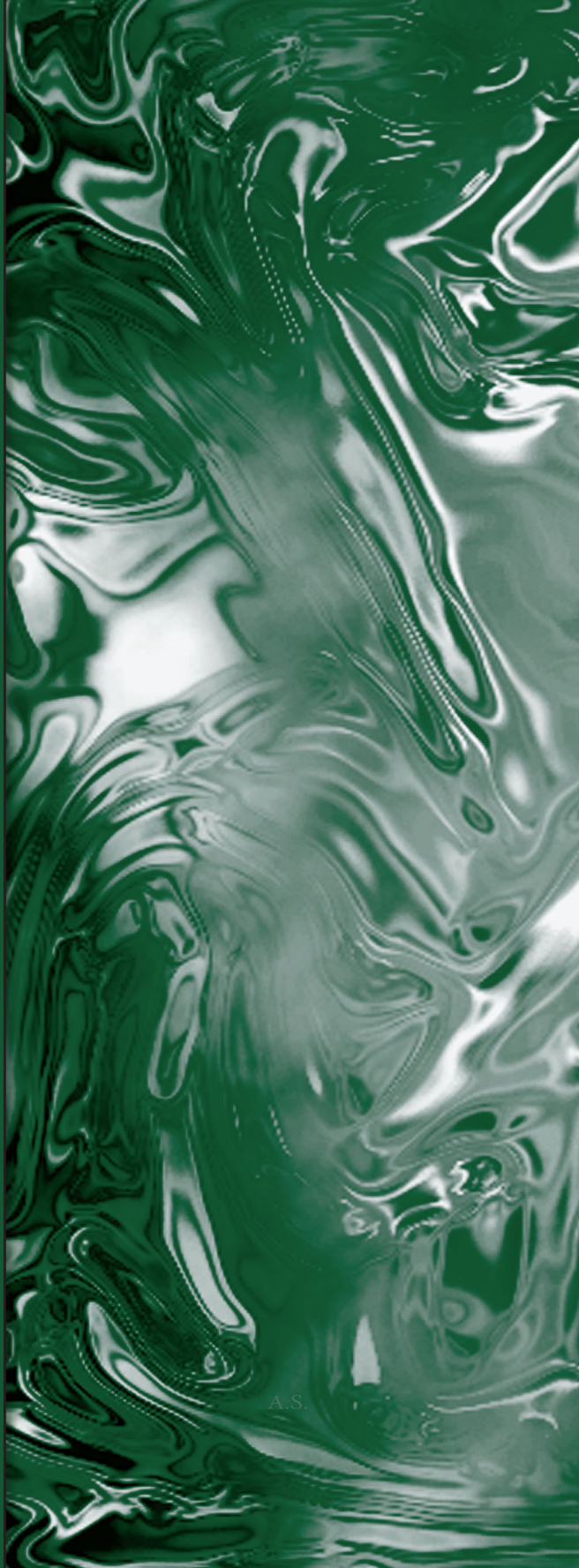


Polymer Surface Modification: Relevance to Adhesion, *Volume 4*

Edited by
K.L. Mittal

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Volume 4

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K.L. Mittal

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Preface

This book chronicles the proceedings of the Fifth International Symposium on Polymer Surface Modification: Relevance to Adhesion held under the auspices of MST Conferences, LLC in Toronto, Canada, June 20–22, 2005. The premier symposium on this topic was held in Las Vegas, Nevada, November 3–5, 1993, the proceedings of which were properly chronicled [1]. The second symposium in this series was held under the aegis of MST Conferences, LLC in Newark, NJ, May 24–26, 1999, which was also documented in a proceedings book [2]. Apropos, it should be recorded that the third symposium in this vein was organized also by MST Conferences, LLC in Newark, NJ, May 21–23, 2001 but, for a variety of reasons, the proceedings of this event were not documented in the form of a hard-bound book. The fourth symposium on this topic was also organized by MST Conferences, LLC in Orlando, FL, June 9–11, 2003 the proceedings of which were documented in a hard-bound book [3].

The topic of polymer surface modification is of tremendous contemporary interest and even a casual look at the literature will attest that there is a brisk R&D activity in this arena. This high tempo of activity and interest emanates from the applications of polymeric materials for a legion of purposes in many and diverse technologies and industries. And the surface behavior (e.g., adhesion, wettability, tribological characteristics, etc.) of polymeric materials is of crucial importance. By suitably modifying polymer surfaces one can obtain the desired surface characteristics without tempering with the bulk properties. Concomitantly, there is much current interest in devising new ways or ameliorating the existing techniques. The techniques for polymer surface modification range from dry to wet, vacuum to non-vacuum, sumptuous to inexpensive, and sophisticated to simple. Apropos, recently much interest has been evinced in the atmospheric pressure plasma treatment as it offers certain advantages vis-a-vis the conventional low-pressure plasmas.

The technical program for this event comprised 46 papers reflecting both overviews as well as original research contributions. The presenters hailed from academia, industry and other research organizations from many corners of the globe. The presentations focussed on various surface treatment methods, analysis and characterization of modified surfaces, understanding the life and durability of treatment methods, and relevance of surface modification in adhesion aspects of polymers.

Now turning to this volume, it contains a total of 18 papers, others are not included for a variety of reasons, which were rigorously peer reviewed, revised

(some twice or thrice) and edited. So it should be recorded that this book is not a mere collection of papers – which is normally the case with many proceedings volumes – rather it represents the highest standard of publication. The book is divided into two parts: Part 1. Surface Modification Techniques; and Part 2. Adhesion Improvement to Polymer Surfaces. The topics covered include: critical assessment of process conditions in polymer surface modification; various dry techniques (e.g., laser, ozone, low-pressure plasma, and atmospheric pressure plasma) to modify polymer surfaces; polymer surface modification by wet chemical techniques (e.g., photosulfonation, grafting, use of chitosan, and use of dendrons); wool surface modification, antimicrobial activity of modified fiber surfaces; AFM study of modified surfaces; relevance of adhesion in nanoimprint lithography; adhesion between polymer films; adhesion of cellulose; adhesion promoters for polyolefin substrates; surface properties of acrylic systems; and detection of contaminants on polymer surfaces by laser induced breakdown spectroscopy (LIBS).

This volume and its predecessors [1–3] contain bountiful information and reflect the latest R&D activity relative to this fascinating and tremendously technologically important arena. Also it is hoped that the information contained here will serve as a fountainhead for new ideas in this field. Anyone with current interest or anticipated need to learn about polymer surface modification should find this book very relevant and of much value.

Acknowledgements

First, as always, it is a pleasure to express my thanks to my colleague and friend, Dr. Robert H. Lacombe, for taking care of the necessary details during the organizational phase of this symposium. Second, thanks are extended to all the contributors to this book for their interest, enthusiasm, patience and cooperation without which the book would not have seen the light of day. The reviewers provided much valuable comments which definitely improved the quality of manuscripts, and they should be thanked for their time and efforts. In closing, my appreciation goes to the staff of VSP/Brill (publisher) for transforming the raw material (manuscripts) into this book form.

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3. K. L. Mittal (Ed.), *Polymer Surface Modification: Relevance to Adhesion*, Vol. 3. VSP, Utrecht, The Netherlands (2004).

Part 1

Surface Modification Techniques

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Importance of process conditions in polymer surface modification: A critical assessment

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Abstract—Plasma web treatment is a common practice for promoting adhesion, wettability and other surface or interfacial properties in the conversion industry. While the objective of creating new surface functional groups is conceptually simple, it can be difficult to choose the most appropriate kind and configuration of plasma source, the most appropriate feed gas composition and the most appropriate operating pressure for a given application. Such difficulties arise from the variety of species that can be formed in the plasma and the variety of possible plasma-surface interactions that can occur. A brief review of the importance of various plasma parameters (e.g., specific energy, species concentrations, and energy distributions) and an example relating nitrogen uptake in poly(ethylene-2, 6-naphthalate) to plasma diagnostic data in a low-radiofrequency capacitively-coupled nitrogen plasma are presented. The importance of driving frequency and treatment configuration is discussed in detail. Uptake kinetics for samples treated at floating potential at low radiofrequency is compared with that for samples treated in the cathode sheath. Analysis of the treatment kinetics is based on a simple model of surface saturation. This approach can be used not only to compare practical treatment results as a function of process conditions, but also to compare different treatment techniques in a practical manner.

Keywords: Polymer surface modification; plasma; capacitively-coupled discharge; process conditions; frequency effects; kinetics.

1. INTRODUCTION

Plasmas are used in a variety of polymer surface modification applications, including adhesion promotion in metallized plastics, wettability control in printing, priming of plastics and elastomers for painting or bonding, and treating catheters and other biomedical devices. Plasma polymerization, plasma treatment and plasma etching of polymers have been the subject of research for several decades, providing review articles and collections of work devoted to plasmas and polymers [1–9]. While the references cited here are by no means exhaustive, they provide a good sense of the broad range of applications, the variety of plasma chemi-

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cal processes that can be employed, and the complexity of the plasma–polymer interaction. Yasuda [1] focuses on the effects of plasmas on the surface chemistry of polymers and discusses the variety of mechanisms of surface chemical modification by plasmas. Liston *et al.* [2] review plasma surface modification of polymers and plasma treatment techniques with a focus on adhesion promotion. Grace and Gerenser [4] review industrial applications and experimental studies of plasma modification of polymers, and then focus on the attempt to connect plasma characteristics with the chemical modifications they produce on polymers. Biederman and Osada [5] provide background on plasma technology and plasma chemistry and discuss applications of plasma polymerized films. The reference edited by d'Agostino [3] provides background on plasma source technology, plasma diagnostic techniques and applications of plasmas to deposition, surface modification and etching of polymers. A broad variety of modification techniques, applications and analytical techniques is presented in the collections edited by Mittal [6–9].

For even a narrow range of applications, one can find a variety of plasma sources used in practice. For example, in plasma treatment of polymer webs, industrialists and academic researchers have employed capacitively coupled low-pressure discharges driven at frequencies ranging from approx. 10 kHz to approx. 20 MHz, microwave discharges, dual frequency discharges and dielectric barrier discharges at atmospheric pressure. Furthermore, a variety of approaches can be found for generating the same chemical functionality on a polymer surface. The diversity of applications, plasma source technologies and gas chemistries employed arises largely because of the rich variety of physical and chemical processes that can occur in even the simplest plasma.

In general, the polymer surfaces to be treated are placed for a specified time in contact with a plasma formed in a particular working gas at a particular pressure and flow rate. The practical dose is considered to be the applied power multiplied by the treatment time. In batch processes, one may consider the power per unit volume in the treatment zone, or one may project the volume upon the surfaces to be treated and consider the power per unit area. In these cases, energy per volume or energy per area is used as a practical treatment dose. In the case of plasma web treatment, the treatment device has some length along the direction of web motion and is at least as wide as the desired width of web to be treated. The treatment dose is found by dividing the power delivered to the treatment device by the device width and the web speed. In none of these cases does the treatment dose represent the actual energy (for example, in the form of ion kinetic energy or chemical potential energy) delivered to the surface of the article to be treated.

Nonetheless, the degree of modification or practical effect of modification as a function of dose (i.e., the dose response) can be used to compare a variety of plasma chemistries and plasma sources, given a particular configuration of treatment device and sample (e.g., elongated sources applied across moving webs). Furthermore, comparing dose responses by varying the treatment time at selected settings of pressure and power can be instrumental in finding the best treatment

conditions, and it can also be helpful in improving one's understanding of the underlying mechanisms.

The effects of the plasma modification are generally confined to the surface region of the treated articles. The ions, electrons and neutral species do not penetrate very far (typically approx. 10 nm), while the vacuum ultraviolet photons may penetrate micrometers deep, depending on the optical absorption properties of the article being treated. Therefore, the progression of surface chemical changes with treatment time follows a saturation curve. After the near-surface region (i.e., approx. 1–2 nm) becomes heavily modified, modification of the subsurface region can occur by diffusion of reactive species from the treated region above. Depending on the depth of analysis, one may observe simple saturation of a surface response with exposure time, or one may observe a region of rapid change with treatment time (reaction-limited regime), followed by a region of significantly slower change (diffusion-limited regime).

While the general description of plasma treatment and the resultant saturation of surface modification with treatment dose are extremely simplified, they provide a useful framework in which to compare different polymer substrates, different sources, different plasma compositions, or different plasma-substrate configurations. At the core of all of these comparisons are the interrelationships among plasma process parameters, treatment configuration parameters and the species distributions that ultimately produce the chemical modification of the substrate surface. A brief discussion of these interrelationships is presented below. In Section 2, as an illustration of the importance of process conditions and treatment configuration, data are presented for treatments of polyester webs using a capacitively coupled radiofrequency nitrogen plasma. The effects of driving frequency, substrate location, power, and pressure are described and discussed.

1.1. Plasma parameters

Plasma surface modification is a consequence of a variety of plasma species distributions impinging on a substrate surface. The process conditions determine the species concentrations and energy distributions. Applied power, as mentioned above, is a critical parameter with respect to the practical treatment dose. Process pressure and gas composition determine reactant concentrations. In addition, total pressure and gas partial pressures influence the energy distributions and concentrations of ions and electrons. The placement of the sample with respect to electrodes influences the relative species concentrations and their energy distributions experienced by the substrate. It is important to note that the external process parameters (i.e., applied power, pressure, gas flow and geometry) do not uniquely influence a particular species concentration and energy distribution.

Of more fundamental significance than the applied power is the power divided by the gas flow through the treatment zone, as it is related to the specific energy (i.e., energy per molecule) deposited in the plasma. For example, a power of 1 W dissipated in a mass flow of 1 sccm amounts to 15.5 eV per molecule. In plasma

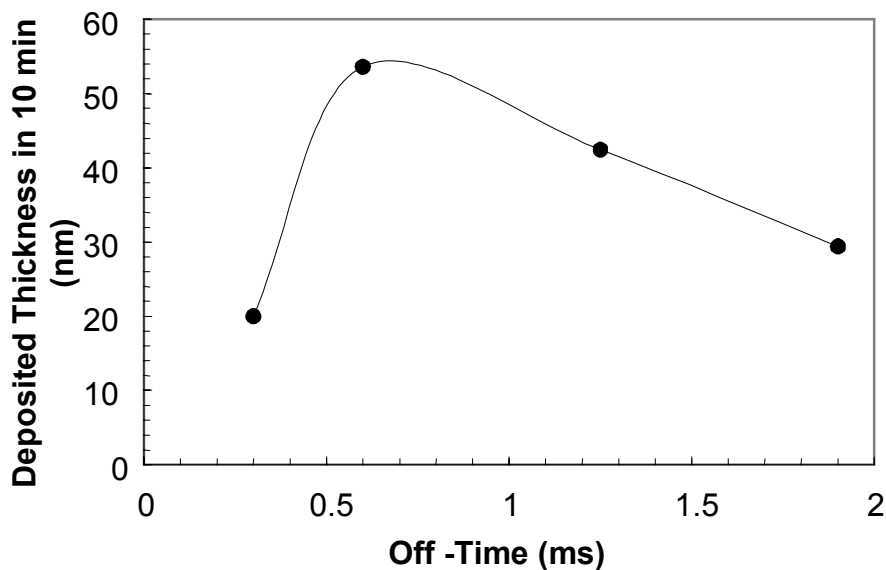


Figure 1. Thickness of deposited fluoropolymer in a pulsed 13.56 MHz capacitively coupled CHF_3 discharge as a function of time between pulses (“off-time”). The discharge pulses were 0.1 ms in duration.

polymerization processes, this parameter has been shown to be of considerable importance [10].

Additional parameters of importance in plasma polymerization using pulsed radiofrequency plasmas are the pulse period and duty cycle. Pulsing the plasma effectively reduces the time-averaged specific energy deposited relative to constant wave (CW) operation at the same driving voltage amplitude. In addition, it has important transient effects. Pulsing the power to the plasma in sufficiently short bursts makes use of higher electron temperatures during the ignition phase of the plasma (measurements and models for pulsed argon plasmas have been presented by Ashida *et al.* for an inductively coupled plasma source [11] and by Booth *et al.* for a capacitively coupled plasma source [12]). Furthermore, with sufficient delay between pulses, relatively long-lived excited neutral species may interact with each other and the substrate in the absence of ions during the period after the plasma is extinguished [13, 14].

An example of the effect of duty cycle on plasma polymerization rate in a capacitively coupled 13.56 MHz discharge in CHF_3 is shown in Fig. 1. In this example, the sample (a silicon wafer) was placed on a 7.6-cm diameter electrode facing a second electrode of equal area on the opposite side of a Teflon[®] cylinder enclosure of 7.6 cm inner diameter and 7.6 cm height. Gas was admitted through a series of holes in the wall of the Teflon cylinder and exited through additional holes in the cylinder wall at a flow of 3 sccm and a pressure of roughly 13 Pa. A 13.56 MHz power generator was used in pulsed mode. The pulse duration (“on-

time”) was 0.1 ms, and the time between pulses (“off-time”) was varied as indicated in the graph. As shown in Fig. 1, the maximum deposition rate does not correspond to the maximum power delivered (i.e., zero “off-time”, 90 W constant wave, as measured at the output of the tuning network). As the “off-time” is increased, the deposition rate increases until a maximum point beyond which it then decreases. In this latter regime, presumably the neutral species responsible for the condensation and polymerization are present in diminishing concentrations as the “off-time” is increased. Similar results have been reported by others [13, 14].

While the ratio of power to gas flow is clearly an important parameter and one of far more fundamental significance than applied power, it gives no indication of how the applied power is partitioned among the various processes occurring within the plasma. In a typical low-temperature nonequilibrium plasma, the applied power couples more effectively to the electrons in the plasma. This energized population of electrons generates ions and excited neutrals by electron impact processes. The types of species formed are determined by the electron impact cross-sections for excitation. Typical electron energy distribution functions have average energies in the range 1–5 eV, with high-energy tails extending into the range of several tens of eV. The electrons in the high-energy tail are important for driving ionization and other excitation processes having thresholds of tens of eV. In discharges sustained by secondary electron emission from the cathodes, a significant population of energetic electrons is generated by acceleration of the secondary electrons in the cathode sheath [15, 16]. These electrons can gain much of the applied voltage amplitude upon traversing the sheath.

Ions traveling from the bulk plasma to surfaces acquire kinetic energy as they traverse the sheaths associated with these surfaces. For a surface floating electrically in the plasma, the ions gain the difference between the plasma potential and the floating potential. This difference scales with the electron temperature and is typically in the range 10–20 V. In contrast, ions entering a cathode sheath gain the difference between plasma potential and the cathode voltage. Depending on the relative areas of cathode and anode, the maximum energy gained by the ions as they approach the cathode can be 1–2 times the driving voltage amplitude, with time-averaged energies of 0.5–1 times the driving voltage amplitude. At low process pressures, the ions do not experience a significant number of collisions in transit to the cathode. At high process pressures, the energy with which the ions arrive is reduced significantly by collisions with neutral gas species.

Neutral reactive species can be extremely important in polymer surface modification processes. For example, monatomic species formed by dissociation of molecular gases can react with polymer surfaces to form new functional groups comprising the atomic species from the plasma and atomic constituents of the polymer repeat unit. In addition, electronically excited atoms and molecules can be important participants in surface reactions leading to the formation of new chemical functionalities. The total pressure and partial pressure of feedstock gases

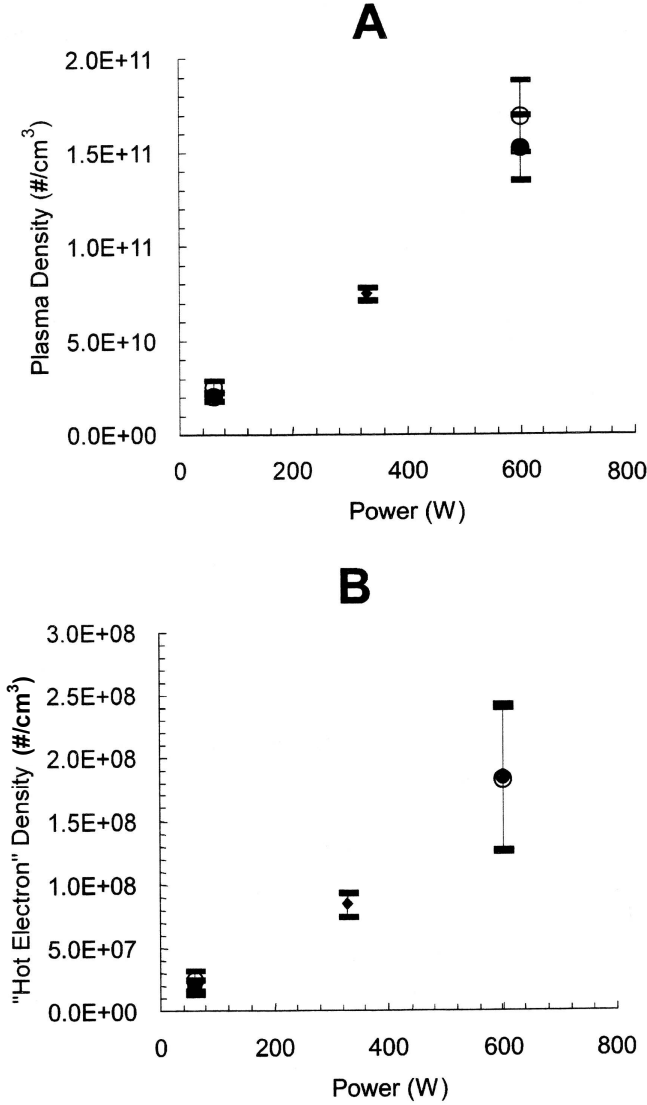


Figure 2. (A) Plasma density and (B) density of "hot" electrons in the high-energy tail of the electron energy distribution, as determined from ion flux probe measurements in a nitrogen plasma driven at 40 kHz using the coplanar electrode configuration (see Fig. 6B). The bulk electron density (i.e., those having the lower temperature population in the bi-Maxwellian distribution) is roughly equivalent to the ion density (i.e., the plasma density), as the electrons in the high-energy tail are of much lower concentration.

influence the types and concentrations of atomic species formed by electron impact dissociation and excited atomic and molecular species formed by electron impact excitation. Furthermore, metastable species formed by electron impact

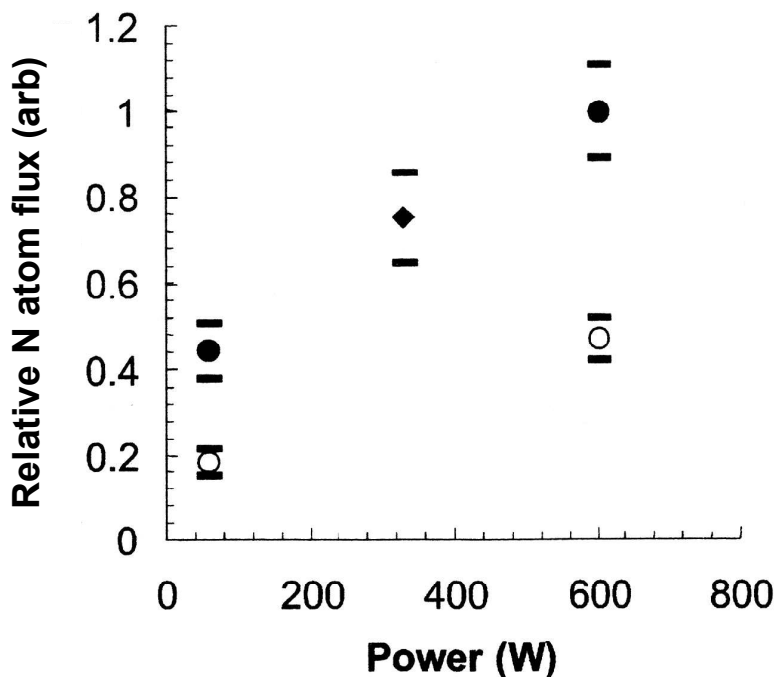


Figure 3. Relative N atom flux as a function of applied power at nitrogen pressures of 10 Pa (O), 20 Pa (◆) and 30 Pa (●). This quantity is found from optical emission measurements by multiplying the ratio of emission intensity from N to that from N₂ by the nitrogen pressure and normalizing this product of pressure and emission intensity ratio to the maximum value for all experimental runs.

(e.g., metastable states of argon or helium) can excite neutral atoms and molecules upon collision to form ions and excited neutral species, and the total system pressure and the partial pressures of the feedstock gases influence the population of products formed by these processes.

A consequence of the presence of excited molecular and atomic species is the emission of photons as the excited states decay. Many of the decay processes include transitions involving the emission of vacuum ultraviolet (VUV) photons. VUV emissions can play a significant role in photochemical reactions during polymer surface modification, as well as in cross-linking reactions at the surface and in the subsurface region of the polymer.

As an example of the importance of ions and reactive neutral species in the polymer surface modification process, ion densities and relative N atom fluxes (respectively from ion flux probe and optical emission data) from a 40 kHz capacitively coupled nitrogen plasma are presented in Figs 2 and 3, and their correlation with surface nitrogen uptake in poly(ethylene-2, 6-naphthalate) (PEN) is shown in Fig. 4. The plasma source, having a coplanar electrode configuration, is described elsewhere [16, 17]. The optical emission and ion flux data are discussed

in Ref. [4]. Relative N atom concentrations were found by taking the ratio of N-atom emission to molecular nitrogen emission and multiplying by the nitrogen pressure (i.e., the total discharge pressure), assuming that the nitrogen was only weakly dissociated. The relative N atom flux (which is taken as equivalent to the relative N atom concentration, as the two quantities are proportional, $\text{flux} \propto \text{concentration} \times \text{velocity}$, and the effects of temperature on velocity are neglected) was normalized to a value of 1 at the maximum value of the product of emission intensity ratio and nitrogen pressure obtained in the experiment. The relative ion flux was found by taking the relative ion saturation current (at a given probe voltage significantly below floating potential) or by fitting the probe current in the ion saturation regime to a simple bi-Maxwellian model for the electrons and using the resultant ion concentration (i.e., plasma density shown in Fig. 2) and the Bohm velocity from the lower electron temperature and normalizing to a maximum value of 1. Nitrogen uptake was determined by XPS analysis of PEN samples at a series of web speeds for each of five combinations of treatment pressure and applied power [17]. A simple model of nitrogen uptake was employed (see Ref. [4] for details):

$$\left. \frac{dN}{dt} \right|_{t=0} = (A\Gamma_i + B\Gamma_N + C\Gamma_N\Gamma_i)N_{\max}, \quad (1)$$

where N is the surface nitrogen content, Γ_i and Γ_N are the respective relative fluxes of ions and N atoms, $N_{\max}$ is the maximum number density of available surface sites for nitrogen incorporation (estimated to correspond to 30 at%), and A , B and C are respective fitting parameters related to the cross-sections for nitrogen incorporation by molecular nitrogen ion impact, atomic neutral nitrogen impact, and incorporation by an interactive process involving ions and neutrals. The value for $N_{\max}$ is a rough estimate and is expected to be similar for both PEN and PET. It is obtained by considering the nonvolatile species produced by adding N atoms to the repeat unit in the polyester.

In Fig. 4, the modeled nitrogen uptake rate at $t = 0$ is plotted against the experimentally determined nitrogen uptake rate at $t = 0$ (as determined from analysis of nitrogen uptake curves (%N vs. t) for each of the five conditions). Using all three processes (i.e., coefficients A , B and C), a good fit is obtained. The quality of fit is degraded significantly by omitting the coefficient C or by using only A , B , or C alone (see Ref. [4]). The interaction term $C\Gamma_N\Gamma_i$ may represent a two-step process, such as formation of surface radicals by ion impact, followed by reaction with atomic neutral nitrogen, or it may represent formation of atomic ions of nitrogen by electron impact processes (the ion flux is directly related to the electron concentration in the plasma).

External plasma parameters, such as power, pressure and gas flow, can be measured and controlled with little difficulty. Unfortunately, these parameters are seldom related in a simple fashion to the fluxes and energy distributions of the species most important for surface modification. The relevant species fluxes and

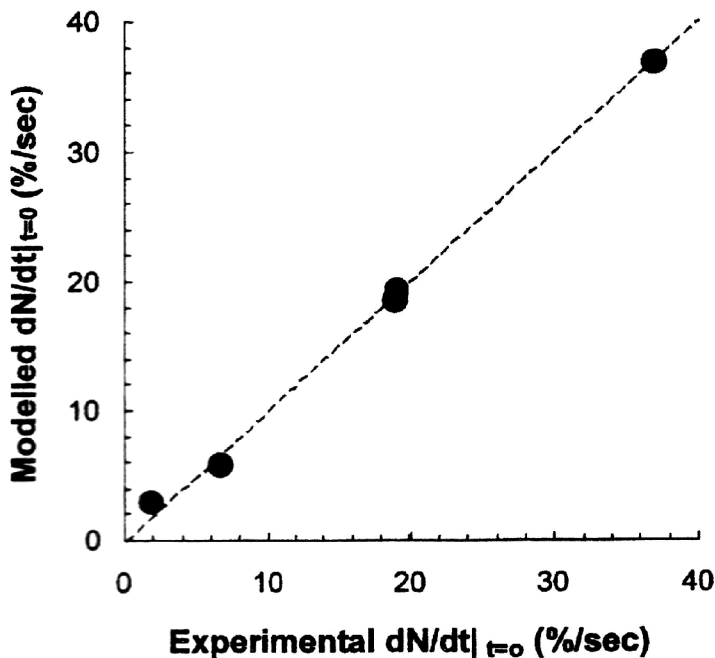


Figure 4. Modeled initial uptake rate vs. experimentally determined uptake rate for surface nitrogen in plasma-treated PEN using a 40 kHz capacitively coupled nitrogen discharge (shown schematically in Fig. 6B). The model used is given by equation (1).

energy distributions, however, can be difficult to measure. Nonetheless, using simple kinetic models, species fluxes and energy distributions can be related to surface modification effects, such as initial uptake rates of chemical species, saturation values for such species, or even distributions of chemical functionalities formed on a treated surface. An excellent example of work relating plasma physical characteristics, gas-phase chemistry and polymer surface chemistry to resultant surface modification is the investigation of the modification of polypropylene in dielectric barrier discharges in air by Dorai and Kushner [18].

2. AN EXAMPLE OF THE IMPORTANCE OF DRIVING FREQUENCY AND TREATMENT CONFIGURATION: CAPACITIVELY-COUPLED RADIOFREQUENCY NITROGEN PLASMA TREATMENT OF POLYESTER WEBS

The example presented below illustrates how considerably different results can be obtained using the same type of treatment apparatus and varying the driving frequency and position of the article to be treated. Other researchers have noted and demonstrated the importance of such differences for steady-state treatments (relatively long exposure times) [19]. In this example, we examine, in addition, the up-

take kinetics in different treatment configurations and observe significant differences in the distribution of chemical species formed for samples floating electrically in the plasma, as compared to samples located in the cathode sheath of a capacitively coupled low-radiofrequency nitrogen discharge.

2.1. Experimental details: plasma treatment

The experimental configuration for treatments of stationary samples is shown in Fig. 5. A pair of water-cooled aluminum electrodes ($16.5\text{ cm} \times 5.1\text{ cm} \times 1.27\text{ cm}$ thick) were housed in a grounded aluminum enclosure (labeled “Support and Side Walls”) and spaced 0.32 cm from the walls and each other. The pair of electrodes was placed on 0.32-cm-thick ceramic spacers (not shown), which, in turn, rested on the aluminum backing plate (approx. $17.1\text{ cm} \times 11.1\text{ cm} \times 1.27\text{ cm}$). The enclosure sidewalls were 1.27 cm thick, providing support for the electrodes and backing plate and extending roughly 2.5 cm above the front surface of the coplanar electrodes. Poly(ethylene-2, 6-naphthalate) samples ($100\text{ }\mu\text{m}$ thick) from Teijin were cut and placed on the electrode assembly and on the upper edge of the grounded enclosure.

The grounded enclosure was installed in a cryopumped chamber (volume about 250 l) and was pumped to a base pressure below $3 \times 10^{-5}\text{ Torr}$. Nitrogen gas was admitted into the chamber at a flow between 80 and 100 sccm . A gate valve

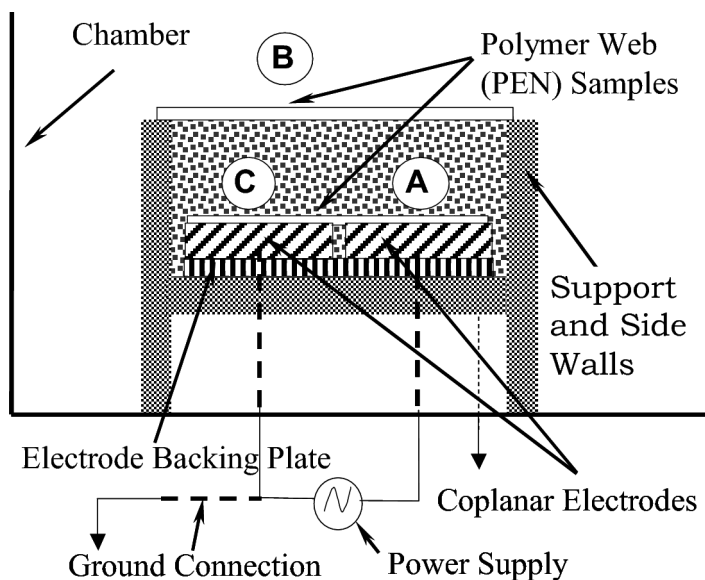


Figure 5. Schematic of apparatus used for treatments of stationary samples.

between the chamber and the cryopump was throttled until the steady-state chamber pressure reached 0.1 Torr. Note that the gas flow in the enclosure was unknown and considerably less than that in the chamber. Comparison with results in a pilot-scale treater with gas flow admitted directly into the electrode gap suggests that the effect of flow is negligible for the 40 kHz nitrogen treatments.

After purging the chamber at steady-state flow for 3 min, power was applied to the electrodes at a specified level for a specified treatment time. Samples in positions A, B, and C were evaluated for three driving frequencies – 40 kHz, 450 kHz and 13.6 MHz. The output of the 40 kHz supply was floating and was applied directly across the two electrodes. The two higher frequency supplies had output referenced to ground; and thus the ground connection indicated in Fig. 5 was

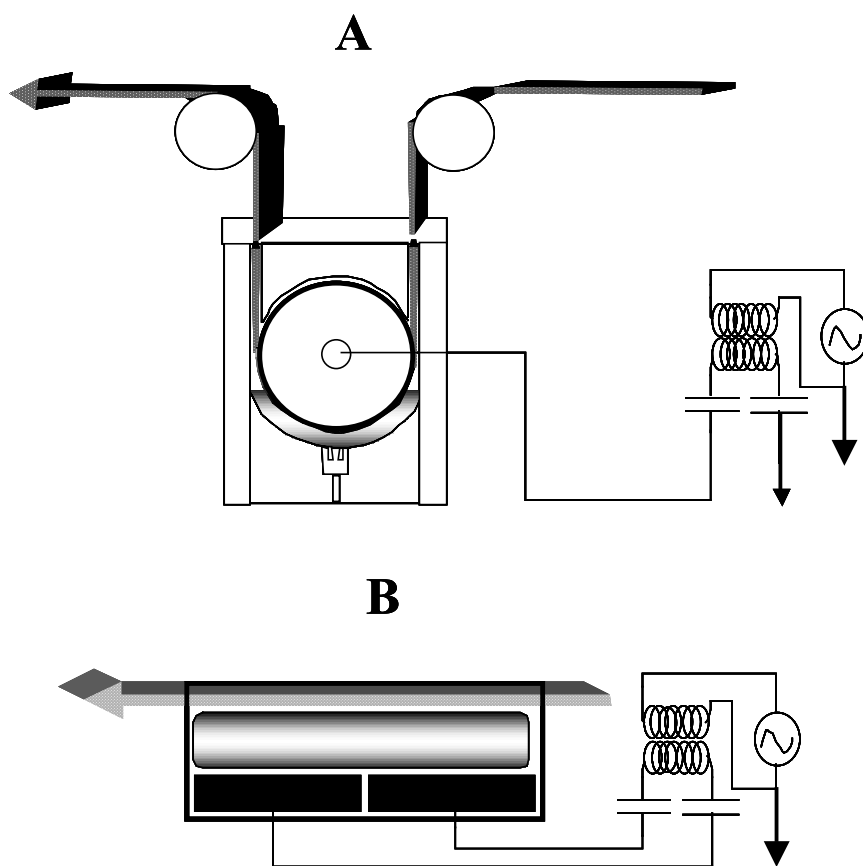


Figure 6. Schematic of pilot-scale apparatuses used for treatments of moving webs: (A) rotating electrode configuration for treatments in the cathode sheath, (B) co-planar electrode configuration for treatments at floating potential.

made. For each power supply configuration, treatment power and time were selected so that the sample in position B (electrically floating) had roughly the same nitrogen content (approx. 10 at%).

For initial treatments of moving webs in the cathode sheath, the electrode assembly shown in Fig. 5 was mounted on an enclosure that was bolted to an aluminum frame with a simple web drive having a friction clutch on the unwind spindle. Web was introduced through slits between the electrode fixture and the enclosure so that the rear surface of the web was in direct contact with the electrode pair. Treatment gas was admitted to the enclosure through a series of orifices in the enclosure walls.

For pilot-scale web treatments, plasma treatment devices were built and installed into an existing vacuum web coater. Schematics for the plasma source for treatments in the cathode sheath and at floating potential are respectively shown in Fig. 6A and 6B. The treatments were carried out at 40 kHz.

For the treatments at floating potential, the web passed through slits in the sidewalls of the enclosure at a distance of roughly 3.3 cm from a pair of $7.6\text{ cm} \times 35.6\text{ cm} \times 1.2\text{ cm}$ co-planar electrodes. Treatment gas was admitted through a series of orifices fed by a manifold along a sidewall of the enclosure, producing treatment pressures from 10 to 30 Pa at nitrogen flows of 230 to 915 sccm.

For treatments in the cathode sheath, the web was admitted to the treatment zone through rectangular ducts in an enclosure and conveyed over a rotating stainless steel electrode having a diameter of 12.7 cm and a length of 33 cm. A grounded counter electrode having a radius of curvature of 8.9 cm was positioned concentric with the rotating electrode to form a gap of 2.54 cm. Treatment gas was admitted through a series of orifices fed by a manifold in the ground electrode assembly, producing nitrogen pressures of 13 to 82 Pa at nitrogen flows of roughly 200–1200 sccm. An aluminum dark-space shield was machined to have a slightly larger radius of curvature than the rotating electrode and was placed roughly 0.3 cm above it. The sides of the shield along the web path were spaced from the enclosure walls to form ducts in series with the entrance and exit ducts.

2.2. Surface analysis

Surface chemical changes in the PEN samples were assessed using X-ray photoelectron spectroscopy (XPS). Analyses were performed using a Physical Electronics 5601 photoelectron spectrometer with monochromatic Al K α X-rays (1486.6 eV). The X-ray source was operated with a 2-mm filament at 350 W. Charge neutralization for these insulating polymers was accomplished by flooding the sample surface with low-energy electrons from an electron gun mounted nearly perpendicular to the sample surface (an emission current $\leq 25\text{ mA}$ and a bias voltage $\leq 0.5\text{ eV}$ were used). The pressure in the spectrometer during analysis was typically 3×10^{-9} Torr. For the high-resolution spectra, the analyzer was operated at a pass energy of 11.75 eV. Under these conditions, the full width at half maximum (FWHM) for the individual components of the C_{1s} peak in an untreated

PEN sample varied from 0.8 to 0.9 eV. All spectra were referenced to the C_{1s} peak for the aromatic carbon atoms in the polyester repeat unit, which was assigned a value of 284.6 eV. Spectra were taken at a 45° electron take-off angle, which corresponds to an analysis depth of approx. 5 nm. XPS metrics found to be helpful in assessing changes for various nitrogen treatments are the incorporated nitrogen and the oxygen loss. In addition, the degree of change in the O_{1s} ester doublet and changes in the chemical environment of the incorporated nitrogen were assessed. The details of the C_{1s} spectrum provided additional information concerning the nature of the surface groups formed by plasma treatment. Detailed surface analyses of nitrogen-plasma-treated PEN with the web at floating potential are presented in Ref. [20]. For the purposes of comparing treatment configurations, quantities derived from XPS core-level spectra are tabulated and plotted below.

2.2.1. Results: treatments of stationary samples at various driving frequencies

The run conditions and results for nitrogen plasma treatments at various driving frequencies for stationary PEN samples are listed in Table 1. U denotes untreated PEN, and the letters in the numbered runs correspond to the sample locations in Fig. 5. In the column headings, ν denotes driving frequency, %N denotes the nitrogen content from XPS, N_{1s} centroid denotes the binding energy at the center of

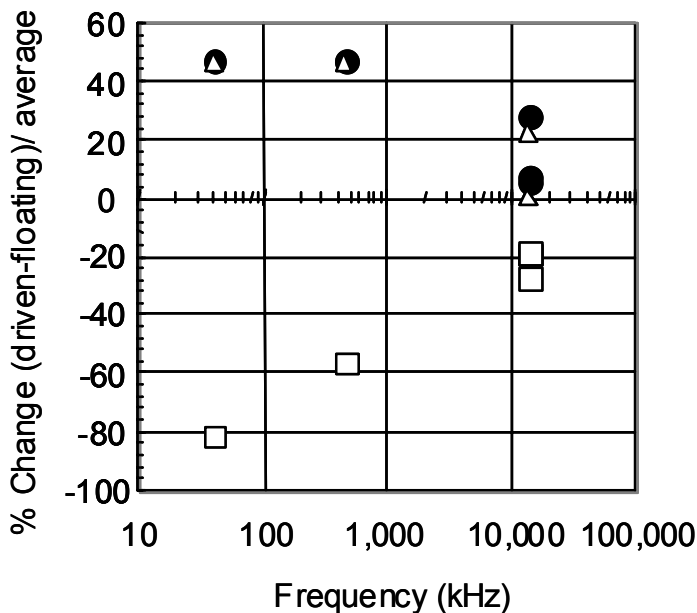


Figure 7. Differences (as a percentage of average value) in nitrogen content (●), oxygen content (□) and ester rearrangement (Δ) as a function of driving frequency for nitrogen plasma-treated PEN samples on the driven (smaller) electrode and at floating potential.

the N_{1s} peak, %O denotes the oxygen content from XPS and Ester rearrangement denotes the degree of rearrangement of the ester portion of the PEN repeat unit (ester rearrangement, as judged from changes in the oxygen doublet of the O_{1s} spectrum is described in Ref. [20]).

From the results shown in Table 1, it appears that the samples in position A (i.e., located on the electrode driven by the power supply) have more incorporated nitrogen, lower N_{1s} binding energy centroids and more oxygen loss than samples located in the other two positions. In general, the samples in position C (i.e., on the grounded coplanar electrode) have the least incorporated nitrogen and least oxygen loss. The differences seen between samples located in position A and position B are plotted in Fig. 7 as a function of driving frequency (except for the binding energy centroid). The graph illustrates that the differences diminish with increasing driving frequency.

Table 1.

Run conditions and XPS results for nitrogen-plasma treatments of stationary PEN samples

Run*	ν (kHz)	Power (W)	Time (s)	%N	N_{1s} centroid (eV)	%O	Ester rearrangement
U	N/A	N/A	N/A	0	N/A	22.2	0
1B	40	100	10	10.4	399.9	22.9	5
1A	40	100	10	16.8	399.0	9.7	8
2B	450	100	15	9.3	399.8	21.1	5
2A	450	100	15	15.0	399.2	11.8	8
2C	450	100	15	6.4	399.5	21.5	4
3B	13600	10	10	8.4	399.7	19.9	4
3A	13600	10	10	11.2	399.5	16.5	5
3C	13600	10	10	8.6	399.8	20.3	4
4B	13600	40	10	15.1	399.8	18.2	5
4A	13600	40	10	16.2	399.5	13.8	5
4C	13600	40	10	13.2	399.7	19.3	5
5B	13600	100	10	17.5	399.6	16.6	6
5A	13600	100	10	18.6	399.5	13.8	6
5C	13600	100	10	16.3	399.7	17.5	6

* U denotes untreated sample; A, B and C refer to positions indicated in Fig. 5.

2.2.2. Results: treatments of moving webs

The simple web treatment device using the co-planar electrode assembly (as described above) was used to obtain dose–response curves at various pressures for samples treated in the cathode sheath. These results could be compared with existing data from pilot-scale treatments of PEN at floating potential. In both cases, various combinations of power and web speed were run at three different pressures.

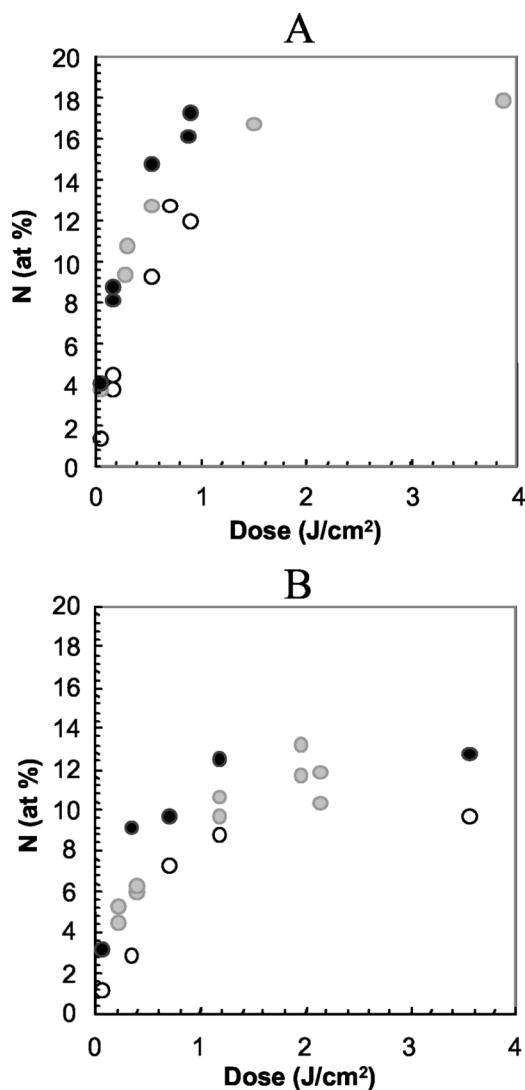


Figure 8. Nitrogen uptake for PEN webs as a function of treatment dose: (A) treatments in the cathode sheath (using a simple web treatment device) and (B) treatments at floating potential (using the pilot-scale apparatus shown in Fig. 6B). Nitrogen pressures in the treatment devices were 6.6 Pa (○), 13 Pa (◐) and 20 Pa (●).

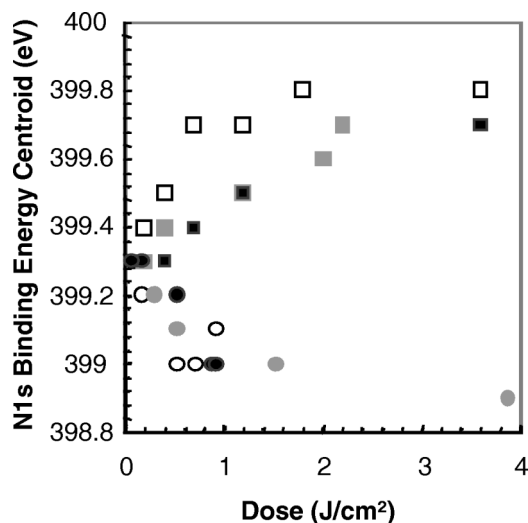


Figure 9. N_{1s} binding energy centroid as a function of treatment dose. Circles: treatments in the cathode sheath (using simple web treatment device). Squares: treatments at floating potential (using the pilot-scale apparatus shown in Fig. 6B). Nitrogen pressures in the treatment devices were 6.6 Pa (white symbols), 13 Pa (gray symbols) and 20 Pa (black symbols).

The treatment dose was taken to be the power per unit width of the treatment device (i.e., in the direction along the web width), divided by the web speed. The data for nitrogen uptake and N_{1s} binding energy centroid as a function of dose are respectively shown in Figs 8 and 9.

The nitrogen uptake for samples treated in the cathode sheath (Fig. 8A) is enhanced relative to that observed for samples treated at floating potential (Fig. 8B). Furthermore, the N_{1s} binding energy centroid shifts to lower values with increasing dose for samples treated in the cathode sheath, in contrast to shifting to higher values with dose for samples treated at floating potential (see Fig. 9).

Poly(ethylene terephthalate) (PET) and PEN have similar nitrogen uptake characteristics when treated at floating potential at 40 kHz using the treater depicted in Fig. 6B. In addition, PET shows the same effects as PEN when treated in the cathode sheath (Fig. 6A); nitrogen uptake is comparably enhanced and the N_{1s} binding energy centroid shifts to lower energy with increased treatment dose.

Nitrogen uptake curves as a function of treatment time for PET at fixed treatment power were obtained using the pilot-scale web treater depicted in Fig. 6A. Similar uptake curves had been previously obtained for PEN [17] using the pilot-scale web treater depicted in Fig. 6B. Uptake curves obtained in this fashion can be fitted to simple kinetic models and allow one to assess the effects of treatment power and treatment pressure on the basic kinetic parameters. The nitrogen uptake curves for PET treated in the cathode sheath, and the previously obtained data for PEN treated at floating potential, are shown in Fig. 10.

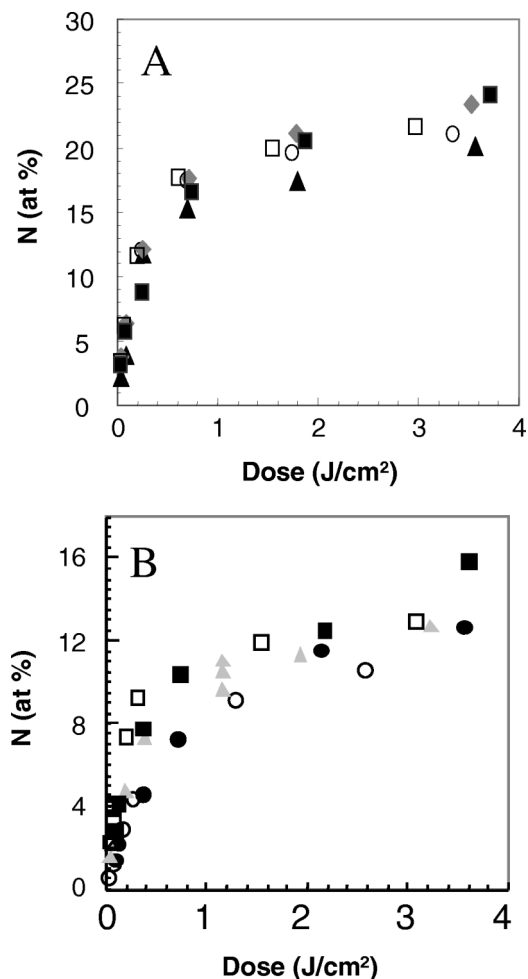


Figure 10. Nitrogen uptake curves obtained at fixed power and varying web speeds. (A) PET treated in the cathode sheath. Treatment conditions: 60 W/13 Pa (○), 600 W/20 Pa (▲), 330 W/48 Pa (◆), 60 W/82 Pa (□), 600 W/82 Pa (■). (B) PEN treated at floating potential. Treatment conditions: 60 W/10 Pa (○), 600 W/10 Pa (●), 330 W/20 Pa (▲), 60 W/30 Pa (□), 600 W/30 Pa (■).

2.3. Analysis

Comparison of PEN treated in the cathode sheath of a capacitively-coupled 40 kHz nitrogen discharge with PEN treated at floating potential in the same discharge reveals enhanced nitrogen uptake, more nitrogen-containing species that have lower N_{1s} binding energies, and increased oxygen loss for PEN treated in the cathode sheath. Furthermore, these differences diminish with increasing driving frequency.

The binding energy shifts suggest a higher degree of amine formation for samples treated in the cathode sheath. N_{1s} binding energies for amine functionalities are typically near 399.1 eV, whereas N_{1s} binding energies for amide functionalities are near 399.9 eV. The enhancement in amine content is consistent with the enhanced ester rearrangement and oxygen loss. See the data in Fig. 7 comparing oxygen content for treatments at 40 kHz in floating and cathode sheath configurations. More detailed studies of the oxygen content as a function of nitrogen plasma treatment dose for moving webs of PEN show that oxygen loss increases with dose in the floating potential configuration [17]. Similar studies for 40 kHz treatments in the cathode sheath configuration, however, reveal a far more dramatic loss of oxygen, consistent with the data presented in Fig. 7. Loss of oxygen lowers the probability of incorporating nitrogen in the form of amide groups.

Because of the relationship between sample position and sheath voltage, and because the driving voltage decreases with increasing driving frequency for comparable applied power (approx. 1000 V at 40 kHz and approx. 100 V at 13.56 MHz for the apparatus used in this work), these results strongly suggest that high sheath voltages are responsible for the differences. These high sheath voltages increase the energy with which ions strike the polymer surface. In addition, they may produce significant shifts in the local species distributions through electron impact processes (secondary electrons are produced at the cathode, in this case the polymer surface, and are accelerated in the high sheath fields). Energetic electrons are capable of producing neutral as well as ionized atomic nitrogen. Furthermore, molecular ions falling in the high-voltage, low-frequency sheaths can produce neutral and ionized atomic nitrogen by dissociative charge exchange collisions.

The data shown in Fig. 10 can be fitted to a simple model of surface saturation [4], where the nitrogen content N of the polyester surface is given by:

$$N = \frac{\alpha \Gamma_I N_{\max}}{\alpha \Gamma_I + \gamma \Gamma_L} (1 - e^{-(\alpha \Gamma_I + \gamma \Gamma_L)t}). \quad (2)$$

Here, Γ_I and Γ_L are respective fluxes of species that result in nitrogen incorporation and nitrogen loss, α is the effective incorporation probability, γ is the effective loss yield, $N_{\max}$ is the maximum possible nitrogen incorporation (based on the number of available sites for incorporation) and t is the treatment time. The terms $\alpha \Gamma_I$ and $\gamma \Gamma_L$ are effectively lumped kinetic terms that represent products of interaction probabilities and species fluxes integrated over the species distributions.

Because the sampling depth of the XPS measurements is greater than the modification depth, the nitrogen uptake curves exhibit a diffusion-limited regime at long times. Nonetheless, the initial linear region of the uptake curves and average saturation values in the diffusion-limited regime can be used to approximate the respective $t = 0$ and long-time behavior of equation (2).

From Fig. 10, it is apparent that the initial uptake rates tend to be somewhat higher, and the saturation values are considerably higher for treatments in the

cathode sheath than for treatments at floating potential. Using a value of 30 at% for $N_{\max}$, the ratio $\alpha\Gamma_I/y\Gamma_L$ (i.e., the ratio of nitrogen uptake to nitrogen loss) can be determined from the initial slopes of the uptake curves (Fig. 10) and their average saturation values. The ratio $\alpha\Gamma_I/y\Gamma_L$ is plotted in Fig. 11 for the two treatment configurations. For the treatments in the floating configuration (Fig. 11A), the ratio $\alpha\Gamma_I/y\Gamma_L$ is in the range 0.5–0.8, with the highest value at the highest treatment pressure and power (30 Pa/600 W). In contrast, the incorporation/loss ratio for the treatments in the cathode sheath (Fig. 11B) increases from 2 to 3 with increasing power, except for the lowest pressures (13–20 Pa), where the ratio

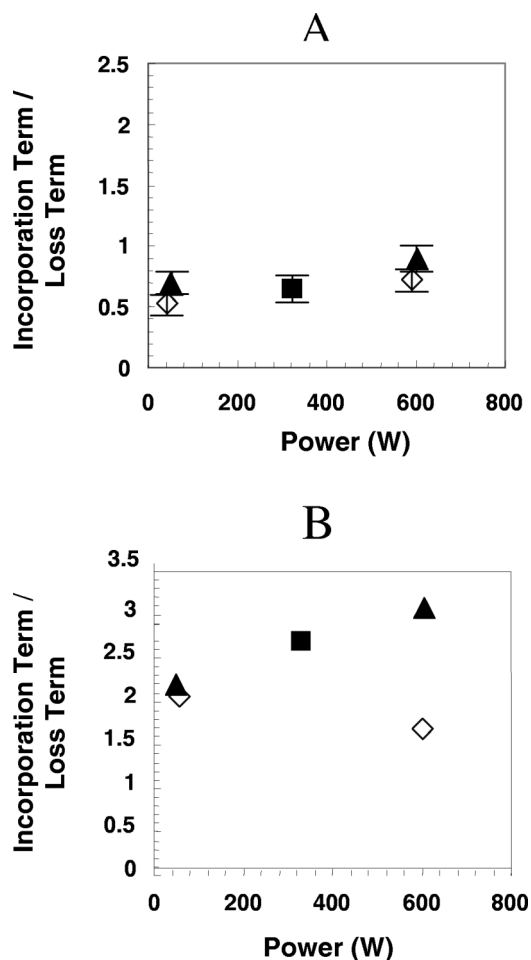


Figure 11. Ratio of incorporation term to loss term as calculated from experimentally observed initial uptake rates and saturation values. (A) Nitrogen plasma treatments of PEN at floating potential at pressures of 10 Pa (◇), 20 Pa (■) and 30 Pa (▲). (B) Nitrogen plasma treatments of PET in the cathode sheath at pressures of 13 Pa (◇), 48 Pa (■) and 82 Pa (▲).

drops from 2 to 1.6 as the power increases from 60 to 600 W. Hence, for both treatment configurations, higher pressures and higher powers shift the uptake kinetics in favor of incorporation processes over loss processes for the polyesters studied. The treatments in the cathode sheath, however, generally have a higher incorporation/loss ratio than those at floating potential. This result is somewhat surprising, as one might expect the increased ion energies to enhance the loss mechanisms considerably.

The diagnostic data in Figs 2 and 3 (applicable to the treatments at floating potential) suggest that the role of applied power is to increase the plasma density and the concentration of dissociated nitrogen. These effects lead to higher fluxes of molecular ions and atomic nitrogen to the polymer surface. In contrast, increasing the pressure has only a small effect on plasma density, while it increases the concentration of neutral atomic nitrogen. The enhanced nitrogen uptake kinetics at high powers and pressures may then be understood as resulting from an increase in species fluxes and an increase in the ratio of the flux of atomic neutrals (and perhaps atomic ions) to the flux of molecular ions. As discussed in Section 1.1, the cause for the importance of the combination of ions and atomic neutrals may be two-step surface reactions (i.e., formation of a surface radical, followed by reaction with atomic nitrogen) or formation of atomic nitrogen ions by electron impact in the plasma. In the case of the treatments in the cathode sheath, additional processes occurring in the sheath itself may generate important species (for example, dissociative charge exchange between molecular nitrogen ions and neutrals to produce atomic nitrogen species).

Implicit in this discussion is the assumption that atomic nitrogen (neutral, ionized, or some combination) will produce higher saturation values of incorporated nitrogen than will molecular ions of nitrogen alone. This assumption is consistent with observations of nitrogen incorporation in poly(methyl methacrylate) surfaces exposed to low-energy (<10 eV) N^+ and N_2^+ [21]. In that work, Gröning *et al.* found that atomic ions produced considerably more nitrogen incorporation than did molecular ions. It is also consistent with observations that polyester surfaces exposed to energetic (approx. 400–1000 eV) N_2^+ (from ion sources) exhibit low saturation values (approx. 2 at% or less) of incorporated nitrogen, as compared to saturation values obtained by exposure to nitrogen plasmas [17]. As molecular nitrogen ions must dissociate upon impact to produce nitrogen incorporation, their loss yields may be significantly larger than their incorporation probabilities. Atomic neutrals and atomic ions of nitrogen, by contrast, may both have incorporation probabilities comparable to their loss yields.

It should be noted that in the case of the treatments at floating potential, increasing the nitrogen pressure significantly above 30 Pa results in a reduced degree of nitrogen uptake. In contrast, treatments in the cathode sheath exhibit this reduced uptake near pressures of 90 Pa. These results are consistent with a decrease in the ratio of the flux of atomic neutrals to the flux of molecular ions with increasing pressure, thereby lowering the effective ratio of incorporation to loss.

The results are also consistent with reduced concentrations of atomic nitrogen from collision processes at higher pressures. The wider useful pressure range for treatments in the cathode sheath is consistent with the notion that the species responsible for surface modification are generated within or near the cathode sheath and cross the sheath to reach the polymer surface, whereas for treatments at floating potential, they must cross the bulk plasma to reach the polymer surface. The relative pressure ranges are consistent with the relative dimensions of the high-voltage cathode sheath and the plasma zone between the cathode and the web at floating potential.

3. CONCLUSIONS

Plasma process parameters and treatment configuration determine the concentrations and energy distributions of species impinging a polymer surface during the plasma-modification process. Geometrical aspects of the treatment configuration (such as placement of sample with respect to the dominant cathode) can have a considerable effect on the nature of polymer surface modification in capacitively coupled radiofrequency plasmas. For example, significant differences are observed between polyester samples treated in the cathode sheath and those treated at floating potential in low-radiofrequency capacitively-coupled nitrogen plasmas. In particular, the incorporation of nitrogen, loss of oxygen, and the degree of amine content relative to amide content are enhanced in the cathode sheath. These differences diminish with increased driving frequency, suggesting that sheath potential is an important factor.

The relationships between the external plasma parameters and the species concentrations and distributions are generally quite complex. Nonetheless, simple analysis of the time dependence of surface modification can provide a basis for comparing different treatment configurations or different processes using the same treatment device. Simple analysis of nitrogen uptake using lumped kinetic terms for nitrogen uptake and loss suggests that surface reactions involving species distributions from the plasma and chemical groups or molecules in the polyester surface favor incorporation mechanisms over loss mechanisms in the cathode sheath of low-radiofrequency nitrogen plasmas. In contrast, for samples at floating potential, the loss mechanisms are favored over the incorporation mechanisms.

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