Preparation and Characterization of Functionalized Polyethylene Surfaces

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ABSTRACT: We describe a procedure to modify the surface of polyethylene (PE) film using a combination of gas discharge and wet chemical techniques. This method generates high densities (10^{14}–10^{16} cm^{-2}) of a specific functionality, largely unaccompanied by other groups, in a 50–100-Å surface layer. The topography of the polymer surface remains unchanged after treatment and functions as an effective starting material for subsequent derivatization by standard synthetic chemical reactions. A plasma of either oxygen, water, or hydrogen is generated under comparable experimental conditions. In all cases a 1–2-s, 5-W, 0.2-Torr treatment produces about the same degree of surface modification as does longer treatment. High-resolution X-ray photoelectron spectroscopy (XPS) shows that either an oxygen or a water plasma produces a variety of oxidation products ranging from alcohols to carboxylic acids. Chromic acid oxidizes the plasma-oxidized surface further to give high densities of carboxylic acid groups which can be readily converted to acid chlorides and derivatized. Borane/tetrahydrofuran reduces the plasma-oxidized surface to give alcohols which can be esterified readily. Contact-angle measurements show that the water-plasma-treated PE surface has a higher surface free energy ($\gamma_s \sim 62$ dyn/cm) than the oxygen-plasma-treated surface ($\gamma_s \sim 50$ dyn/cm). A 5-s, ambient-temperature, 0.2-Torr, 2-W hydrogen plasma generates a significant number of quenchable radical sites. XPS spectra of this treated surface, exposed to either nitric oxide or nitrosotrifluoromethane, show that both compounds bond to the surface.

Introduction

In many regards, organic polymer surface chemistry is an established and intensely studied discipline. That this should be so follows naturally from the commercial and technological importance of polymeric materials. Often in their application, problems arise which are related to the surface and interfacial chemistry of these materials. For example, the phenomena of wear, adhesion, wetting, and aging involve, to varying degrees, processes occurring at or near the surface of the polymer.[1] Historically, these isssues have been addressed in a largely empirical manner. While more detailed information about polymer surfaces has become available due to the dramatic increase in sophistication of the means for studying surfaces in general, it is still difficult to relate such macroscopic behavior (i.e., wetting, adhesion, etc.) to a system's microscopic characteristics. In order to elucidate the nature of such relationships, several key problems must be addressed. First, methods have to be developed for functionalizing and modifying polymer surfaces to give materials whose structures are well understood at the molecular level. Second, detailed studies are needed of the structure–reactivity relationships exhibited by these materials. Third, and perhaps most important, the molecular basis of gross surface properties needs to be elaborated through the use of specific, well-defined changes in the microscopic structure of the material. In our view, little progress will be realized without the availability of flexible, well-characterized preparative methodologies for polymer surfaces.

The chemical modification of polymer surfaces has an extensive literature.[2] The procedures employed for a wide range of materials show a considerable degree of commonality. Rather than present a general overview, we will restrict our discussion to procedures which have been employed successfully on polyethylene.

Considerable attention has been devoted to the use of gas discharges for surface modification of polyethylene.[2,3] Depending on conditions, the use of any plasma often results in considerable cross-linking and/or oxidation of the polymer.[3] The magnitude of these changes depends on such factors as the nature of the gas, the power density of the discharge, and the length of time of exposure. The cleanliness of the experimental system and the purity of the gas feed are also critical factors in determining the nature of the surface modification achieved. A number of studies have appeared recently which use X-ray photoelectron spectroscopy (XPS) to characterize the chemical consequences of plasma treatment of polymers such as polyethylene.[3a-e] These studies showed that even low-power-density plasmas can result in the formation of considerable chemical heterogeneity. This is not too surprising in view of the diverse number of highly reactive species generated in a gas discharge.[4] Even so, a great deal of "surface" selectivity was observed.[5]

Another approach for modifying the surface of polyethylene with the view of introducing heteroatom functionality, involves the use of highly reactive chemical agents in solution. The most extensively examined of these is aqueous chromic acid.[6,7] The chemical changes effected with this wet chemical procedure have been described in detail.[7]

Common to each of the above procedures is the use of highly reactive reagents, a necessary condition due to the very stable nature of both the carbon–carbon and carbon–hydrogen bonds in polyethylene. What is sacrificed in using such procedures is selectivity in product formation and structural integrity in the polymer surface. For example, chromic acid significantly damages the surface; extensive pitting and chain scission are observed under the forceful conditions needed to generate high densities of surface functional groups.[7]

We describe in this paper a detailed study of several procedures which have been used to modify the surface of polyethylene film. Common to each procedure is the combined application of plasma and wet chemical techniques. These plasma–wet chemical methods can be employed to generate high densities of a specific functionality largely unaccompanied by other groups in a sharply defined surface layer. The polymer surfaces thus obtained are smooth (in that the surface topography, consisting of diffuse lamellar structure, is *unchanged* by the treatment) and have been shown to function as effective starting materials for subsequent derivatization by standard organic synthetic techniques.

Experimental Techniques

Spectroscopic Methods. ATR-IR spectra were recorded on a Nicolet MX-1 FT-IR spectrometer using a 45° KRS-5 ATR crystal. XPS spectra were recorded on a Physical Electronics Model 548 spectrometer. Base pressures of the order of 8×10^{-9} Torr were typically achieved during analysis. All spectra were

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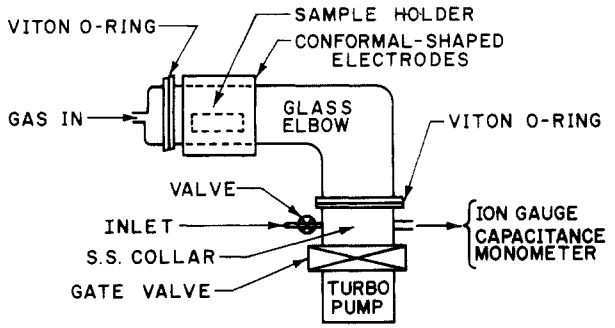


Figure 1. Schematic representation of the reaction chamber.

recorded using AlKα excitation with the main C1s peak arbitrarily referenced to a binding energy of 285 eV.

Polyethylene Preparation. Low-density (ρ = 0.9205), blow-molded polyethylene film was extracted by immersion for 10 min in boiling methylene chloride (reagent grade); the extraction was repeated twice with fresh solvent. After drying in a vacuum overnight, samples of the film were cut with a sharp scalpel. Care was exercised to avoid contacting the polymer surface with a potential source of contamination.

Gas Discharges. A schematic representation of the discharge chamber is shown in Figure 1. The diameter of the L-shaped glass cylinder was approximately 80 mm. The external hemicylindrical electrodes were 76 mm wide, while the cylindrical aluminum sample holder was 25 mm high by 56 mm in diameter. Power from a 13.56-MHz radio-frequency generator was supplied to one of the electrodes through a π-impedance-matching network while the other electrode was maintained at ground potential. Oxygen (Air Products, 99.5%) was metered into the reactor through an electronically controlled mass-flow meter at a rate of 10 sccm and a total pressure of 0.2 Torr. Water (twice distilled and outgassed) or hydrogen (Matheson, 99.9995%) was admitted into the reactor to a total static pressure of 0.2 Torr. Before placing a polyethylene sample in the reactor, the impedance of the π-network was tuned for minimum reflected power with the sample holder in place for the desired reaction conditions of gas, flow, and pressure. A circular polyethylene sample was held flush to the aluminum sample holder with a suitable glass or aluminum cover plate. The sample surface was oriented parallel to the electric field (perpendicular to the surface of the electrodes). Before exposing the polymer to the discharge, the loaded reactor was evacuated to a pressure between 3×10^{-8} and 6×10^{-8} Torr, which usually required several hours to achieve. After plasma treatment, the system was evacuated to a suitable low pressure and back-filled with the desired gas via the inlet shown in Figure 1.

Chromic Acid Oxidation. Aqueous chromic acid was prepared from chromium trioxide, water, and sulfuric acid in the ratio of 3:4:3 by weight. An oxygen-plasma-treated sample of polyethyene was floated on this solution for varying lengths of time at ambient temperature. The treated sample was washed thoroughly with distilled water, once with acetone, and dried in vacuo.

Derivitization of Surface Carboxylic Acids. The procedures employed were similar to those reported in the literature.[7] Carboxylic acid groups were converted to the corresponding acid chloride by treatment for 1 h with a solution formed by reacting 3.2 mL (45 mmol) of thionyl chloride with 3.9 mL (51 mmol) of dimethylformamide, removing the products SO_2 and HCl with an argon purge, and diluting with 8.0 mL of dry methylene chloride. The treated film was washed thoroughly with 2 × 5 mL portions of *dry* methylene chloride and used immediately for the preparation of derivatives.

In two representative treatments, films obtained by the above procedure were immersed in neat ethylenediamine or 0.1 M *p*-iodoaniline in methylene chloride. After incubating the samples for 30 min, the films were washed thoroughly with 5 × 20 mL portions of methylene chloride and dried in vacuo. The ethylenediamine derivative contained significant amounts of the monoamide product whose pendant amino groups were suitable for subsequent derivatization with typical acylating agents (anhydrides, acid halides, active esters, etc.). The *p*-iodoaniline derivative was used directly for XPS analysis.

Borane Reduction. Circles of plasma-oxidized polyethylene, PE(Ox), were covered with 1.0 M borane in tetrahydrofuran (Aldrich) and allowed to stand overnight at room temperature. The excess borane was destroyed by the slow addition of methanol. The sample was washed three times with methanol, and then immersed overnight in an approximately 5% solution of triethanolamine in methanol, and again washed with methanol followed by methylene chloride. The film thus obtained (containing hydroxyl surface groups) was dried and stored in vacuo.

Derivitization of Surface Alcohols. The procedures employed were unexceptional. Samples of oxidized polyethylene (borane reduced or PE(Ox)) were incubated with the selected acylating agent (anhydride, active ester, or acid halide) either as a neat liquid or in solution, washed thoroughly, and dried in vacuum.

In a representative procedure, a 1.5-cm diameter circle of PE(Ox) (cut with a sharp scalpel from an oxygen-plasma-treated sample) was placed in a scintillation vial and covered with 4 mL of a solution of trifluoroacetic anhydride in methylene chloride. After standing overnight, the sample was removed, washed with 2 × 10 mL portions of methylene chloride, and dried under reduced pressure (1×10^{-6} Torr). The product film was stored in vacuo.

Radioisotopic Labeling. Nonradioactive *N*-succinimidyl propionate was prepared by the standard reaction of equimolar quantities of *N*-hydroxysuccinimide and propionyl chloride in the presence of 1 equiv of pyridine in methylene chloride at 0 °C. The crude product was recrystallized twice from ether–cyclohexane to give white needles, mp (uncorrected) 48–50 °C; NMR ($CDCl_3$) δ 2.82 (s, 4 H), 2.65 (q, 2 H), 1.25 (t, 3 H).

N-Succinimidyl propionate-2,3-^3H with a specific activity of 91.5 Ci/mmol (New England Nuclear) dissolved in 1.0 mL of benzene was diluted with 5.40 mg (0.032 mmol) of unlabeled material. The resulting solution was used in subsequent labeling studies.

In a typical experiment, a circle of treated polyethylene film was incubated in the radiolabeling solution for 2 days, and then washed in repeatedly changed 10-mL portions of toluene over a period of 3 days. The film was washed finally in 20 mL of Aquasol-2 scintillation cocktail (New England Nuclear) for 1 day and counted in fresh scintillation fluid in a Beckman 300 scintillation counter.

Contact-Angle Measurements. Five solutions of ethanol and water were prepared having the compositions (V/V) of 0, 2.5, 5.0, 7.5, and 10.0% ethanol. By use of literature values[8] for γ_L, γ_L^D, and γ_L^P, the corresponding γ values for the 2.5, 5.0, and 7.5% solutions were calculated from fourth-order, least-square-determined equations. The values, respectively, are given in the order γ_L, γ_L^D, γ_L^P: 65.9, 21.4, 44.5; 60.7, 20.9, 39.8; 56.2, 20.5, 35.7. γ values for the liquids water, glycerol, formamide, and methylene iodide were taken from the literature.[9]

The contact angle of a liquid on a sample was measured with a Rome-Hart, Inc., contact-angle goniometer. Angles were measured on both sides of each liquid drop, usually using two separate drops for each liquid, and the values obtained averaged.

Results and Discussion

It is not uncommon for the surface composition of commercial polyethylene to differ substantially from that of the pure hydrocarbon. Spurious contamination, bloomed additives, and extensive surface oxidation are all major contributors to the structural and compositional heterogeneity typically seen. To ensure that the chemistry examined in this study truly reflected reactions of polyethylene, a brief study was conducted to identify techniques which consistently gave high-quality starting polymer surfaces. Unless great care is taken,[10a] films prepared by melting polyethylene in contact with other surfaces usually appeared to be grossly contaminated and/or oxidized when examined by XPS.[10b] Significantly, attenuated total reflectance infrared spectroscopy (ATR-IR) is an insufficiently sensitive probe to detect this condition. The best films were obtained consistently by using low-density polyethylene, heavily protected by anti-

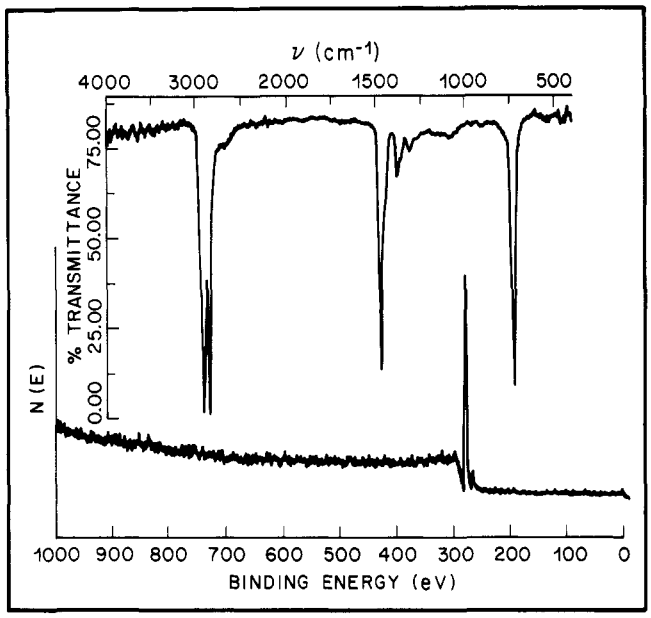


Figure 2. XPS and ATR-IR spectra of the extracted, low-density polyethylene film used as the starting material. The XPS spectrum shows very little oxygen-bearing functionality.

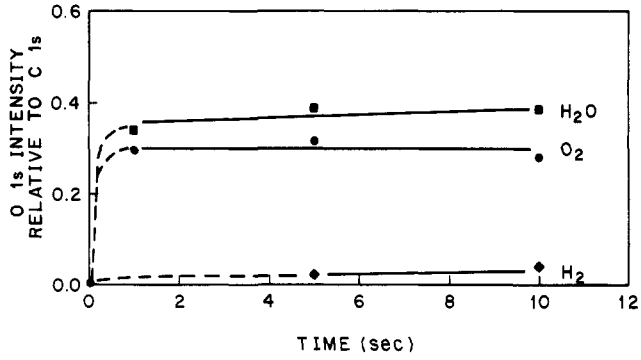


Figure 3. The ratio of the peak heights of oxygen 1s to carbon 1s, as determined by XPS, as a function of the length of treatment of polyethylene surfaces with discharges of various gasses (0.2 Torr, 5 W).

oxidants, which had been processed into a film by blow molding. Prior to use, the antioxidants were solvent extracted (see Experimental Techniques). When necessary, strain in the samples was removed by annealing in vacuum. Figure 2 shows the XPS and the ATR-IR spectra (low resolution) of a typical sample used in this study. These spectra are significantly different from those obtained before extraction; the XPS spectrum of an unextracted film showed high levels of oxygen functionality, while the ATR-IR spectrum exhibited strong additional absorption bands at 3100–3000 and 900–700 cm^{-1} due to the presence of phenolic antioxidants.

We investigated three gases—oxygen, water vapor, and hydrogen—as plasma reagents. A discharge was established in each gas under comparable experimental conditions of power, pressure, and duration of treatment time. We discuss each gas plasma in turn.

Oxygen. Figure 3 shows a plot of the relative ratio of oxygen to carbon, as determined by XPS, for an oxygen-plasma-treated polyethylene sample as a function of the duration of the discharge. Figure 4 shows a high-resolution XPS spectrum of a sample plasma treated for 1 s. This spectrum agrees generally with the conclusions of an earlier study which fit the asymmetry of the carbon 1s peak as an apparent convolution of at least three distinct oxygen-bonded carbon species.[3a,d] The most significant feature

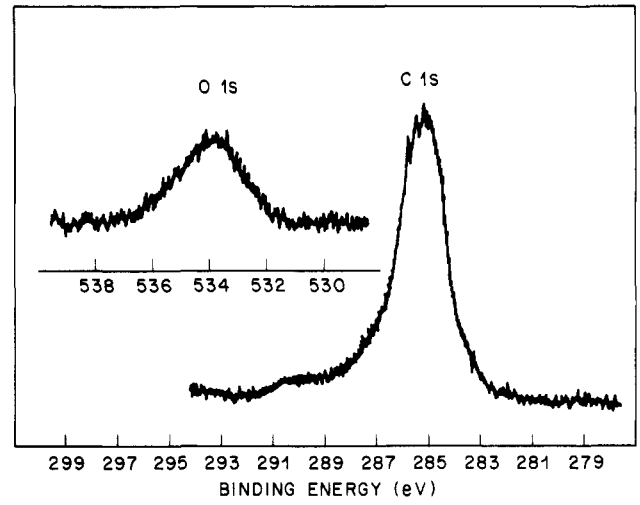
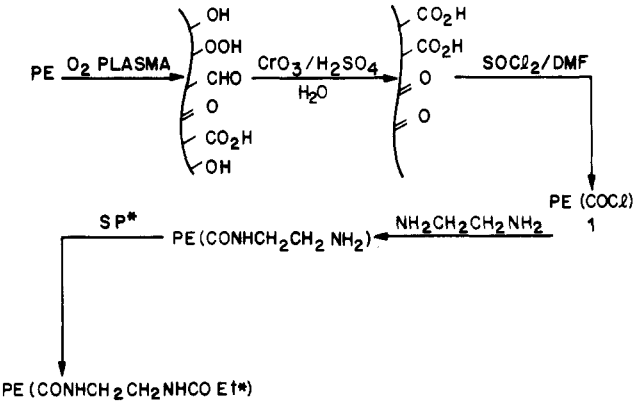


Figure 4. A high-resolution XPS spectrum (with the same vertical scale for each peak) of a 0.2-Torr, 2-W, 1-s oxygen-plasma-treated polyethylene film.

Scheme I



of the data in Figure 3 is that, as measured by XPS, little change occurs in the sample composition after 1 or 2 s of exposure to the plasma. Examination of these plasma-treated samples by scanning electron microscopy (SEM), showed that the surface topography of the film was unchanged (within the limits of resolution of the SEM) even after treatments of 30 min.

A 2-W, 1-s plasma-exposed polyethylene film, PE(Ox), was oxidized in aqueous chromic acid. Site densities of carboxylic acid groups were determined by radioisotopic labeling with *N*-succinimidyl propionate-2,3-^3H (Sp*) according to the procedure in Scheme I.

Derivatives for examination by XPS were prepared by reaction of 1 (Scheme I) with excess *p*-iodoaniline in CH_2Cl_2 to give the corresponding amide, PE($CONHC_6H_4I$).

In a second series of reactions, PE(Ox) films were treated with excess trifluoroacetic anhydride and reserved for XPS analysis. Samples of PE(Ox) which had been reduced first with borane–tetrahydrofuran (BH_3/THF) were similarly treated to incorporate trifluoroacetate labels for XPS analysis. This series of reactions was repeated, substituting radioactively labeled succinimidyl propionate-2,3-^3H for trifluoroacetic anhydride (Scheme II).

Table I shows the results of the radioactive labeling studies for the plasma-only- and plasma/borane-treated samples. Figure 5 shows the results of the XPS study using trifluoroacetate labels. Representative low- and high-resolution XPS spectra are shown in Figures 6 and 7, respectively. Several features of the data deserve specific comment. First, there exists in the plasma-only-treated samples a considerable amount of functionality which

Scheme II

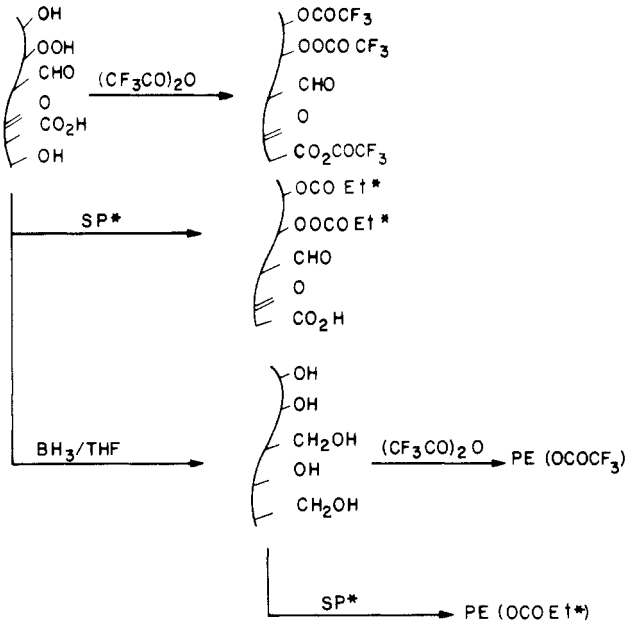


Table I
Site Densities As Characterized by Radioisotopic Labeling

plasma (time, s)	posttreatment	sites labeled/cm²
none	none	$<<1 \times 10^9$ (background)
O_2 (1 s)	none	$\sim 2.48 \times 10^{14}$
	BH_3/THF	$\sim 2.38 \times 10^{15}$
O_2 (10 s)	none	1.21×10^{14}
H_2O (1 s)	none	3.08×10^{14}
	BH_3/THF	3.17×10^{15}
H_2 (1 s)	(1) BH_3/THF (2) MeOH	$<1.1 \times 10^{12}$
	(1) BH_3/THF (2) pyridine *N*-oxide	1.6×10^{14}

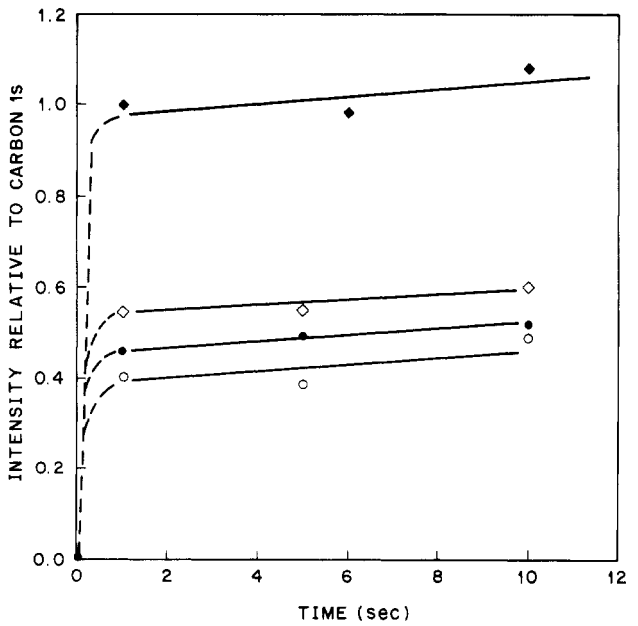


Figure 5. An XPS determination of the effect of oxygen-plasma treatment time on the amount of fluorine label incorporated after surface functionalities are allowed to react with trifluoroacetic anhydride. The closed symbols denote that the polyethylene sample was reduced with borane before esterification (●, ○ = peak height ratio oxygen 1s:carbon 1s; ♦, ◇ = fluorine 1s:carbon 1s).

reacts slowly with the radioisotopically labeled succinimidyl propionate. On the basis of an analysis of the

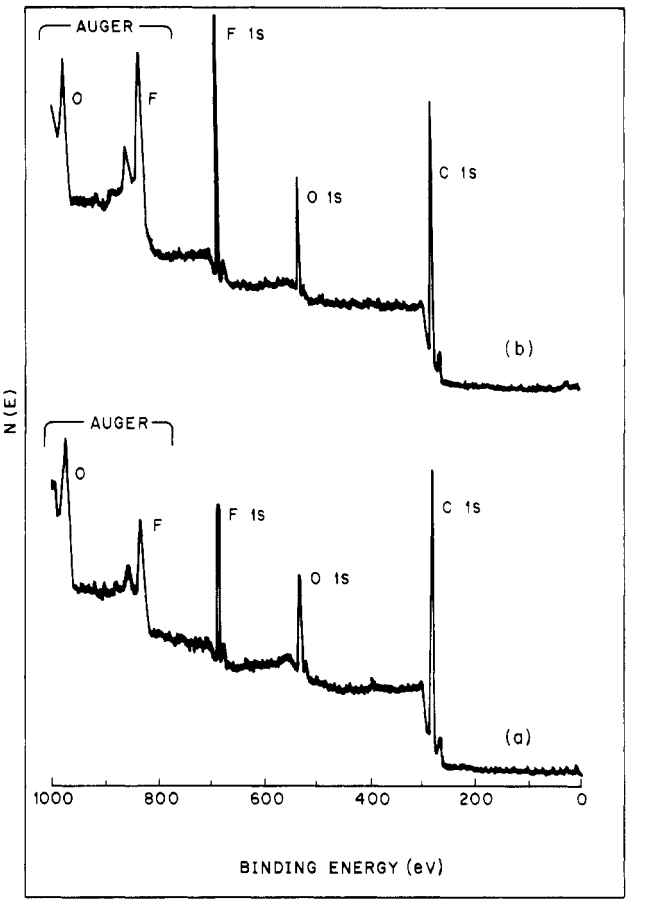


Figure 6. Low-resolution XPS spectra of trifluoroacetate-labeled, 1-s, oxygen-plasma-treated polyethylene films. Spectrum (a) is from a surface not reduced with borane while (b) is from a borane reduced surface.

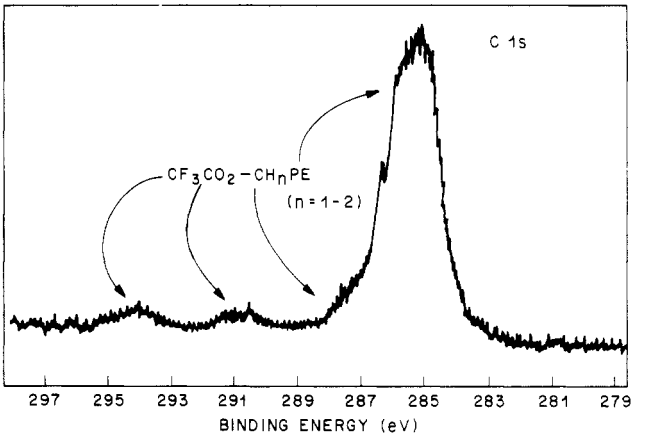


Figure 7. A high-resolution, carbon 1s, XPS spectrum of the material in Figure 6b.

high-resolution XPS data, most of these labeled groups are assumed to be hydroxyl moieties primarily belonging to alcohols, although the presence of hydroperoxides and other hydroxyl containing functionalities cannot be discounted (carboxylic acids do not react with the radioactive reagent). Second, reduction of the original plasma-oxidized film with borane produces a dramatic increase in the number of groups labeled by either procedure.[11] A qualitative evaluation, based on photoelectric cross sections from the literature,[12] indicates that the ratio of fluorine to oxygen in the borane-reduced material (Figures 5 and 6) is close to that which would be predicted for a trifluoroacetate derivative containing no other source of oxygen. Although the foregoing is not a rigorous analysis,

the result strongly suggests that a nearly homogeneous hydroxyl-functionalized surface is generated by the plasma/borane procedure.

When the XPS data in Figure 5 are compared to the results of the radioisotopic labeling study (Table I), a significant discrepancy is apparent. Both types of label indicate the same general trend; i.e., reduction with borane increases both the homogeneity and number of "surface" groups which react with the label. The apparent magnitude of this increase, however, differs markedly as measured by the two procedures. This difference was consistently reproducible. Two reasonable explanations come to mind. First, the "surface" functionality may not be distributed in a simple manner within the depth sampled by XPS, or second, the labeling of sites by either trifluoroacetic anhydride or *N*-succinimidyl propionate may not be specific for one type of oxygen-containing functionality.[13]

Several workers[3a,5] have shown that plasma treatment of polyethylene is "surface selective" in that only a few tens of angstroms are affected under the conditions employed in this study. Thus, the plasma-oxidized surface region is expected to be reasonably well-defined; however, this definition need not be, nor is it anticipated to be preserved in the subsequent derivatization reactions since reagents and solvents are used which are known to swell polyethylene. Nevertheless, control experiments in which PE(Ox) samples were immersed at room temperature in swelling solvents such as toluene or tetrahydrofuran showed no significant changes by XPS in surface composition (ratio of carbon to oxygen). On the basis of this finding, we conclude that organic-solvent-induced surface rearrangement is not an important contributor to the differences observed in the two labeling measurements. Our feeling is that, after borane reduction, the differences in the number of sites labeled by the two reagents reflect their chemical selectivity. *N*-Succinimidyl propionate reacts cleanly with alcohols to give propionate esters (and, in this case, incorporates tritium into the polyethylene film) but does not react with carboxylic acid groups to give anhydrides. Conversely, trifluoroacetic anhydride is expected to react readily with the hydroxyl groups of both alcohols and carboxylic acids to give the corresponding esters and mixed anhydrides, respectively. The XPS data in Figures 5 and 6 suggest that such is indeed the case. Specifically, the changes observed in the relative ratios of fluorine to carbon, oxygen to carbon, and especially fluorine to oxygen indicate strongly that the fluorine label is incorporated into "oxygen rich" functionalities in the unreduced film. Thus, this procedure results in an underestimation of the increase in the alcohol sites labeled after borane reduction.

We note that labels incorporated by either procedure are readily accessible to reagents in nonswelling solvents. At ambient temperature, more than 85% of the tritium activity is removed from radiolabeled films after incubation with aqueous ammonia, and trifluoroacetate labels are rapidly cleaved by treatment with aqueous methanol.

Chromic acid oxidation of oxygen-plasma-treated polyethylene samples proceeds in a much more complicated manner than that observed with the oxygen-plasma/borane-reduced samples. Treatment of PE(Ox) films with chromic acid (see Experimental Techniques) gives surfaces containing high densities of carboxylic acids as measured by radioisotopic labeling (Scheme I). After a treatment of 2–3 s, site densities of $\sim 5 \times 10^{15}$ CO_2H groups/cm^2 were obtained. Longer oxidation times (up to 30 min) did not significantly change the number of sites labeled.[14] Subsequent studies by XPS, based on the reaction of *p*-iodoaniline with surface acid chloride groups, showed definitively that the oxygen-containing functionality present on the film surface was grossly heterogeneous. Carboxylic acids were only a small fraction of this functionality, never more than about 50 mol %. On the basis of the radioactive labeling data and on the high-resolution carbon 1s spectra of these samples, we conclude that most of the excess, nonlabeled, oxygen-containing groups are ketones. Analysis of chromic acid oxidized samples by SEM revealed a further complication. After 15 s, and possibly sooner, the polymer surface was heavily pitted. This contrasts markedly with the behavior of a non-plasma-oxidized film, which was not pitted even after 30 min of chromic acid treatment at ambient temperature.

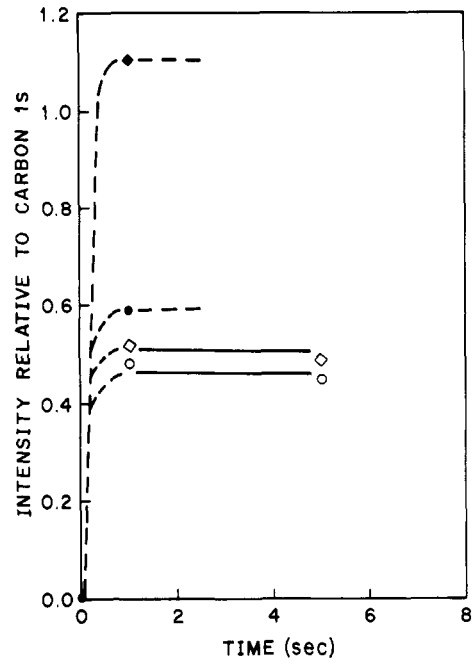


Figure 8. An XPS measurement of the effect of water-plasma treatment time on the amount of fluorine label incorporated when surface functionalities are allowed to react with trifluoroacetic anhydride. The closed symbols denote that the film was reduced with borane prior to incubation with the anhdyride (●, ○ = peak height ratio oxygen 1s:carbon 1s; ♦, ◇ = fluorine 1s:carbon 1s).

Water. It is well-known that a water plasma contains a number of strongly oxidizing neutral species.[4] Principal among these are oxygen atoms as well as a small amount of hydroxyl radicals. It is thus unlikely that a water plasma will generate, directly, high densities of alcohols by reaction of hydroxyl radicals with the polyethylene surface. This assertion is borne out by the data in Table I. The nearly 10-fold increase in the amount of tritium incorporated after borane reduction (Scheme II) illustrates that a large portion of the oxygen-containing groups are initially present in the film in a nonreactive form (see above).

Figure 8 shows the results of an XPS study using trifluoroacetate as a marker (Scheme II). The chemical consequences of a water plasma are seen to be very similar to those observed with an oxygen plasma. In complete analogy, a high site density, nearly monofunctional surface is obtained after borane reduction. A careful comparison of the XPS (Figures 5 and 8) and radioisotopic labeling data (Table I) for the two plasma systems indicates that a water plasma is slightly more reactive. As is found for the oxygen plasma, the rate of oxidation, as measured by XPS, declines rapidly after the first second of a water discharge. The surface morphology, when examined by SEM, is also found to be unchanged within the limits of

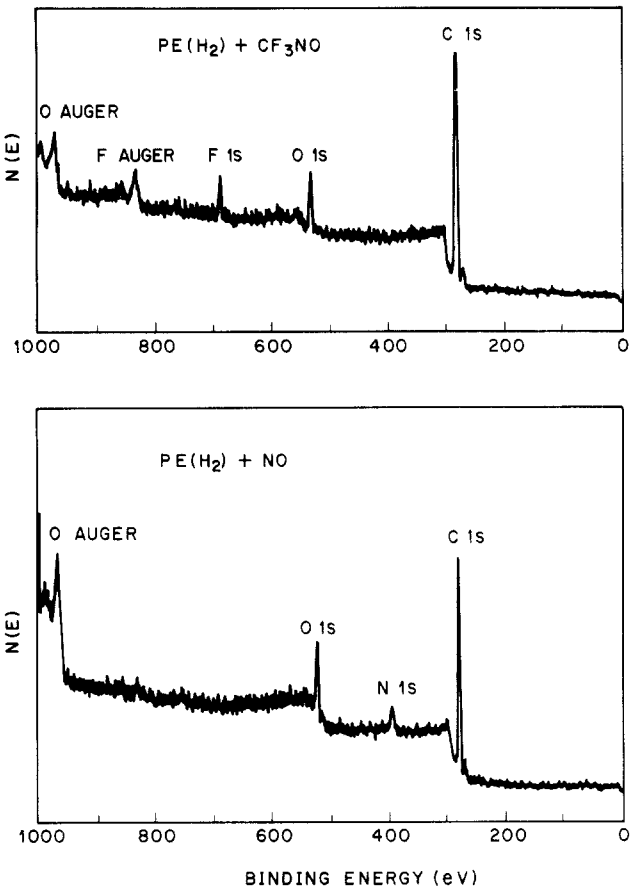


Figure 9. Low-resolution XPS spectra of hydrogen-plasma-treated polyethylene films reacted with either NO or CF_3NO.

instrumental resolution (~0.01 μm).

Hydrogen. Treatment of polyethylene with a hydrogen plasma represents a fundamentally different type of surface derivatization from that described thus far. It is believed that hydrogen atoms are the major reactive species which reach the surface.[4] Their reaction with the polymer is expected to result in the formation of alkyl radicals by either carbon–carbon bond cleavage or hydrogen atom abstraction. As such, two different types of derivatization could be effected as described in eq 1 and 2. In the first case (eq 1), the initially formed radicals

$$2RCH_2\dot{C}HR' \rightarrow RCH_2CH_2R' + RCH{=}CHR' \rightarrow (RCH_2CR'H)_2 \quad (1)$$

$$RCH_2\dot{C}HR' + Y \rightarrow RCH_2CH\dot{Y}R' \quad (2)$$

decompose by the normal recombination–disproportionation reactions of alkyl radicals.[15] Subsequent functionalization would ensue by some high-yield reaction of an olefin. In the second case (eq 2), the intermediate radicals would be quenched directly by a suitable trap. In either case the utility of these reactions depends strongly on some nontrivial considerations. First, the relative rates of disproportionation vs. recombination in a system such as this are unknown.[15b,16] Second, radicals in polymers can be very long-lived, requiring that the reactor be devoid of radical traps; the feed gas and reactor walls must also be free of potential oxidants such as water vapor or oxygen. Finally, the flux of reactants should be tailored so as to maximize the amount of disproportionation. With care, this procedure can be successfully employed.

A 5-s, ambient-temperature, 0.2-Torr, 2-W hydrogen plasma generates a significant number of quenchable radicals. Figure 9 shows the XPS spectra of the products

Table II
Surface Properties of Polyethylene Samples[a]

substrate	γ_s	γ_s^D	γ_s^P
PE(H)	40[b]		
PE(O_2)	50[b]		
	50[c]	28	22
PE(H_2O)	61[b]		
	64[c]	27	37

[a] Apparent surface free energies (dyn/cm) as calculated from contact-angle data. [b] Zisman method. See ref 22. [c] Kaeble method. See ref 9.

obtained with two different quenching gases, nitric oxide (NO) and nitrosotrifluoromethane (CF_3NO), both of which are highly reactive toward free radicals in solution. The NO reaction product contains a significant amount of nitrogen, which indicates a very clean reaction. The results from the CF_3NO reaction are less clear-cut in that a larger amount of oxygen appears in the product than is expected. The CF_3NO quenched material shows no electron spin resonance, suggesting that the nitroxyl radical product is itself unstable.[17,18]

In a separate experiment, a polyethylene film was treated with a hydrogen plasma for 1 s and then held in the reaction chamber in high vacuum (4×10^{-8} Torr) for several days to allow the initially formed radicals to react. The presence of olefins was then assayed by two independent procedures. First, examination by XPS of a sample which had been immersed for 1 h in a ~0.01 M solution of I_2 in CH_2Cl_2, followed by repeated washes with CH_2Cl_2, showed the iodine had been incorporated into the polymer surface.[19] In the second procedure, two samples which had been treated with a 1.0 M solution of borane in THF were removed from the borane solution and quenched with either methanol or pyridine *N*-oxide in benzene. The methanol quench results in the protonation of boron–carbon bonds which are formed in the hydroboration of olefins. The pyridine *N*-oxide treatment results, after workup, in hydroxylation of boron–carbon bonds.[20] Radioisotopic labeling of these two differently treated films according to the procedure in Scheme II indicates that the pyridine *N*-oxide treated sample contains a significantly higher number of alcohol sites (Table I) than the methanol-treated sample, strongly suggesting the formation of olefins. Indeed, the number of olefin sites produced is comparable to the number of hydroxyl functionalities formed from an oxygen or water plasma (see Table I).

Wetting Properties of Polyethylene Treated in Oxygen or Water Plasmas. Traditionally, studies on the effects of surface modification have relied heavily on the interpretation of contact-angle data. To complete our analysis and provide a reference for comparison with earlier work, we have examined the wetting behavior of films oxidized in either an oxygen or a water plasma. Our films are unique in that the oxidations employed are much milder (1 s at 2 W and 0.2 Torr) than those previously reported.[21] Data are presented only for samples which have not been exposed subsequently to organic solvents. Figure 10 shows typical Zisman plots[22] for three substrates: oxygen-plasma- or water-plasma-treated polyethylene and, as a control, an untreated, polyethylene sample. The liquids used consisted of solutions of ethanol and water (see Experimental Techniques). Qualitatively, the water-oxidized sample appears to be a more polar material, paralleling the somewhat higher oxygen content seen by XPS. The same general trends are indicated by a separate analysis of wetting behavior with several polar liquids (see Experimental Techniques) according to the method of

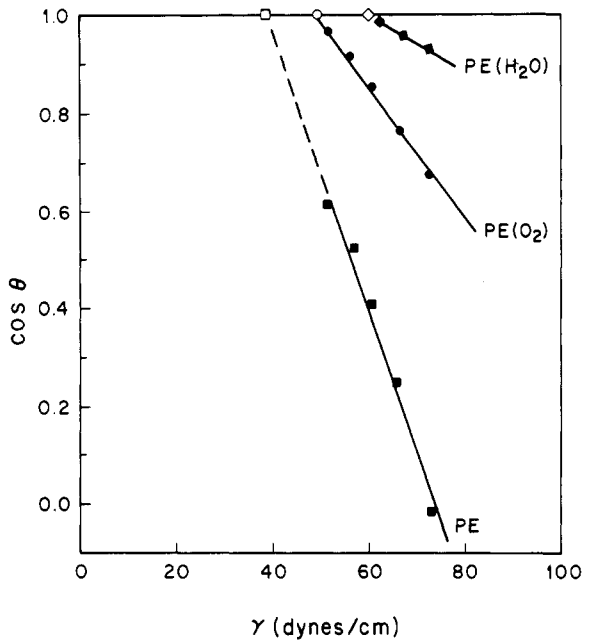


Figure 10. Plot of the cosine of the contact angle, θ, made by droplets of a series of ethanol/water solutions on three polyethylene substrates: solvent extracted (PE), oxygen-plasma-treated ($PE(O_2)$), and water-plasma-treated ($PE(H_2O)$), low-density polyethylene.

Kaeble.[9] The results shown in Table II factor the apparent solid surface free energy (γ_s) into "dispersive" (γ_s^D) and "polar" (γ_s^P) components, and again indicate that the water-plasma-treated sample is a more polar material. It is interesting to note that both oxidants give a product containing a large component of the total surface free energy which is due, formally, to dispersive interactions, the magnitude of which is essentially the same for each sample. From a chemical point of view, it is not obvious why a water plasma should produce a "more polar surface" nor is the physical basis for this increased "polarity" clear.

Conclusions

Functionalized polyethylene surfaces can be prepared by a combination of plasma and wet chemical techniques. The reactions appear to be limited to a very thin polymer surface layer, leave the surface undamaged, and are capable of generating high densities of a *single* functional group suitable for subsequent derivatization. We will report on the use of these materials in subsequent communications.

Acknowledgment. We thank H. Schonhorn for helpful comments and discussions and G. Schwartz for the use of his XPS system.

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