



Industrial processing of polymers by low-pressure plasmas: the role of VUV radiation

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Abstract

The use of low-pressure plasmas for materials processing, pioneered by the semiconductor industry since the 1960s, is now also a commercial reality in technologies which make extensive use of plastics (automotive, aerospace, packaging, pharmaceutical, textile, and other industries). A large fraction of these processes involve the surface modification of polymers for improved adhesion, and many of these use air or oxygen plasma to incorporate polar functional groups into the polymer surfaces. Interaction mechanisms between a plasma and a polymer surface are very complex, for they include synergistic effects of physical bombardment by energetic particles and by ultraviolet photons, and resulting chemical reactions at and below the surface.

In this article we present an overview of plasma surface modification of polymers, in which we identify the main variables for process control, illustrated by examples. We then show, on hand of a series of specially designed experiments, how the effects of ultraviolet photons generated in the plasma can be assessed separately from those of other energetic and reactive species, especially in the case of oxidizing plasmas. Finally, we comment on the merits and drawbacks of industrial plasma processes in comparison with other competing technologies, especially those based on ultraviolet radiation. © 1999 Elsevier Science B.V. All rights reserved.

PACS: 61.80.B; 61.82.P; 52.25.Q

Keywords: Ultraviolet; Plasma; Polymers; Surface treatment

1. Introduction and background

1.1. Adhesion of polymeric systems

Polymers are increasingly used in both high-tech and consumer-product applications on ac-

count of their advantages over more traditional engineering materials such as metals. But these advantages (for example, high strength-to-weight ratio, resistance to corrosion, relatively low cost) are also accompanied by certain drawbacks, which manufacturing operations must overcome. One such challenge is the characteristic low surface energy of polymers and their resulting intrinsically poor adhesion; the term “adhesion” may be loosely defined as the mechanical resistance to

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separation of a system of bonded materials [1]. Since adhesion is largely 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, and these have become the object of a vast literature [2–4]. They include mechanical treatments, wet-chemical treatments, exposure to flames, photons, ion beams and other types of ionizing radiation, corona discharges, and glow discharge plasmas (both high and low-pressure). Also over the years, numerous theoretical models of adhesion have been proposed to account for a wide range of experimental observations. While none of these models is entirely satisfactory so far, there is a growing body of evidence that chemical reactions at the interface can play a key role in many cases [2–4].

A concept which has gained much support among adhesion scientists is the existence of an “interphase” (see Fig. 1), 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 [5] argues very convincingly that interphases exist in many

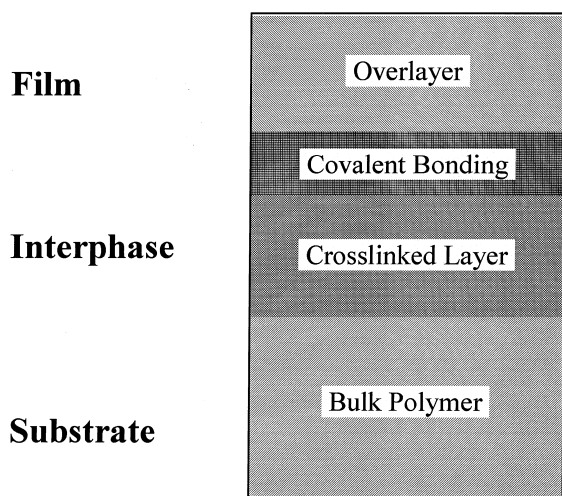


Fig. 1. Schematic diagram of the interphase structure between an adhering overlayer and a plasma-treated polymer base.

polymeric macro-systems such as adhesive joints, coating/substrate systems, fibre-or particulate-reinforced composites, etc., 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.

Among the techniques for modifying polymer surfaces mentioned above, those based on both atmospheric-pressure and low-pressure plasmas present certain important advantages over the others [2,3]. In the remainder of this article we focus on plasma processes, particularly those which lead to surface oxidation of polymers; we begin briefly with the longest-established, corona treatment, but then emphasize low-pressure plasmas which have become wide-spread in recent years. The main emphasis will be on ultraviolet-induced photochemical effects, which accompany all such processes.

1.2. Surface modification of polymers by plasma

1.2.1. Fundamental principles

A plasma can be succinctly defined as a partially or fully ionized, macroscopically neutral gas, in which the charged particles possess collective interactions [6]. Apart from the special case of corona discharges, discussed below, we will mainly be concerned with “glow discharge” plasmas at reduced pressures (typically $0.1 \lesssim p \lesssim 10^3$ Pa). Among the important parameters which characterize such discharges are the charged particle density, n (electrons or positive ions), and the electron temperature, T_e (or mean kinetic energy, \bar{u}). A key feature is the fact that T_e is high, typically above 10^4 K (~ 1 eV), while the temperature of heavy particles (ions, molecules, molecular fragments) remains near ambient (300 K, or 0.025 eV). This is an obvious prerequisite for treating polymers, which would rapidly degrade if exposed to a very hot gas. On the other hand, the hot electrons, which acquire their kinetic energy directly from the applied electromagnetic field, collide with gas molecules and thereby transfer energy through ionization, bond breakage (molecular fragmentation), and other forms of excitation. Excited molecular and atomic species in the plasma, in turn, can emit photons over a very broad

portion of the electromagnetic spectrum, ranging from X-rays to the infrared (IR). As we shall see, photons in the vacuum ultraviolet (VUV) or ultraviolet (UV) range, which have energies comparable to or exceeding those of covalent bonds (a few eV, typically), can readily initiate photochemical reactions in polymers. The reader is referred to recent reviews [2,3] for other important aspects of plasmas in the present context.

Regarding the interaction of plasma with a polymer surface, four major effects may be distinguished:

1. surface cleaning, that is, removal of contamination from the surface;
2. ablation, or etching, of surface material;
3. cross-linking or branching of macromolecules, which can cohesively strengthen the near-surface layer; and
4. modification of surface-chemical structure; this can occur during plasma treatment, but also upon re-exposure of the polymer to air, at which time residual free radicals can react with atmospheric oxygen and water vapor.

In the case of oxygen-containing plasmas, the case we wish to emphasize here, these effects can all coexist; however, depending on the choice of processing parameters, one or the other can be made to dominate.

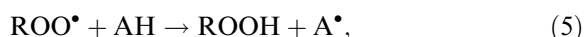
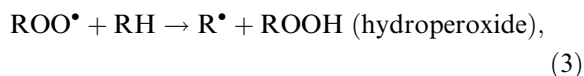
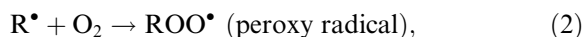
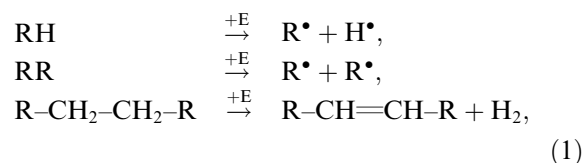
1.2.2. Oxygen-containing plasmas

Polymeric surfaces are quite reactive towards oxygen, which comprises roughly 20% of the ambient atmosphere. However, with additional energetic activation of the polymer and/or O₂ molecules, the reactivity can be very greatly enhanced. Not surprisingly, therefore, corona discharge treatments in atmospheric air, used industrially since the 1950s, still represent a major process for surface treating polymer films, textiles, and other flexible substrates of simple geometry. This is accomplished in so-called dielectric barrier discharge systems comprising two electrodes, of which at least one is covered with a layer of dielectric material [7]. The corona discharge, operated at high voltage in the 10–30 kHz frequency range, is not homogeneous, for it consists of a multitude of filamentary microdischarges some 100 μm in diameter and 100 ns or less in duration

[7]. This tends also to result in surface-chemical inhomogeneity; furthermore, it is well known that the effectiveness of corona treatment generally fades quite rapidly with time.

To counter these drawbacks, and to render plasma surface modification amenable to polymeric products with more complex shapes than flexible webs or filaments, low-pressure glow-discharge treatments have seen a remarkable growth, beginning roughly in the mid-1980s. This type of treatment is homogeneous on a microscopic scale, and tends to be effective for a longer period of time, for reasons discussed below. However, it comes with the economic penalty of higher capital outlay for a vacuum chamber and pumps, and other ancillary equipment. Nevertheless, this has not prevented low-pressure plasma from making inroads even where economic margins are slim, since plasma treatments have “unique” capabilities, and are environmentally benign (contrary to many processes – e.g. wet-chemical ones – they can replace).

We have mentioned above that plasma treatments (both high and low-pressure) of polymers give rise to modification of the surface-chemical structure, and that chemistry at the interface (or, rather, the interphase) is often believed to be a dominating mechanism of adhesion. In the case of oxidizing plasmas, the following set of free-radical reaction pathways and molecular reaction products are known to occur:

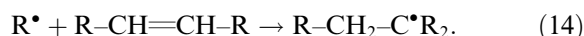
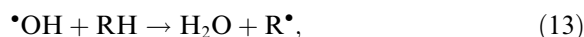


where “E” in Eq. (1) designates a source of energy capable of bond breakage (e.g. VUV photons,

energetic ions or electrons), and reactions Eqs. (2)–(5) are chain-propagating radical reactions. The peroxy intermediates can lead to three possible reaction pathways, namely crosslinking, and functionalization with or without scission of the polymer chain. Examples of the former, which terminate the chain reaction, are



while examples of the latter and further chain propagating reactions are



Clearly, the reaction scheme (1)–(14) is not complete; for example VUV photons with $\lambda < 100$ nm can give rise to ionization reactions. This scheme can evidently lead to a wide variety of oxidation products, including C–OH (alcohol), C=O (carbonyl, – ketone or aldehyde), C–O–C (ether), COOH (carboxylic acid), COOC (ester),



(epoxide), etc. Fig. 2 represents the curve-fitted C(1s) X-ray photoelectron spectrum (XPS or ESCA) of polyethylene (PE) treated in low-pressure air microwave (MW) plasma; indeed, the spectrum of corona-treated PE is very similar [8]. While the XPS spectrum of virgin PE displays only the C1 peak at 285.0 eV, Fig. 2 clearly reveals three new peaks resulting from the plasma-induced ox-

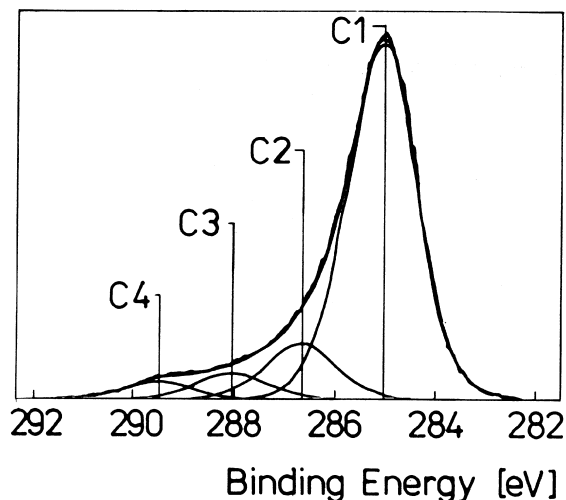


Fig. 2. High-resolution C(1s) X-ray photoelectron spectrum (XPS) of PE treated in a low-pressure air microwave plasma for 30 s.

idation. These are C2 at 286.5 eV (C–O groups, due to hydroxyl, ether, or epoxide), C3 at 288.0 eV (due to C=O carbonyl, or O–C–O double ether), and C4 at 289.4 eV (due to ester or carboxylic acid groups). Clearly, XPS alone cannot distinguish the various functionalities associated with any given sub-peak, a task which can be resolved in combination with chemical derivatization reactions [9].

The total amount of oxygen incorporated into the PE surface can readily exceed 20 at. %, even after only a few seconds of exposure to plasma [8]. Clearly, these drastic changes in surface composition, particularly the presence of highly polar groups such as carbonyl, drastically alter the surface free energy, γ , of a polymer, particularly its non-dispersive component [2,10]; this rise in surface energy is readily demonstrated by increased wettability, for example by water. Instead of forming a bead with a large contact angle, a water drop will flatten on the surface, resulting in a smaller contact angle; that is, the surface has become highly hydrophilic. This also translates into greatly increased adhesion by inks, paint, dyes, or adhesive compounds, which can chemically react with the new surface functionalities, or with long-lived radicals residing near the polymer surface.

1.3. Industrial processes and equipment

In a recent review chapter entitled “Plasma sources for polymer surface treatment” [3], both high- and low-pressure plasma systems for industrial processing of polymers have been described in considerable detail. This includes general design considerations for both radiofrequency (RF) and microwave (MW) plasma systems, as well as plasma sources for specific tasks and applications. This latter topic covers the treatment of flexible substrates (e.g. films, fabrics, etc.), large objects such as moulded automotive parts, for example polypropylene (PP) or ethylene-propylene-diene-terpolymer (PP/EPDM) bumpers, or many small parts and particulates. Many of these processes are based on oxidizing plasmas of the types discussed in Section 1.2.2. In view of the limited space here, and since the interested reader can readily find desired information in the richly-illustrated reference [3], we shall restrict ourselves to one typical example how oxidizing plasma can modify polymer adhesion in a very dramatic manner: Ultrahigh molecular weight PE (UHMW PE) particles are included in cast polyurethane (PU) matrix components for a number of reasons, namely improved abrasion resistance, lower friction coefficient, enhanced tear resistance, and lower weight. Fig. 3 shows scanning electron micrographs of tensile test sample surfaces of PU matrix containing UHMW PE particles, after failure in tensile tests. Fig. 3(a) illustrates the poor bonding of the untreated par-

ticles to the PU – the particles were pulled away from the matrix during the tensile test, as evidenced by the voids left behind at the interface. However, a very different picture emerges when the particle surfaces have been modified by exposure to an oxygen plasma; this is accomplished industrially by gravity-feeding them through a long, vertical, low-pressure RF (13.56 MHz) plasma reactor. Fig. 3(b) shows that the particles are torn apart during the tensile test, since the bond strength between the modified UHMW PE and the PU surfaces exceeds the internal cohesive strength of the particles. Similar performance enhancements are observed for paint adhesion on plasma-treated plastic bumpers, and many other situations discussed in Refs. [2–4] and elsewhere.

2. VUV/UV photochemistry of polymers in plasma

While Section 1 of this article has dealt with the overall effects of (O₂-based) plasma treatments on polymers, the objective of this second section is to underline the specific contribution due to short-wavelength radiation originating from the plasma. We begin, in Section 2.1, with a brief historical review, followed by a precis on ultraviolet emission characteristics and how these photons interact with polymers (Section 2.2), and by a brief overview of our own research results on polymer photochemistry in oxidizing plasmas (Section 2.3).

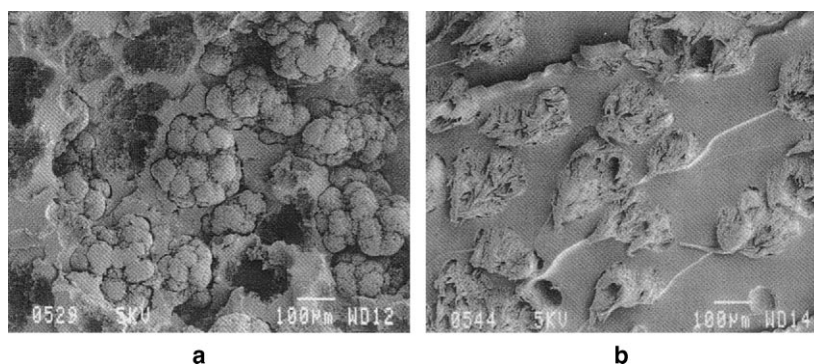


Fig. 3. Scanning electron micrographs of failed tensile test sample surfaces of a polyurethane matrix composite containing UHMW PE particles: (a) untreated particles; (b) oxygen plasma-treated particles.

2.1. Evidence for a “VUV” contribution

Hudis [11,12] was the first to investigate the relative importance of VUV/UV radiation during low-pressure plasma treatment of polymers: In a series of elegant experiments, he used an inductively coupled plasma reactor with two exchangeable sample chambers, one permitting direct exposure of a high-density polyethylene (HDPE) sample to a H₂ plasma, the other in which the HDPE sample was also under vacuum but exposed only to the H₂ plasma radiation through a LiF window. Following exposures of varying durations he measured crosslinking by gelation, and found that the variation of the depth of crosslinking with exposure time was very similar in the two chambers. In the case of the irradiation experiment, he attributed the gelation to light covering the range from 120 to 190 nm. A few years later, Yasuda used electron spin resonance (ESR) spectroscopy [13], while Clark and Dilks [14] used ESCA to also demonstrate UV-induced effects well below the immediate surface region of plasma-treated polymers. The latter authors exposed ethylene-tetrafluoroethylene copolymer to inductively coupled RF plasmas in argon, following which they measured the angularly resolved ESCA spectra. They interpreted their results in terms of a two-component, direct and radiative energy-transfer model, showing that the outermost monolayer crosslinks rapidly via direct energy transfer from Ar ions and metastables. On the other hand, the observed chemical modification of the subsurface and bulk regions was attributed entirely to UV radiation ($\lambda \lesssim 380$ nm).

During the ensuing 20 years many other researchers, too numerous to cite here, have studied the effects of short-wavelength radiation on polymers. Materials examined include PE [15–19], polypropylene, PP [17–20], polystyrene, PS [19,21], fluoropolymers [22,23], polyimide [22,23], and others; some authors [22, 23] used window materials with different short wavelength cutoffs, λ_c , ranging from 104 nm for LiF to 160 nm for SiO₂, and higher (KBr and Crown glass), to study irradiation-induced effects under otherwise constant exposure conditions. However, even to this day there is some controversy, since not all researchers

in the field of polymer modification by plasmas agree that VUV/UV plays a key role [24].

2.2. Plasma emission and polymer absorptions

Fig. 4 shows emissions from a few technologically important plasmas, namely those of H₂, N₂, O₂, He and Ar, in the VUV to visible wavelength range of interest to the present context, 100 nm $\lesssim \lambda \lesssim$ 400 nm. Hydrogen plasma, particularly, shows very intense VUV emission below 160 nm due to the Lyman and Werner bands, and the Lyman α atomic resonance line (Ly α) at 121.5 nm. Nitrogen and oxygen also possess certain intense emission lines in the VUV, for example the 130.5 nm resonance line of atomic oxygen, accompanied by weaker molecular bands. However, it is the rare gas (He and Ar) spectral emissions which display rather remarkable characteristics, in that many of the intense VUV features (e.g. the atomic lines mentioned above) do not originate from these gases, but rather from ubiquitous impurities such as water vapor, or small air leaks: By virtue of the extremely efficient (Penning) energy transfer from long-lived He* or Ar* metastables, even trace amounts of impurities can evidently lead to quite intense emissions. In an industrial plasma process involving a polymeric substrate, gas desorption

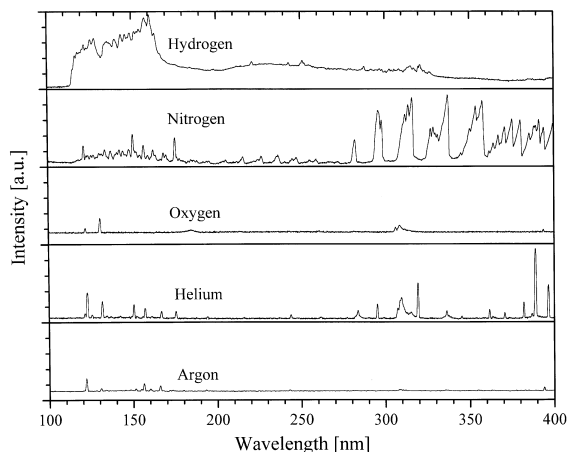


Fig. 4. Vacuum ultraviolet to visible emissions of several gases used in plasma processing ($P = 250$ W, $p = 2$ Torr, $\phi = 10$ sccm).

(H₂, H₂O, air, hydrocarbons, etc.) can all lead to VUV emissions of the types exemplified in Fig. 4.

PE possesses the simplest structure among commercial polymers, namely a CH₂ backbone, which also results in the simplest absorption spectrum [25] – the absorption coefficient, $\alpha(\lambda)$, is small for $\lambda > 160$ nm, but rises sharply for λ below this value, reaching $\alpha \simeq 10^5$ cm⁻¹ at 120 nm and a maximum of $\sim 3 \times 10^5$ cm⁻¹ near 80 nm. This absorption results in dissociative excitation (bond breakage) of C–C and C–H bond electrons, hence in the formation of radicals, as expressed in Eq. (1). All other polymers with only C–C and C–H single bonds, e.g. PP, display very similar absorption, while those with multiple bonds or aromatic rings possess additional strong absorption features in the range $170 \text{ nm} \leq \lambda \leq 190 \text{ nm}$. For the benzene ring, in PS for example, α is almost two orders of magnitude greater at 190 nm than near 240 nm, the wavelength region in which traditional organic photochemistry based on the forbidden $\pi \rightarrow \pi^*$ transition is carried out. Polymers which incorporate in their structure atoms with lone electron pairs (oxygen, nitrogen) also absorb quite strongly at $\lambda > 160$ nm [26].

Evidently, the knowledge of $\alpha(\lambda)$ allows one to estimate the penetration depth, $D(\lambda)$, of VUV and UV radiation below the polymer surface, where D is defined as the layer thickness below which the intensity at the particular λ has dropped to 10% of its initial value. For example, for normally incident Ly α radiation on PE, $D \simeq 60$ nm, while $D \simeq 20$ nm at $\lambda = 80$ nm. For $160 \text{ nm} \leq \lambda \leq 200 \text{ nm}$, polymers with O-containing functional groups can have $D > 100$ nm, while in the UV ($\lambda > 200$ nm) these and aromatic polymers have D values well in excess of 1 μm .

2.3. Photochemistry of polymers

The photochemistry of polymers in the near-UV and visible ranges has been extensively studied for most commodity polymers [27], since their environmental stability depends on it. A tendency towards UV instability can be remedied by the addition of stabilizing compounds or fillers such as carbon black. In Section 2.2 we noted, however, that α can be orders of magnitude greater in the

VUV range, so that chemical instability here is virtually assured. We have shown that photons with $\lambda \leq 160$ nm are absorbed by alkyl chains, giving rise to the formation of radicals, and ensuing reactions (so-called type 1 initiation). An example of this is the photochemical attack of polyolefins (PE and PP), see Eq. (1). A radical formed this way can, for example, recombine with another radical (Eqs. (6) or (9)), split off hydrogen from a neighboring carbon atom (Eq. (4)) and form a double bond, or it can react with species from the gas phase (O₂, O[•], etc., see Eq. (2)) to form a variety of functional groups, as discussed in Section 1.2.2. At $\lambda > 160$ nm, absorption of photons by functional groups gives rise to so-called type 2 initiation. This includes the well-known Norrish-type reactions of carbonyl groups (C=O); similarly, hydroxyl (C–OH), ether (C–O–C), or double bond structures can give rise to the formation of various kinds of radicals after photoexcitation.

In this laboratory, we have recently conducted extensive studies of VUV-induced photochemical effects on a variety of polymers [9,17,18,28,29]. For this purpose, we have used the emission from a microwave (MW, 2.45 GHz) plasma in ultrapure H₂ gas [30], or in mixtures of H₂ with He or Ar [18,30] or with O₂ [31], the resulting radiation being directed into the sample chamber through various windows, for example MgF₂ ($\lambda_c = 112$ nm), CaF₂ ($\lambda_c = 122$ nm), or SiO₂ ($\lambda_c = 160$ nm). As explained elsewhere [30,31], each of the above-named plasma VUV emissions has certain advantageous characteristics, such as a near-continuum (H₂ plasma, see Fig. 4), or near-monochromatic Ly α radiation (Ar/H₂ mixture). If H₂ plasma is used as the light source, and if molecular O₂ at low-pressure is deliberately introduced into the sample chamber, the O₂ molecules absorb VUV radiation in the range $130 \lesssim \lambda \lesssim 170$ nm. This results in photodissociation, by which one O¹D and one O³P oxygen atoms are produced, which are obviously far more reactive towards a polymer surface than ground-state molecular oxygen. More will be said about this further below.

The VUV irradiation of PE in an O₂ atmosphere results in O incorporation into the polymer surface (see Eq. (2), for example), and the surface concentration [O] can be determined by XPS. Fig. 5

shows how [O] evolves with exposure time, when the radiation source is a H₂ plasma (see Fig. 4), and when the window materials separating the H₂ plasma from the sample chamber are varied: When the window is MgF₂ ($\lambda_c = 112$ nm) [O] rises quite rapidly to its asymptote (~ 25 at.%), while the somewhat slower oxidation rate for CaF₂ ($\lambda_c = 122$ nm) is due to the lower VUV power density. The plateau at [O] $\simeq 25$ at% signals an equilibrium between O incorporation and the removal of volatile oxidized species (“etching”) which results from chain scissions (see below). When the window is SiO₂ ($\lambda_c = 160$ nm) the oxidation rate is very low, and it can be attributed to type 2 initiation via absorption by additives (antioxidants) and irregular structures in the polymer, rather than by the structure of PE itself.

We have measured the rate, ε , of H₂ plasma radiation-induced etching of various polymers by depositing thin films of these onto the surface of a quartz crystal microbalance (QCM), placed inside the sample chamber. ε values were measured under three sets of conditions, namely [29]:

1. sample surface exposed to the VUV irradiation, 0.3 Torr of O₂ in the sample chamber;
2. sample surface exposed, but vacuum ($\sim 10^{-4}$ Torr) in the sample chamber;

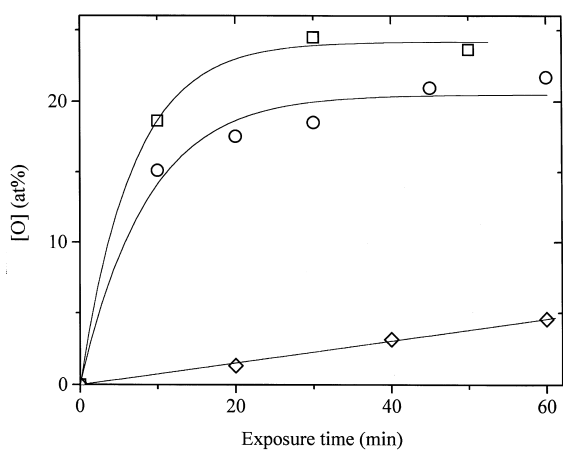


Fig. 5. Evolution of the surface oxygen concentration [O] of a PE film irradiated in O₂ with the emission of a hydrogen plasma through a magnesium fluoride (\square), calcium fluoride (\circ), and a silica (\diamond) window.

3. sample surface not exposed (parallel to incident radiation), 0.3 Torr of O₂ in chamber.

The results of these experiments, shown in Fig. 6, may be briefly summarized as follows: The materials investigated (PE, PS, PMMA and hexatriacontane, HTC, a C₃₆ alkane with the same $-\text{CH}_2-$ repeat unit as PE) display widely-varying ε values under given experimental conditions, with ε decreasing as follows: PMMA > HTC > PE > PS, as expected on the basis of the α values of these materials. In all cases ε increases with rising VUV radiation power density (integrated between 112 and ~ 200 nm). Comparing ε values for cases (1) and (2) above, we notice that etching can occur under the sole influence of VUV irradiation, but that it is much enhanced in the presence of oxygen. However, under condition (3) (and (2) for PS), ε values are too low to show on this plot. This, evidently, demonstrates that the etch mechanism involves a strong synergy between VUV-induced radical formation at the polymer surface, and attack of these radical sites by atomic oxygen (AO). AO alone (case (3)) results only in a very small etch rate, unless the atoms possess several eV of kinetic energy (hyperthermal AO) [32].

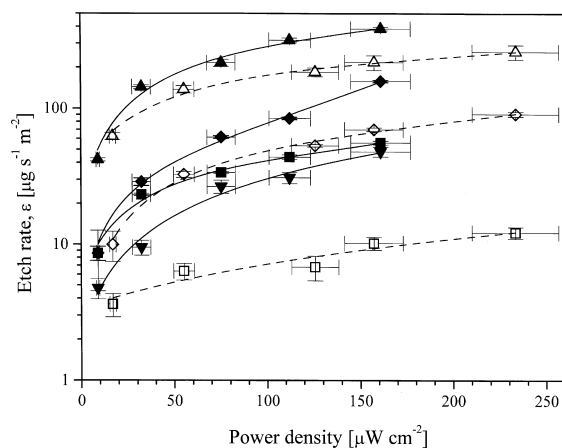


Fig. 6. Polymer etch rate, ε , dependence on integrated VUV radiation power density: Polymethyl methacrylate (PPMA): \blacktriangle VUV/O₂, \triangle VUV; hexatriacontane (HTC): \blacklozenge VUV/O₂, \diamond VUV; Polyethylene (PE): \blacksquare VUV/O₂, \square VUV; Polystyrene (PS): \blacktriangledown VUV/O₂.

3. Comparison of plasma with UV processing

Whether we use direct exposure of a polymer, for example PE, to oxygen-containing plasma, or VUV-induced surface oxidation, XPS results will show the same maximum [O] value ($\sim 25\%$, see Fig. 5) and the same C(1s) spectrum (see Fig. 2). The only difference is that the kinetics are much slower ($\sim 20\times$) in the VUV case, but this can be attributed here to the fact that the source has not been optimized for VUV power emission (irradiance): As we have shown elsewhere [29,30], the total power density emitted by a H_2 plasma in the $112 \leq \lambda \leq 200$ nm wavelength range is $225 \mu W/cm^2$, when the total power absorbed by the plasma is 350 W; this translates into an efficiency for VUV generation of roughly 0.05%, evidently quite low. However, much effort has been devoted, over the years, to develop both coherent (laser) and incoherent VUV and UV light sources of high efficiency. We will now briefly describe incoherent far-UV sources which can be used for photochemical treatment of relatively large surface areas; lasers are known to have an important pyrolytic contribution [33], are rather difficult to scale up for large surface area treatments, and will therefore not be discussed further. The interested reader will, however, find a large literature on excimer laser processing of materials, for example Ref. [33].

Low-pressure lamps (several Torr and less) are often used as sources of high-intensity VUV light; as already mentioned above, the radiation of atomic resonance lines of argon, krypton, xenon, together with the molecular bands in the case of mixtures with molecular gases (nitrogen or hydrogen) are excited in glow discharges. The most common low-pressure gas discharge sources and window materials are listed in Ref. [34]. A VUV source with a broad, continuous emission spectrum, widely used also for calibration purposes, as in our own experiments [29,30], is the deuterium arc lamp which peaks around 160 nm in the Lyman band, and extends to about 300 nm due to the recombination continuum. For a very long time, the most important far-UV source was the mercury lamp, with its two strong emission lines at 254 and 185 nm, arising from the following atomic transitions:

$$^3P_1 \Rightarrow ^1S_0 + h\nu \text{ (253.4 nm),}$$

$$^1P_1 \Rightarrow ^1S_0 + h\nu \text{ (184.9 nm).}$$

Irradiances of about 10 mW cm^{-2} at 185 nm, and up to 100 mW cm^{-2} at 254 nm, have been reported. When raising the current density to several $A \text{ cm}^{-2}$, these characteristic lines saturate and a previously weaker one, at 194.2 nm, becomes dominant.

During the past decade a new family of high-irradiance UV lamps has been developed, in the form of incoherent, pseudo-continuous excimer sources, using dielectric barrier discharges [34–40]. Since the radiative emission is due to a transition between a weakly-bonded upper state (excimer means *excited dimer/trimer*) and a repulsive ground state, no trapping of the radiation occurs, contrary to the case of resonant line sources. The plasma characteristics are determined by such external parameters as gap spacing, gas mixture and filling pressure, thickness and characteristics of the dielectric barrier, and others. Lamp performance can be optimized via the formation of the desired excimer species. Emissions in the VUV to UV-A range are obtained by choosing appropriate excimers, namely rare gas dimers [35,36], halogen dimers [36], rare gas halide excimers [36,37], or mercury rare gas excimers [36,38], see Table 1.

All of the above-mentioned sources have been used for large-area photochemical processing, in two basic configurations, namely:

- linear arrays, or large-area single lamps, where the treatment chamber is separated from the reaction chamber by transparent dielectric windows [33,40–42];
- “internal” lamps, where there is no window barrier between the photon source and the processing chamber [33,43].

While in the first case care must be taken to prevent any deposition on the window materials, the latter case has the drawback that radicals created in the lamp may participate in the process chemistry.

Microelectronics-oriented applications provided a strong impetus for investigating VUV-polymer interactions since at least 20 years: In photolithography, for example [44,45], the short

Table 1
Excimer complexes with their corresponding peak wavelength, photon energy and UV domain, after Ref. [50]

Excimer	Wavelength (nm)	$h\nu$ [eV]	UV range
Ar ₂ ⁺	126	9.8	VUV
Kr ₂ ⁺	146	8.5	VUV
F ₂ ⁺	158	7.8	VUV
ArBr*	165	7.5	VUV
Xe ₂ ⁺	172	7.2	VUV
ArCl*	175	7.1	VUV
KrI*	190	6.5	VUV
ArF*	193	6.4	VUV
KrBr*	207	6	UV C
KrCl*	222	5.6	UV C
KrF*	249	5	UV C
XeI*	253	4.9	UV C
Cl ₂	259	4.8	UV C
XeBr*	283	4.4	UV B
Br ₂	289	4.3	UV B
XeCl*	308	4	UV B
I ₂	342	3.6	UV A
XeF*	354	3.5	UV A

wavelengths permit higher resolution and smaller features, while all-dry processing via direct etching and self-development provide additional benefits. Both negative and positive photoresists with high absorption coefficients and sensitivity have been developed [46], permitting high aspect-ratio structures to be achieved by appropriate choices of exposure dose and contrast [47]. Multilevel metallization represents another area for VUV processing in microelectronics, where polyimide (PI) is an attractive interlevel dielectric material. Using VUV contact lithography with deuterium lamps, 50 nm line patterns of PI have been obtained [48]; hundred-fold higher dry etching rates can be achieved by replacing mercury lamps with an incoherent excimer source [49]. High quality homogeneous metal films can then be deposited in a two-step process [50], also using excimer lamps. The above-described successes in photolithography have led to further research in VUV imaging, for contact printing and holography, with promising results [51].

The development of large area, high intensity incoherent UV light sources is also benefiting

photo-induced modification of polymeric substrates in application areas other than microelectronics: VUV radiation has been shown, depending upon treatment conditions, to result in cleaning and cross-linking [11,12], fluorination [52], de-fluorination [22], enrichment in C–O bonding of the surfaces [22,23], with applications in barrier film deposition [53], metallization [50], enhancement of wettability [22] and of biocompatibility [54], and numerous others.

4. Conclusions

In this article we have shown that plasmas, both at atmospheric and reduced pressures, are increasingly being used in industry for processing polymeric materials. If the feed gas is oxygen or air, a particularly important subset of such processes, the polymer surface can be controllably oxidized, and its physical characteristics (wettability, adhesion, etc.) can thereby be greatly enhanced. We have also shown that similar changes can be brought about on the polymer surface if it is exposed to a particular constituent of the complex plasma environment, namely its VUV/UV radiative emission. Normally, the power level of such short wavelength radiation is relatively low, but in recent years new lamp technologies have been developed, based both on low-pressure and atmospheric pressure gas discharges, in which the VUV/UV efficiency has been optimized. Numerous photochemical processes which use such light sources have been investigated and commercialized. At this point in time it appears that both plasma and VUV photochemical processes have promising futures in the industrial processing of polymers, for they both have their particular sets of advantages and drawbacks.

Acknowledgements

This work was supported by research grants and fellowships from the Natural Sciences and Engineering Research Council of Canada (NSERC), and from the Fonds Formation de Chercheurs et Aide à la Recherche (FCAR) of

Québec. The authors are grateful to their colleagues for assistance and many valuable discussions, particularly to J. Behnisch, G. Czeremuszkina, J.E. Klemberg-Sapieha, A. Kruse, E.M. Liston and L. Martinu.

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