Plasma modification of polymer surfaces for adhesion improvement

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Polymers have wide-ranging applications in food packaging and decorative products, and as insulation for electronic devices. For these applications, the adhesion of materials deposited onto polymer substrates is of primary importance. Not all polymer surfaces possess the required physical and/or chemical properties for good adhesion. Plasma treatment is one means of modifying polymer surfaces to improve adhesion while maintaining the desirable properties of the bulk material. This paper addresses the interaction of organic surfaces with the various components of a plasma, with examples taken from a review of the pertinent literature.

Introduction

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 [1–5]. These applications include films for food packaging, electrical insulation, resins for photoresists, advanced composites possessing superior mechanical properties, and a variety of biopolymers. Polymers are selected for a given application on the basis of their physical, electrical, and chemical properties, e.g., thermal stability, coefficient of thermal expansion, toughness, dielectric constant, dissipation factor, solvent absorption, and chemical resistance. However, seldom if ever is adhesion a criterion for polymer material selection.

Means of modifying polymer surfaces to improve adhesion include mechanical abrasion, treatment with solvents, caustic solutions, or acids [6], graft polymerization of polar monomers from reactive sites generated on the surface (by wet or plasma techniques) [7, 8], adsorption of a polymer from solution [9], or plasma-induced polymer deposition [10]. Fluoropolymers, which are intrinsically difficult to adhere to, require an aggressive surface treatment with reagents such as sodium/naphthalene which have been shown to defluorinate, unsaturate, and partially oxidize the surface a few hundred nanometers deep [11].

The literature contains numerous examples and several reviews [12] of plasma treatment for polymer surface modification. Plasmas have been used to provide biocompatibility [13] of materials such as poly(methyl methacrylate) (PMMA) [14], poly(vinyl chloride) (PVC) [15], and polyurethane [16]. For example, treatment of PMMA intraocular lenses, used to replace the natural lens of the eye during cataract surgery, imparts hydrophobic properties and minimizes adverse interactions.

Early investigations of plasma–polymer interactions for purposes of improving wetting and adhesion of metal–polymer laminate systems included studies by Schonhorn and Hansen [17] using helium plasmas. They attributed polymer modification to crosslinking by activated species of inert gases (CASING). In other applications, plasma surface treatments have been used to improve polymer/polymer adhesion [18, 19]. In 1969, Hollahan et al. [20] found that low-temperature gaseous plasmas of ammonia or nitrogen–hydrogen mixtures resulted in the creation of surface amino groups and 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 [21] used low-temperature discharges of oxygen and helium to increase the joint strength of epoxy–polymer–epoxy laminate structures.

Plasma treatment of organic fibers that are used as reinforcement in polymer composites enhances interlaminar adhesion to organic matrices, thereby improving structural stability [22]. Nitrogen plasmas have been used to improve the adhesion between poly(ethylene terephthalate) (PET) or Nylon-6 tire cord and rubber [10, 23]. Air plasmas can preferentially modify noncrystalline regions of Nylon-66 and PET to effect the dye uptake of these fibers [24]. Golf balls can be treated with plasma to prevent paint from chipping [25].

A polymer's chemical structure and composition are key 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. Commercial films may differ from those films prepared in the laboratories, 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]. Accurate interpretation of analytical results that are used to follow surface modification reactions requires careful sample preparation to eliminate surface impurities. Takahagi et al. [27] used X-ray photoelectron spectroscopy (XPS) to show the effects of solvent cleaning on the surfaces of PTFE and other polymers. Such impurities can affect wetting behavior, surface chemical composition, and trends in modification-induced surface properties. For example, hydrocarbon contaminants found in fluoropolymer films [28–31] can be removed or altered under conditions that would affect the uncontaminated fluoropolymer.

Impurities in some commercial films are added intentionally, e.g., as stabilizers [32] or slip additives to reduce friction [4]. Preferential segregation of such stabilizers has been shown to decrease wetting of polyethylene [32].

Plasmas are collections of charged particles, most commonly occurring in the gaseous state. Plasmas are, on the whole, electrically neutral, with number densities of electrons and positive ions about equal. Plasmas are characterized by the energies and densities of these electrons and ions. "Hot" plasmas possess ions with energies approaching that of the electrons, while in "cold" plasmas the energy of the ions is orders of magnitude less than the electron energies. The latter category of plasmas are referred to as nonequilibrium plasmas. These are typically generated at low pressures, for example, between 10^{-3} and 10^{1} torr. This paper focuses on the types of cold-gaseous plasmas used for surface modification of organic polymers. The gases in these plasmas are not fully ionized, and it is not unusual that only one in 10^{4} particles is an ion. The ions, electrons, photons, and highly reactive neutral atoms and molecules in the plasma each have the potential of modifying surfaces with which they come in contact. To best utilize this potential, one needs to understand the nature and effects of these interactions and the means by which they modify surfaces.

In general, the nature of the interaction of the plasma constituents with solid surfaces is determined by plasma reactor configuration and processing parameters that can be adjusted to modify (chemically and/or physically) the various polymer surfaces. Plasma-enhanced chemical vapor deposition occurs when precursors to the deposited film are generated by fragmentation of the gas in the plasma and transported to a surface where they react to form a stable solid film. Proper selection of gases from which the plasma is generated can result in deposition of organic or inorganic films. Chemical surface modification results when the species generated in the gas react at a surface to form stable products with physical and/or chemical properties that are different from those of the bulk. In many instances, etching and modification occur simultaneously. Without proper selection of process gases, plasma system configuration, and operating parameters, undesirable properties of the plasma-modified polymer surface can result. One such undesirable property is the presence of a weak boundary layer (WBL). For example, plasma treatment can produce low-molecular-weight fragments at the surface that do not strongly adhere to the bulk. Materials deposited onto the WBL exhibit low values of practical adhesion, with fracture occurring at the WBL/bulk interface.

Under certain circumstances, plasma processing is an attractive alternative to other techniques of modification. Plasmas modify surface properties without affecting the favorable characteristics of the bulk. Modification is typically very fast, in many instances taking only seconds. In addition, because plasma processes are "dry," the need for undesirable wet chemical etching processes and the associated waste disposal problems is eliminated. As a result, plasma modification of polymer surfaces is becoming more widespread and is utilized on a wide range of part sizes and shapes [25].

This review gives a brief description of plasma systems and processes as they relate to modification of polymer surfaces for improving adhesion. Relationships among surface chemical composition, wettability, and adhesion are presented. Reactive neutrals, ions, photons, and electrons are discussed with respect to their effects on a variety of polymers.

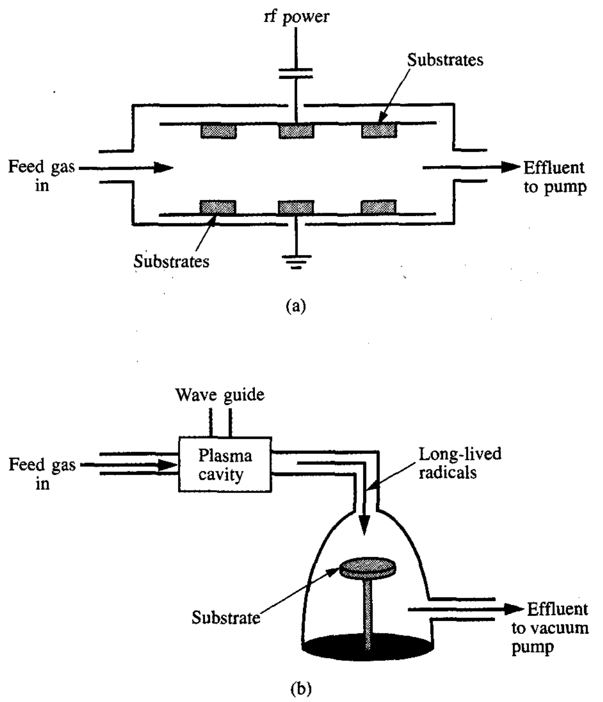


Figure 1

(a) RF-planar diode plasma system configuration with substrates positioned on the rf-driven (top) or grounded (bottom) electrodes. Energies of ions bombarding the substrate surfaces are typically greatest for substrates positioned on the rf-driven electrode. (b) Microwave plasma system configuration with a substrate positioned downstream from the plasma and not exposed to ion bombardment.

Plasma system configurations

The major structural components of plasma processing systems are a vacuum chamber, a pumping system, a gas introduction system, and an excitation source. The size and shape of vacuum chambers are largely determined by the size and shape of the material being processed. Chamber construction materials should not interact with the processing gases and their dissociative products; such interaction could result in contamination of the surfaces being processed. Chamber pressure and gas flow rates determine the gas flow regime, gas flow velocities, and, hence, residence times of gases in the plasma.

Free electrons in the plasma interact with atoms and molecules in the gas phase, leading to fragmentation (dissociation) and ionization. These fragments can be highly reactive. Although the probability that 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 result in greater dissociation efficiencies and, subsequently, higher processing speeds.

Schematic representations of plasma system configurations for processing of materials "in the plasma" and "remote from the plasma" are shown in **Figure 1.** In Figure 1(a), substrates reside directly in the chamber housing the plasma. Plasma excitation sources in this configuration are commonly either direct current (dc) or radio-frequency (rf, typically 13.56 MHz). 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, in a direction normal to that surface. These ions can attain energies from several electron volts (eV) to greater than 1.0 keV. In Figure 1(b), samples reside in a location remote from the plasma and are therefore not subjected to energetic ion bombardment. Microwave (MW) frequencies are common (but not exclusive) excitation sources in these systems.

Surface analytical techniques

Certainly, the list of techniques available for polymer surface analysis is quite extensive. The techniques that have been most frequently used for characterization of plasma-modified polymer surfaces include XPS, static secondary ion mass spectrometry (SSIMS), and contact angle measurements. Other techniques that have been used to complement these methods, namely Rutherford backscattering spectroscopy (RBS) [33, 34], reflection-absorption Fourier transform infrared spectroscopy (FTIR) [35], and laser desorption coupled with Fourier transform mass spectrometry (LD–FTMS) [36], are listed and

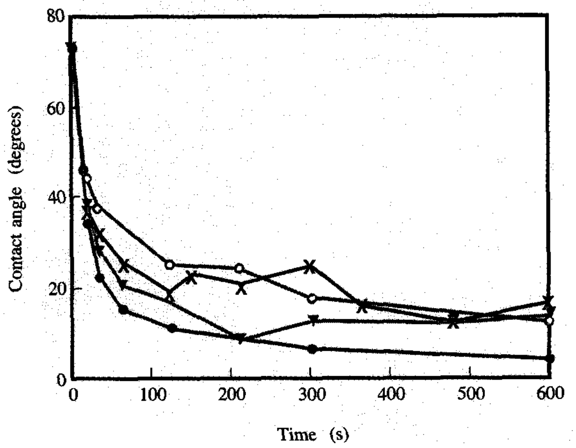


Figure 2

Change in advancing DI water contact angle with plasma treatment duration for Kapton films downstream from oxygen microwave plasmas at 30 W (○), 60 W (×), and 120 W (▼), and for an 85/15 mixture of oxygen and nitrogen at 60 W (●).

summarized in **Table 1**. The interested reader can find a detailed discussion of these techniques as they apply to plasma processing and surface modification in [37] and [38].

Measurement of the contact angle of a liquid drop on a solid surface is a technique which is much more accessible than XPS, RBS, or SSIMS, but which yields information with monolayer sensitivity [39]. The most commonly used approach for measuring contact angle is the sessile drop method. A liquid drop is placed on the surface to be analyzed and allowed to spread. Wettability of the surface can be gauged by the angle made by the advancing liquid with the surface, θ_a, i.e., the advancing contact angle.

The contact angle is a measure of the surface energy of the polymer. Higher polymer surface energy results in lower contact angles, or greater wettability. The relatively high surface tension of water (about 73 mN/m in air) provides measurable angles over a wide range of polymers with differing surface energies.

Often water is withdrawn and the volume decreased until the footprint of the drop begins to recede over the previously "wetted" surface. The receding contact angle, θ_r, is often reported as the angle made by the liquid drop just as the total circular area of the drop on the surface begins to decrease. Contact angle hysteresis, namely the difference between θ_a and θ_r, is indicative of surface contamination, surface roughness, or surface immobility (substrate drag), for example, for some anisotropic polymers [39, 40].

Relationship among surface composition, wettability, and practical 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. Kapton® film, a polyimide formulation produced by curing a polyamic acid whose precursors are pyromellitic dianhydride (PMDA) and oxydianiline (ODA), is made commercially via a chemical imidization reaction and some thermal treatment. **Figure 2** shows the reduction in advancing DI water contact angle which results from treatment of Kapton films downstream from oxygen microwave plasmas. High-resolution XPS spectra in the C 1s region are shown both for untreated and for treated films in **Figure 3**. Peak 1 represents the contribution from C–C and C–H bonds, peak 2 that of C–N and C–O; peak 3 arises from carbonyl groups in the imide rings (O=C–N). Peak 4 has been attributed to formation of carboxylates [41], and peak 5 to a carbonate or peroxy species [42]. Similar functional groups have been observed on surfaces treated using both rf- and dc-generated oxygen plasmas [42, 43], although the type and degree of treatment affects their concentration.

The concentration of certain surface functional groups can often be related to the wettability determined from contact angle measurements. **Figure 4** shows the advancing DI water contact angle as a function of [O]/[F] atomic ratios measured by XPS for films of PTFE, the copolymer of tetrafluoroethylene and perfluoroalkoxyvinyl ether (PFA), and Teflon–AF–2400® (amorphous fluoropolymer) modified using plasmas under a variety of conditions [36] and exposed to air. Also shown, for comparison, are the data of Momose et al. for plasma treatment, and subsequent exposure to air, of PFA [44] and poly(vinylidene fluoride) (PVdF) [45]. Although the data are plotted without regard for the chemical environment of oxygen and fluorine, a relationship is observed, such that the advancing contact angle is inversely proportional to the ratio of atomic concentrations of oxygen and fluorine, [O]/[F], found on the surfaces. The straight lines are least-squares fits for the data of [36] and for the combined data from [44] and [45], respectively. The latter data exhibit consistently lower contact angles for a given value of [O]/[F]. This difference may be attributed to several factors, including a potential difference in the method used to calculate elemental composition (peak height vs. peak area) and/or the presence of hydrocarbon impurities in the control samples of the fluoropolymers used in the previous reports [44, 45]. In addition to being more hydrophilic, these hydrocarbons possess a lower energy threshold for modification [46]. Golub et al. [30, 47] have proposed that the presence of such impurities, inferred from atomic ratios and high-resolution C 1s XPS spectra, affects the degree of surface modification in plasmas, specifically the [O]/[C] and [F]/[C] ratios.

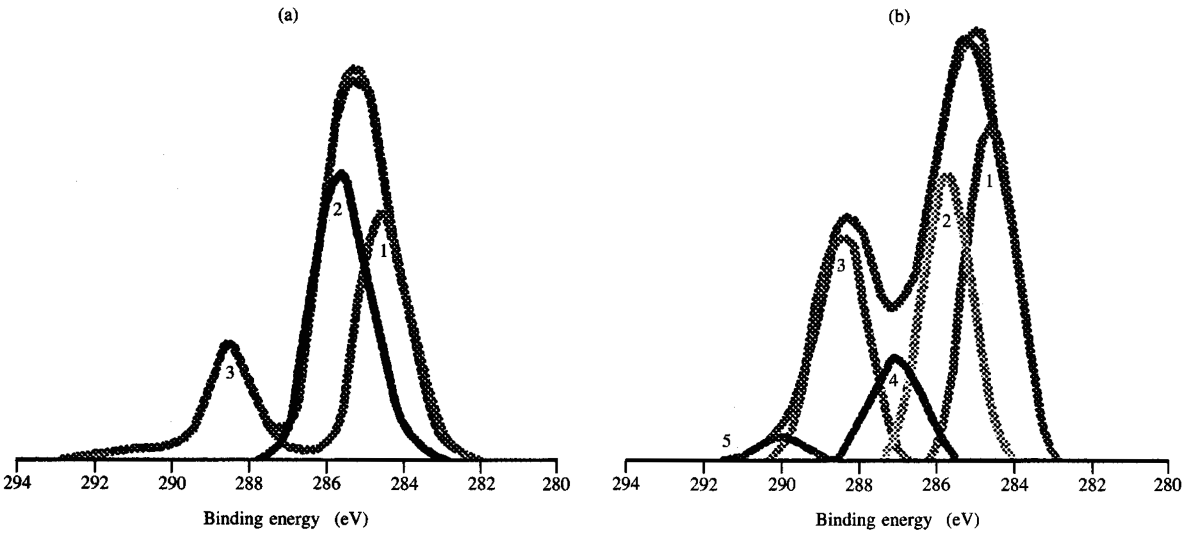


Figure 3

High-resolution C 1s XPS spectra for Kapton films (a) not treated and (b) treated downstream from an oxygen plasma for ten minutes.

Table 1 Some useful techniques for surface analysis of plasma-modified polymers.

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	20 to 10^4 nm	Elemental composition, depth profiles
SSIMS	Ions (3–5 keV)	Sputtered ions	<0.5 nm	Fragmentation pattern, relative molecular weight, and crosslinking density
FTIR	IR radiation (5000 to 400 cm^{-1})	Bond vibrations	1 nm to bulk	Chemical groups, molecular orientation
LD–FTMS	Laser	Ablated fragments	~20 nm (depends on laser and material)	Fragmentation pattern, relative molecular weight, and crosslinking density

Katnani et al. [48] have shown a correlation among the peel strengths of chromium films deposited onto PMDA–ODA polyimide treated for various durations using an oxygen plasma, the intensities of the C 1s XPS peak attributed to C=O groups, and the water contact angles. Liston [11] suggested that wetting, enhanced by an increase in polar groups from plasma treatment, results 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.

However, the practical adhesion, or bondability, between polymer surfaces and other materials deposited onto them cannot always be correlated with wettability [43, 49]. The presence of a highly wettable, but weak, boundary layer leads to a low value of practical adhesion. Such weak boundary layers can result from excessive

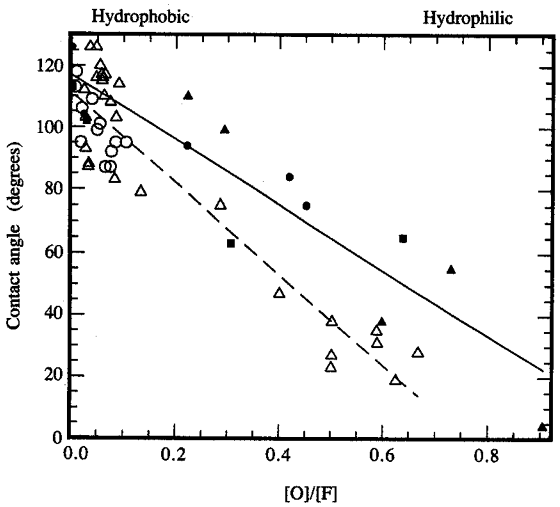


Figure 4

Advancing DI water contact angle as a function of [O]/[F] atomic concentration ratios (determined by XPS) for surfaces of several fluoropolymers modified using a variety of processing conditions. Fluoropolymers are PVdF (△, Ref. [45]), PFA (○, Ref. [44]), PTFE (●, Ref. [36]), PFA [■, Ref. [36]), and AF-2400 (▲, Ref. [36]).

chain scission processes and/or lack of crosslinking at the surface [50], or surface contamination (see the discussion of ion-induced modification in the section which follows).

Adhesion between two surfaces results from a combination of mechanical, chemical, and electrostatic contributions. In addition to these contributions, diffusion characteristics of materials, especially polymers, must be considered. Surface micro-roughness can induce mechanical interlocking and produce a greater surface area for chemical interactions between the components of the interface. Roughening of polymer surfaces is induced by ion or photon treatments (see below). Chemical interactions include acid–base and dipolar effects. Interfacial characteristics are determined primarily by the strength of chemical bonding between the two joining surfaces. Ho and co-workers [51, 52] found that for polyimide (not plasma-treated), the calculated chemical bond strengths to metals increase in the order Cu < Al < Cr. This order of metal reactivity is used to explain the experimental observations that 1) Cu atoms diffuse into polyimide to form clusters, 2) Al intermixes with polyimide without cluster formation, and 3) Cr reacts with the polyimide surface almost immediately upon deposition, leading to a uniform interface with little intermixing. Tead et al. [53] demonstrated that diffusion of molten polystyrene into a film of plasma-modified polystyrene was affected by the mode of plasma modification. The permeability to diffusion was least for treatments having a large contribution from ion bombardment. It was suggested that these treatments resulted in relatively more crosslinking than obtained for treatment in the absence of ion bombardment.

Acid–base interactions between a polymer surface and an overcoat layer play an important role in adhesion [54, 55]. In a Lewis sense, polymers can be classified as acidic, basic, amphoteric, or neutral. For example, post-chlorinated poly(vinylchloride) is an acidic polymer, while PMMA is basic [54]. 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. Reactive metals such as chromium deposited in systems that typically operate at $\geq 10^{-6}$ torr are likely to oxidize in the gas phase [56]. Chromium oxides are more acidic than chromium metal [57]. Therefore, electron donors such as carbonyl groups interact more strongly with the oxide.

Lavielle et al. [58] improved the adhesion of gelatin (considered to be a basic polymer) to PET by microwave plasma treatments in air at 0.2 torr for three seconds. Enhanced adhesion was observed as a result of treating either polymer. Treatment imparted a more basic character to the gelatin by formation of additional carbonyl groups. A more acidic character was imparted to the PET, since the formation of carboxylic acid groups dominates over the formation of carbonyl and hydroxyl groups.

Burkstrand has shown that the formation of metal–oxygen–polymer complexes on oxygen-plasma-treated polymer surfaces correlates with adhesion of the metal film [59]. Metals interact with hydroxyl (–OH), carbonyl (–C=O) and ester (–COOR) groups (typically basic in nature) on a plasma-modified surface. Carbonyl groups on polymer surfaces are sites for reaction with Cr during the initial steps of evaporative deposition [60, 61]. It has been suggested that charge transfer occurs from Cr atoms into the carbonyl groups of the PMDA portion of polymide, leading to the coordination of Cr^{+2} with two ligands from different monomers [62].

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 (**Figure 5**). **Table 2** 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,

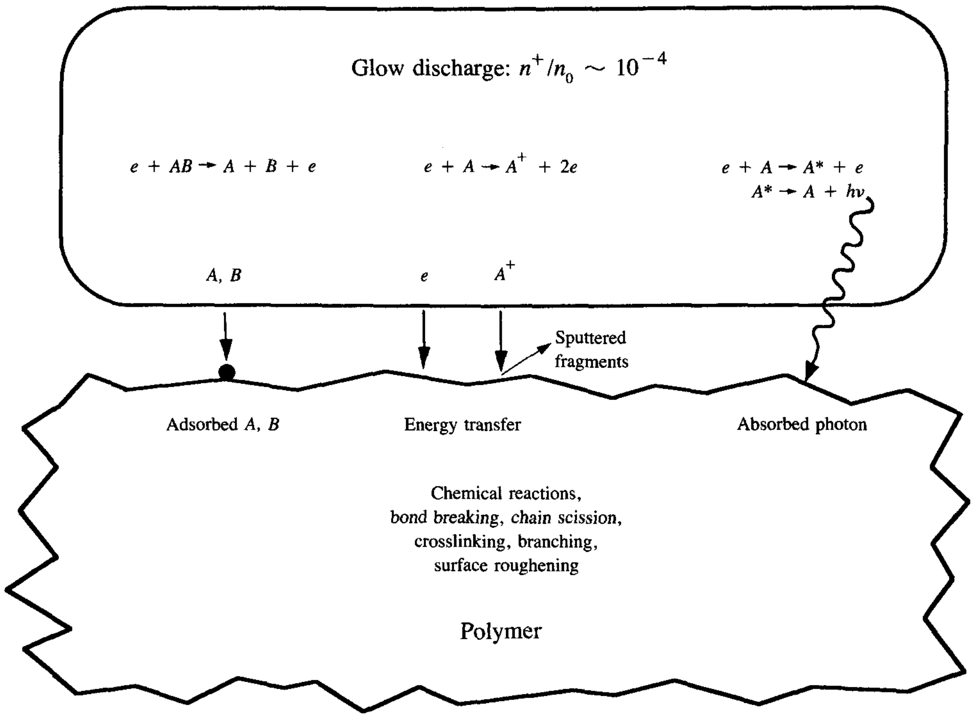


Figure 5

Representation of plasma constituents and their roles in polymer surface modification.

are used to illustrate the effects of those components that are present 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, and ductility of the metal. Furthermore, adhesion of as-deposited films has been shown to diminish upon thermal annealing or with time, especially upon exposure to ambient conditions of elevated temperature and humidity. Although the table is somewhat simplistic, it indicates the degree of change in adhesion one might expect for a diverse combination of polymers, metals, and surface 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 weaken polymer chemical bonds and change surface chemical composition. To simplify discussions of plasma modification as they relate to polymer chemical structure, the various chemical configurations can be reduced and referred to generically as –C–C–, –C=C–, or RX, where X is an element (e.g., hydrogen) attached to an organic functional group, R.

By far, the gas most often used for plasma modification of polymers is oxygen, but other commonly used gases include ammonia, nitrogen, and water vapor. Hall et al. [21] concisely listed several mechanisms by which plasmas act to modify polymer surfaces. These include removal of a weak surface layer by oxidation, cleaning by removal of adsorbed materials, crosslinking, and chemical reaction. 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 a modification reaction sequence [69–71]. In addition to the removal of organic materials, oxygen plasmas leave many polymers more wettable. Hansen and co-workers [72] proposed that this resulted from the formation of C=O, OH, and $-CO_2H$ groups at the polymer surface. Gerenser et al. [73] used XPS to study oxygen corona-discharge-treated polyethylene surfaces. In addition to carbonyl, hydroxyl, and carboxylic acid groups, epoxy and

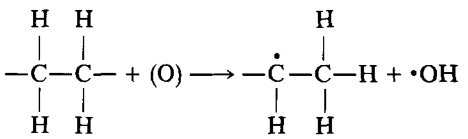
Table 2 Some examples of metal/polymer adhesion obtained by a variety of polymer-surface modification methods involving reactive-neutral chemistry, ion or electron bombardment, and photon irradiation.

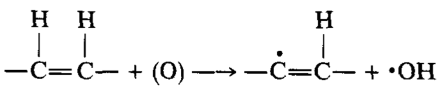
Polymer	*Polymer surface treatment*	*Metal*	*Peel strength of as-deposited metal films 90° peel test (g/mm)*		*Reference*
			No treatment	*Treated*	
Reactive neutrals only					
Kapton 200 H (PMDA–ODA)	O_2 MW plasma downstream	Cr	23	16	[43]
Reactive neutrals + ions + electrons + photons					
Kapton 200 H (PMDA–ODA)	O_2 dc glow	Cr	20	50–67	[43]
Polyimide*	O_2 rf plasma	Fe	<5	80†	[63]
PET	O_2 rf plasma	Co	<5	80†	[64]
	NH_3 rf plasma		<5	<5†	
Polyimide*	O_2 RIBE	Cu	2	70	[65]
Ions only					
BPDA–PDA	Ar ion beam	Cr	14	17	[66]
PMDA–ODA	Ar ion beam	Cr	24–28	53–58	[66]
Photons only					
PET	Laser irradiation (248 and 308 nm)	CoCr	3	>40‡	[67]
		CoNi	10	>40‡	
PTFE	X-rays	Ni & Au	Improved, Tape test		[68]
Electrons only					
PTFE	Electrons (2 keV)	Ni & Au	Improved, Tape test		[68]

*Unspecified polyimide.
†90° peel of polymer, not metal.
‡Ethylene–acrylic acid (EAA) copolymer peel test.

hydroperoxy groups were also detected via gas-phase derivatization reactions.

Among the commonly proposed reactions by which atomic oxygen initiates polymer modification is hydrogen abstraction [21, 74–76]:


(1)

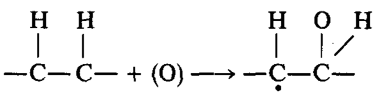

(2)

$RH + \cdot OH \rightarrow R\cdot + H_2O$ (3)

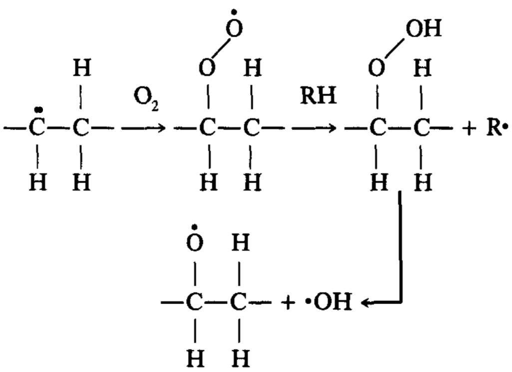
Hudis [77] suggested the possibility of a more indiscriminate abstraction,

$RH + (O) \rightarrow R'\cdot + R''O\cdot$ (4)

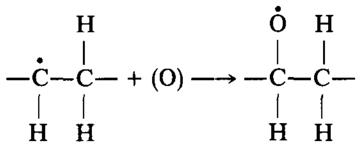
where R, R′, and R″ are different polymer fragments. A well-known class of reactions is radical addition to olefins [78–80]; addition of oxygen atoms to unsaturated groups can initiate modification according to


(5)

Subsequent reactions involving either atomic or molecular oxygen can weaken polymer bonds. However, several investigators [71] have shown that the etching rate of some polymers is unaffected by the presence of molecular oxygen, and is controlled only by the concentration of atomic oxygen in the plasma. A possible reaction involving O_2 is autoxidation [81]:

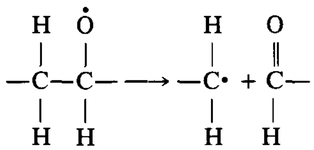

(6)

Another possible pathway involves reaction with an oxygen atom [21, 74]:



(7)

The resulting alkoxyl radical possesses a weakened C–C bond [82], and bond breaking can proceed according to the well-known alkoxy degradation reaction



(8)

Radical sites on treated polymer films may remain active for some time after plasma treatment. Exposure to other gaseous environments can result in radical quenching to yield other products. For example, transfer in air from the plasma chamber for purposes of *ex situ* analysis may result in incorporation of oxygen [26, 44–46] and/or nitrogen [36].

A key to increasing modification rates is, therefore, increasing oxygen atom concentrations in the plasma. Oxygen atom concentrations increase with electron energy and/or density in the plasma, or changes in gas-phase chemistry that reduce oxygen atom recombination reactions. Increases in electron energy and/or density can result from changes in power and frequency of the source. Gas additives can affect both electron density and gas-phase chemistry. N_2 [83] and N_2O [84] are among the gases added to oxygen. Both of these additives produced increased oxygen atom concentrations in the plasma and resulted in greater polymer etching rates.

When polymer etching is performed at or near room temperature, polymer etching rates using oxygen plasmas in the absence of ion bombardment are much smaller than in the presence of ion bombardment. Etching in the absence of ion bombardment is often achieved with samples positioned downstream from the plasma, in a region known as the afterglow. Although there are no reports of differences in the rate of modification (e.g., based on wetting behavior or surface composition) in these two conditions, structural differences such as degree of crosslinking of the modified polymer surfaces may result.

For both hydrocarbon and fluorocarbon polymers, plasmas of ammonia or mixtures of nitrogen and hydrogen can improve wettability by attachment of amine groups to the surface of the polymer [20]. Clark and Hutton [85] 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 in a reaction analogous to that of Equation (1). The water contact angle was reduced from about 90° to 50°.

Exposure of polymer surfaces to helium plasmas improves the wetting of a variety of polymers [86], as well as bondability to the treated surface [17, 21]. Schonhorn and Hansen [17] suggested that CASING due to bombardment by He ions in an rf plasma resulted in increased bondability to PTFE. Two other components of helium plasmas which can induce such crosslinking are metastable species (possessing an energy of 19.8 eV) and high-energy photons (UV and VUV). Egitto et al. [87] have previously summarized the effect of O_2, He, and CF_4 plasmas on the wettability of a variety of polymers.

Fluorination of a variety of polymers using different fluorine-containing gases and system configurations has been reported[1] [33, 88–90]. Fluorination tends to increase the contact angle, θ, i.e., decrease the wetting of polymer surfaces. The degree of wettability is controlled by adjusting the relative amounts of oxygen- and fluorine-containing gases in the gas feed and has been shown to depend directly on the atomic percent coverage of fluorine on the polymer surface [91]. In one study, rf plasma treatment with mixtures of CF_4 and O_2 in equal amounts increased polyimide/polyimide adhesion by thirty times, a much greater improvement than obtained with either gas used alone [92]. This was attributed to 1) the formation of F–C=O functional groups on the polyimide surface, which were more reactive toward amino or peptide groups in a polyimide resin than oxygen that is not bonded to fluorinated carbon, and 2) a reduced degree of fluorination and structural degradation of the polymer molecules when compared with the changes that occur in pure CF_4 plasmas.

- *Ion-induced modification; ion beams*

Several ion beam techniques are used to promote adhesion [93, 94]. These include treatment of the substrate prior to deposition, simultaneous beam irradiation and deposition, and treatment following deposition [93]. This paper addresses only the first technique. Although ion beam treatments are not a form of plasma modification, bombardment by energetic ion beams can be similar to that occurring at surfaces residing in the plasma. Table 2 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 of ions incident on the surface (that is, the ion density, energy, and duration of exposure). The energy of ions bombarding surfaces in plasma systems typically does not exceed a few

[1] J. Dedinas, M. M. Feldman, M. G. Mason, and L. J. Gerenser, presentation given at the Second Annual International Conference on Plasma Chemical Technology, San Diego, 1984.

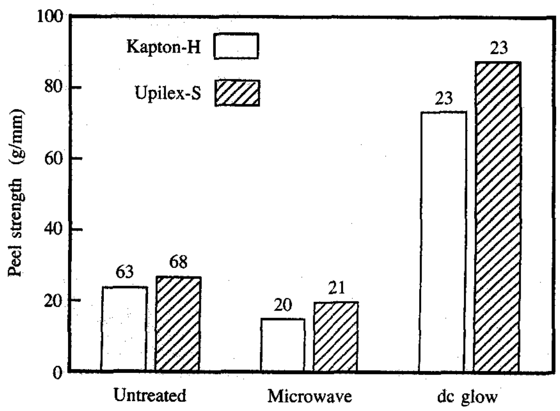


Figure 6

Peel strengths for Cr/Cu lines on Kapton-H and Upilex-S films. Shown are results for the untreated polymers and for films treated downstream from a microwave plasma and in a dc-glow discharge. Advancing DI water contact angles are shown above the bars.

hundred eV. The ion penetration depth at this energy is of the order of a few angstroms. Polymers bombarded with energetic ions are altered with respect to chemical composition and structure of the surface. For example, the bombardment of spin-coated polyimide films on silicon wafers with Ar ions results in surfaces that are rich in graphite-like structures which enhance conductivity at the surface [95].

Ion beam experiments have been performed using ion energies less than 1.0 keV, representative of those commonly found in plasma systems. For example, Pappas et al. [66] used energetic ions at 200 eV to modify surfaces of both PMDA–ODA polyimide and another polyimide film having the polyamic acid precursors biphenyl tetracarboxylic dianhydride (BPDA) and phenylene diamine (PDA), prior to sequential metallization with chromium and copper. With argon ions, PMDA–ODA films gave 90° peel strengths that were about twice the values measured for untreated polymer films. On the other hand, very little adhesion improvement was observed for BPDA–PDA films with the same treatment. For PMDA–ODA films treated with argon ions and subsequently with oxygen ions, or using only oxygen ions, peel values improved by a factor of two relative to the untreated film. These treatments resulted in a factor of four increase in peel values for the BPDA–PDA films. Hence, chemical structure of the polyimide must play a role in the modification and resulting adhesion.

- *Ion-induced modification; effect of ion bombardment in plasmas*

Furman et al. [96] observed that the adhesion of Cr on argon-plasma-treated PMDA–ODA polyimide was somewhat insensitive to ion dose, actually decreasing as the dose increased. However, higher doses of energetic ions resulted in greater durability of the metal/polymer bond, as shown by reduced adhesion loss upon heating due to hydrothermal weakening of the polymer or oxidation of the Cr. It was suggested [96] that the modified polyimide serves as a barrier against transport of water from the bulk to the metal.

Tead et al. [53] have proposed that for modification of polystyrene in the absence of ion bombardment, the ratio of chain scission to crosslinking events occurring during treatment is much greater than for modification performed in the presence of ion bombardment, as occurs during reactive ion etching (RIE) and reactive ion beam etching (RIBE). Crosslinking promotes improved cohesive strength in polymers and increased resistance to solvents and moisture diffusion. On the other hand, low-molecular-weight fragments resulting from excessive chain scission can result in a weak boundary layer leading to poor practical adhesion. Hence, treatments that improve the wetting properties of polymer surfaces are not always conducive to reliable adhesion of metal films, especially when the treatment results in the formation of a weak boundary layer. Burger and Gerenser [97] proposed that excessive treatment of polymers in oxygen plasmas produced more chain scission, leading to a surface that is rich in low-molecular-weight fragments. This results in a weak boundary layer that is detrimental to metal/polymer adhesion. Hence, the characteristics of surfaces suitable for vapor deposition of metals include 1) an abundance of reactive functional groups on the surface, e.g., for acid-base-type interactions with deposited-metal atoms, and 2) no treatment-induced degradation of the structural/mechanical integrity (e.g., cohesive strength) near the polymer surface.

Chin and Wightman [49] proposed that in addition to creating a more hydrophilic, polar surface, O_2 rf-plasma treatment of LARC-TPI® polyimide caused chain scission. This led to the formation of a weak boundary layer that lowered the adhesion strength, as measured by 180° peel tests with a pressure-sensitive adhesive. In this study, samples were placed on an electrically insulated substrate[2] in a plasma operating at high pressures and relatively low power density. In this configuration, ions striking the polymer surface have relatively low kinetic energies. The presence of a weak boundary layer was consistent with the observation that rinsing the plasma-treated samples in methanol resulted in peel strength values of about 520

[2] J. W. Chin, private communication, 1993.

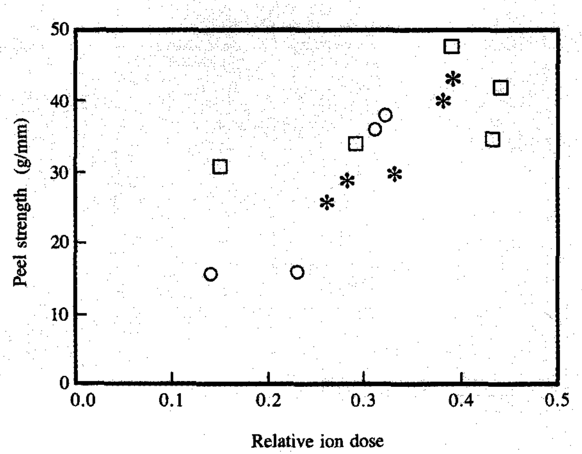


Figure 7

Peel strengths from 90° peel tests of chromium on Kapton films that were treated using a dc-glow discharge at various values of gas pressure and dc power level and plotted as a function of relative ion dose. Data are shown for 100 mtorr (□), 125 mtorr (*), and 150 mtorr (○).

N/m, greater than those observed for both untreated films and plasma-treated films, about 460 N/m and 250 N/m, respectively. For comparison, high-density polyethylene exhibited improved adhesion with plasma treatment because of surface crosslinking upon exposure to the high-energy radiation present in plasmas.

Practical adhesion of metal films to Kapton-H and Upilex-S (BPDA–PDA)® polyimides, as determined by 90° peel tests, is shown for the untreated polymers, with treatment downstream from an oxygen microwave plasma, and with treatment in a dc-glow discharge in **Figure 6**. Downstream-plasma treatment, in the absence of ion bombardment, reduced practical adhesion levels for both Kapton-H and Upilex-S, while treatment in the dc glow produced adhesion about triple the value measured for untreated films. In addition, adhesion was found to increase with the degree of ion bombardment in the dc glow discharge plasma (**Figure 7**).

Roughening of a polymer surface can result from ion bombardment due to differences in etching rates between crystalline and amorphous regions of the polymer [98, 99]. The degree of texturing depends upon the selectivity and directionality of the etching process. Cross et al. [99] found that although sputter-etching rates in oxygen plasmas were roughly four times greater than in argon, the latter generated microtexture features more rapidly. Roughening of the surface can improve adhesion, but this effect appears to play a minor role compared to chemical-bonding-induced adhesion enhancement [91]. For example, Chang et al. [100] have shown that thirty seconds of presputtering of Teflon using 500-eV Ar^+ ions, prior to evaporation of Cu, increased adhesion by fifty times. Although this may be due to mechanical enhancement offered by the fine surface texture produced by the sputtering, continued roughening did not improve adhesion. Chemical bond formation, in this case Cu–C and Cu–F (as indicated by XPS analysis), probably dominated.

Paik and Ruoff [65] used oxygen RIBE to improve the adhesion of Cu to polyimide. By comparing results to oxygen 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 roughening at moderate doses, and a decrease (to values comparable to those achieved by chemical bonding) due to structural failure at the highest doses.

Tissington et al. [101] made observations similar to those of Paik and Ruoff [65] for oxygen plasma treatment of polyethylene fibers. Specifically, short treatment times led to oxidation of the surface, intermediate treatment crosslinked the surface (by virtue of UV radiation from the plasma), increasing the cohesive strength of the fiber in that region, and long exposures roughened the surface.

- *Photon–polymer interactions*

Because of their electronic configurations, most polymers absorb well in the UV and VUV regions. As a result, photon irradiation at such wavelengths can be used to modify polymer surfaces. Modification by high-energy photons can occur by crosslinking [17, 102], desaturation (e.g., for PTFE and PE), removal of surface atoms or groups [46], or photoablative roughening [103].

Groups having aromatic functionality, such as polyimides and PET, are particularly sensitive to UV irradiation and can be modified by exposure at much longer wavelengths [104] than are required for the modification of saturated polymers such as PE and PTFE because of differences in the electronic configuration of these polymers. For absorption to occur, higher photon energies are required to induce electronic transitions in the saturated polymers. For PE, photons are absorbed only by $\sigma \rightarrow \sigma^*$ electronic transitions. For PTFE, photons are absorbed by $\sigma \rightarrow \sigma^*$ and $n \rightarrow \sigma^*$ transitions. The polyimide structure, having a high degree of conjugation, possesses lower-energy transitions such as $n \rightarrow \pi^*$, $n \rightarrow \sigma^*$, $\pi \rightarrow \pi^*$, and $\sigma \rightarrow \pi^*$, in order of increasing energy.

Photoablation of the aromatic polymers is possible using uv lasers. It is convenient to refer to a threshold in fluence (energy per unit area per laser pulse), F_{th}, below which negligible ablation occurs. At fluences below F_{th}, excimer

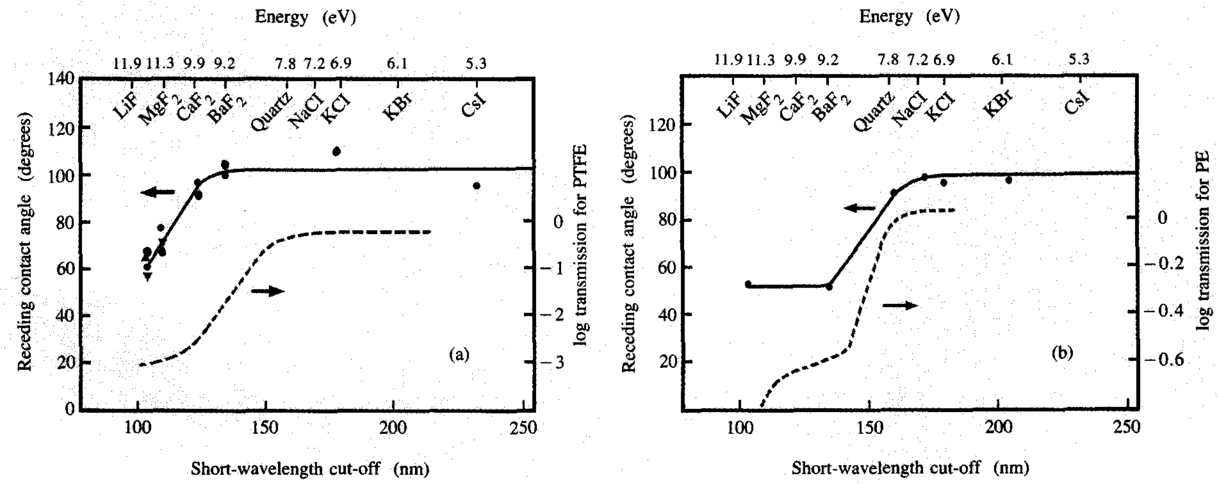


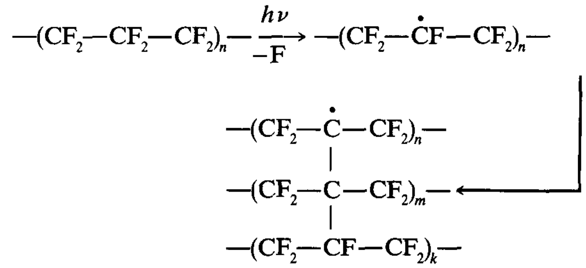
Figure 8

Comparison of receding DI water contact angles following exposure to VUV radiation at various wavelengths with transmission spectra for (a) PTFE and (b) PE. Transmission data for (a) and (b) are from Refs. [108] and [109], respectively.

laser irradiation at 193 nm in air can induce significant chemical surface modification of PTFE (defluorination and oxidation) and PET (deoxidation) [105]. For PET, some nitrogen incorporation occurred during laser irradiation in an NH_4OH ambient. Heitz et al. [67] improved the adhesion of several cobalt alloys on PET by laser irradiation at 248 and 308 nm (see Table 2).

Helium plasmas emit strongly in the UV and VUV regions. Impurities in the process gas can greatly enhance or decrease the intensities of this radiation [106]. The effect of irradiation wavelength on the treatment of several saturated and unsaturated polymers has been investigated [46, 102, 103] by inserting crystal filters having various short-wavelength cutoffs between the plasma and the polymer sample. Arc plasmas at high pressure in helium and argon have also been used as a VUV source for surface modification of PTFE [103] and polyimide [103, 107]. Receding DI water contact angles on surfaces of PTFE and polyethylene (PE), treated using a helium microwave plasma as the irradiation source and with different filters, are compared with the VUV transmission spectra of those polymers in **Figures 8(a)** and **8(b)**, respectively.

As mentioned, high-energy radiation can induce crosslinking and branching in polymers such as PTFE. Results obtained by Fourier transform mass spectrometry with laser-assisted pyrolysis suggest that VUV induces crosslinking in both PTFE and PFA films [36]. VUV-induced defluorination and crosslinking of PTFE can proceed according to the reaction sequence



Further reaction with nitrogen and air introduces carbon–nitrogen and carbon–oxygen bonds on these surfaces [36, 44, 45]. This results in improved wetting (Figure 4). The crosslinking may also enhance those properties of the fluoropolymer surface that are related to adhesion [50], such as cohesive strength and resistance to solvents and moisture, as long as extensive crosslinking does not embrittle the polymer film.

Wheeler and Pepper [68] used Mg K_a X-rays (1254 eV) and electrons (2 eV) to improve wetting and adhesion of evaporated Ni and Au films to PTFE. Analysis by XPS revealed a modified layer of crosslinked or branched PTFE, potentially denser and with higher surface energy, that accounted for the improved wetting and adhesion. Removal of fluorine free radicals by the radiation to leave active chain sites for branching or crosslinking was proposed. 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, forming crosslinked films without the need for a curing agent [110]. Electron beam bombardment prior to evaporation of gold onto Teflon–FEP has been shown to increase gold–Teflon bond strengths by a factor of six compared to those for untreated Teflon films [111]. 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 value (crosslink density was proportional to electron energies), and then decreased at still higher energies.

Treatment of polymer fibers

Plasmas are used extensively to modify the surfaces of fibers to improve the mechanical stability of composite structures. For example, extended chain polyethylene (ECPE) has many desirable characteristics (e.g., high modulus and strength, good chemical resistance), but its adhesion to organic matrices such as epoxies is poor. Better adhesion performance can be obtained by surface modification of the fibers with ammonia and oxygen plasmas [22]. Surface analysis and mechanical testing (shear test) have been used to evaluate the adhesion performance of ECPE/epoxy composites. The ammonia-plasma-modified ECPE surfaces show a correlation among amine concentration, treatment time, and adhesion. However, although the concentration of surface amine groups increases with ammonia plasma treatment time up to twenty minutes, the interlaminar shear strength does not increase significantly after one minute of treatment. SEM revealed that the locus of failure of untreated ECPE composites was at the interface, but, after plasma treatment, failure involved fiber fibrillation and internal shear fracture. The interfacial shear strength was proportional to surface amine concentration until it was greater than the shear strength of the fiber. XPS was used to assess changes in chemical bonding on the surface; the increase in adhesion was attributed to specific chemical interaction between the fiber surface and the resin. Similarly, ammonia plasmas have been used to attach amino groups to a fairly unreactive organic aramid fiber (Kevlar®) and thereby increase adhesion to brominated epoxy resin matrices [112].

Woods and Ward [113] suggested three possible mechanisms associated with improvement in interlaminar shear strength for polyethylene fiber/epoxy resin composites with oxygen plasma treatment of the polyethylene fibers. First, with short plasma treatments, surface oxidation improves wetting of the fiber surface by the resin. Second, ultraviolet radiation from the plasma strengthens the polyethylene surface by crosslinking reactions. Third, longer plasma treatment times result in micro-roughening of the polyethylene, resulting in mechanical keying of the fiber to the resin.

Kevlar fibers, modified in oxygen plasmas, contain carboxylic, hydroxyl, and amino surface groups that can be reacted chemically with $TiCl_4$ to serve as a support catalyst for ethylene polymerization [114]. Upon addition of the co-catalyst (triethyl aluminum) and ethylene gas, polymerization takes place on the fiber surface. The polyethylene-encased Kevlar is then compatible with a polyethylene matrix.

Reversion of treatment with time, temperature, and humidity

Wettability of plasma-modified polymer films has been shown to decrease with time after plasma treatment. This decrease is accelerated by higher temperatures [115]. Occhiello et al. [116] proposed that for polystyrene at low temperatures, increased hydrophobicity as a function of time was independent of molecular weight and was probably due primarily to rearrangement of the modified surface. At higher temperatures, reversion to a more hydrophobic surface occurred more rapidly for polystyrene having lower molecular weights. In the latter case, reversion was attributed to diffusion of unmodified polystyrene chains from the bulk to the surface. 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 [44]. 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 adhesion characteristics [11].

Exposure to humid environments can degrade adhesion. The humidity resistance of polyimide/polyimide plasma-treated interfaces was shown to be much higher for plasma treatment using mixtures of O_2 and CF_4 than for treatment in O_2, CF_4, or N_2 [92].

Following metallization of polymers, 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 [96]. 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 [117].

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 removing contaminants, roughening surfaces, and/or introducing reactive chemical groups. Surface chemical species that interact chemically with deposited films can improve adhesion by orders of magnitude. However, extensive chain scission must be avoided because it can lead to weak boundary layers. Crosslinking, enhanced by bombardment of ions, electrons, and photons from the plasma, can improve the cohesive strength of a polymer film. In general, the effective modification of a polymer surface requires the incorporation of adhesion-promoting chemical functional groups at the surface without degrading the structural integrity of the near-surface region.

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