Atmospheric Pressure Plasma Treatment of Polyethylene via a Pulse Dielectric Barrier Discharge: Comparison Using Various Gas Compositions Versus Corona Discharge in Air

JOHN B. LYNCH,¹ PAUL D. SPENCE,^{2,*} DAVID E. BAKER,¹ TIMOTHY A. POSTLETHWAITE¹

¹ Cryovac North America, Sealed Air Corporation, Columbia, Maryland 21044-4098

² Textille and Nonwoven Development Center, University of Tennessee, Knoxville, Tennessee 37996

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ABSTRACT: Modification of polyolefin surfaces is often necessary to achieve improved printability, lamination, etc. Although corona discharge and flame treatments can produce the higher surface energy needed for these applications, the properties of the resulting surfaces are not always optimal. Atmospheric pressure plasma is a surface modification technique that is similar to corona discharge treatment, but with more control, greater uniformity, and higher efficiency. Using an atmospheric pressure plasma unit with a dielectric barrier discharge generated using an asymmetric pulse voltage, the effects of different gases, powers, and linespeeds on polyethylene surface treatment were studied. Our results show that atmospheric pressure plasma can be used to achieve higher long-term wettability, higher surface oxygen and nitrogen, and a greater range of surface chemistries with better robustness versus standard corona treatment. Atomic force microscopy results suggest significant differences in the mechanism of surface functionalization versus etching and ablation depending on the gases used. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 319–331, 1999

Key words: plasma; polymer; wettability; surface; XPS; AFM; contact angle; acid/ base; atmospheric pressure plasma; surface energy

INTRODUCTION

Although polyolefins exhibit many valuable bulk properties at a low cost, they have low surface energy (i.e., low wettability), making them difficult to print or laminate. Flame and corona discharge treatments have been used to increase the surface energy for printing and lamination; however, there are issues with flame and corona discharge treatments (CDT) including longevity, robustness, homogeneity, and process control. The wettability of corona discharge-treated surfaces is limited by competing reactions such as chain scission and surface ablation. Increased robustness and optimized surface chemistry from plasma treatments would aid in achieving higher surface wettability over a longer period of time.

Plasma treaters are generally thought of as operating in low-pressure conditions (*vide infra*) to achieve a stable plasma with a variety of gases doped into the reaction chamber. The use of different gases allows for increased control of the final surface chemical and physical properties. Low-pressure plasma (LPP) treatments are well known for their ability to impart a variety of surface chemistries to polymers through the use of various gases.^{1–5} Examples include air,^{6,7} nitrogen,^{8,9} ammonia,^{10,11} carbon dioxide,¹² noble

Correspondence to: J. B. Lynch.

^{*} Present address: Cryovac North America, Sealed Air Corp., Duncan, SC 29334.

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gases,¹³ nitrogen oxides,¹⁴ and oxygen.^{15–19} The acid/base properties resulting from these treatments are important for adhesives.²⁰

The equipment for plasma treatment of continuous polymer webs at low pressure is costly and requires the upkeep of large vacuum systems. Atmospheric pressure plasma affords the control of surface chemistry through the choice of reactive gases, but without the need for vacuum conditions.^{21–24} A continuous atmospheric pressure plasma treater using a dielectric barrier discharge (APP-DB) has been developed at the Textile and Non-woven Development Center (TAN-DEC, University of Tennessee, Knoxville) for the treatment of nonwoven polymers. Stable plasma under atmospheric conditions is made possible through the use of specific gas mixtures, gashandling systems, impedance matching, pulse shapes, and unique electrode designs.²⁵

LPP provides a surface treatment with the highest degree of control and efficiency, mostly because it is performed at low pressure. Ambient pressures present problems with increased collisions, which lead to dissipation of the plasma effectiveness, especially in air. The goal of the development of atmospheric pressure plasma is to give the control, versatility, and effectiveness of LPP under the more economical ambient pressure conditions of corona treatment.

Relative to CDT, APP-DB gives higher electricfield uniformity, versatility, and control, similar to LPP, but without the need for a vacuum. Although one can obtain a corona in many types of gases, conventional corona treaters do not allow for economical and effective operation in anything but air. One unique aspect of the atmospheric pressure plasma electrode design is the controlled gas delivery for increased versatility and efficiency. Proper electrode and power supply designs, along with controlled gas flow, help minimize or eliminate the filamentary discharges (or "streamers") that characterize a corona discharge and often lead to nonuniform surface treatment and/or pinholes. The present study compares APP-DB with a commercial corona discharge treater to determine its relative value based on degree of wettability achieved, level of functionalization, degree of substrate damage, longevity of the treatment, and robustness of the treated surface.

The plasma-treatment process conditions that govern the nature of the resulting polymer surface are the flux of the reactive species (a relationship of power and treatment time), gas composition, polymer type, pressure or gas flow, temperature, humidity, and nature of the electrodes used. In this study, gas, power, and linespeed (treatment time) were varied for comparison with the CDT of polyethylene. A designed study was undertaken whereby four different gas mixtures with or without helium (air, CO₂/O₂/He, O₂/He, and NO/N_2) were used for treatment at high and low power with high and low treatment times (i.e., slow and fast linespeeds). Every effort was made to keep other variables constant, but there are likely some secondary effects that introduce uncertainty into the data. This report summarizes the results of that designed study. A future report will be issued with an in-depth study of the effects of other plasma-treatment factors on the resulting surface chemistry.

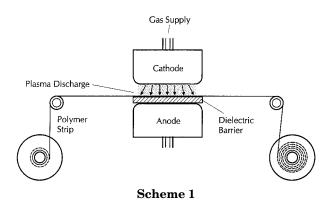
Treated samples were studied by contact angle (CA), X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM), and surface acidity/basicity. The water CA was used to follow the robustness and longevity. Since some applications require that the resulting surfaces have a reasonable shelf life (greater than 1 month), the surface wettability was monitored over time as part of the study. It is important to note that many studies reported in the literature report wettability immediately after treatments (within 1 h) when the wettability is at its highest and the surface is still reactive. Some reports do not make mention of the age of the sample at analysis.

The "robustness" of the resulting surface (i.e., resistance to being rinsed off) was also monitored because some applications require that the newly created surface polar species be well anchored to the bulk of the polymer. The water CA was used as a measure of aging since it appears to be the most sensitive parameter to changes in the surface.

EXPERIMENTAL

Materials

Polyethylene films were extruded as 3-in. tapes from Dowlex 3010 (Dow Chemical Co., Midland, MI). The gases (He, O_2 , CO_2 , 10% NO in N_2) used for the plasma studies were of the highest possible purity. For CA and robustness studies, 18 MOhm Milli-Q water was used. High-purity formamide and diiodomethane were used for the acid/base analyses. The diiodomethane was stored in the dark. All treated films were stored at



room temperature in either roll form or folded over (treated side on the inside) and placed in plastic bags. Care was taken during handling to ensure no contamination.

Atmospheric Pressure Plasma Treatment

Atmospheric pressure plasma treatments were performed at TANDEC at the University of Tennessee using a specially designed system for treating continuous webs at high powers with strict control of the atmospheric composition (monitored by mass spectrometry) and gas flow rates. A uniform, one-atmosphere plasma suitable for plasma processing of thin films and webs was generated using a dielectric barrier discharge. The discharge used for this study (see Scheme 1) consisted of two cup-shaped electrodes approximately 11 cm in diameter, with the lower electrode covered by a dielectric insulator. The electrodes and supply and take-up reels were housed inside a stainless-steel enclosure to allow containment and recycling of the process gas. The electrode gap was typically 1 mm, with the polymer translated through the discharge zone at a uniform rate using a feedback regulated stepper motor.

With the application of a suitable, high-voltage signal to the discharge electrodes, the working gas between the electrodes can be made to break down and produce a uniform, small volume, weakly ionized, nonequilibrium plasma rich in excited and electronic states. These excited-state species serve to activate and functionalize the polymer surface. The number density of these species is strongly dependent on the discharge power of the treatment zone.

The power density, P, used (dependent on the atmospheric composition) is expressed in watts (power in the plasma monitored using an *in situ* power meter) per cubic centimeter, W/cm^3 :

$$P = \frac{W}{Ad}$$

where A is the area of the discharge (9.6 cm^2) and d is the gap distance (0.1 cm). Treatment times are calculated based on the linespeeds and the length of the treater head (11 cm) to give the total residence time of a particular spot in the plasma. Immediately after treatment, the treated samples were overnight mailed for surface analyses and aging studies.

Corona Treatment

Corona treatment was performed using an Enercon system that employs a 14-in. Bare Roll Treater Station (Model TL11V-150), a 1 kW power supply, and a custom-built web handling system with tension control for varying the linespeed. The power density, P, used (dependent on the atmospheric composition) is expressed as the power at the electrode in watts (estimated from an Enercon readout) per cubic centimeter, W/cm^3 :

$$P = \frac{W}{Ad}$$

where A is the surface area of the electrode $(3 \times 33.5 \text{ cm})$ and d is the gap distance (0.15 cm). Treatment times are calculated based on the linespeeds and the length of the treater head (3 cm) to give the total residence time of a particular spot in the plasma.

Contact Angles

CA measurements were performed using a CAM-Micro Tantec system. Strips $(1 \times 5 \text{ cm})$ of the polymer film from the center of the web were cut and mounted on copper plates (to reduce static charging effects) using two-sided tape to ensure a flat surface. Multiple readings (3–8) were recorded and averaged to obtain the results listed in the tables; variations were generally less than 2°.

X-ray Photoelectron Spectroscopy

XPS data were obtained in a Physical Electronics Model PHI5600*ci* spectrometer using a monochromated Al K_{α} (1486.6 eV) X-ray source, with a 45° take-off angle. Data were acquired with the X-ray source operated at 250 W of power. The analysis area was 800 μ m in diameter. Quantitative analysis (generally considered accurate to $\pm 10\%$, relative) was performed by analyzing XPS peak areas using atomic sensitivity factors provided by Physical Electronics Inc. The binding energy analysis was referenced to the C 1s signal of the aliphatic hydrocarbon at 284.8 eV. Sample charging was neutralized using an electron flood gun. The %C, %O, and %N are atomic concentrations for about the first 5 nm of the surface. The samples were 2–10 days old when the analyses were done.

Atomic Force Microscopy

AFM data were obtained with a Digital Instruments Nanoscope III microscope in ambient conditions operating in either a tapping mode (using single-crystal silicon cantilevers) or a minimized force contact mode (using silicon nitride cantilevers). Images obtained in either mode were essentially identical. Image processing generally consisted of a real-time plane-fit, an off-line flatten (second order), and a contrast enhancement. Several areas were imaged to ensure the validity and uniformity of the results. Images presented are representative of multiple areas analyzed.

Surface Tension Parameters/Acid and Base

Surface energy (or surface tension of liquids), γ , can be broken up into two primary components²⁶:

$$\gamma = \gamma^{\rm LW} + \gamma^{\rm AB}$$

where γ^{LW} is the Litshitz–van der Waals component due to nonspecific dispersive interactions and γ^{AB} is the acid/base component encompassing specific interactions such as dipolar, induction, and hydrogen-bonding. Further,

$$\gamma^{AB} = 2 \sqrt{\gamma^+ \gamma^-}$$

where γ + is the Lewis acid component and γ^{-} is the Lewis base component.

Calculation of Surface Tension Components $(\gamma^{LW}, \gamma^+, \text{ and } \gamma^-)$

The following general equation is used to determine the surface-energy components of a solid. CA measurements $(\theta_1, \theta_2, \theta_3)$ are made with three liquids (methylene iodide, water, formamide) on the solid surface and the known liquid surfacetension components are used to solve three simultaneous equations for each liquid:

$$\gamma_{\lambda}(1 + cos \ \theta) = 2(\sqrt{\gamma_{\lambda}^{LW}\gamma_{S}^{LW}} + \sqrt{\gamma_{\lambda}^{+}\gamma_{S}^{-}} + \sqrt{\gamma_{\lambda}^{-}\gamma_{S}^{+}}$$

Caution must be taken in the use of the results from these calculations since small errors in the CA, even as low as 2°, can have large effects on the values obtained. Thus, this information is used to give only a general idea of the surface acidity and basicity.

Aging and Robustness

Aging studies were based on changes in the water CAs. For samples that changed dramatically, XPS was also used to look for differences (e.g., contamination); no significant changes in the XPS were recorded. Robustness (i.e., whether or not the surface can be rinsed off) studies were performed by soaking the samples in either roomtemperature or 70°C water with gentle agitation for 2 min. The samples were then air-dried before analyzing via water CAs.

RESULTS

Treatment conditions are listed in Table I. Efforts were made to keep conditions similar between different gases and powers; however, some conditions are interrelated. For example, the mean field strength correlates very strongly with the watt density. Since dosage and gas composition were determined to be the most significant factors, these were used to identify and graph the samples throughout the article.

Surface analytical results are listed in Tables II–IV and plotted in Figures 1–5. Besides gas composition, dosage (J/cm^3), which is defined as a product of the watt density (W/cm^3) and treatment time (seconds), was seen to be the most important factor. It is generally seen that higher dosages lead to higher functionalization and lower water CAs within certain gas mixtures; however, when ablation becomes the predominant process at even higher dosages, the functionalization plateaus and CAs begin to rise again.

Effect of Dosage and Gas on Surface Oxygen and Nitrogen Content

Surface oxygen and surface nitrogen are plotted versus dosage and gas in Figures 1 and 2, respec-

Gas	Treat Time (s)	Watt Density (W/cm ³)	Dosage (J/cm ³)	Flow Gas 1 (Lpm)	Flow Gas 2 (Lpm)	Flow He (Lpm)	Electrode Temperature (°C)	Mean Field Strength (kV/cm)	Pulse Rise (µs)
Air Corona	0.5	4	2	n.a.ª	n.a.	n.a.	n.a.	n.a.	n.a.
	0.5	16	8	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
	0.5	40	20	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Air	0.5	3.9	2	15	n.a.	n.a.	42	24	0.88
	0.5	15	7.3	15	n.a.	n.a.	42	40	1.40
	3	3.9	12	15	n.a.	n.a.	42	24	0.88
	3	15	44	15	n.a.	n.a.	42	40	1.40
CO ₂ /O ₂ /He	0.5	4.9	2.5	8.1	2.9	1.4	43	29	1.28
	0.5	13	6.5	8.1	2.9	1.4	43	41	1.34
	3	4.9	15	8.1	2.9	1.4	43	29	1.28
	3	13	39	8.1	2.9	1.4	43	41	1.34
NO in $\rm N_2$	0.5	10	5	7	n.a.	n.a.	40	31	0.80
	0.5	14	7.2	7	n.a.	n.a.	40	36	1.00
	3	10	30	7	n.a.	n.a.	40	31	0.80
	3	14	43	7	n.a.	n.a.	40	36	1.00
O ₂ /He	1	13	13	2.8	n.a.	5.4	33	37	0.92
-	5	13	67	2.8	n.a.	5.4	33	37	0.92

Table I Treatment Conditions for APP and CDT-Treated Polyethylene

^a Not applicable.

tively. The surface oxygen concentration increases until 10-20 J/cm³ and then plateaus. The plateau indicates where surface ablation becomes

Table II	XPS Results of Surface-Treated	d
Polyethy	ene Samples	

Gas	J/cm ³	% C	% O	% N
Air Corona	2	89	11	_
	8	87	13	
	20	85	15	0.6
Air	2	88	12	0.4
	7.3	85	15	0.5
	12	81	18	0.9
	44	81	18	0.9
CO ₂ /O ₂ /He	2.5	93	7	0.2
	6.5	89	11	0.1
	15	85	14	0.7
	39	82	17	0.9
NO in N_2	5	87	10	2.6
	7.2	90	8	2.1
	30	78	18	4.2
	43	79	17	4.1
O ₂ /He	13	87	13	0.1
-	67	85	15	0.1

a major process. Dosage is the single most important factor under the conditions that were explored, but the gas type and treater type also play significant roles.

APP-DB with air results in more oxygen incorporation than does CDT in air, suggesting more efficient functionalization of the surface by APP-DB. Both treatments in air incorporate more oxygen, especially at low dosages, than do CO_2/O_2 and O_2 . It is important to note that both the CO_2/O_2 and O_2 plasmas involved the presence of He to facilitate a stable, uniform plasma at 760 Torr; the effect of the He on the efficiency of functionalization is not known. Despite a slow start, the NO/N₂ treatment is able to achieve the highest levels of functionalization, possibly due to lower levels of ablation.

The flow rate of the reactive gases (i.e., not He) also seemed to be an important factor in determining the amount of oxygen incorporated (graph not shown). One possibility is that more efficient removal of volatile organic species and other interfering species allows for more interactions of the reactive species with the polymer substrate. However, more studies would have to be done to explore this.

Gas	Dosage (J/cm ³)	CA ^a -1 (Days)	CA-7 (Days)	CA-30 (Days)	CA-90 (Days)	$\Delta \mathrm{RT}$ Wash ^b	$\Delta 70^{\circ} \mathrm{C}$ Wash ^c	$\gamma^{(+)}$	$\gamma^{(-)}$
Air Corona	2	72	71	75	79	5	9	0.1	11
	8	68	73	68	77	13	13	0.2	7
	20	59	70	72	72	10	10	0.5	9
Air	2	69	74	76	82	2	-4	0.3	6
	7.3	64	66	71	75	2	-3	0.03	11
	12	71	61	67	79	2	-9	0.1	13
	44	63	66	64	65	5	-10	0.4	14
CO ₂ /O ₂ /He	2.5	80	73	77	86	16	13	0.01	7
	6.5	72	76	76	88	7	4	0.1	9
	15	63	71	79	89	7	7	0.5	3
	39	72	68	70	69	9	1	0.2	9
NO in N_2	5	74	76	80	83	2	$^{-2}$	0.1	8
	7.2	79	82	82	84	3	3	0.1	7
	30	71	71	76	74	-2	-2	5	0.6
	43	74	76	80	80	2	-5	4	0.2
O ₂ /He	13	68	72	76	75			0.5	5
	67	65	66	69	77			0.1	12

Table III CA Studies of Surface-Treated Polyethylene

^a Water CA in degrees.

 $^{\rm b}$ Change in water CA after a water wash at room temperature. $^{\rm c}$ Change in water CA after a water wash at 70°C.

The surface nitrogen concentrations are highest for those samples that were treated with nitrogen-rich, O_2 -deficient plasmas, that is, NO/N₂, followed by APP-DB with air as a distant second. The rest show very low nitrogen incorporation, possibly due to the higher reactivity of oxygen

Gas	J/cm ³	$_{ m CH}^{\%}$	% CO	% C==0	% 0-C==0	% 398 eV	% 401 eV	% 403 eV	$^{\%}_{ m 407~eV}$
Air Corona	2	75	9	4	2				
	8	73	8	3	3		_		
	20	65	12	4	3	0.1	_	_	0.5
Air	2	74	11	4	1	_	_	_	_
	7.3	70	8	4	3	_		_	
	12	65	8	5	3	0.3	0.4		0.2
	44	66	8	3	4	0.2	0.6	—	0.2
CO ₂ /O ₂ /He	2.5	82	8	3	1	_	_	_	_
	6.5	74	12	2	1	_	_	_	
	15	69	10	3	3	0.5	0.3	_	
	39	67	9	2	4	0.4	0.5	—	—
NO in N_2	5	70	14	3	1	0.8	0.3	_	1.4
	7.2	64	22	4	1	0.6	0.3	0.2	1.0
	30	53	16	5	4	1.6	0.6		2.0
	43	62	13	2	2	0.7	1.1	0.3	2.1
O ₂ /He	13	75	8	2	3	_	_	_	_
	67	67	11	3	3	—	—	—	—

Table IV High-Resolution XPS Results of Surface-Treated Polyethylene Samples

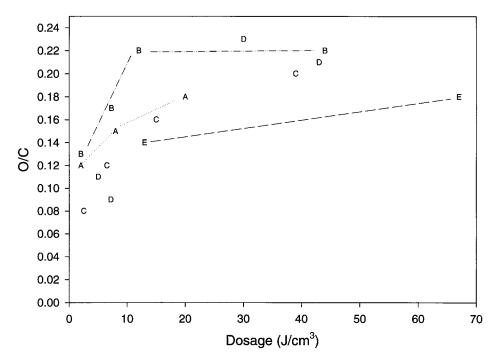


Figure 1 Surface oxygen-to-carbon ratio versus dosage with different gas compositions, where (A) is CDT in air, (B) is APP-air, (C) is APP-CO₂/O₂/He, (D) is APP-NO in N_2 , and (E) is APP-O₂/He. Lines were drawn to connect points for (A), (B), and (E) to guide the reader.

versus nitrogen in a plasma. It is interesting to note that APP-DB is able to incorporate more nitrogen than is CDT with air, suggesting that APP-DB more efficiently produces reactive nitrogen fragments than does CDT.

Long-Term Wettability Versus Surface Composition and Gas Type

Figure 3 shows the relationship between the cosine of the water CA 30 days after treatment versus the total surface oxygen and nitrogen content. There is nearly a linear relationship for all treater types and gases except NO/N_2 . The high surface oxidation and nitrogenation of the polyethylene by APP-DB with NO/N $_2$ does not lead to high long-term wettability. Since aging and robustness do not appear to be issues with these samples (vide infra), it is unclear what the reason(s) for this difference is. One possibility is that the polar functionalities are trapped just below the surface that the CA probes. Another possibility is that the nature of the oxygen and nitrogen species formed are not as hydrophilic or interact with each other so strongly that they are not available for interaction with the water.

The surface acidity (γ^+) and basicity (γ^-) are fairly similar for most samples within the reproducibility of the three solvent methods. The notable exceptions are the high-dosage, APP-DB NO/ N₂-treated samples, which show a dramatic increase in surface acidity with a subsequent reduction in surface basicity. These samples have the highest levels of nitrate species by high-resolution XPS (*vide infra*), which may explain this finding.

Aging and Robustness of Treated Polyethylene Samples

Table II lists the water CAs 1, 7, 30, and 90 days after treatment as a way of monitoring the aging of the treated surfaces. Most samples show changes less than 10°. Changes are more likely as the 1-day CA drops below 70°, as might be expected due to the higher surface energy. Some noteworthy samples are the high-dosage samples of APP-DB containing O_2 where CAs below 70° were maintained. This may be due to much thicker zones of functionalization such that the polar species have nowhere else to go. The lack of additives and the nonpolar nature of the bulk are

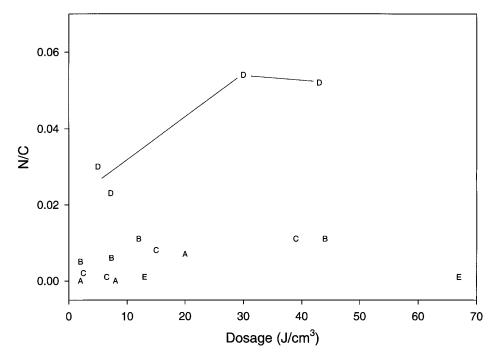


Figure 2 Surface nitrogen-to-carbon ratio versus dosage with different gas compositions, where (A) is CDT in air, (B) is APP-air, (C) is APP-CO₂/O₂/He, (D) is APP-NO in N₂, and (E) is APP-O₂/He. A line was drawn to connect the points for (D) to guide the reader.

the likely reasons for none of the samples returning to the original CAs of the untreated polyethylene (102°) .

Surface Composition by High-Resolution XPS

The results from high-resolution XPS analysis of the treated surfaces are listed in Table IV. The results are listed as absolute percents of the overall surface. The assignments are discussed below.

C 1s Spectra of Oxygenated Polymer Surfaces

High-resolution C 1s spectra were generally peak fit to four or less constituents (Fig. 4). The lowest binding-energy component, ascribed to aliphatic hydrocarbon, was set to a binding energy of 284.8 eV. The higher binding-energy components were ascribed to -C-O- (e.g., alcohol, ether, ester, or hydroperoxide) at \approx 286.0–286.5 eV, C=O (e.g., aldehyde, ketone) at \approx 287.5–288.0 eV, and O-C=O (e.g., carboxylic acid, ester) at \approx 288.8– 289.3 eV.²⁷ Plasmas that led to nitrogen incorporation undoubtedly contributed to the higher binding-energy C 1s shoulder, but total O and N surface concentrations suggested that oxygenated species were the major component in all the samples.

Figure 4 shows the C 1s spectra of (a) an untreated polyethylene control and (b) an APP-DB treated (air, low power, low linespeed) polyethylene sample. The polyethylene control spectra consists of a single peak at 284.8 eV, assigned to the aliphatic hydrocarbon C 1s. The treated polyethylene surface also displays a major component at 284.8 eV as well as three higher binding-energy minor components at 286.3, 287.6, and 289.1 eV. These are ascribable to -C-O-, C=O, and O-C=O species, respectively, as described above. These species result from surface oxidation of the polymer film in the plasma.

Besides small variations with the dosage, the carbonyl-containing species do not vary much between the different gases. The higher level of organic nitrogen is probably the reason for the higher CO (CN) species in the NO/N₂-treated samples.

N 1s Spectra of Nitrogenated Polymer Surfaces

High-resolution N 1s spectra were generally fit by as few as two and as many as four components (Fig.

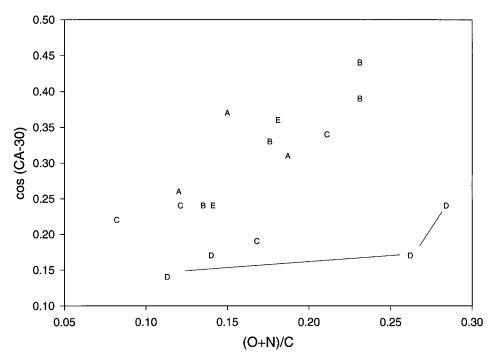


Figure 3 Wettability (i.e., $\cos \theta_{H_2}$ 0) 30 days after treatment versus dosage with different gas compositions, where (A) is CDT in air, (B) is APP-air, (C) is APP-CO₂/O₂/He, (D) is APP-NO in N₂, and (E) is APP-O₂/He. A line was drawn to connect the points for (D) to guide the reader.

5). All spectra displayed a low binding-energy component that was generally fit to two components, the first around 399.5–400.5 eV, ascribable to species such as $-C-NH_2$ or $-C-C\equiv N$ and the second around 400.5–401.5 eV, attributable to functionalities like $-CONH_2$ or $-CONH^{.28}$ Several higher binding-energy (\geq 403 eV) N 1s signals were occasionally seen, these being the major nitrogen components on the surfaces treated with nitrogen-containing plasmas. These peaks can be ascribed to species containing directly oxidized nitrogen such as nitrites (around 405–406 eV) and nitrates (around 407–408 eV).²⁹

Figure 5 shows a typical N 1s spectrum of a NO/N_2 atmospheric pressure plasma (low power, low linespeed)-treated polyethylene sample. As discussed above, the lower binding-energy signal was fit to two components at 399.5 and 400.7 eV. The highest binding energy signal (fit to a single peak at 405.8 eV) is ascribable to a nitrite. Occasionally, a minor component is seen around 403 eV, the identity of which is unknown at this point. Several of the air plasma-treated films that showed nitrogen incorporation had minor components in the 407–408 eV range, likely corresponding to nitrites or nitrates.

For those samples with significant levels of nitrogen, the nature of the nitrogen is predominantly reduced (e.g., amines, amides). The exception is the NO/N₂-treated samples, especially at high dosages, which show a significant level of nitrates.

Atomic Force Microscopy

AFM was employed to examine the morphological changes induced on polyethylene by atmospheric pressure plasma as well as corona discharge. It is known that polymer surface treatment with coronas and plasmas can result in both surface crosslinking and chain scission. These treatments have also been shown to lead to changes in the polymer surface morphology, especially at very high dosages.^{30,31} Based on observations from these results, it has been hypothesized that the low molecular weight organic material (LM-WOM), which results from chain scission, coalesces to form mounds or droplets on the surface. Representative $5 \times 5 \ \mu m$ AFM images are shown in Figure 6(A–K).

In general, mound formation was seen at high dosages (greater than about 15 J/cm³, see

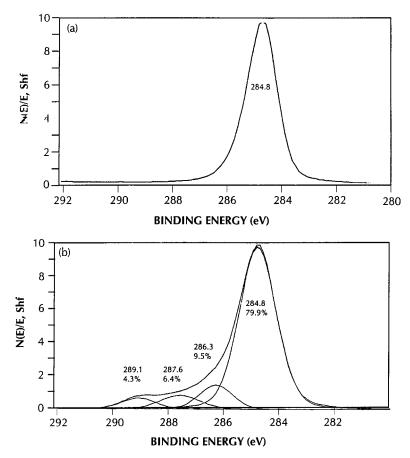


Figure 4 C 1s spectra of (a) untreated and (b) APP-air-treated polyethylene. Fits shown in (B) are expressed in percent of total carbon peak.

Images C, E, G, K) on all treatments (plasma and corona) with the exception of NO/N_2 plasma. Treatment with NO/N_2 leads to the formation of ridges on the polymer surface at high and low dosages (images H and I). APP-DB O_2 /He treatment at low dosages appears to etch the surface (image J), while both low-dosage air treatments suggest a "melting" of the original features (images B and D). The low-dosage CO_2 / O_2 /He treatment leads to a "pebbly" surface (im-

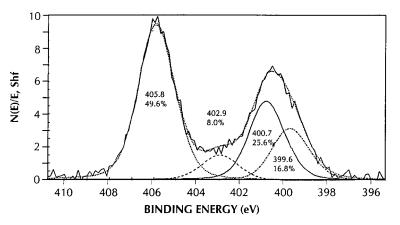


Figure 5 N 1s spectra of APP-NO in N_2 -treated polyethylene. Fits shown are expressed in percent of total nitrogen peak.

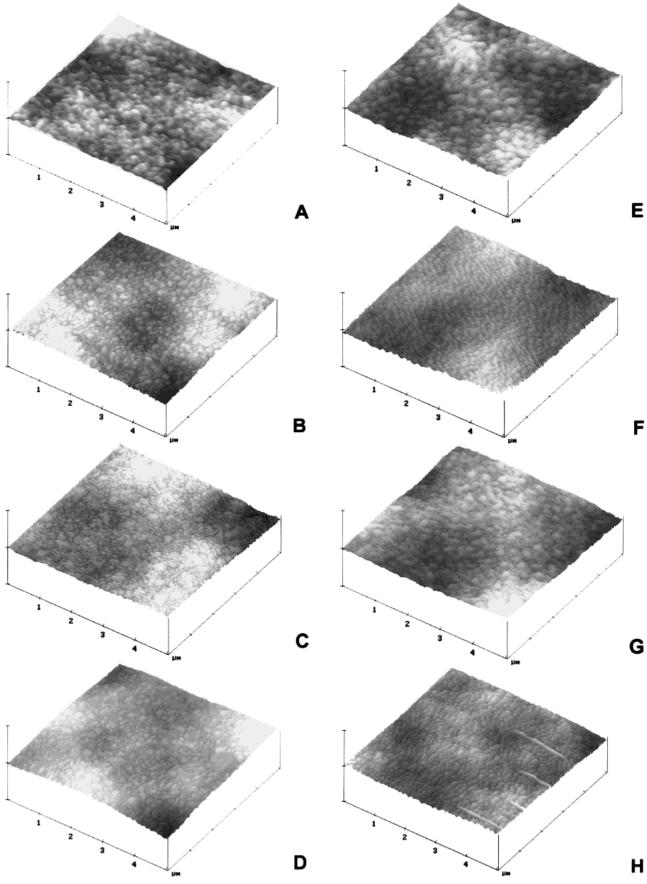


Figure 6 (Continued on next page)

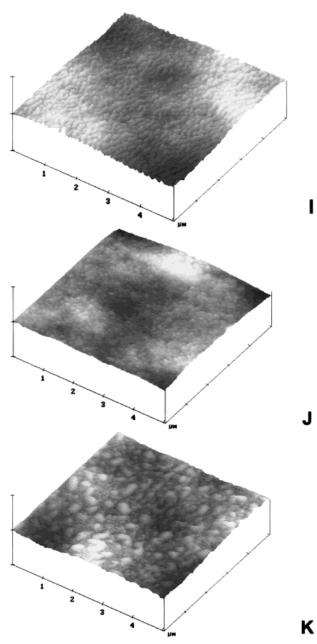


Figure 6 AFM images $(5\mu \text{m x and y}, 200\text{nm z})$ of treated and untreated polyethylene, where (A) is untreated, (B) is CDT in air at 8 J/cm³, (C) is CDT in air at 20 J/cm³, (D) is APP-air at 12 J/cm³, (E) is APP-air at 44 J/cm³, (F) is APP-CO₂/O₂/He at 15 J/cm³, (G) is APP-CO₂/O₂/He at 39 J/cm³, (H) is APP-NO in N₂ at 5 J/cm³, (I) is APP-NO in N₂ at 5 J/cm³, (J) is APP-O₂/He 30 J/cm³ and (K) is APP-O₂/He 67 J/cm³.

age F). The differences in morphology after surface treatment further support variation in the relative amounts of ablation, chain scission, and other functionalization.

CONCLUSIONS

Using an atmospheric pressure plasma (APP-DB) treater developed at the University of Tennessee, polyethylene was treated under a range of conditions to investigate the extent of surface chemistries possible. Specifically, four gas mixtures (dry air, O_2 /He, CO_2/O_2 /He, and NO/N_2) were employed at atmospheric pressure in a dielectric barrier, parallel-plate plasma treater at high and low power and high and low linespeeds. The wettability, polar surface tension components, surface atomic concentration and bonding, and morphology of the resulting polymer surfaces were analyzed with static CA, XPS, and AFM.

Our results show that

- Atmospheric pressure plasma (APP-DB) provides more control over the final surface chemistry and also higher efficiency relative to CDT.
- The resulting surface chemistry is strongly dependent on the gas used in the plasma and the dosage.
- Using APP-DB, more wettable surfaces were produced than by CDT; under the right conditions, these wettable surfaces are also more robust.

Future studies will involve further investigations of specific gas combinations such as NO/N_2 and with other polymers in order to better understand the chemistry involved.

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