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Plasma surface modification of polymers for improved adhesion: a critical review

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Abstract—Since the earliest systematic research during the 1960s, the field of materials surface modification by 'cold', low-pressure plasma treatment has undergone an enormous expansion. Much of this expansion has taken place in recent years, particularly in the surface modification of polymeric materials, for which there now exist numerous industrial applications (enhancement of paint adhesion, improved bonding in polymer matrix composites, etc.). In this paper, we provide a critical review of the development and trends in this field; reference is also made to other surface modification techniques, particularly to corona treatment, and comparisons are made wherever appropriate. We begin with a brief overview of adhesion theory, and of the physics and chemistry of 'cold' plasmas. Next, interaction mechanisms between a plasma and a polymer surface are examined; these include physical bombardment by energetic particles and by ultraviolet photons, and chemical reactions at or near the surface. The resulting four main effects, namely cleaning, ablation, crosslinking, and surface chemical modification, occur together in a complex synergy, which depends on many parameters controlled by the operator. In spite of this complexity, for there are still many unanswered questions, it is nevertheless possible to optimize the main set of parameters governing a given process, and then to reliably reproduce the process outcome. Three industrially important systems, for which many research results exist, are then separately examined, namely: (i) polymer–polymer bonding, (ii) polymer–matrix composites, and (iii) metal–polymer bonding. Finally, we present a brief overview of commercial plasma reactors for industrial (non-semiconductor) purposes, and of process considerations for efficient use of such equipment. We foresee that the use of plasma processes will continue to expand, because they have unique capabilities, are economically attractive, and are 'friendly' towards the environment.

Keywords: Low-pressure plasma; polymers; surface modification; adhesion; polymer–matrix composites.

1. INTRODUCTION

1.1. Background

In recent years, we have witnessed a remarkable growth in the use of synthetic organic polymers in technology, both for high-tech and for consumer-product applications. Polymers have been able to replace more traditional engineering materials such as metals, on account of their many desirable physical and chemical characteristics (high strength-to-weight ratio, resistance to corrosion, etc.) and their relatively low cost. However, fundamental differences between polymers and other engineering solids have also created numerous important technical challenges, which manufacturing operations must overcome. An

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important example is the characteristic low surface energy of polymers and their resulting intrinsically poor adhesion [1–4]; the term ‘adhesion’, as it is used here and in the following text, may be briefly defined as the mechanical resistance to separation of a system of bonded materials [5]. Since adhesion is fundamentally a surface property, often governed by a layer of molecular dimensions, it is possible to modify this near-surface region without affecting the desirable bulk properties of the material.

Over the years, several methods have been developed to modify polymer surfaces for improved adhesion, wettability, printability, dye uptake, etc. These include mechanical treatments, wet-chemical treatments, exposure to flames, corona discharges, and glow discharge plasmas. A basic objective of any such treatment is to remove loosely bonded surface contamination and to provide intimate contact between the two interacting materials on a molecular scale, for molecular energies across an interface decrease drastically with increasing intermolecular distance [1]. The simplest method that one can envisage for improving adhesion is to mechanically roughen a surface, thereby enhancing the total contact area, and mechanical interlocking, which is one of several basic mechanisms that have been proposed to explain adhesion. Theoretical adhesion models have been proposed by various authors to account for a wide range of related experimental observations (for reviews of these theories, see, for example, refs 6 and 7); they are, very briefly:

- (i) the adsorption or chemical reaction theory, which states that bond strength is mainly determined by physi- or chemisorption at the interface;
- (ii) the electrostatic theory of Deryagin [8], which is based on contact charging when two dissimilar materials are intimately joined;
- (iii) the diffusion theory of Voyutskii [9], which claims that the bond strength of polymers is governed by diffusion across their interface;
- (iv) the rheological theory of Bikerman [10], which states that the performance of a bonded system is governed by the mechanical properties of the materials comprising the joint, and by local stresses in the joint; and
- (v) the mechanical interlocking or ‘hooking’ theory, based on the micro-geometry of the interface, as already mentioned above.

As discussed in some detail by Sharpe [7], each of these ‘theories’ has certain merits, but also many weaknesses; at present, none of them taken alone can adequately account for any large subset of all of the experimental observations relating to the bond strengths of joined materials. We feel, however, that there is a growing body of evidence that chemical reactions at the interface [mechanism (i) above] can play a key role in many cases, and we illustrate this with many examples in the remainder of this review.

A concept which has been gaining much support among adhesion scientists in recent years is the existence of an ‘interphase’, loosely defined as a region intermediate to two contacting solids, which is distinct in structure and properties from either of the two contacting phases. Sharpe [7] argues very convincingly that interphases exist in many macro-systems such as adhesive joints, coating/substrate systems, and fibre- or particulate-reinforced composites; that they may control the overall mechanical behaviour of these systems; and that failure to take them into account will likely lead to flawed models. We

are in general agreement with these statements, and we present numerous examples of 'interphase' effects in the course of this review.

Returning to surface treatments for adhesion enhancement, mechanical roughening alone has limited effectiveness; wet-chemical treatments with solvents, strong acids or bases, or the sodium/liquid ammonia treatment for fluoropolymers [11], are becoming increasingly unacceptable because of environmental and safety considerations. Furthermore, wet-chemical treatments tend to have inherent problems of uniformity and reproducibility, criticisms which are also often levelled against flame treatment. Modification of polymer surfaces by plasma* treatment, both corona and low-pressure glow discharges, presents many important advantages and overcomes the drawbacks of the other processes mentioned above—reasons why these plasma processes have been gaining wide acceptance over the years in diverse industrial applications. Corona treatment is the longest established and most widely used plasma process [12]; it has the advantage of operating at atmospheric pressure, the reagent gas usually being ambient air. However, this circumstance is also an important limitation in that chemical effects other than surface oxidation, achievable by using reagent gases other than air, tend to be uneconomical or hazardous, or both. These restrictions are largely absent in the case of low-pressure glow discharge treatments, the plasma type that we will address almost exclusively in the remainder of this text. We have recently compared corona and low-pressure plasma surface treatments [13], and have reviewed polymer surface modification by glow discharge plasma [14, 15], as other authors have done [16]. The purpose of the present paper is to provide a critical, up-to-date overview of plasma surface modification science and technology for polymers from the viewpoint of adhesion, wettability, and surface chemistry. Considering the very extensive literature which now exists in this field, we have not attempted to list all relevant publications, but a selection which represents the particular viewpoints advanced in this paper.

1.2. Low-pressure plasma processes

1.2.1. General comments. The industrial use of plasma processing has been spearheaded by the microelectronics industry since the late 1960s (a) for the deposition of thin film materials [17], and (b) for plasma etching of semiconductors, metals, and polymers such as organic photoresists [18–20]. Several dozen plasma equipment manufacturers in North America, Europe, and the Far East cater to this market, and their combined annual sales exceed US\$ 10⁹; they have recently been joined by other equipment builders who specialize in 'industrial' (non-semiconductor oriented) plasma applications.

Contrary to processes (a) and (b) above, where material is added to or removed from the surface, respectively, the third type of plasma process—surface modification (of particular interest in the context of this review)—does neither of these in significant amounts. Instead, the composition and structure of a few molecular layers at or near the surface of the material are changed by the plasma.

*A plasma may be succinctly defined as a partially ionized gas, with equal number densities of positive and negative charge carriers, in which the charged particles are 'free' and possess collective behaviour.

Largely thanks to this third process category, we are currently witnessing a vigorous expansion of industrial plasma processes into areas other than micro-electronics, namely into the automotive, aerospace, and packaging sectors, to name but a few examples.

In spite of this proliferation of applications, there are still many unresolved questions regarding the most efficient use of plasma processing, largely due to the inherent complexity of the plasma state. In order to ensure the high quality and the reproducibility of a given plasma process, numerous parameters must be controlled with care, such as the pressure and flow rate of the reagent gas or gas mixture, the discharge power density, the surface temperature and electrical potential of the workpiece, etc. Currently, the effects of excitation frequency and of plasma-surface interactions are still only partially understood, and these are the objects of much ongoing research. These are discussed briefly in the remainder of this section, along with low-pressure plasma principles.

1.2.2. The physics and chemistry of low-pressure plasmas. In a low-pressure (≤ 1 Torr = 133 Pa), high-frequency (≥ 1 MHz) discharge, the heavy particles (gas molecules and ions) are essentially at ambient temperature (~ 0.025 eV), while the electrons have enough kinetic energy (several eV) to break covalent bonds, and even to cause further ionization (that is, to sustain the discharge). The chemically reactive species thus created can partake in homogeneous (gas-phase) or heterogeneous reactions with a solid surface in contact with the plasma. Since this type of plasma chemistry takes place at near-ambient temperature, it is well suited for processing thermally sensitive materials such as semiconductors and polymers [21, 22].

As mentioned above, the creation of reactive species (radicals, ions, molecular excited states, etc.) in a plasma results primarily from inelastic collisions between 'hot' electrons with energy $u = (mw^2)/2e$ (w , m , and e are the electron velocity, mass, and charge, respectively) and ground-state atoms or molecules. The rate coefficient C_j for excitation of a particular species or state ' j ' is given by

$$C_j = \left[\frac{2e}{m} \right]^{1/2} \int_0^\infty \sigma_j(u) F_0(u) u \, du, \quad (1)$$

where $\sigma_j(u)$ is the particular process cross-section and $F_0(u)$ is the electron energy distribution function (EEDF). It is noteworthy that nearly all processes of importance here possess an energy threshold u_j for which

$$\sigma_j(u) \equiv 0, \quad u \leq u_j. \quad (2)$$

The number density \dot{n}_j of species ' j ' produced per second in the plasma from ground-state molecules (of number density $N \text{ cm}^{-3}$) clearly also depends on the electron density n ; that is,

$$\dot{n}_j = C_j N n. \quad (3)$$

The power balance between the applied electromagnetic field (of frequency $f = \omega/2\pi$) and the plasma can be expressed by

$$P_a = \xi n V, \quad (4)$$

where P_a is the power absorbed in the volume V of plasma and ξ is the average

power absorbed per electron. The parameter ξ , which is readily measurable, can also be considered as the power required to sustain an electron-ion pair in the plasma. Ferreira and Loureiro [23] have calculated ξ values for the 'simple' case of a low-pressure argon plasma; their model shows that at constant pressure, ξ decreases as f is raised from 'low frequency' (≤ 100 MHz) to microwave (MW, > 100 MHz) frequencies. In other words, the efficiency of producing electron-ion pairs is greater at MW than at 'low' frequency, for a given power density absorbed in the plasma. Indeed, the yields of other types of chemically reactive particles such as free radicals, which at 20% or more of all species are the majority constituent, are also found to be higher in MW plasmas. As recently reviewed by Moisan *et al.* [24], this is attributed to a significantly higher fraction of energetic electrons in the tail of the EEDF and to a higher n value than for lower-frequency plasmas. It is therefore not surprising that among recent generations of commercial plasma reactors, an increasing number of these systems operate at the 2.45 GHz MW frequency [20, 22] (see also Section 4).

Rather than use either MW or RF (radiofrequency) power to sustain the plasma, we (LM, MRW) often combine the two power sources to generate a so-called 'mixed' (or dual-) frequency plasma [25]. While MW excitation generates a high concentration of active species in the gas phase, as noted above, the role of the RF power is to create a negative DC self-bias voltage, V_B , on the powered, electrically isolated substrate-holder. This causes ions to be accelerated by the potential drop ($V_p - V_B$) across the RF-induced plasma sheath, or 'dark space', to their maximum kinetic energy:

$$E_{i,\max} = e |V_p - V_B|, \quad (5)$$

where V_p , the plasma potential, is generally a few tens of volts positive with respect to ground. In practical situations, at higher gas pressures of ~ 100 mTorr, the ions lose part of their energy through inelastic collisions. The average energy is then typically

$$\bar{E}_i \approx 0.4 E_{i,\max}. \quad (6)$$

In other words, in dual-frequency (MW-RF) processing, independent control of the RF power allows us to vary the energy of the ions bombarding the substrate surface, with values ranging from a few eV to several hundreds of eV, and with fluxes of up to $\sim 10^{16}$ ions/cm² s [25], conditions comparable to the operating parameters of low-energy ion beam systems. The commercial plasma equipment (whether RF or MW) described in Section 4 can, in principle, be readily modified for use in the dual frequency (MW-RF) mode of operation.

2. INTERACTION OF PLASMAS WITH ORGANIC SURFACES

2.1. Types of plasma-polymer interactions

2.1.1. General discussion. In the plasma treatment of polymers, the subject on which we henceforth focus our attention, energetic particles and photons generated in the plasma interact strongly with the polymer surface, usually via free radical chemistry [15, 19, 21, 22]. For lack of space, we choose not to discuss a related field, plasma polymerization, for which the reader is referred to an excellent recent monograph [19].

In plasmas which do not give rise to thin film deposition (see Section 1.2.1), four major effects on surfaces are normally observed. Each is always present to some degree, but one may be favoured over the others, depending on the substrate and the gas chemistry, the reactor design, and the operating parameters. The four major effects are:

- (i) surface cleaning, that is, removal of organic contamination from the surfaces;
- (ii) ablation, or etching, of material from the surface, which can remove a weak boundary layer and increase the surface area;
- (iii) crosslinking or branching of near-surface molecules, which can cohesively strengthen the surface layer; and
- (iv) modification of surface-chemical structure, which can occur during plasma treatment itself, and upon re-exposure of the treated part to air, at which time residual free radicals can react with atmospheric oxygen or water vapour.

All these processes, alone or in synergistic combination, affect adhesion, as will be discussed in detail in Section 3.

We now briefly examine each of these four effects, frequently using an oxygen plasma as an example. The reason for this choice is not only that oxygen plasmas lead to strong effects in all four categories, but that they also have much technological importance in semiconductor and 'industrial' (non-semiconductor) processing.

(i) Cleaning. This is one of the major reasons for improved bonding to plasma-treated surfaces. Most other cleaning procedures leave a layer of organic contamination that interferes with adhesion processes; of course, any clean surface rapidly reacquires a layer of contamination when exposed to ambient atmosphere. For example, it is known that as little as $0.1 \mu\text{g}/\text{cm}^2$ (a single molecular layer) of organic contamination on a surface can interfere with bonding if the bonding material cannot dissolve or remove the contaminant from the surface to be bonded [26]. This amount of contamination is the residue from $0.01 \text{ cm}^3/\text{cm}^2$ of a liquid containing 10 ppm of non-volatiles. It is difficult and expensive to obtain solvents or water, in industrial quantities, with less than 10 ppm non-volatiles, so that, almost by definition, a surface will remain contaminated after any cleaning process that finishes with a liquid rinse.

In some cases, it has been reported that contamination on the surface to be bonded did not interfere with bonding. It was concluded that the interaction of the substrate and the adhesive was sufficiently strong to cause displacement of the surface contamination by the adhesive, or that some incorporation mechanism existed between the contamination and the adhesive.

Oxygen-containing plasmas are capable of removing organic contamination from inorganic and polymeric surfaces, but it is critically important to plasma-clean a polymer for a sufficiently long time to remove all of the surface contamination. Almost all commercial polymer films, and most moulded parts, contain additives or contaminants such as oligomers, anti-oxidants, mould release agents, solvents, or anti-block agents, which are oily or wax-like. Most of these are deliberately incorporated into the polymer formulation to improve its properties or manufacturability, and they are designed to 'bloom' to the surface and to coat that surface.

Because these materials often have a very similar chemistry to that of the base polymer, they are generally difficult to detect with X-ray photoelectron spectroscopy (XPS) or other analytical techniques. Typically, these additives can be present in layers 1–10 nm thick, even after solvent cleaning; they simply continue to diffuse to the surface.

The surface contamination will react with the plasma in a similar way to the polymer. That is, if the plasma cleaning is not of sufficient duration to completely remove it, the contaminant will become wettable and will have a modified XPS pattern similar to that of the polymer. However, it will still remain a loosely-bonded, albeit plasma-treated, contaminant layer, not a plasma-modified polymer surface. At normal power levels (typically, a few mW/cm²), it is necessary to clean most polymers for some tens of seconds. A treatment of a few seconds is generally not long enough (unless very high power densities, many tens of mW/cm², are used) to remove the contaminants, only to treat them and give the false impression of a wettable and properly treated surface.

(ii) Ablation. Ablation, or plasma etching, is distinguished from cleaning only by the amount of material that is removed. Ablation is important for the cleaning of badly contaminated surfaces, for the removal of weak boundary layers formed during the fabrication of a part, and for the treatment of filled or semi-crystalline materials. Since amorphous polymer is removed many times faster than either its crystalline counterpart or inorganic filler material, a surface topography can be generated, with the amorphous zones appearing as valleys. For example, plasma surface treatment of fluoropolymers for short times improves their wettability without modifying their surface texture, but overtreatment gives a very porous surface [27, 28]. The same is true for polyethylene terephthalate (PET) [29]. This change in surface morphology can improve mechanical interlocking and it can increase the area available for chemical interactions (see Section 1.1). Some ablation of reinforcing fibres tends to improve composite properties, but the fibres must not be significantly reduced in diameter by overtreatment because thinner fibres will be weaker [30–33] (see Section 3.3).

(iii) Crosslinking. CASING (Crosslinking via Activated Species of INert Gases) was one of the earliest-recognized plasma treatment effects on polymer surfaces [34]. As suggested by the acronym, CASING occurs in polymer surfaces exposed to noble gas plasmas (e.g. He or Ar), which are effective at creating free radicals but do not add new chemical functionalities from the gas phase. Ion bombardment or vacuum ultraviolet (VUV) photons* can break C—C or C—H bonds, and the free radicals resulting under these conditions can only react with other surface radicals or with other chains in chain-transfer reactions; therefore, they tend to be very stable [36]. If the polymer chain is flexible, or if the radical can migrate along it, this can give rise to recombination, unsaturation, branching, or crosslinking. The latter may improve the heat resistance and bond strength of the surface by forming a very cohesive skin, the effect so dramatically illustrated by the early CASING experiments [34].

In the past it has been assumed that it was necessary to use an inert gas to obtain crosslinking, but there are some reports on the crosslinking of poly-

*Vacuum ultraviolet light is defined as electromagnetic radiation with wavelengths $\lambda < 175$ nm, the absorption edge of oxygen [35].

propylene (PP) even in oxygen plasmas [37, 38]. In this case, the crosslinked skin is much thinner (~ 300 Å) than on polyethylene, not only because VUV radiation is absorbed in a much thinner layer in PP than in PE [39], but also because O_2 plasma ablates the polymer surface at the same time as the cross-linked layer is being formed in the sub-surface region. This has been discussed in detail in a series of papers by Clark and co-workers (e.g. refs 40 and 41).

(iv) Chemical modification. The most dramatic and widely reported effect of plasma is the deliberate alteration of the surface region with new chemical functionalities capable of interacting with adhesives or other materials deposited on the polymer. Being a core subject of the present review paper, much of the remaining text is devoted to chemical modification and its diverse applications.

2.1.2. Vacuum ultraviolet photochemistry. There have been many studies of the optical emissions from plasmas in the near-ultraviolet and visible region [42]. However, the photon energy at wavelengths longer than the ultraviolet (about 180 nm) region is insufficient to initiate rapid photochemical reactions without some photoinitiator. But the VUV radiation in plasma reactors can break any organic bond and initiate rapid free-radical chemistry. There are very few data in the literature on the emission from real process plasmas in the VUV region, or on the effect of VUV radiation on polymer surfaces. Notable exceptions are the work of Hudis and Prescott [43], and of Clark and co-workers during the 1970s. In an excellent paper [41], Clark and Dilks show the relative effects of VUV and of gas-phase excited species on the depth of reaction in polymers. Their work and other experiments show that the modern plasma reactor is essentially the same light-producing device as those used by researchers in VUV spectroscopy [44], or in some commercial UV lamps [45]. In plasma reactors, the parts are directly immersed in this light source without any intervening windows!

It is important to stress the difference between a 'pure' plasma and a 'real process' plasma: practically all of the published VUV emission data for low-pressure discharges pertain to spectroscopic studies in which extreme care was taken to ensure pure gases. However, plasma reactors, by definition, are used to process materials, and the plasma gas therein will rapidly become contaminated with the volatile byproducts of that processing. For example, when polymers are exposed to oxygen-containing plasmas, 20% or more of the gas phase can be volatile compounds of carbon, hydrogen, and oxygen, all of which can interact with the surface, both chemically and energetically.

The VUV emission from a large number of plasmas has been measured [46], and in all cases the spectra were found to include components of intense, extremely energetic VUV radiation. These emission spectra are usually complex and strongly dependent on experimental parameters such as the gas composition, power, pressure, and the concentration of contaminants. In addition to the complexity arising from the variables just mentioned, the plasma excitation frequency also has a major effect. For example, visible and VUV spectral emissions from MW (2.45 GHz) and RF (13.56 MHz) plasmas show important differences in ion and excited species concentrations [20], which result from their different EEDFs [see equation (1), Section 1.2.2]. In RF and MW oxygen plasmas, our measurements show higher concentrations of O^+ and O^*

(electronically excited atomic oxygen) in the former, but more neutral atomic oxygen in the latter.

Figure 1 illustrates the differences in VUV emission between RF and MW plasmas in nitrogen. This spectrum is a semi-logarithmic plot of the photo-multiplier current vs. the wavelength λ , so apparently small differences in the line height, in fact, represent very significant differences in intensity. Also, it must be stressed that because all of the radiation at $\lambda < 200$ nm is photochemically active, the RF plasma is much more active than its MW equivalent, while the dual-frequency (MW-RF) plasma is more active than MW or RF alone [47].

This VUV radiation will increase the rate of initiation of surface reactions on polymers, while the increased gas-phase concentration of ground-state free radicals (from the MW excitation) will enhance the overall rate of surface reactions. This synergistic effect between MW and RF excitation, along with RF-induced self-bias, can help to explain the advantages that we observe in mixed-frequency plasma processing [13, 25, 48, 49].

As mentioned above, VUV radiation is sufficiently energetic to break any organic covalent bond [40, 50]. These photons are absorbed in a very shallow layer near the polymer surface (or in the surface contamination), typically a few tens of nanometres deep [38, 51–54]. Indeed, differences in the absorption spectra among polymers [51, 54] make it possible, in principle, to tailor the plasma emission spectra to maximize the photochemical effect on different materials. This is illustrated by the data of Egitto and Matienzo [55] shown in Fig. 2; it shows that the receding contact angle of water on polyethylene (PE) is not affected by light with wavelengths longer than about 170 nm (the cut-off of quartz). The absorption spectrum of PE is also shown in Fig. 2. These data indicate that the contact angle is affected by photons with an absorption coefficient greater than about 10^4 (an absorption depth of about 50 nm). It is obvious that there is a very strong relationship between the two sets of data. Our results show that an oxygen plasma is not very effective for treating poly(tetrafluoroethylene), PTFE; a possible reason for this is that PTFE does not strongly

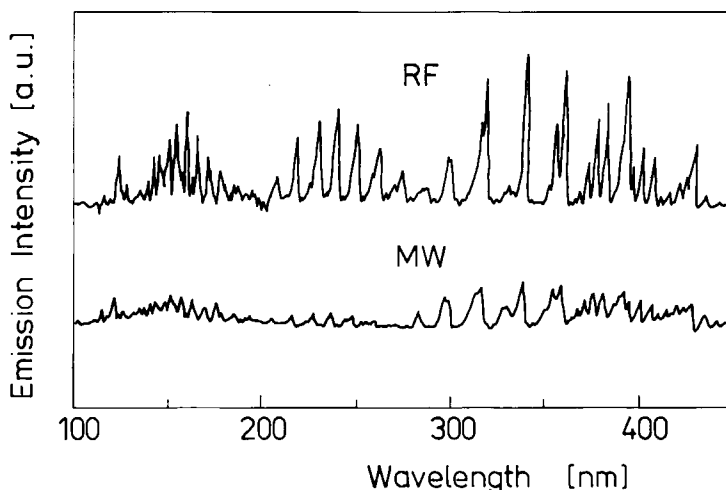


Figure 1. VUV spectra emitted from a MW and an RF discharge in nitrogen. The intensity is shown on a logarithmic scale.

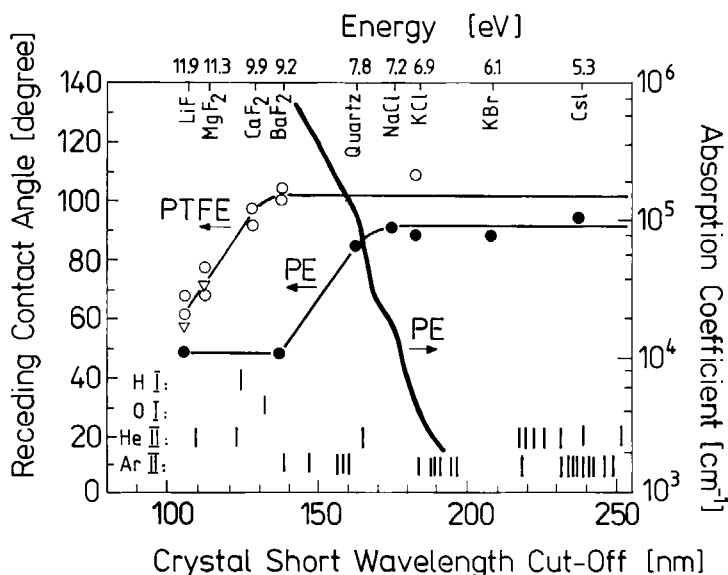


Figure 2. Effect of the short wavelength cut-off on the receding water contact angle on PE and PTFE (after ref. 55), with an overlay of the PE absorption spectrum (after ref. 52).

absorb the 130.5 nm emission from an oxygen plasma. We do not have the absorption spectrum for PTFE, so this cannot be confirmed at the present time, but the similarity in shape between the PTFE and PE data from Egitto and Matienzo suggests that it is probably true. In addition, it is known that hydrogen-containing plasmas (which emit at 121.5 nm) and He plasmas (emitting at 59.0 nm) are efficient at reducing the contact angle on PTFE.

Clearly, then, a very important phenomenon operating in plasma reactors is the VUV photochemistry at surfaces. For the case of polymer surfaces, this is supported by literature references to improved wetting [55], cleaning [56], crosslinking [43, 57], fluorination [58], functionalization [48, 59], and free-radical generation [36]. In all of these examples, the polymer surfaces were separated from the active plasma by a VUV-transparent window, which allowed VUV photons to reach the sample surface, but not the reactive radicals or ions from the plasma. In some cases, the reported results showed that VUV radiation alone can account for as much as 80% of the surface reactions that result when the sample is directly immersed in the plasma.

A recent paper [60] dealt with the treatment of polypropylene in a downstream plasma system that also used a mercury quartz lamp to illuminate the sample. These authors came to the erroneous conclusion that UV had no influence on surface treatment. This conclusion is unjustified for two reasons: first, the 185 nm radiation from a mercury lamp has a wavelength longer than the absorption edge of PP [39] ($\lambda \approx 170$ nm, see Fig. 2), so it will not be effective for the treatment of this polymer; second, the PP surface was about 40 cm below the surface of the mercury lamp. Oxygen-plasma products (O , O_3) and their reaction products with PP (CO , CO_2 , H_2O , etc.) all possess strong VUV absorption cross-sections [35], so that the 40 cm-long optical path through these species results in

absorption of most of the UV radiation from the lamp before it can reach the PP surface. This absorption of radiation is one of the main reasons for using downstream strippers in the semiconductor industry [20], that is, machines in which photoresist removal is due to long-lived oxygen species only.

In conclusion, the reaction of polymer surfaces near ambient temperature is very slow in the presence of only ground-state atoms or molecules because these do not possess sufficient energy to cause rapid reaction rates [61, 62]. However, when acting in synergy with elevated surface temperature, bombardment by energetic ions, exposure to VUV photons, or a combination of these, the overall reaction rate will increase by several orders of magnitude. The complex interdependence of these effects is the primary reason why theoretical analysis and modelling of plasma chemical reactions is so difficult.

2.2 Characterization of modified surfaces

2.2.1. General description of techniques. As discussed in Section 2.1, energetic particles and VUV photons generated in the plasma interact strongly with organic polymer surfaces. This interaction gives rise to cleaning, ablation or etching, breakage of bonds, reaction of surface free radicals, crosslinking, and incorporation of chemical groups originating from the plasma or from subsequent exposure to selected gases or vapours. Since all these processes can affect adhesion, it is crucial that one be able to characterize a given plasma treatment in terms of the resulting changes in surface chemical composition, structure, and physical or functional properties.

A variety of surface-specific techniques are available for the characterization of polymers. Among the most powerful and frequently used are X-ray photoelectron spectroscopy (XPS or ESCA) [3, 4, 13, 16, 40, 41, 49, 58], static secondary ion mass spectrometry (SSIMS) [3, 63], Fourier transform infrared spectroscopy (FTIR) [3, 4, 38], and contact angle goniometry [1, 4, 28, 48, 55]. Also very useful are high-resolution electron energy loss spectroscopy (HREELS) [64], scanning electron microscopy (SEM), and techniques based on ion beam probes such as elastic recoil detection (ERD) analysis [65], ion scattering spectroscopy (ISS) [66], and Rutherford backscattering spectroscopy (RBS) [66]. Of course, a wide variety of 'functional' test methods have been devised to evaluate the relative merits of a given surface treatment, e.g. mechanical peel or lap-shear tests, electrical property measurements, and others. These are too numerous to recite here, and the reader is directed to ref. 67. The same applies to plasma diagnostic techniques [42], the most common of which are optical emission and mass spectrometries, and electric probe measurements.

2.2.2. Surface chemical structure. In Sections 1.1 and 2.1.1, we have already expressed our belief that the chemical modification of a polymer surface is one of the most powerful ways of enhancing its bond strength with another surface; the inherently low surface free energy of untreated polymers hinders the wetting by liquid adhesive systems [68, 69], or the interaction with deposited layers of metal or other materials. Typically, a reactive plasma is used to add polar functional

groups, which can dramatically increase the surface free energy of the polymer. For example, oxidation is known to enhance metal–polymer adhesion [48, 64], while surface nitrogenation with nitrogen-containing plasmas introduces basic groups that can enhance dyeability with acid dyes [70], printability, or cell affinity in biocompatibility [71]. Some of these are discussed in more detail further below. Of course, plasma can also be used for surface fluorination [72–74] and silylation [75], surface-chemical changes which tend to impart greater hydrophobicity, i.e. reduced wettability and bond strength (this being desirable in some instances). In the remainder of this sub-section, we briefly illustrate and discuss some of the above-mentioned chemical changes.

2.2.2.1. Nitrogenation. In the opening remarks above, we already mentioned how basic groups deriving from surface nitrogenation of polymers can be useful. Two commercial polymers, Kapton[®] polyimide (PI) and linear, low-density polyethylene (PE) have been exposed to MW and MW–RF plasmas in pure N₂ gas. Figure 3 shows C(1s) XPS spectra of the untreated, clean polymer surfaces (lower spectra), and of surfaces following MW and MW–RF plasma treatments [49]. Plasma treatment of PE is seen to result in three new spectral features (peaks C2 to C4), besides the original C1 peak at 285 eV associated with carbon bonded to carbon or hydrogen only; the new features arise from the chemical bonding of nitrogen in amine (C2), imine (C3), and amide or nitrile (C4) groups. The relative concentrations of these various functionalities (proportional to the relative peak areas) show a strong, systematic dependence upon V_B , the RF-induced bias voltage during MW–RF plasma treatment. While the N₂ plasma treatment leads to bonded nitrogen primarily in the form of imine or imide groups (C3: C=N, 287.0 eV), amine groups (C2: C–N, 285.8 eV) are in the majority following NH₃ plasma treatment. In the N₂ plasma case, the total bonded-nitrogen concentration can exceed 40 at % on PE [49], while exposure to NH₃ plasma at comparable conditions systematically results in less nitrogen uptake. It has been estimated that up to 20% of the total nitrogen uptake can be photochemically induced by VUV radiation with $\lambda \gtrsim 120$ nm [48]; the VUV radiation from an NH₃ MW plasma was found to be more pronounced than that from an N₂ plasma due to the intense H _{α} emission at 121.5 nm; this observation is in agreement with other published data [15, 43]. Following the plasma treatment and the subsequent exposure of samples to the atmosphere during their transfer to the XPS instrument, oxygen can also become incorporated. Typically, the highest concentration of oxygen in PE (~8 at %) is found after N₂ plasma treatment, while NH₃ plasma treatment results in a somewhat lower oxygen concentration (~4 to 6 at %) [49].

Referring again to Fig. 3, strong effects may also be noted for the case of Kapton[®] PI [poly(*N,N'*-*P,P'*-oxydiphenylene) pyromellitimide], whose virgin C(1s) spectrum is evidently much more complex than that of PE: the C1 peak is attributed to carbon in oxydiphenylene, while the C2 peak corresponds to carbon singly bonded to oxygen and nitrogen, plus the carbons in the pyromellitic dianhydride ring. The C3 and C4 peaks are associated with the carbonyl carbon in imide linkages and the shake-up satellite associated with aromatic structure, respectively. Following N₂ plasma treatment, the spectra show

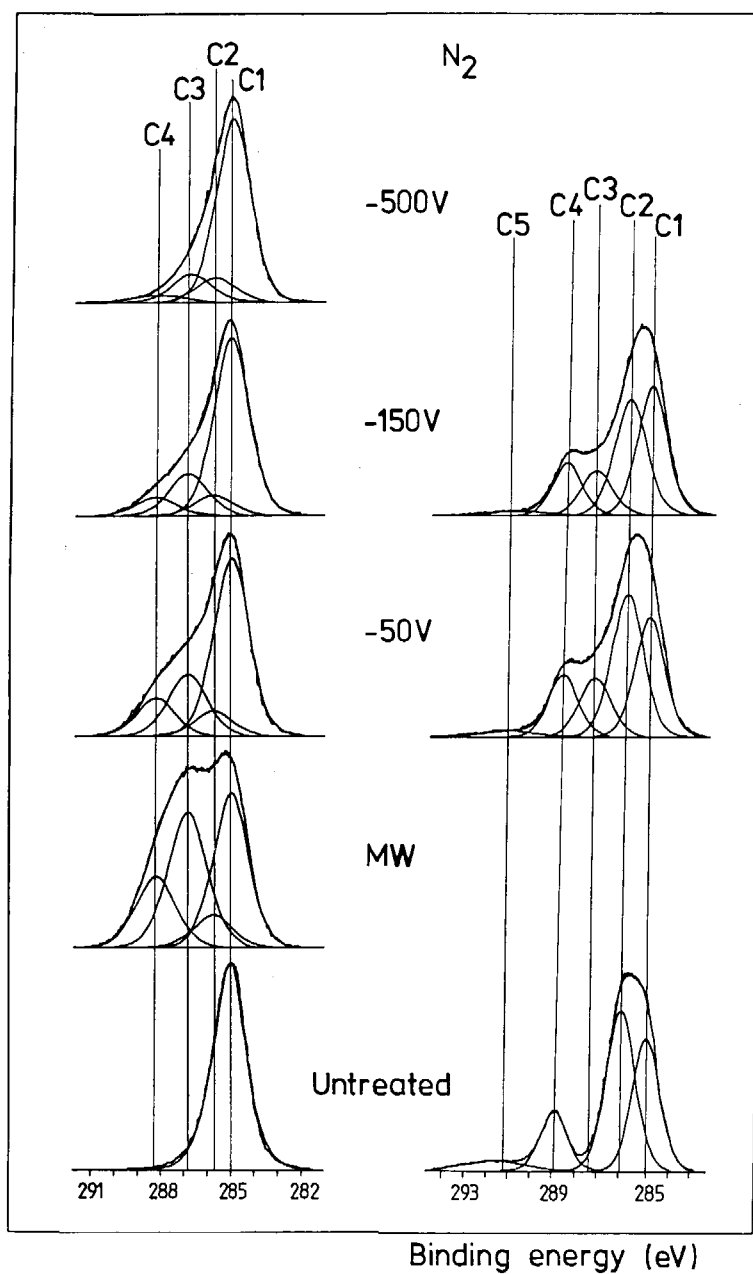


Figure 3. C(1s) XPS spectra for MW and MW-RF N_2 plasma-treated polyethylene (left column) and Kapton® polyimide (right column). Modified after ref. 49.

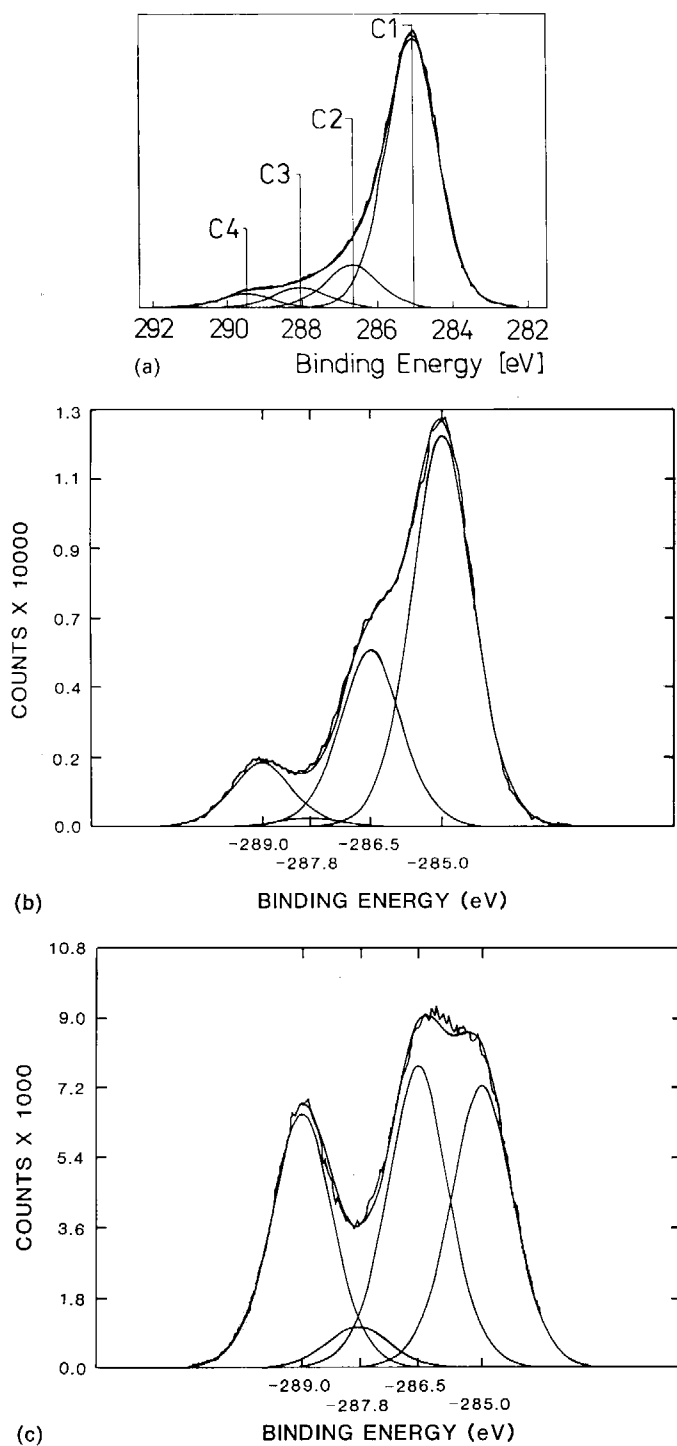


Figure 4. C(1s) XPS spectra: (a) PE treated in a low-pressure air MW plasma for 30 s, which results in O/C = 0.30 (after ref. 114). (b) Untreated epoxy, and (c) epoxy degraded by exposure to a corona discharge for 900 h. After ref. 84.

important changes in structure and composition, such as a sharp increase in the amide functionality (C3). Particularly noteworthy, however, is the surface damage induced by ion bombardment. It is manifested by decreases in C4 and C5 intensities, caused by the breakage of C=O bonds in the PI structure, and to the opening of benzene rings, respectively.

The results above, obtained in this laboratory, are presented only by way of illustration, for similar observations have been reported by many others [30, 33, 38, 63, 71, 76, 77].

2.2.2.2. Oxidation. The vast majority of commercial processes involving the corona treatment of polymer surfaces, carried out in ambient atmospheric air, are designed to create polar moieties (carboxyl, ether, carbonyl, hydroxyl, etc.) by reaction with activated oxygen species [12, 78–80]. As will be shown in Section 2.2.3, the presence of such polar groups raises the surface free energy of the polymer, which permits wetting by printing inks and substantially higher bond strengths than those obtained with the untreated surfaces. Low-pressure air or oxygen plasmas may also be used for this purpose, but the need to operate in a partially evacuated chamber adds to the treatment cost. Low-pressure O₂ plasma is, however, employed extensively in microelectronics for the removal (stripping) of polymeric resists, used for microlithography [18, 20], and for the surface treatment of complex shapes, such as car bumpers, where corona cannot be implemented (see also Section 4).

Figure 4a represents the curve-fitted C(1s) XPS spectrum of PE treated in an air MW plasma. This spectrum (compared with that of 'virgin' PE, see Fig. 3) clearly reveals the new peaks resulting from plasma oxidation, namely C2 at 286.5 eV due to C—O groups (hydroxyl, ether, or epoxide), C3 at 288.0 eV due to C=O or O—C—O (carbonyl or double ether), and C4 at 289.4 eV due to O=C—OH or O=C—O—C.

The total surface oxygen concentration can be controlled by varying process parameters such as the plasma treatment time and the power density, but care must be exercised not to 'overtreat' the surface, a problem well known to the corona community. Gross overtreatment can lead to excessive bond breakage and oxidation, manifested by the massive formation of 'low-molecular-weight oxidized molecules' (LMWOM) [28, 38, 80–84], which appear on the surface as solid debris or liquid droplets, readily visible under an optical or a scanning electron microscope [82–84]. An extreme example of this can occur during the faulty operation of high-voltage equipment, when an organic insulation (e.g. epoxy resin) may be exposed to an air corona for tens or hundreds of hours. Figures 4b and 4c show, respectively, the XPS spectra of the untreated epoxy and resulting liquid and solid LMWOM (formic, glycolic, and oxalic acids) [84]. In order to distinguish LMWOM from other low-molecular-weight products in the following text, we refer to the latter as 'LMW species'.

2.2.2.3. Fluorination and silylation. As mentioned above, it is sometimes advantageous to render a surface hydrophobic, that is, non-wettable by water or aqueous solutions. An obvious example is the surface treatment of textiles;

perhaps less well known is the fluorination of the inner surfaces of the plastic gasoline tanks of automobiles, to provide a barrier against gasoline-vapour permeation. For several years this has been done using molecular fluorine, a process that is now becoming outlawed for environmental and safety reasons. Plasma-based fluorination, on the other hand, uses stable, saturated fluorine compounds (perfluorocarbons such as CF_4 , C_2F_6 , or sulphur hexafluoride, SF_6), and these in much smaller quantities. Surface fluorination can also be achieved by the deposition of a thin layer of a perfluorinated plasma polymer; here, an unsaturated fluorocarbon feedgas such as C_2F_4 or C_4F_8 is best used [85], but excellent water repellancy can also be obtained by the plasma polymerization of organosilicone 'monomers' such as hexamethyldisiloxane [75, 86, 87].

Figure 5 shows the $\text{C}(1s)$ XPS spectra of PE film following 30 s of treatment in a CF_4 or a C_2F_4 MW plasma (upper and lower spectra, respectively; unpublished results from this laboratory). While the C_2F_4 -based plasma polymer is richer in fluorine ($\text{F}/\text{C} = 1.40$, as compared with 0.70 for the CF_4 case), the two surfaces displayed almost identical water contact angles ($\theta_a = 122^\circ$, $\theta_r \approx 60^\circ$, see

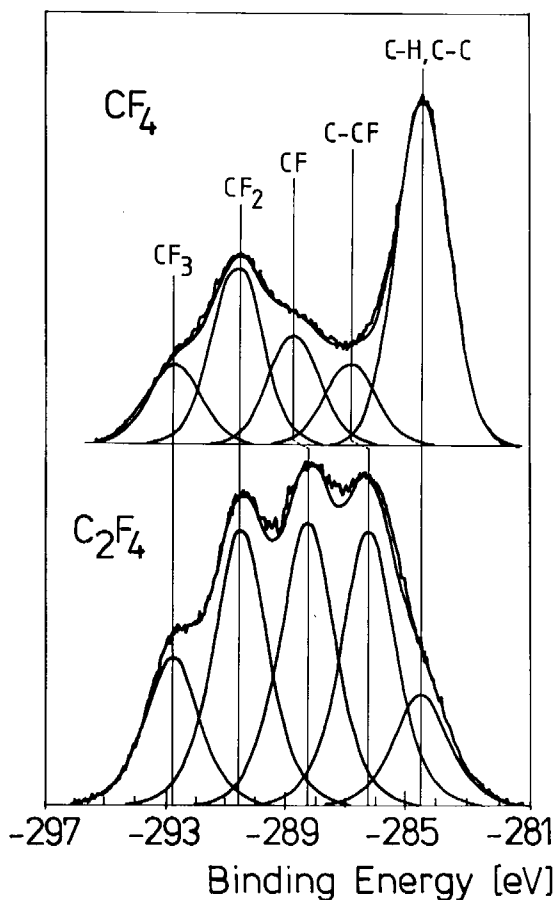


Figure 5. $\text{C}(1s)$ XPS spectra of PE treated in a low-pressure MW plasma for 30 s: (top) CF_4 plasma; (bottom) C_2F_4 plasma. Peak positions and assignments are in accord with the literature (see, for example, ref. 85).

Section 2.2.3). Very similar results have also been obtained here for the case of kraft paper (lignocellulose, a natural polymer) [74, 88], and numerous other workers have also reported data resembling the ones above [58, 72, 73, 85].

2.2.2.4. Post-plasma reactions. In the description of crosslinking by the CASING treatment (Section 2.1.1), we mentioned that free radicals are formed at or below the polymer surface; these radicals may be stable for long durations, and they thereby have an opportunity to react. This opportunity often arises on exposure to atmospheric oxygen or water vapour, which explains the omnipresence of bonded oxygen species in the XPS spectra of He, Ar, or N₂ plasma-treated polymers [38, 49, 77].

Although usually undesirable, post-plasma reactions can also be used deliberately to bond desirable species onto the surface of polymers. In the 1970s, the grafting of acrylic acid to synthetic fabrics, immediately following surface activation in a pure Ar plasma (without intermediate exposure to air), was one of the earliest industrial applications of plasma chemistry [89].

2.2.3. Wettability. Because modified wettability is one of the most apparent results of plasma treatment, a common method of characterizing a given treatment is to measure the contact angles of drops of various liquids on the surface. Untreated polymeric surfaces are usually hydrophobic, displaying advancing and receding water contact angles from 60° to 90° or more. Plasma-produced polar groups increase the surface free energy, γ , of the polymer; the accompanying decrease in contact angle, θ , usually correlates with better bonding of adhesives, and θ has often been used as an estimate of bonding quality [15]. The wettability enhancement differs among various polymers, but it is always significant, even for fluorocarbons [27, 90] and silicones [91].

The value of γ is usually determined from measurements of the static contact angles of a selected series of liquids [92, 93]. However, for rigorous interpretation of contact angle measurements one must take into account the facts that real surfaces possess microroughness, and that the relative concentrations of hydrophobic and hydrophilic molecular groups may vary. The surface heterogeneity gives rise to contact angle hysteresis, that is, a difference between the advancing, θ_a , and receding, θ_r , contact angles. One must therefore take into account deviations from an ideal surface (rigid, smooth, and homogeneous) when evaluating experimental and theoretical data, as discussed in detail in a recent review by Morra *et al.* [94].

The effect of nitrogen concentration, produced by NH₃ plasma treatment, on the contact angle hysteresis of low-density polyethylene (PE) and polyimide (PI, DuPont Kapton® H) is illustrated in Fig. 6. Even on the untreated PE surface, the θ_r value is seen to be lower than θ_a ; this is probably due to the presence of surface roughness, or of polar surface contaminants, or of both. With increasing nitrogen concentration, the θ_r values drop rapidly because of the resulting rise in the concentration of hydrophilic groups. However, the hysteresis ($\theta_a - \theta_r$) remains high until the concentration of hydrophobic groups has become small, at which point θ_a also decreases. Similar behaviour is seen to apply to polyimide, with the difference that this polymer already contains nitrogen and oxygen in its original structure. The measurement of contact angle hysteresis can thus serve as

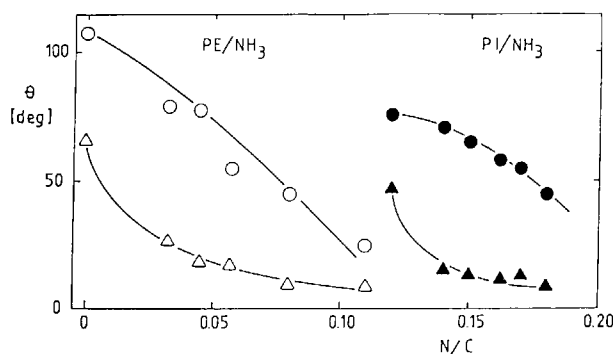


Figure 6. Effect of the XPS atomic ratio N/C on the advancing (○, ●) and receding (△, ▲) water contact angles on PE (○, △) and PI (●, ▲) treated in an NH₃ MW-RF plasma. After ref. 108.

an indicator of the relative concentrations of hydrophilic and hydrophobic groups, and also of the Lewis acid–base characteristics of the surface, a concept of rapidly growing importance in adhesion science [95–97]. The surface characteristics just mentioned are also accessible through other experimental techniques, such as inverse gas chromatography [98, 99].

In practical applications, the stability of the plasma-treated polymer surface is an important issue, but very often a surface rendered wettable by the treatment is found to revert to a less wettable state with time [16, 28, 29, 38, 48, 91, 100–105]. This process, which we call ageing, may result from a combination of four effects [106]: (i) the thermodynamically driven reorientation of polar moieties away from the surface into the sub-surface; (ii) the diffusion of mobile additives or oligomers from the polymer bulk to the surface; (iii) the formation of LWM species in the sub-surface and their subsequent migration to the surface; and, finally, (iv) the reaction of residual free radicals, i.e. chemical change.

The effect of storage time on the wettability of NH₃ plasma-treated PE is illustrated in Fig. 7. The initial contact angle values, $\theta_a = 105^\circ$ and $\theta_r = 70^\circ$, drop to $\theta_a = 30^\circ$ and $\theta_r = 5^\circ$ after plasma exposure. These values increase only slightly during the first few days of storage and remain stable, even at the elevated temperature of 90°C . However, some increase in θ_a and θ_r is noted when the samples are exposed to high humidity, probably resulting from chemical reaction, mechanism (iv) in the above-cited list.

In practice, it is difficult to distinguish the relative contributions of the four effects listed above to the observed ageing (reversion) process. In the case of very clean polymer films, Occhiello *et al.* [102] have used plasma-induced isotopic labelling to demonstrate the importance of entropy-driven molecular relaxation [mechanism (i) above], the rate of ageing apparently depending on the mobility of polar moieties about the polymer chain. The most pronounced ageing process has been observed for polypropylene (PP); poly(ethylene terephthalate) (PET) and polystyrene (PS) showed a lesser tendency to age [107], while PE [48, 107] (see Fig. 7) and PI [48] are quite stable. Attempts have been made to suppress ageing phenomena by stabilizing the surface layer via crosslinking using controlled ion bombardment during MW plasma exposure [48, 49, 108].

As a rule, therefore, ageing rate data cannot be generalized or predicted. The rate of reversion must be measured for every new batch of material, because

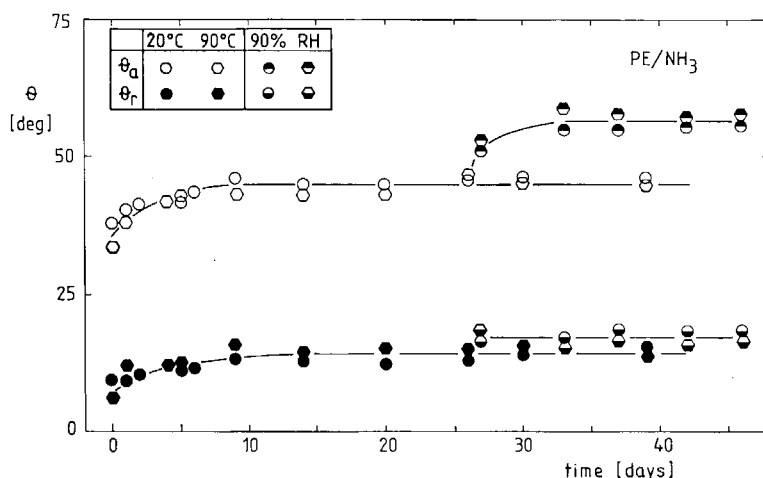


Figure 7. Advancing (θ_a) and receding (θ_r) water contact angles on PE treated at substrate temperatures of 20 and 90°C in MW plasma of NH_3 , plotted vs. the storage time in ambient air and at 90% relative humidity. After ref. 48.

small changes in polymer formulation can produce large rate changes. It is insufficient to measure the wetting once; it must be followed with time unless the parts are bonded, printed, or painted immediately after plasma treatment.

3. BONDING ENHANCEMENT THROUGH PLASMA TREATMENT

3.1. General considerations

The various effects of the plasma-surface interactions discussed in the earlier sections contribute in a synergistic manner to the different mechanisms of adhesion. Indeed, bonding enhancement can be regarded as resulting from the following overlap of effects: (a) removal of organic contamination and of weak boundary layers by cleaning and ablation; (b) cohesive strengthening of the polymeric surface by the formation of a thin crosslinked layer that mechanically stabilizes the surface and serves as a barrier against the diffusion of LMW species to the interface; and (c) creation of chemical groups on the stabilized surface that result in acid-base interactions and in covalent linkages believed to yield the strongest bonds.

Experience has shown that the plasma treatment conditions necessary to achieve maximum bond strength must be optimized for any given materials combination. This is accomplished by exercising control over the effects mentioned above, a process in which the chemistry of the substrate material, the energetics at the plasma-polymer interface (ions, photons), and the gas-phase plasma chemistry play the major roles. In the following, we discuss the effects of plasma treatment for different materials combinations, divided into three representative groups: polymer-polymer bonding, polymer-matrix composites, and metal-polymer bonding.

3.2. Polymer-polymer bonding

Plasma treatment can be used with great effect to improve the bond strength to

polymers. In these cases, the improved properties result from both increased wettability of the treated polymer by the adhesive and the modification of the surface chemistry of the polymer. The changed surface chemistry facilitates reaction of the adhesive with surface species during curing, to form covalent bonds with the plasma-treated interphase. Figure 8 illustrates the relation between the advancing water contact angle and the shear strength for the polyphenylene sulphide (Ryton® R-4)/epoxy system, following different plasma treatments. Most of these data follow the expected relationship that the bond strength will improve with improved wetting; oxygen and O_2/CF_4 mixtures give both the best wetting and the best bond strength. However, the data in Fig. 8 also show that in certain cases (for example, 4% O_2 in 96% CF_4), it is possible to obtain excellent bonding with very poor water wetting. XPS analysis of the polymer surface after this plasma treatment shows a large amount of fluorine substitution, but also about 5–10% of oxygen-containing moieties. Apparently, the fluorinated surface is sufficiently hydrophobic to repel water, but it is still wettable by the epoxy.

Reference 109 presents what is believed to be the first direct experimental evidence for the formation of covalent bonding between plasma-generated surface functionalities and an epoxy adhesive. The proof of this covalent bonding is extremely important because it would predict greatly improved hot-wet (100% relative humidity, 100°C) stability of the adhesive bonds to plasma-treated polymers. In fact, it has been reported that O_2 plasma treatment of the surface of graphite/PI parts improves the hot-wet stability by a factor of 2, as compared with solvent wiping [110].

Tables 1 and 2 give examples of typical bonding improvement data for a number of polymers. It must be stressed that these data are intended only to show the trend and the magnitude of improvement that can be obtained through

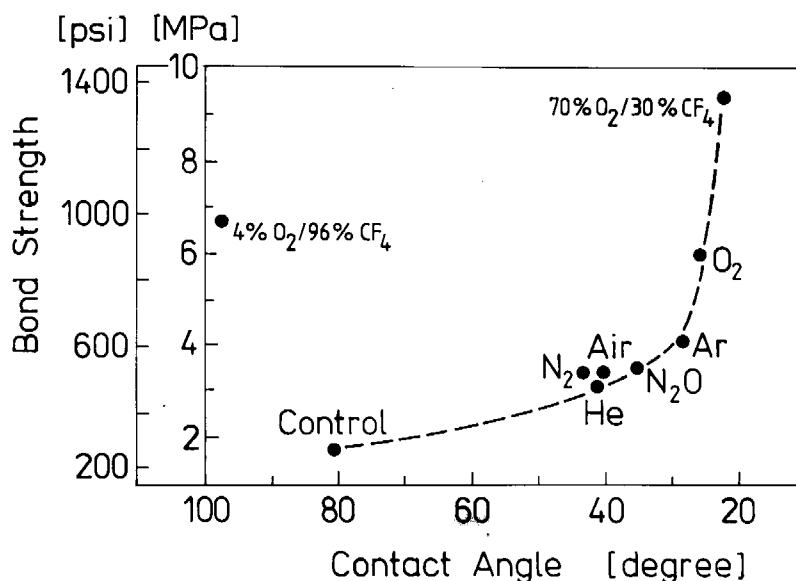


Figure 8. Shear strength vs. static water contact angle for polyphenylene sulphide (Ryton® R-4)/epoxy laminates for different plasma treatments. After ref. 15.

Table 1.

Typical examples of lap-shear bonding improvement after various plasma treatments

	Control		Plasma-treated	
	MN/m ²	psi	MN/m ²	psi
Polyimide (PMR [®] -15)/graphite	2.90	420	17.93	2600
Polyphenylene sulphide (Ryton [®] R-4)	2.00	290	9.38	1360
Polyether sulphone (Victrex [®] 4100G)	0.90	130	21.65	3140
Polyethylene/PTFE (Tefzel [®])	—	Very low	22.06	3200
HDPE	2.17	315	21.55	3125
LDPE	2.55	370	10.00	1450
Polypropylene	2.55	370	21.24	3080
Polycarbonate (Lexan [®])	2.83	410	6.40	928
Nylon [®]	5.86	850	27.58	4000
Polystyrene	3.93	570	27.58	4000
Mylar A [®]	3.65	530	11.45	1660
PVDF (Tedlar [®])	1.93	280	8.96	1300
PTFE	0.52	75	5.17	750

Table 2.

Typical examples of peel-strength improvements after various plasma treatments.

	Control		Plasma-treated	
	N/m	lb/in	N/m	lb/in
Silicone (red, Durometer 50)	70.1	0.4	3330	19
RTV silicone (D.C. type E)	—	Very low	403	2.3
Perfluoroalkoxy (PFA)	17.5	0.1	1450	8.3
Fluorinated ethylene propylene (FEP)	17.5	0.1	1820	10.4
Tefzel [®]	17.5	0.1	2770	15.8
PTFE	17.5	0.1	385	2.2
Polyimide (Kapton [®])	700	4	2800	16

plasma treatment. These data only represent typical values, which will differ from one experimenter to the other depending on the polymer formulation, the type and amount of additives, the adhesive, the cure cycle, the time between plasma treatment and bonding, and, of course, the other plasma parameters.

It is also important to stress that there is no 'standard' plasma process. There are normal starting processes for various polymers that are learned through experience, but it is usually necessary to optimize these to obtain the best processing conditions for each application. Under optimum conditions for a given polymer/adhesive system, the bond strength can generally be improved to the point where the bond failure is cohesive in the weakest material, and not in the bond line. For example, a five- to seven-fold bond strength improvement has recently been found for PP to epoxy [111]. Improvements by factors of 3 and 7 were observed for the peel strength of pressure-sensitive adhesive tape to PFA [27] and to PE [81], respectively, and a four-fold improvement in the epoxy bonding of PE or PP to aluminium [6, 112].

Besides polymeric laminated structures using adhesives, efforts are continuing to achieve good polymer-polymer bonding by mere plasma activation. Interfacial

phenomena have recently been studied for the cases of PE/PE and PE/PET laminates without adhesives, following treatment in a low-pressure MW air plasma or in an ambient air corona discharge [113, 114]. The adhesion force was found to exhibit a pronounced maximum for a surface concentration of bound oxygen between 11 and 14 at%, independent of the type of treatment (see Fig. 9). Based on high-resolution XPS, such as that illustrated in Fig. 4a, it has been concluded that the maximum adhesion occurs when the XPS peak C2 is highest (i.e. when the concentration of hydroxyl, ether, or epoxide groups is highest) and that of carboxyl (acid) groups is lowest (see Fig. 10). These results

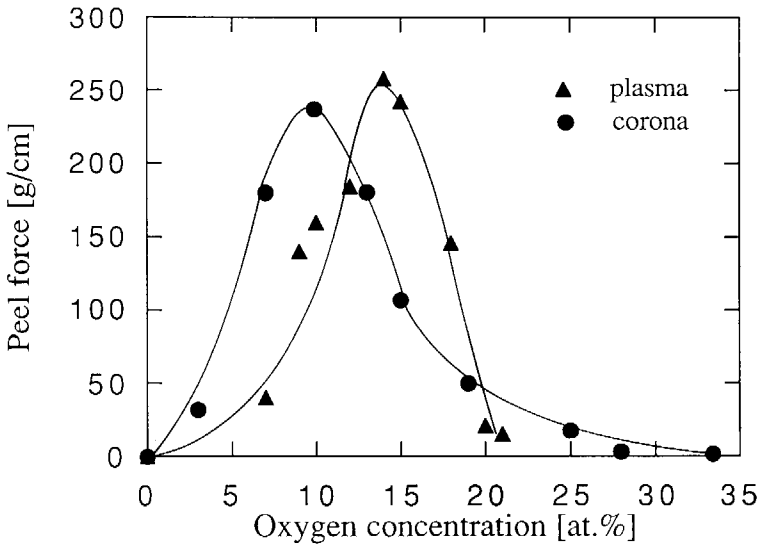


Figure 9. Peel force of PE/PE laminates without adhesive as a function of the oxygen concentration after low-pressure plasma (\blacktriangle) or corona (\bullet) treatment in air. After ref. 114.

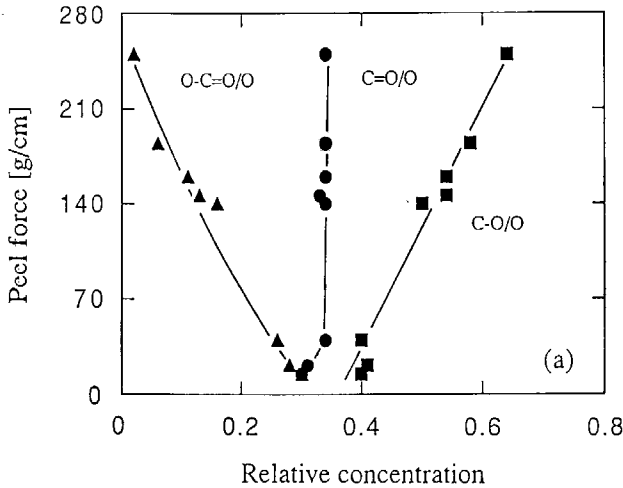


Figure 10. Peel force of PE/PE laminates without adhesive plotted against the relative concentration of oxygen-containing groups following treatment in a low-pressure air plasma. After ref. 114.

suggest that the highest adhesion force appears when the surface is mechanically stabilized by crosslinking and when the effect of a weak boundary layer due to excessive LMWOM is minimal (low carboxyl concentration) [114]. Association of the C4 (carboxyl) group with LMWOM is confirmed by the fact that rinsing the plasma-treated surface with distilled water substantially decreases the C4 peak intensity. It has yet to be established whether the maximum bond strength, observed above, results in part from direct covalent bonding across the interface between the two laminated surfaces.

The acidity of a strongly oxidized surface suggests that another type of chemical bonding mechanism might be of importance here, namely acid–base interactions [95–97]. Adhesion of dye molecules, an example drawn from our own experience, strongly supports this view: non-polar polymers such as PE or polypropylene (PP) cannot be treated with inexpensive water-based acid dyes. If, however, basic (Lewis base) moieties are grafted to the surface, the acid–base interactions between these and the dye (Lewis acid) can give rise to strong (chemical) adhesion at the polymer surface. Surface nitrogenation (amination) using a plasma of N_2 , NH_3 , or volatile amines has been shown [70] to yield the desired results, which are attractive for both economic and environmental reasons.

3.3. Polymer–matrix composites

In the case of composite materials, the plasma treatment of the filler can be very effective in promoting adhesion because of the large treated surface area. The modification of interfaces not only enhances the bond strength between the components, but it can also improve the electrical and ageing characteristics of the composite by reducing the penetration of water vapour and other contaminants.

Regarding the mechanical properties, in many fibre-reinforced polymer composites, toughness is derived from energy dissipation that occurs when bonds between the fibres and the matrix fail. After plasma treatment, the peel and flex properties of the composite tend to improve, but the toughness can decrease because the above-described energy loss mechanism is no longer available. Therefore, toughness must be achieved through another mechanism. The easiest way to develop the requisite toughness is to use a toughened (lower modulus) matrix, an approach that will not only add energy dissipation, but also increase the critical flaw size and thus increase the strength of the composite.

The following are typical illustrations of the trends discussed above. Once again, due to large variations among the reinforcing filler and matrix materials, detailed optimization must be performed for each proposed composite system, in order to obtain reliable engineering data.

Much research has been done over the years on the treatment of particulate filler materials, such as $CaCO_3$ powder [115] and mica flakes [116, 117], by exposure to selected plasma gases. The objective was to impart either acidic or basic properties by chemical surface modification, or to deposit strongly adhering plasma–polymer layers, thereby enhancing interfacial compatibility with various polymeric matrix materials. Among the matrices examined were PE, PP, PS, and polyvinyl chloride (PVC). In all cases, mechanical properties (for

example, tensile strength) could be significantly enhanced in the plasma-treated samples, as compared with untreated control samples. Depending on the particular materials/treatment combinations, the improved properties could be explained in terms of acid–base interactions [115] or ‘bridging’ via compatible polymer/plasma–polymer homologues [116, 117].

Aromatic polyamide or ‘aramid’ (DuPont Kevlar®-29) fibres or fabric were also modified by plasma treatment or coated with plasma polymer before encapsulation in a triazine resin matrix [118]. Here too, very significant increases in the bond strength (peel strength of two-ply laminates) could be attributed to the plasma treatments; this was not entirely surprising, since untreated aramid fibres are known to have superb mechanical characteristics, but are also known to present bonding difficulties.

In a detailed study by Ismail and Vangeness [119], different graphite composites were compared following oxygen-plasma treatment or high-temperature oxidation. The authors found that the plasma treatment had no substantial effect on the surface area of pitch fibre or carbonized polyacrylonitrile (PAN), but that it increased the BET surface area (measured by Kr adsorption) of graphitized rayon by almost an order of magnitude. For comparison, the high-temperature treatment of PAN (without plasma) increased the BET area by three orders of magnitude. Even though the BET area of the graphite fibres increased only slightly following both types of treatment, the O₂ adsorption on the plasma-modified surface rose by 430%. This difference has been attributed to chemical adsorption of the O₂ by active sites left on the fibre surfaces. The authors recommended that plasma treatment be used on pitch-carbon fibres if primarily chemical bonding is sought, while high-temperature oxidation is preferred for primarily physical bonding.

Jang and Das [120] reported the results of tests on a high modulus graphite/epoxy composite following both O₂ and N₂ plasma treatments. They found that after a 1 min N₂ plasma treatment of the graphite, the composite shear strength increased by 55%, the flex strength decreased by 7%, and the toughness decreased by 24%. However, the toughness could be restored by the addition of less than 5% chlorotributynitrile (CTBN) rubber to the matrix. Significant improvements have also been observed for high modulus graphite in high modulus epoxy (Thornel T-300 in DER 332/T403) [33]. Increases of the T-peel force by 41%, 32%, and 22% were observed following plasma treatment in air, Ar, and NH₃, respectively, while a decrease by 18% after O₂ plasma exposure was felt to indicate that the treatment conditions had not been fully optimized.

Interesting results have also been reported for polyaramide/epoxy composites [33, 121]. Allred *et al.* [121] studied commercial Kevlar® cloth; SEM examination of the surface showed that the fibres were very smooth before and after NH₃ plasma treatment, which they believed healed small surface flaws. After plasma treatment, they observed a change in the failure mode of the composite from matrix–fibre debonding to cohesive failure in the fibre (splitting, fibrillation, separation of the skin and core of the fibre, and crack propagation through the epoxy matrix), implying covalent bonding between the epoxy and the fibres. After 1 min of NH₃ plasma treatment, a 114% increase in T-peel, a 31% increase in interlaminar strength, and a 5% decrease in toughness were observed.

Chemical derivatization analysis of the plasma-treated surface using a dye

showed that there was about one NH_2 group per polymer-repeat unit after 1 min of N_2 plasma treatment. Oxygen contamination of the NH_3 plasma interfered with the incorporation of NH_2 into the surface, probably because of the competition for the active sites by oxygen species. No change in the NH_2 concentration on the surface was observed, even after 18 months of storage in air.

The plasma treatment also reduced the water absorption of the composite system by a factor of 3, and it converted from a capillary (wicking along the fibre-matrix interface) to a Fickian (diffusive) absorption through the body of the matrix [121]. The rate of water absorption in the composite was found to be less than that in a block of neat epoxy of the same size; water uptake was found to be equivalent to the volume fraction of epoxy in the composite. This change in the absorption mechanism would suggest a great improvement in the hydrothermal stability of plasma-treated composites.

The results of a series of T-peel tests on three different types of polyaramide and two different polyethylene yarns, each treated for 1 min in four different plasma gases [33], are summarized in Table 3. Kevlar® 29 has a lower modulus and a greater elongation than Kevlar® 49; when type 29 is plasma-treated and bonded to the matrix, it has a much greater peel strength than the best results for type 49, namely 5.25 N/mm vs. 2.70 N/mm (30 lb/in vs. 15.4 lb/in). This is another indication that a lower-modulus system is needed in composites that possess good bonds between the matrix and the fibres. The first material, 49/7100, showed no ageing or loss in performance even after 300 days of storage in air. The T-peel performance of polyethylene yarns illustrated in Table 3 shows large variations in peel strength depending on which plasma gas is used, illustrating, once again, that the plasma process must be optimized for each material used. These data pertain to a medical-grade material, while the standard-grade material had so much surface contamination that plasma treatment made no difference to the performance of the composite.

The data shown above illustrate the great improvements that can be achieved in most composites after plasma treatment of the reinforcing material, without affecting the other properties of the composite.

Table 3.

Per cent improvement of the T-peel force for two types of high-modulus fibres (after ref. 33)

Fibre type	Denier	Plasma			
		O_2	Air	Ar	NH_3
Aramid (DuPont Kevlar® 49)	7100	318	218	204	169
Aramid (DuPont Kevlar® 49)	380	129	154	169	83
Aramid (DuPont Kevlar® 29)	1500	2383	—	—	2486
Polyethylene yarn (Spectra® 900)	1200	360	380	220	150
Polyethylene yarn (Spectra® 1000)	660	153	100	87	45

3.4. Metal-polymer bonding

There is strong evidence in favour of the chemical reaction mechanism (see Section 1.1), the one which should, in principle, lead to the strongest bonds, to explain strong metal-polymer adhesion. Burkstrand [122] was among the first to

show that evaporated metals can react with oxygen-containing polymer surfaces, which can lead to metal–oxygen–carbon (M–O–C) type linkages.

Plasmas can be used with success to provide the necessary surface functionalities that can form strong bonds. For example, *in situ* XPS studies have revealed the presence of Ag–O–C and Ag–N–C linkages [123] after exposing PE to oxygen and nitrogen plasmas, respectively, as illustrated by the XPS spectra in Fig. 11. For this particular system, the metal–PE adhesion was found to improve according to the following sequence of plasma gases used: $\text{Ar} < \text{O}_2 < \text{N}_2$. Similar effects were observed in another *in situ* study of Mg on PP [124]. The highest sticking probability for evaporated Mg atoms was found on a PP surface following exposure to an N_2 plasma or, for comparison, following argon ion bombardment at a dose of 5×10^{15} ions/cm².

In practical situations, the plasma conditions needed for treatment of a given polymer surface must be optimized for every metal/polymer combination. Departure from optimum treatment conditions can lead to various effects, often involving the presence of a weak boundary layer. For example, if the surface is insufficiently treated, the ubiquitous contamination layer (lubricant, mould release, anti-blocking agents) is incompletely removed or additives from the polymer's bulk can diffuse to the interface and contribute to the formation of a weak boundary layer. Therefore, even if the surface is found to be wettable and to contain the desired oxygen or nitrogen moieties, adhesion does not improve

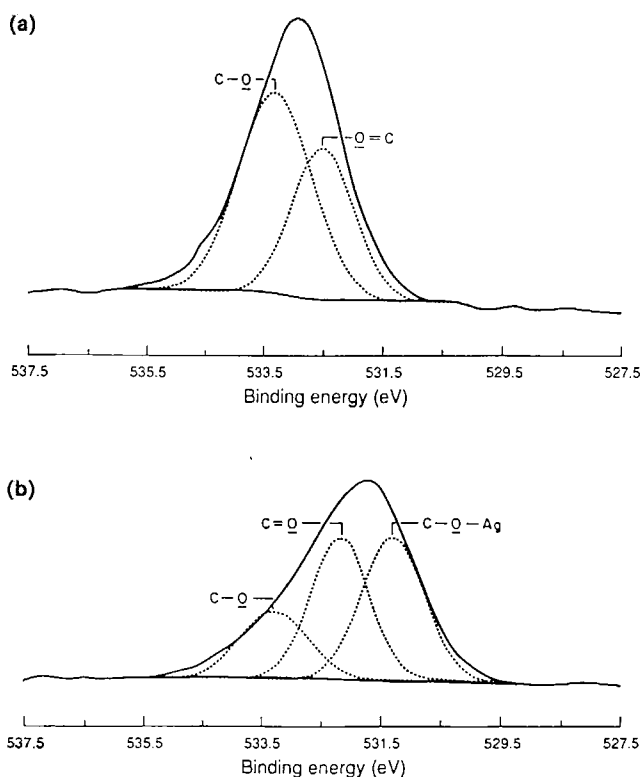


Figure 11. Line-shape analysis of the O(1s) spectrum of oxygen-plasma-treated PE: (a) before Ag deposition; (b) after deposition of nominally 5×10^{14} atoms/cm² of silver. After ref. 123.

because one is attempting to bond to a plasma-treated layer of contamination. Also, the surface can be grossly over-treated, which leads to the formation of excessive LMWOM [80, 83, 84], as already discussed in Section 2.2.2.2.

An example of the mechanical failure of a weak boundary layer is the case of polytetrafluoroethylene (PTFE); this material can readily be plasma-treated for cleaning and surface modification, to give good wetting and to provide oxygen-containing or nitrogen-containing groups. The adhesion, however, is still found to be poor, because the sub-surface structure of PTFE remains weak and not easily stabilized by crosslinking.

It follows that an 'optimum' plasma treatment should yield two simultaneous effects: surface crosslinking and the formation of the requisite chemical functionalities. Such a composite interphase is illustrated schematically in Fig. 12. The crosslinking process not only leads to mechanical strengthening of the interface, but the crosslinked interface sublayer simultaneously provides a barrier against diffusion of LMW species from the polymer bulk. In practice, the control of crosslinking can be achieved by using plasma gases which strongly emit VUV radiation, the efficiency of which roughly follows the sequence $\text{He} > \text{Ne} > \text{H}_2 > \text{Ar} \approx \text{O}_2 \approx \text{N}_2$ [125]. Therefore, plasma surface treatments using mixtures such as He/O_2 or He/N_2 should, in principle, lead to the most pronounced adhesion improvements.

It follows that the thickness and properties of the composite interphase in Fig. 12 depend on the substrate material, on the penetration depth of the crosslinking agents (photons, ions), and on the plasma characteristics. Therefore, as already stressed on several occasions above, it is important to optimize the quality of this interphase for every materials combination.

In some cases, improved adhesion cannot be achieved merely by plasma

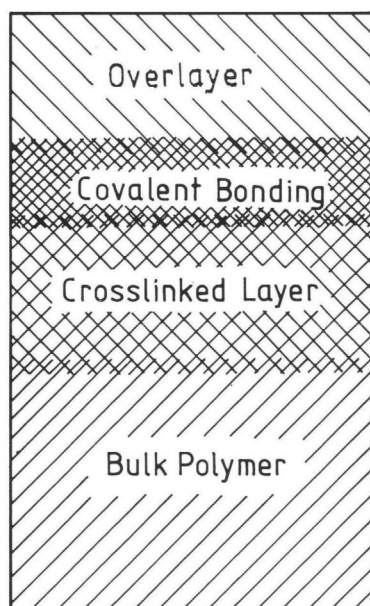


Figure 12. A schematic diagram of the interphase structure between the adhering layer and a polymer base.

surface modification, and another intermediate layer is needed; such a layer increases the thickness of the interphase and may also play additional roles. Metal-containing plasma polymers have been suggested as a means of improving the adhesion of structures such as Au-PTFE [126], where chemical bonding is practically excluded. In this case, metal clusters are incorporated into the intermediate layer by simultaneously sputtering or evaporating metal during the plasma polymerization of a fluorocarbon or hydrocarbon monomer [127]. The metal concentration can be gradually increased from the polymer side towards the metal side, so that adhesion improvement is achieved by complete mechanical interlocking. The composite metal-polymer structure can also be used to tailor the optical properties for use in decorative applications [127].

Low-pressure plasma treatment has been suggested as a means of improving the adhesion of copper to polyimide or to fluorocarbons, as used in multilayer printed circuit boards. In a simple case, polyimide must be pretreated by oxygen plasma to increase the adhesion of a Cr intermediate layer, onto which Cu is then deposited by electroless plating [128]. When PTFE is used, on account of its good thermal and dielectric properties, the surface can be activated by a hydrogen plasma to achieve wettability, following which copper formate is applied by spin coating [129]. The copper formate is then converted to metallic copper by chemical reduction, again in a hydrogen plasma.

Metallic intermediate layers of Pd, Pt, Au, or Cu, obtained by the plasma decomposition of organometallic compounds, have also been investigated for improved adhesion of electroplated Cu to PTFE [130].

Intermediate layers appear to be necessary for good adhesion in corrosive and other chemically active environments. Their role is to suppress the diffusion of destructive agents towards the interface. In this capacity, plasma polymerized hydrocarbon (CH_4) films have been found to improve the bonding of Pt electrical contacts to Parylene® or other polymers that are used as implantable, biocompatible sensors [131].

4. PLASMA EQUIPMENT FOR INDUSTRIAL PROCESSING

Plasma technology has been used in the laboratory for at least 50 years but it has not been a practical industrial or commercial technology until the last 15 years. As already mentioned above (Section 1.2.1), commercial equipment development was originally driven by the requirements of the semiconductor market, but more recently equipment designed specifically for the industrial market has also become available. The 'industrial market' is defined here as any application that does not involve semiconductor wafers.

Plasma equipment usually consists of six modules or functions: vacuum system, power supply, matching network, power monitor, reactor chamber, and controller.

Low-pressure plasma systems for surface modification generally operate in the pressure range from 10 to 500 Pa (about 0.1–3.5 Torr), with a continuous gas flow into the reactor. Therefore, the vacuum system must be able to maintain this pressure/flow regime; this moderate vacuum level does not require sophisticated pumps, so that two-stage mechanical pumps are generally satisfactory. The pump package is usually sized to allow pumpdown to the operating pressure in less

than 1 min and to maintain an inlet gas flow of 50 sccm for the smallest systems to several 1000 sccm for systems of several cubic metres in volume. Pump maintenance, and the perfluorinated pump fluid that is required if an oxygen plasma is to be used, tends to be the largest part of the total plasma-system operating and maintenance costs.

A major advantage of plasma surface treatment as compared with most other treatment processes is the lack of harmful byproducts from the treatment process. There are no toxic or hazardous liquids or gases that must be disposed of. Usually, the main process byproducts are CO, CO₂, and water vapour, none of which is present in toxic quantities. We are unaware of any users of plasma for polymer surface treatment who need scrubbers on their pump exhausts; in other words, plasma surface treatment is very benign towards the environment.

The plasma excitation power of industrial systems generally ranges from 50 to 5000 W, again depending on the size of the reactor. Plasma reactors have been built utilizing a wide range of excitation frequencies, from DC to microwave; DC plasmas are not advantageous, primarily because of the need for a current-limiting resistor to stabilize the plasma and prevent arcing, and because of the very large bias effects that are present. Most plasma reactors, therefore, use AC electrical power supplies, operating at audio-, radio-, or microwave frequency [21, 22]. More specifically, international regulatory agencies have allocated certain 'ISM' (industrial, scientific, medical) frequencies for use in applications other than telecommunications, and it is these frequencies which equipment builders favour for obvious technical and economic reasons. Commercial plasma systems, therefore, usually operate in the low-frequency (LF, 50–450 kHz), radiofrequency (RF, 13.56 or 27.12 MHz), or microwave (MW, 915 MHz or 2.45 GHz) ISM frequencies. There are numerous vendors who offer highly efficient and cost-effective power supplies, matching networks, and other accessory hardware in these frequency ranges.

LF plasmas (50–450 kHz) are sometimes used because the generators are somewhat less expensive than those operating at other frequencies, and because they do not require precise impedance matching. However, our studies have shown that the reaction rates tend to be significantly slower than those at RF or MW frequencies, and that there is more of a tendency to arc at LF.

RF plasmas (13.56 MHz) are easily generated with equipment that is stable and reliable, and which has been commercially available from several vendors for many years. It is necessary to use a matching network to match the impedance of the plasma to that at the generator output (usually 50 Ω , resistive), a task that can be accomplished either manually or with automatic, servo-driven devices. At 13.56 MHz or higher, the plasma is very stable and reactive because the quench time of the plasma species is longer than the half-cycle period of the applied field.

MW plasma (2.45 GHz) is often more reactive than RF, as explained in Section 1.2.2, and the MW generator may be less expensive. However, if the cost of all of the peripheral equipment, such as wave guides, power meters, dummy loads, stub tuners, and applicators is included, the total system cost tends to be similar to that of an RF system. Nevertheless, in recent years there has been a gradual shift from RF to MW, a trend that we believe will continue in the foreseeable future.

A recurring problem in characterizing plasma processes, or in transferring a plasma process from one type or size of reactor to another, is the specification of the 'power density' in the plasma. This can be defined in at least three ways, namely (1) power per unit area of electrode; (2) power per unit volume of primary plasma; or (3) power per unit volume of the entire reactor. As each of these is deficient in some way, it is usually difficult to predict the best process parameters for transferring a process from one reactor to another. Instead, one needs to start with a reasonable set of parameters and then optimize the process experimentally in the new reactor.

There are several types of plasma reactor chambers: dielectric (e.g. fused quartz) or metal, and batch or continuous. Quartz chambers are important in the semiconductor industry because of the requirements for extreme cleanliness and particle-free operation, but they may also have advantages in some industrial applications. In the present context, plasma treatment for improved adhesion, extreme cleanliness is rarely required, and the danger of breakage favours the use of metal. Aluminium is the metal of choice for constructing plasma reactors, because it has excellent thermal and electrical conductivity, and chemical resistance. Aluminium is not readily attacked by any plasma gas except the heavy halogens (Cl_2 , Br_2 , or I_2). Aluminium has been fabricated into cylindrical vessels (known as 'barrel' reactors), and into rectangular reactor chambers, with shelf or cage electrodes. It is also possible to fabricate specially shaped electrodes for particular applications. The only size limitation on metal reactors is the strength of large vacuum vessels; the largest currently available commercial reactors have dimensions in excess of 2 m [132, 133]. These are used to process plastic automobile parts (e.g. bumpers or dash assemblies) in plasma generated either in an electrodeless MW plasma from a cluster of MW sources or in large, specially shaped RF electrodes.

Most commercially available plasma systems are designed for batch operation, which involves loading a batch of parts, evacuation, plasma processing, purging to atmospheric pressure, and removal of the parts. While this has been satisfactory for many applications, the use of polymers in ever more sophisticated applications, such as composite structures, increasingly calls for the continuous processing of filaments, yarn, film, and fabric. Therefore, plasma systems have been built for continuous processing, either using 'air-to-air' or 'cassette-to-cassette' ('batch-continuous') configurations.

In air-to-air systems, there are sequentially pumped chambers on either side of the reactor chamber, which are connected by some form of material feed-through system. This feed-through system makes it possible to continuously bring material from atmospheric pressure to the low reactor pressure, and then back to ambient atmosphere; the major engineering problem in air-to-air systems is the design of the feed-through.

Cassette-to-cassette systems have been built in which the source and takeup spools are both under vacuum. This configuration minimizes the abrasion of fragile materials, such as graphite yarn, when they are drawn through a feed-through, and it facilitates materials treatment in plasma gases with very little oxygen contamination. One commercially available RF (13.56 MHz) plasma machine (Fig. 13) has a double-sided electrode system that is 0.67 m (26 in.) square, so that the film or yarn traverses 1.34 m of plasma on each pass through

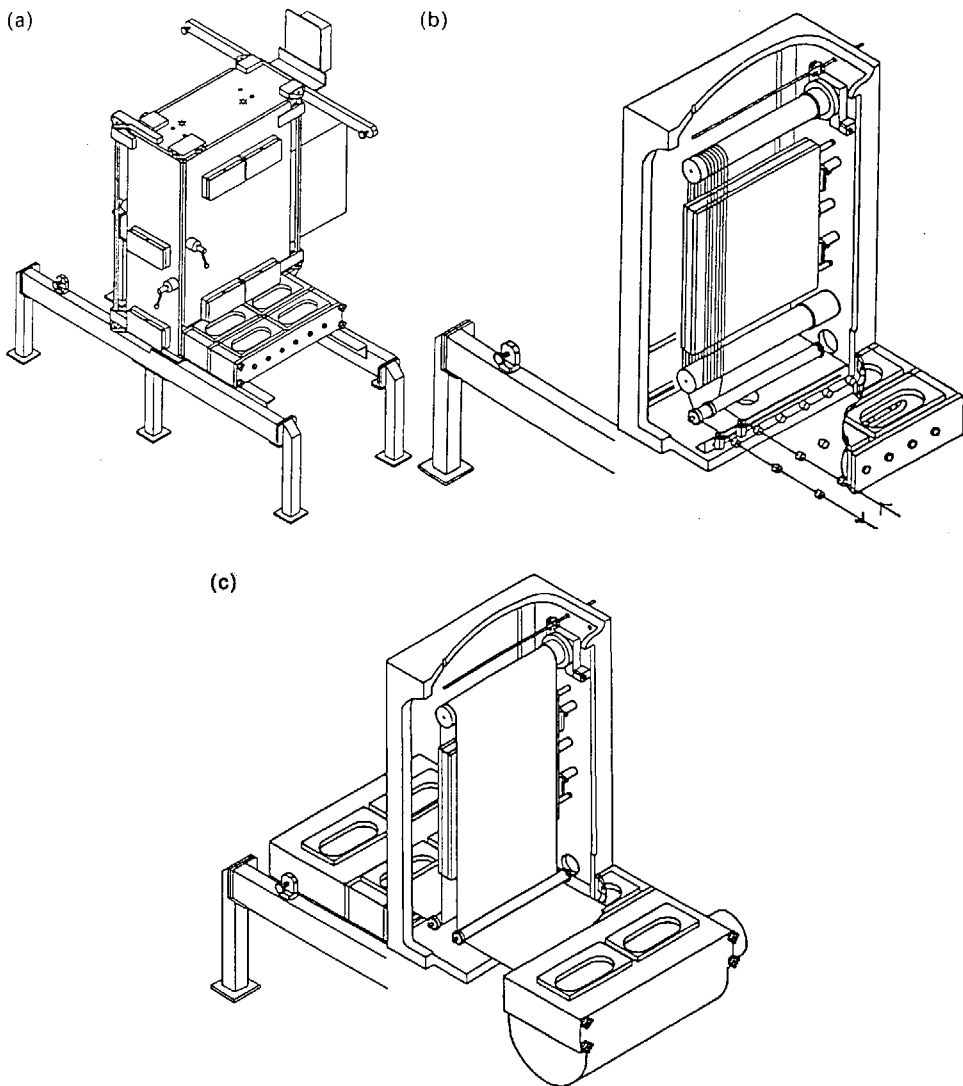


Figure 13. Drawings of industrial-scale continuous plasma treaters: (a) overview; (b) yarn-treatment configuration; (c) continuous cassette-to-cassette treatment configuration. (Courtesy of GaSonics/International Plasma Corp.)

the plasma zone [134]. The design of the upper and lower rollers makes it possible to run yarn through the plasma several times, thus assuring a sufficiently long residence time in the plasma, even at high line speed. This machine is available in either an air-to-air (Figs 13a and 13b) or a cassette-to-cassette configuration (Fig. 13c).

Two large 'batch-continuous' machines have been built for plasma deposition onto flexible web substrates, one for LF (50 kHz) operation [135], the other operating at MW (2.45 GHz) frequency [136]. The latter, based on the LMP[®] (Large volume Microwave Plasma) principle [137, 138], uses pairs of counter-activated, linear slow-wave microwave applicators which mutually compensate

fringing-field inhomogeneities. As mentioned above, MW plasma has the economic advantage of higher product throughput rates than lower frequency counterparts. Of course, any plasma system designed for plasma deposition can also be used for surface treatment.

In all types of continuous systems, the maximum processing speed ('line speed') is determined by the residence time in the plasma required to assure the appropriate treatment. Our data show that for reasonable power densities (0.1 W/cm^3) in existing equipment, clean polymers (e.g. some polyethylenes, polyimide, or polyamide) can be treated in less than 10 s residence time, which corresponds to a line speed of 150 m/min (500 ft/min) or more. Graphite yarn, however, requires a longer residence time because it is usually desired to etch the fibre surface rather than to merely change its chemistry. Processing speeds for graphite are, therefore, usually less than 30 m/min (100 ft/min). However, multiple tows of yarn can be processed in parallel so that the net processing speed can be much greater.

Discrete-continuous machines have been designed and built, systems where discrete parts, or racks of parts, enter the reactor on one side and exit on the other. A typical application is the treatment of plastic automobile bumpers.

The last of the six equipment modules mentioned earlier is the controller, and, as the name implies, its role is to control all of the operations of the system. In all modern systems, the controller is based on a microprocessor that can be programmed to remember a large number of 'recipes', any one of which can be called up, depending on what is to be treated. The controller determines all of the machine parameters (operating pressure, type of plasma gas, gas flow rate, power level, processing time) and the sequence of processing steps, if a multi-step process is being used. The processing information is displayed on a screen, so that the operator is constantly informed. The more sophisticated controllers are capable of communication with a host computer for data logging and process verification, and can be linked with plasma diagnostic techniques such as optical emission spectroscopy.

The best plasma equipment will do very little of benefit for the surface modification of materials without the proper plasma process. Unfortunately, this is the area where there is the least scientific knowledge, and where the most 'art' is involved. As we have shown in Section 2, the interactions between a plasma and a surface, especially a polymer surface, are extremely complex. It must always be remembered that a 'real' plasma contains not only the feed gas, but also all of the volatile products of the interaction between the starting plasma and the surface; the composition and concentration of these products are very rarely known, especially in the boundary layer (the few millimetres closest to the polymer surface) where most of the reactions occur that affect the surface. It is extremely difficult to perform analyses in this region because any sampling technique will affect the composition and concentration of the unstable transient species in the boundary layer. Analysis of the plasma outside the boundary layer is of relatively little value because of the myriad reactions that the boundary-layer species undergo during their diffusion into the bulk of the plasma.

The development of the proper process is nearly always the result of a series of optimization tests in which the plasma parameters are varied, and these changes are then correlated with the results obtained by testing the properties of the

treated parts. The literature, for example this paper, and the experience of others working in this field, especially the manufacturers of plasma equipment, will give a good starting point for process development; however, final refinement and implementation of any given plasma process must be accompanied by verification, testing, and optimization.

5. CONCLUSIONS

We have shown in this review that 'cold', low-pressure plasma treatment can give rise to profound changes in the surface and interfacial properties of materials, particularly of polymers. Corona treatment, a similar process in several respects, has been in industrial use for several decades. However, unlike corona, in which the reactive gas is usually air and which is generally restricted to simple surface geometries such as flexible webs, plasma treatment is extremely versatile in its capabilities.

Following brief reviews of adhesion theory and of the physics and chemistry of 'cold' plasmas, we examined the all-important mechanisms by which a plasma interacts with a polymer surface. These include physical bombardment by energetic particles and by ultraviolet photons, particularly vacuum ultraviolet (VUV, $\lambda \leq 175$ nm), which are energetic enough to break most organic bonds, and cause chemical reactions at or near the surface. The resulting four main effects—cleaning, ablation or etching, crosslinking, and surface chemical modification—occur together in a complex synergy, which depends on many parameters controlled by the operator.

Plasmas can readily be applied to objects of all possible geometries, ranging from webs or films to large solid objects with complex shapes, and to small discrete parts in large quantities (even including fine particles such as powders, fibres, or flakes). Industrial plasma systems are available for treating webs, either in a continuous air-vacuum-air or in a batch-continuous (cassette-to-cassette) mode of operation, while other reactor designs are readily adapted for treating discrete parts with the characteristics listed above.

The most important advantage of a low-pressure plasma, however, is the fact that it offers virtually limitless possibilities for tailoring the surface structure and chemistry of a given polymer. Of course, like corona, this plasma treatment can comprise a controlled surface oxidation with air or oxygen designed to create polar (e.g. carboxyl, hydroxyl, etc) moieties. Polar groups greatly increase the surface energy of the polymer, thereby enhancing its wettability by liquids and adhesives; this in turn, improves bond strength, printability, and dye uptake, to name but a few attributes. Nitrogen-containing functionalities can be created by exposing the surface to a plasma of nitrogen, or nitrogen-containing gases (e.g. ammonia), with additional advantages. In contrast, a surface can also be rendered more hydrophobic (*less* wettable) by plasma fluorination or silylation with a variety of reagent gases or vapours, all offering particular characteristics and advantages. It is noteworthy that only very small quantities of reagents are consumed, and that these can almost always be chosen from among inexpensive, non-toxic compounds. In some processes, hazardous byproducts may be created (e.g. HCN), but only in sufficiently small quantities that can be readily collected from the pump exhaust and then neutralized. These are routine procedures, as

has been proved by the semiconductor industry, for many years the leading user of plasma processing.

The very richness of choices offered by plasma processing can also be construed as an important drawback: each new application requires that the process conditions be clearly identified and optimized. Because there are numerous parameters (power, pressure, gas composition and flow rate, treatment duration), optimization can be tedious. Furthermore, owing to the inherent complexities of the plasma state and, even more, of its interactions with solid surfaces, there are still many unanswered questions and much ongoing research. We have pointed out some such unknowns in the preceding text, but have also emphasized that they pose no fundamental obstacles to process optimization by semi-empirical procedures. Once the key process variables have been identified and optimized, modern control instrumentation can ensure that the process outcome is reliably reproduced. In conclusion, we are convinced that industrial plasma processing will continue its vigorous expansion because it has unique capabilities, because it is economically viable, and because it is 'friendly' towards the environment.

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