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# The Effects of Plasma Irradiation on Saccharides*

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## ABSTRACT

Monosaccharides and polysaccharides are chemically modified when they are subjected to rf plasmas derived from oxygen, nitrogen, or argon. The plasma treatment converts hydroxyl groups within the bulk to carbonyl groups on the order of one per anhydroglucose unit. On the surface, the concentration of carbonyl groups is greater than in the bulk. The activated surfaces formed by the plasma treatments are stable for at least 1.5 h. The observed spectral (IR, ESCA, and ESR) changes of the irradiated samples are the direct result of the plasma and not the secondary result of plasma-activated surfaces reacting with the atmosphere.

## INTRODUCTION

Modifications of surfaces of natural polymers by radio frequency (rf) cold plasmas have been reported [1-4]. Recently it has been reported that paramagnetic species are formed in polysaccharides

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during their treatment with cold plasmas. The paramagnetic species are destroyed by either moisture or oxygen. As the electron spin resonance (ESR) spectra of these species decrease, intensities of chemiluminescence increased [5]. The ESR signals were attributed to the formation of free radicals produced as the carbon-to-oxygen bonds of the polysaccharides were cleaved in the plasma. The chemiluminescences were attributed to the reaction of oxygen with the free radicals to produce oxetanes, activated carbonyls, or activated oxygen species. Electron emission spectroscopy for chemical analyses (ESCA) was used to observe surface changes in the binding energies ($E_B$) of the $C_{1s}$, $O_{1s}$, and $N_{1s}$ electrons of the polysaccharides during plasma treatments. However, in that study [5] the plasma-irradiated saccharides had to be transferred from the plasma chamber into the ESCA spectrophotometer. In spite of efforts to transfer the plasma-irradiated samples in an inert atmosphere, the spectra may have been influenced by traces of oxygen or moisture contacting the samples during transfer procedures.

This is a report of experiments designed to treat saccharides with cold plasma of argon, nitrogen, or oxygen within the reactor chamber of the ESCA spectrophotometer in order to observe changes in surface composition brought about by the cold plasma treatment without interference from transfer procedures.



## EXPERIMENTAL

### Materials

Monosaccharides and polysaccharides were obtained from Sigma Chemical Corporation. (Names of companies or commercial products are given solely for the purpose of providing specific information; their mention does not imply recommendation or endorsement by the U.S. Department of Agriculture over others not mentioned.) Sorbital, although not a saccharide, was used for comparative purposes. It too was obtained from Sigma. The dry argon, oxygen, and nitrogen (99.99% pure) were obtained from Union Carbide Corp.

### Plasma Generator

An all-glass cylinder with external electrodes was constructed to fit onto the reaction chamber of the Varian IEE-15 spectrophotometer (Fig. 1). The cylinder served as the cold plasma generating chamber that was modeled after the rf cold plasma apparatus described previously [4]. The rf field was generated from a Tegol 100-W generator that operates at 13.56 MHz. Fifty watts of continuous rf power was used to generate the plasma in the chamber at a

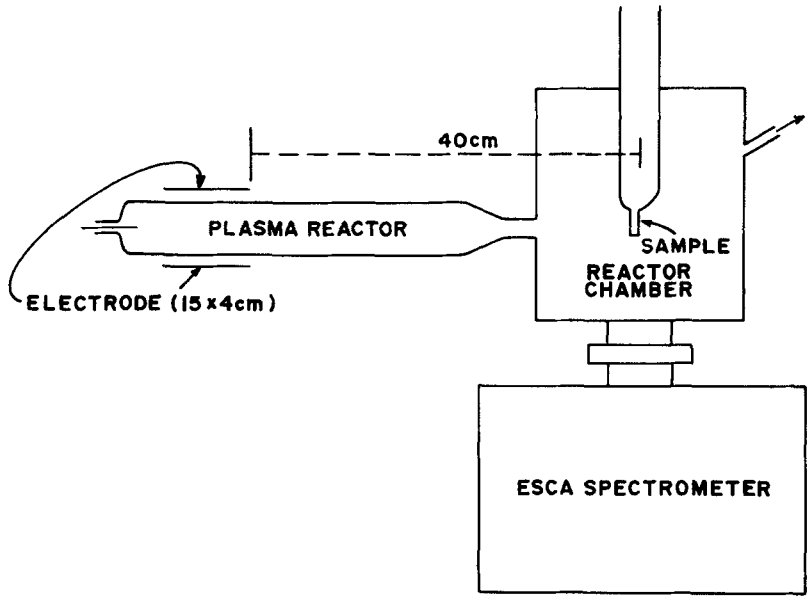


FIG. 1. Arrangement of the plasma reactor in relationship to components of ESCA spectrometer.



gas pressure of 200 mt. The apparatus allowed for the mounting of samples on a metal cylinder directly in line with the plasma flow. Samples were located about 40 cm downstream from the electrodes and beyond the visible glow discharge area. Samples were rotated 90° every 5 min during the 20-min exposure to cold plasma to insure uniform treatment. The cylindrical sample holder was covered with "Scotch Magic Tape" and the compound attached to the tape [6]. The entire surface of the sample holder was covered by each compound.

## Electron Spectroscopy for Chemical Analyses (ESCA)

The cylinder to which the plasma irradiated sample was attached could be lowered directly into the cavity of the Varian IEE-15 spectrophotometer equipped with a magnesium anode without the sample being subjected to another atmosphere. For each sample, ESCA spectra were obtained before and after subjection to the cold plasma. Typical spectrometer parameters were: pressure ($10^{-6}$ t), x-ray voltage (9 kV), filament current (120 mA), analyzer voltage (100 eV), sweep width (20 eV), and sweep time (20 s). The binding energies

($E_B$) of the centers of the spectra were 284, 399, and 532 eV for $C_{1s}$, $N_{1s}$, and $O_{1s}$, respectively.

## Infrared Analyses

Infrared (IR) spectra were obtained on a Digilab FTS 15B spectrometer. Samples were in the form of disks. One milligram of sample was mixed with 350 mg of dry KBr, and 300 mg of mixture was used to prepare the disk. After the spectra were obtained, some of the disks were stored for 30 d in desiccators over $CaSO_4$, in an argon or oxygen atmosphere.

# RESULTS AND DISCUSSION



Plasmas affected both the IR and ESCA spectra of all samples. ESCA spectra obtained from α-D-glucose before and after exposure to an oxygen plasma (Fig. 2) are typical of spectra obtained with all saccharides. The $C_{1s}$ spectra of the treated samples contain clearly discernible shoulders at about 289 eV. The $O_{1s}$ spectrum broadens as a result of the plasma treatment, and its intensity, as determined from the area of the peak, increases. The uppermost curves in Fig. 2 were obtained by subtracting the spectrum before irradiation from that obtained after irradiation. These difference curves illustrate that the treatment of α-D-glucose with the rf cold plasma of oxygen causes an increase in the $E_B$ peaks at 289 eV for the $C_{1s}$ spectra. Similarly, for the $O_{1s}$ spectra, the increase in intensity and the broadening of the $O_{1s}$ spectrum after plasma treatment can be attributed to increases in the peaks with $E_B$ of 533.6 and 531.6 eV, respectively.

The changes observed after plasma treatments can be explained on the basis of chemical and physical modification of the surface. The plasma can etch away surface contaminants and activate molecules of the substrate to react chemically with like molecules or with gaseous molecules in the plasma. Each original compound contains carbons of approximately the same electron density and gives rise to a relatively narrow $C_{1s}$ peak with a maximum at 286 eV. After plasma treatment, a $C_{1s}$ peak of higher binding energy (288/289 eV) emerges, indicating modification of the surface. Surface modification is also indicated by the appearance of $O_{1s}$ peaks at higher and lower binding energies than that of the control.

The IR spectrum of fructose, which contains one keto group, had an absorbance at 5.75 nm. The other saccharides do not absorb in

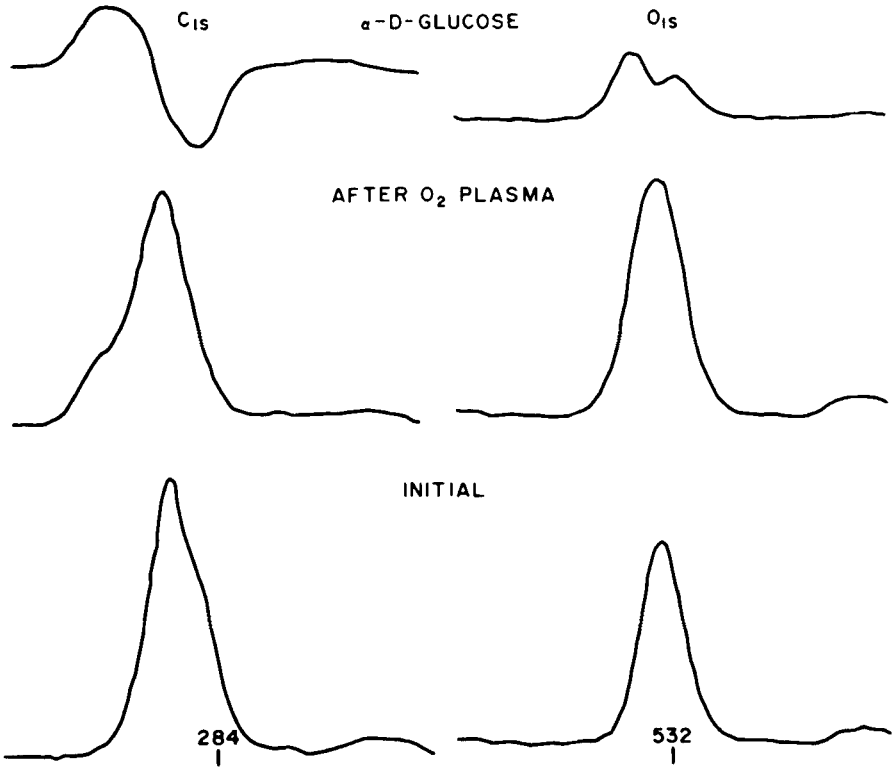


FIG. 2. $C_{1s}$ and $O_{1s}$ spectra of α-D-glucose before and after treatment with oxygen plasma. Upper curve is difference obtained by subtracting spectrum of untreated from treated sample. Sweep width: 20 eV; Initial binding energy: $C_{1s}$, 294 eV; $O_{1s}$, 542 eV.

this region before argon plasma irradiation. After plasma treatment, all samples had some absorbance at that wavelength. When the IR spectrum of each of the saccharides is subtracted from the spectrum obtained after treatment in an argon plasma, decreases in absorbance near 3.3 nm and near 6.2 nm, and an increase at 5.75 nm are observed. The argon plasma treatment of fructose does not cause an increase in absorbance at 5.75 nm. The changes in percent absorbance at 5.75 nm resulting from the argon plasma varied from 1.8 for Sigma-cell to 3.1 for both cellobiose and maltose (Table 1). Based on the observed percentage of absorbance of the fructose spectrum of 2.6 ± 0.4%, which corresponds to one carbonyl group per saccharide unit, these data suggest that one alcohol group per saccharide unit is

TABLE 1. Effect of Inhibited Plasma on IR and ESCA Spectra

| Compound | Absorbance Ar[a] | Height at 288 eV (Δ% A) | | | $N_{1s}$ area (arbitrary units) | | | $\Delta C_{1s}$ (%)[b] | | | $\Delta O_{1s}$ (%)[c] | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Ar | $O_2$ | $N_2$ | Ar | $O_2$ | $N_2$ | Ar | $O_2$ | $N_2$ | Ar | $O_2$ | $N_2$ |
| α-D-Glucose | 2.8 | 57 | 65 | 42 | 250 | 25 | 60 | 6 | 11 | 5 | 8 | 10 | 7 |
| β-D-Glucose | 2.0 | 51 | 35 | 49 | 200 | 25 | 80 | 10 | 13 | 9 | 13 | 6 | 5 |
| α-D-Fructose | 0 | 35 | 58 | 25 | 100 | 10 | 30 | 19 | 15 | 9 | 12 | 7 | 4 |
| Sorbitol | 3.0 | 39 | 40 | 27 | 300 | 10 | 70 | 10 | 4 | 4 | 20 | 3 | 3 |
| Maltose | 3.1 | 60 | 62 | 37 | 300 | 30 | 80 | 10 | 12 | 9 | 32 | 11 | 11 |
| Cellobiose | 3.1 | 43 | 49 | 47 | 350 | 30 | 80 | 7 | 11 | 10 | 12 | 11 | 13 |
| Sigmacell | 1.8 | 38 | 103 | 57 | 600 | 55 | 130 | 5 | 23 | 5 | 28 | 12 | 11 |
| α-Cellulose | 2.9 | 56 | 61 | 33 | 350 | 20 | 70 | 8 | 12 | 7 | 23 | 22 | 26 |
| Amylose | 2.1 | 27 | 56 | 33 | 400 | 30 | 80 | 4 | 16 | 11 | 14 | 7 | 13 |
| Amylopectin | - | 66 | 102 | 50 | 500 | 45 | 80 | 8 | 15 | 7 | 15 | 24 | 20 |

[a] [% A of treated sample - % A of untreated sample] at 3.75 nm as measured by FTIR.

[b] [(The area increase at 289-288 eV after plasma treatment) ÷ (total $C_{1s}$ area before irradiation)] × 100 as measured by ESCA.

[c] [(The area increase at 531 eV after plasma irradiation) ÷ (total $O_{1s}$ area before irradiation)] × 100 as measured by ESCA.

converted to a carbonyl group during argon plasma treatments of saccharides other than fructose.

The ESCA data that summarize effects of cold plasma of argon, oxygen, or nitrogen on the saccharides are also in Table 1. Although there is no increase in the IR absorbance at 5.75 nm in argon plasma treatments of fructose, its ESCA spectrum of the $C_{1s}$ peak near 289/288 eV increases in intensity. The increase in the $C_{1s}$ component of higher energy may be attributed to some species other than, or in addition to, carbonyl groups. Or perhaps, plasma treatments increase the concentration of that component on the surface of fructose only and not within the bulk, thus permitting its detection by ESCA but not by IR.

The $C_{1s}$ spectra of all compounds after plasma treatment with argon and oxygen contain the easily discernible shoulder at $E_B$ of 288 eV. This peak is not as obvious in the spectra of the compounds treated with nitrogen plasma. However, the increase in the component is obvious when the differences in the $C_{1s}$ spectra after and before treatment in nitrogen plasmas are examined. The $C_{1s}$ peak at 288 eV is absent in the untreated saccharides. The heights of the $C_{1s}$ spectra at 288 eV (Table 1) do not differ greatly with the type of plasma treatment except for the Sigmacell and amylopectin samples treated in oxygen plasma.

Ward et al. [5] found that cellulose subjected to either an argon or a nitrogen plasma gave an EPR signal. The signal intensity was greater for the argon-treated sample than for the nitrogen-treated sample. An unpaired electron on a carbon free radical formed during plasma radiation would affect the electron density on the carbon and cause $E_B$ of the $C_{1s}$ electrons to increase. The same would be true if the unpaired electron were on an oxygen attached to a carbon. The presence of both free radicals and carbonyl groups on the surface of the plasma-treated saccharides would explain both the observed IR and $C_{1s}$ spectra.

When the $C_{1s}$ spectrum of the untreated saccharides is subtracted from that of the argon plasma-treated sample, an increase in the intensity between 289 and 288 eV is observed for every compound. These intensity increases are reported in Table 1 as (area of peak/area of original $C_{1s}$ peak) $\times$ 100.

The plasma treatments also affect the $O_{1s}$ ESCA spectra. Any of the saccharides treated with any of the plasmas experienced a net increase in surface oxygen. No shoulders or new peaks were observed after the plasma treatments. The $O_{1s}$ spectra were all broadened by the treatments. From analyses of the difference spectra, each treated

saccharide had an increase at 531 eV. This increase indicates the presence of oxygen with an electron density higher than that of the oxygens present originally in the saccharides. This change might result from conversion of some hydroxyl groups to carbonyl groups or to free radicals. These difference spectra show that with argon plasma the changes in $O_{1s}$ spectra were greater than changes in $C_{1s}$ spectra for every compound except fructose, for which the change in $C_{1s}$ was greater. In contrast, with the oxygen plasma, the changes in $O_{1s}$ spectra were greater than changes in $C_{1s}$ spectra only for α-cellulose and amylopectin. With nitrogen plasma, the change in $O_{1s}$ spectra were greater than changes in $C_{1s}$ spectra for all except sorbitol, glucose, and fructose.

When oxygen plasma is utilized, there is also a significant increase in a component of even higher binding energy (about 533 eV). The increase of the latter is greater than or equal to that observed at 531 eV. None of the plasma used was more effective than any other in increasing this surface oxygen on all saccharides. For example, the increase of surface oxygen in α-cellulose after oxygen plasma treatment was 50%, whereas with argon plasma it was 18%. The corresponding increases in maltose were 35 and 40%, respectively.

Each treated saccharide, regardless of the plasma employed, experienced a buildup of surface nitrogen. These increases in nitrogen are indicated by peak areas of the $N_{1s}$ spectra at 400 eV (Table 1). With argon and oxygen, nitrogen is present in very small amounts as impurities in the gas or from leakage of air into the chamber. The surface nitrogen is not related to the concentration of nitrogen in the plasma, as the nitrogen concentrations on the surface of samples subjected to argon plasmas were from twofold to fivefold those treated with nitrogen plasmas. In each plasma, Sigmacell, a purified cellulose fiber, showed the greatest concentration of nitrogen, which was about twice that experienced by α-cellulose, a purified cellulose insoluble in 17% NaOH. The least susceptible to addition of the nitrogen was fructose. As a generalization, the polysaccharides, when treated with the plasma, achieved a higher level of surface nitrogen than did the monosaccharides; the disaccharides were intermediate.

The area difference at 289/288 eV resulting from plasma irradiation and the area resulting from added nitrogen can be used to approximate the ratios of lower electron density carbon atoms to nitrogen atoms resulting from the plasma treatments (Table 2). The ratio varies with the plasma treatment. Except for fructose that had the largest ratio in each plasma, the ratio is relatively constant for samples in a given plasma. In a given compound, the ratio is largest for the oxygen plasma and least for the argon plasma.

Similarly, ratios of oxygen with a binding energy of 531 eV to carbon with a binding energy of 288/289 eV were calculated (Table 2). This ratio was greatest for the samples treated with argon plasma.

TABLE 2. Effect of Plasmas on Atom Distribution on Surfaces Atom Ratio[a]

| | C/N[b] | | | O/C[c] | | |
|---|---|---|---|---|---|---|
| Compound | Ar | $O_2$ | $N_2$ | Ar | $O_2$ | $N_2$ |
| α-D-Glucose | 2 | 30 | 7 | 1.0 | 1.0 | 1.0 |
| β-D-Glucose | 3 | 30 | 8 | 1.0 | 0.5 | 0.5 |
| α-D-Fructose | 13 | 90 | 13 | 0.2 | 0.2 | 0.2 |
| Sorbitol | 3 | 40 | 4 | 1.5 | 0.5 | 0.5 |
| Maltose | 3 | 40 | 7 | 2.0 | 1.0 | 1.0 |
| Cellobiose | 3 | 30 | 7 | 1.0 | - | 0.5 |
| Sigmacell | 1 | 50 | 4 | 2.5 | 0.5 | 1.0 |
| α-Cellulose | 2 | 50 | 3 | 1.5 | 1.0 | 1.0 |
| Amylose | 1 | 50 | 8 | 2.0 | 0.5 | 0.5 |
| Amylopectin | 2 | 40 | 7 | 1.5 | 0.5 | 0.5 |

[a]Atom ratios determined from area of ESCA peaks and Wagner's atom sensitivity factors [7].

[b]The C area used was that at 289/288 eV.

[c]The O area used was that at 531 eV and the C area that at 289/288 eV.



The ratio in argon plasma for all samples, except fructose, varied from 1.0 to 2.5. The maximum ratio obtained with nitrogen or oxygen plasma was 1.0. With every plasma the ratio for fructose was 0.2.

Not only can carbonyl groups be formed within saccharides by argon plasma irradiation, but once formed, they tend to be stable. This stability was demonstrated by examination of the IR immediately after irradiation of a saccharide and examination of the same pellet following storage in either a dry oxygen or a dry argon atmosphere for 30 d. In either case there was no detectable loss in the intensity of the absorption at 5.75 nm during the storage. However, there is a decrease in the intensity of the $C_{1s}$ peak in the ESCA characteristic of carbon atoms of low electron density (higher binding energy) as a function of time after irradiation. The loss of carbon atoms of low electron density is best illustrated by observing changes in difference spectra for $C_{1s}$ electrons with time elapsed after plasma irradiation. Such difference spectra are illustrated by curves in Fig. 3 which were obtained with α-D-glucose immediately after its treatment with an oxygen plasma and after 1.5 h after its irradiation. A similar decrease

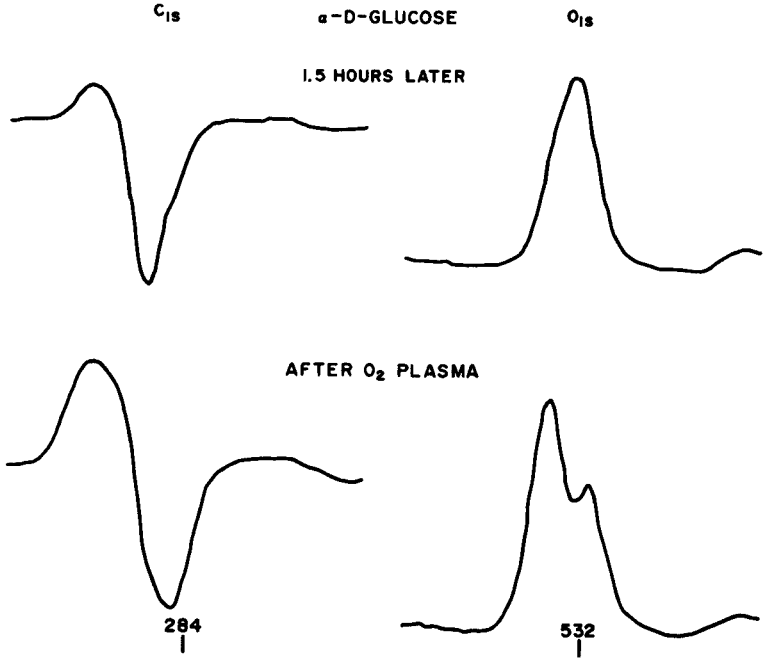


FIG. 3. $C_{1s}$ and $O_{1s}$ difference spectra obtained from subtraction of the spectrum of α-D-glucose from that of α-D-glucose treated in an oxygen plasma. Spectrum recorded immediately after plasma treatment (lower) and after 1.5 h in ESCA reaction chamber following plasma treatment. Sweep width: 20 eV; Initial binding energy: $C_{1s}$, 294 eV; $O_{1s}$, 542 eV.

in the $C_{1s}$ peak of low electron density with time after irradiation was observed with each type of plasma, but the greatest decrease was observed for that sample treated with oxygen plasma.

The difference spectra for the $O_{1s}$ peaks included in Fig. 3 show that with time after irradiation, there is a loss in the component of $E_B$ equal to 531 eV and an increase in the component of $E_B$ of 533 eV. The latter represents an oxygen of lower electron density. The data indicate that the IR band at 5.75 nm, which is present in fructose before plasma irradiation and in all compounds after plasma irradiation, even after long exposures to air, oxygen, or moisture, probably results from carbonyl groups. The $C_{1s}$ component that decreases as time after plasma irradiation increases represents a carbon of lower electron density than is present in the original compounds. It might

result from either a free radical or from more positive carbon than that of a ground state carbonyl group. Because the $C_{1s}$ component was absent in the untreated fructose and decreases on exposure to oxygen after its plasma treatment, that component is likely due to a carbon free radical or to an electronically excited carbonyl. Earlier work [5] has shown that the disappearance of this $C_{1s}$ component is accompanied by a decrease in intensity of the ESR spectra of the plasma-treated saccharide.

Loss in the ESR signal was accompanied by an increase in chemiluminescence (CL). The CL is increased when the plasma irradiated sample is exposed to oxygen or moisture. The decrease in this most positive carbon component as detected by ESCA simply proves that this component is disappearing from the surface, as ESCA measures surface changes only. However, reflectance IR has shown that the carbonyl groups on the surfaces of plasma-treated samples are stable even long after irradiation. These facts and the fact that an $O_{1s}$ component of highest $E_B$ (533 eV) increases as the $C_{1s}$ component of high $E_B$ decreases with time after plasma treatment indicate that perhaps there is a reaction between molecular oxygen and carbon atoms containing a free electron to produce a new type of free radical or peroxy type of compound. Peroxy compounds can also be formed by the reaction of molecular oxygen with activated carbonyls.

## CONCLUSIONS

Bulk as well as surface properties of saccharides can be changed by subjecting the compounds to rf-generated cold plasmas. Surface changes occurring during plasma irradiations can be detected by ESCA techniques. The subjection of saccharides to cold plasmas within the ESCA spectrophotometer eliminated the possibility that the surface changes observed previously were caused by contamination occurring during the transfer of samples from the rf generator to the ESCA spectrophotometer.

Plasmas of argon, nitrogen, or oxygen all produced an average of one carbonyl group per monosaccharide unit. The carbonyl groups occurred in the bulk as well as on the surfaces of the irradiated samples. Those in the bulk were stable for long periods after irradiation. However, surface changes, as detected by the decrease in a $C_{1s}$ component of highest $E_B$ and the accompanying increase in an $O_{1s}$ component of highest $E_B$ with length of time after plasma irradiation, occurred with all samples. Changes in these two components might account for the decrease in ESR signal and for the increase in chemiluminescence after exposure of plasma-treated polysaccharides to

oxygen or moisture. Nitrogen was bound to the surfaces of all plasma-irradiated saccharides, with the greatest amount of bound nitrogen resulting from argon plasmas. This study indicates that, on plasma irradiations, traces of nitrogen and oxygen are present regardless of the plasma used and that activated species of these elements are bound to the surfaces of the polysaccharides during their irradiation in cold plasmas.

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