylic acid groups (-COOH) into a polymer imparts an acidic character to the surface whereas incorporation of amino groups ($-NHR_2$ or $-NH_2R$) or carbonyls (-C = O) imparts a basic character. Metal films deposited in industrial systems that typically operate at 10^{-6} Torr or above are likely to oxidize reactive metals such as chromium in the gas phase [37]. Chromium oxides are more acidic than chromium metal [38]. Therefore, electron donors such as carbonyl groups can interact more strongly with the oxide.

Burkstrand has shown that the formation of metal-oxygen-polymer complexes formed on oxygen plasma-treated polymer surfaces correlates with adhesion of the metal film [39]. Metals were observed to interact with hydroxyl (-OH), carbonyl (-C = O) and ester (-COOR) groups (typically more basic in nature than the untreated polymer, with respect to the metal) on the plasma-modified surface.

EFFECT OF PLASMA CONSTITUENTS ON POLYMER-SURFACE PROPERTIES

Reactive neutrals, ions, electrons and photons generated in the plasma can all interact simultaneously with polymers to alter surface chemical composition, wettability, and adhesion. Table III is a summary of several investigations using various plasma and beam techniques to provide reactive-neutral chemistry, ion bombardment, electron bombardment and photon irradiation to modify polymer surfaces for adhesion to vacuum-deposited metals. The beam studies, although not strictly plasma techniques, are used to illustrate the effects of those components formed in the plasma environment. In most cases, adhesion was measured using 90° peel tests. Factors that can affect peel strength include thickness of the film being peeled, width of the peeled line, peel rate, ductility of the metal and peel technique. Furthermore, adhesion of as-deposited films has been shown to diminish upon thermal annealing or with time, especially upon exposure to ambients of elevated temperature and humidity. Although the table is somewhat simplistic, it is shown here as an indication of the degree of change in adhesion one might expect for a diverse combination of polymers, metals and treatments.

Neutral/polymer Interactions

For polymer modification to proceed by virtue of interaction with reactive neutral species in the plasma, the reactive dissociation products of the parent gas must serve to weaken polymer chemical bonds and change surface chemical composition. To simplify discussions of plasma etching and modification as they relate to polymer chemical structure, the various chemical configurations can be simplified and referred to generically as -C-C-, -C = C-, or RX where X is some element (like hydrogen) attached to some organic functional group, R.

By far, the gas most commonly used for plasma modification of polymers is oxygen, but other commonly used gases include ammonia, nitrogen, and water vapor. Although a large number of chemical reactions are possible in oxygen plasmas, oxygen atoms are generally accepted as being the primary reactive species in initiating the modification reaction sequence [48-50]. In addition to removal of organic materials, oxygen plasmas leave many polymers more wettable. Hansen and coworkers [51] proposed that this presumably resulted from formation of C = O, OH, and $-CO_2H$ groups. Gerenser, et al. [52], used XPS to study oxygen corona discharge-treated polyethylene surface. In addition to carbonyl, hydroxy and carboxylic acid groups, the presence of epoxy and hydroperoxy groups was measured via gas-phase derivatization reactions.

Among the possible initiating reactions for surface modification are abstraction

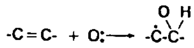
$$\text{-C-C-} + \text{O:} \longrightarrow \text{-}\dot{\text{C}}\text{-C-} + {}^{\bullet}\text{OH} \tag{1}$$

$$\text{-C=C-} + \text{O:} \longrightarrow \text{-}\dot{\text{C}}\text{=C-} + {}^{\bullet}\text{OH} \tag{2}$$

$$\text{RH} + {}^{\bullet}\text{OH} \longrightarrow \text{R}^{\bullet} + \text{H}_2\text{O} \tag{3}$$

$$\text{RH} + \text{O:} \longrightarrow \text{R}^{\bullet\prime} + \text{R}''\text{O}^{\bullet} \tag{4}$$

and addition of oxygen atoms to unsaturated groups



$$\text{-C=C-} + \text{O:} \longrightarrow \text{-}\overset{\text{O}}{\dot{\text{C}}}\text{-}\overset{\text{H}}{\text{C}}\text{-} \tag{5}$$

Subsequent reactions can weaken these bonds. These subsequent reactions may involve either atomic or molecular oxygen, although several investigators [50] have shown that the etching rate of some polymers is unaffected by the presence of molecular oxygen, controlled only by the concentration of atomic oxygen in the plasma.

A key to increasing etching and modification rates is, therefore, increasing oxygen atom concentrations in the plasma. Increased oxygen atom concentrations typically result by virtue of increases in electron energy and/or density in the plasma, or changes in gas phase chemical reactions. Increases in electron density and/or energy can result from changes in power and frequency of the source (described above). Gas additives can affect both the plasma density and gas-phase chemistry. Some gases that have been added to oxygen are N_2 [53] and N_2O [54].

Polymer etching rates downstream from pure oxygen plasmas (in the absence of ion bombardment) are much smaller (at or near room temperature) than etching rates in the presence of ion bombardment. Although there are no reports of differences in rate of modification (e.g., by virtue of changes in wetting behavior or surface composition) in these two configurations, it is suspected that structural differences may result, for example, degree of crosslinking of the modified polymer surfaces.

For both hydrocarbons and fluorocarbons, plasmas of ammonia or mixtures of nitrogen and hydrogen can improve wettability, possibly by virtue of attachment of amine groups to the surface of the polymer [12]. Clark and Hutton [55] used a hydrogen plasma to achieve defluorination of PTFE surfaces. The formation of the defluorinated layer (approximately 2 nm thick) was achieved via abstraction of fluorine by hydrogen, the fluorine analogue of equation (1). It was possible to reduce water contact angle from about 90° to about 50°.

Ion-induced Modification

Several ion beam techniques have been used to promote adhesion. These include treatment of the substrate prior to deposition, simultaneous beam irradiation and deposition, and treatment following deposition. These techniques are reviewed in reference [56]. This paper addresses only the first technique. Table III gives several examples of improved adhesion for metal films evaporated onto a number of different polymers that had been pretreated by sputter etching with argon ions or by irradiation with argon (and oxygen) ion beams.

The degree of enhancement in etching or modification due to ion bombardment depends on the dose and energy of ions incident onto the surface. The energy of ions bombarding surfaces in plasma systems typically does not exceed a few hundred eV. The ion penetration depth at this energy is on the order of a few angstroms. The surface properties of polymers subjected to interactions with energetic ions are altered with respect to chemical composition and structure. Werner, et al. [57], used a 1 MeV beam of protons or helium ions to enhance the adhesion of gold to Teflon. Cheeks and Ruoff [58] bombarded various polymers, including PTFE, with H_2 and He ion beams. Both served to defluorinate the surface with H_2 being more effective. This was attributed to abstraction of fluorine by hydrogen.

Furman, et al. [59], also observed that initial adhesion of as-deposited Cr to PMDA-ODA polyimide was somewhat insensitive to dose in radio-frequency argon plasmas, actually decreasing somewhat as the dose increased. However, greater doses of energetic ion bombardment resulted in greater durability of the metal/polymer bond manifested by less adhesion loss upon heating (due to hydrothermal weakening of the polymer or oxidation of the Cr). It was suggested that the modified polyimide serves as a barrier against transport of water from the bulk to the metal.

During oxygen plasma treatment, addition of oxygen-containing groups to the polymer surface is accompanied by crosslinking and chain scission events. Reaction of oxygen with polymer radical sites can retard crosslinking and oxidative degradation can remove crosslinked material. It has been suggested that UV radiation from the plasma can cause crosslinking, to a depth dependent upon its intensity, countering the reduction in polymer molecular weight induced by atomic oxygen [60].

Tead, et al. [61] have proposed that the ratio of crosslinking events to chain scission events in polystyrene is enhanced by ion bombardment during oxygen plasma treatment, a natural occurrence when samples are processed directly in the plasma, but a phenomenon which is lacking when treatment is performed in a position remote from the plasma (e.g., downstream from the plasma). Hence, it is possible that oxygen plasma treatment in the absence of ion bombardment (and/or photon irradiation), although resulting in extremely hydrophylic surfaces, can produce a weakly bound surface layer of low molecular weight material which effectively yields poor values of practical adhesion of subsequently deposited materials. This is consistent with the observation that wetting of Kapton surfaces treated downstream from oxygen microwave plasmas is diminished after rinsing with water, apparently removing such low molecular weight fragments [27]. Interestingly, after rinsing, surface wetting reverted to a value comparable to that obtained for Kapton films exposed to argon plasma or vacuum ultraviolet radiation, both of which can serve to crosslink polymers.

Such behavior has been observed for chromium films deposited onto films of Kapton polyimide which had been treated with oxygen plasmas in two configurations; downstream from a microwave plasma and in a DC glow discharge [41]. Although wetting and XPS analysis of films treated in these configurations were similar, the downstream plasma treatment resulted in reduced values of adhesion (as determined by peel tests of lines etched into the metal) when compared to untreated polyimide films. On the other hand, films treated in the DC glow discharge were exposed to bombardment by ions having kinetic energies on the order of 10 eV [62], as determined by Langmuir probe measurements. Metal lines formed on these films exhibited peel strengths more than three times greater than those for untreated films. It appears that the ideal modified polymer is one that contains a high density of the chemical surface functionalities requisite for good adhesion while maintaining durability in the near surface region. This durability can be achieved by enhancing those processes that promote crosslinking and inhibiting those that result in a low molecular weight weak boundary layer.

Roughening of a polymer surface can result from ion bombardment, in some cases due to differences in etching rates between crystalline and amorphous regions of the polymer [63,64]. Paik and Ruoff [44] used oxygen reactive ion beam etching (RIBE) to improve the adhesion of Cu to polyimide. By comparing results to oxygen reactive ion etching (RIE) at similar doses (lower energy ions and less roughening), they proposed chemical bonding as the primary mechanism for adhesion enhancement at low doses, a stronger contribution due to rough-

Table III. Some examples of polymer/metal adhesion obtained by a variety of polymer-surface modification methods involving reactive-neutral chemistry, ion or electron bombardment and photon irradiation.

POLYMER	POLYMER SURFACE TREATMENT	METAL	PEEL STRENGTH OF AS-DEPOSITED FILMS 90 DEG PEEL (g/mm)		REFERENCE
			NO TREATMENT	TREATED	
REACTIVE NEUTRALS ONLY					
Kapton 200 H (PMDA-ODA)	O2 MW Plasma Downstream	Cr	20	4	40
REACTIVE NEUTRALS + IONS + ELECTRONS + PHOTONS					
Kapton 200 H (PMDA-ODA)	O2 DC Glow	Cr	20	50-67	41
Polyimide	O2 RF Plasma	Fe	<5	80*	42
PET	O2 RF Plasma NH3 RF Plasma	Co	<5 <5	80* <5*	43
Polyimide	O2 RIBE	Cu	2	70	44
IONS ONLY					
BPDA-PDA	Ar Ion Beam	Cr	14	17	45
PMDA-ODA	Ar Ion Beam	Cr	24-28	53-58	45
PHOTONS ONLY					
PET	Laser Irradiation (248 and 308 nm)	CoCr CoNi	3 10	>40** >40**	46
PTFE	x-rays	Ni & Au	Improved, Tape Test		47
ELECTRONS ONLY					
PTFE	electrons (2 KeV)	Ni & Au	Improved, Tape Test		47

NOTES:
* 90 degree peel of polymer, not metal.
** Ethylene-Acrylic Acid (EAA) copolymer peel test.

ening at moderate doses, and a decrease (to values comparable to those achieved by chemical bonding) due to structural failure at the highest doses.

Photon-polymer Interactions

Because of their electronic configurations, most polymers absorb well in the UV and VUV. As a result, photon irradiation at such wavelengths can be used to modify polymer surfaces. Modification by high energy photons can occur by virtue of cross-linking [11,65], desaturation (e.g., for PTFE and PE), removal of surface atoms or groups [66], or photoablative roughening [67].

Groups having aromatic functionality, like polyimides and PET, are particularly sensitive to UV irradiation and can be modified by exposure at much longer wavelengths [59] than required for modification of saturated polymers like PE and PTFE. This can be explained on the basis of the electronic configuration of these polymers. The difference in energy between the highest occupied molecular orbital and the lowest unoccupied molecular orbital is greater for saturated polymers than for unsaturated polymers. That is, for absorption to occur, greater photon energy (shorter wavelength) is required to induce any electronic transitions in the saturated polymers.

Helium plasmas emit strongly in the UV and VUV. Impurities in the process gas can greatly enhance or decrease the intensities of this radiation [68]. The effect of irradiation wavelength on the treatment of several saturated and unsaturated polymers has been investigated [65-67] by inserting crystal filters having various short wavelength cutoffs between the plasma and the polymer sample. Receding DI water contact angles on surfaces of PTFE treated using a helium microwave plasma as the irradiation source and with different filters, are compared with the VUV absorption spectrum of that polymer in Figure 5. Arc plasmas at high pressure in helium and argon have also been used as a VUV source for surface modification of PTFE and polyimide [67].

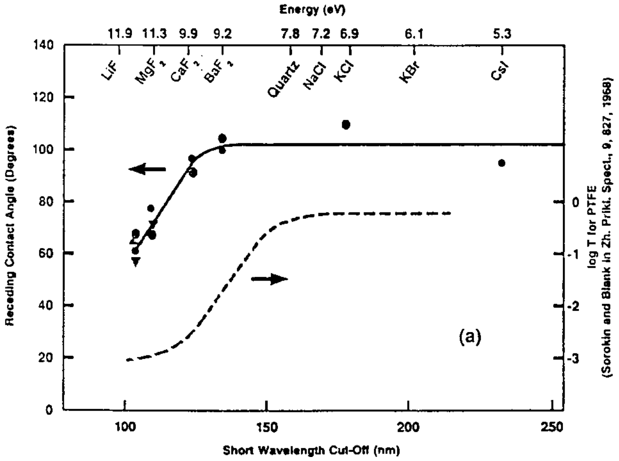


Figure 5. Comparison of receding DI water contact angles following exposure to VUV radiation at various wavelengths with the transmission spectrum for PTFE.

Wheeler and Pepper [47] used Mg Kα x-rays (1254 eV) and electrons (2 KeV) to improve wetting and adhesion of evaporated Ni and Au films to PTFE. Analysis using XPS revealed a modified layer of crosslinked or branched PTFE, potentially greater in density and surface energy, accounting for the improved wetting and adhesion. Removal of fluorine free radicals by the radiation was suggested to leave active chain sites for branching or crosslinking. No incorporation of oxygen (or other non-fluorocarbon species) was detected, nor was any surface texturing observed.

Electron Bombardment

Irradiation by x-rays or electrons was also used to open epoxide ring structures in epoxy precursors, leading to crosslinked films without the need for a curing agent [69]. Electron beam bombardment prior to evaporation of gold onto Teflon-FEP® has been shown to increase gold-Teflon joint strengths by a factor of six compared to those for untreated Teflon films [70]. This was attributed to increased crosslinking caused by the electron bombardment; this crosslinking enhanced the cohesive strength of the Teflon. Bond strengths increased with electron energy to a maximum (increased crosslinking at higher energies), but decreased at still higher energies at which the increased range of electrons reduced modification in near surface region.

REVERSION OF TREATMENT

Wettability of plasma-modified polymer films has been shown to degrade with time after treatment and this degradation is accelerated by higher temperature [71]. When plasma-modified films are exposed to oxygen or air prior to metal deposition, radicals formed during treatment can react to form more stable surfaces [72]. Hence, adhesion obtained for in-situ modification and deposition may differ from that resulting when a transfer in air is required between modification and deposition processes. Migration of "contaminant" from the bulk to a treated surface can also serve to degrade wetting and adhesive characteristics [19].

Following metallization, moisture in the polymer can result in adhesion degradation with time and temperature, either as a result of hydrothermal weakening of the surface region or oxidation of the metal by the absorbed water at elevated temperatures [59]. In addition, moisture movement through a film may also serve as a transport medium for ions that can cause corrosion reactions at the interface of dissimilar metal layers such as chromium and copper [73].

SUMMARY

Effective plasma modification of polymer surfaces for adhesion enhancement requires a thorough knowledge of the effects of system configuration and processing parameters on the plasma constituents and the effect of these constituents on polymer surfaces. The system configuration and parameters used for a given application determine whether the plasma environment acts primarily chemically, physically, or as a combination of both. Plasmas can enhance adhesion by cleaning contaminants and/or roughening surfaces. Surface chemical species that can interact chemically (electron interactions) with deposited films can improve adhesion by orders of magnitude. However, chain scission leading to weak boundary layers must be avoided. Crosslinking, enhanced by bombardment of ions, electrons and photons from the plasma can improve the polymer's cohesive strength. In general, effective modification involves addition of "favorable" chemical functional groups at the surface while improving (or at least not degrading) the structural stability of the near-surface region.

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