Characterization and Use of Radio Frequency Plasma-Activated Natural Polymers

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Synopsis

A group of natural materials having anhydroglucose units linked by glycosidic bonds, as well as other related compounds, were irradiated with plasmas generated by a radio frequency field (13.56 MHz). Reactive sites created were characterized by electron spin resonance, chemiluminescence, infrared, and x-ray photoelectron spectroscopy. The free radicals are related to the number of glycosidic bonds, and their decays result in chemiluminescence. In the absence of moisture and oxygen, however, the radicals are stable. During plasma irradiation, carbonyl groups as well as free radicals are formed on surfaces, and the atom ratio of oxygen to carbon on surfaces increases. Within the reactor, thin films of polymers can be deposited on cotton fabrics by allowing the monomer to enter the reactor above the fabric that is in a horizontal position downstream from the external electrodes.

INTRODUCTION

Our interest is in the use of radio frequency (rf) cold plasma to increase the reactivity of natural polymers through the introduction of active centers and in the use of those centers as either catalysts or reactive sites. Cold plasmas have been used, for example, to produce pinhole-free polymer films on glass and other nonconducting substrates,[1] to graft acrylic acid to polymeric substrates,[2] to modify the surfaces of natural polymers,[3–5] and to improve the wettability of cotton fabric.[6] It was recently reported that rf plasma produced macroradicals on threads of regenerated cellulose and caused its degree of polymerization to decrease and its solubility in weak base to increase.[7] A mechanism of radical formation based on similarity to irradiation by ^{60}Co was proposed.[8]

This report concerns the use of rf-generated argon plasma to produce reactive sites in a group of cellulose or starch materials. Each compound within the model group has one or more anhydroglucose units (agu) with glycosidic bonds between the units. Electron spin resonance (ESR), x-ray photoelectron spectroscopy (ESCA), infrared spectroscopy (IR), and chemiluminescence (CL) were used to locate and characterize the reactive sites produced by the plasma on the natural polymers.

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EXPERIMENTAL

Materials

Model compounds were purchased from Sigma Chemical Company. Dialdehyde starch, which was 91.2% oxidized, was obtained from Miles Laboratories, Inc. Cotton cellulose was purified by extraction with hot ethanol followed by boiling in 1% sodium hydroxide solution. The sodium hydroxide solution was removed by washing the cellulose with distilled water, then with dilute acetic acid, and again with distilled water. Methanol and chloroform were reagent grade.

Argon and dry nitrogen were commercial-grade cylinder gases purchased from Union Carbide Corporation.

Cold Plasma Treatments

The rf generator, plasma reactor, and general operating procedure were described previously.[6] Precautions were taken to ensure that irradiated samples were exactly 50 mg each and that they were centrally located in the reactor

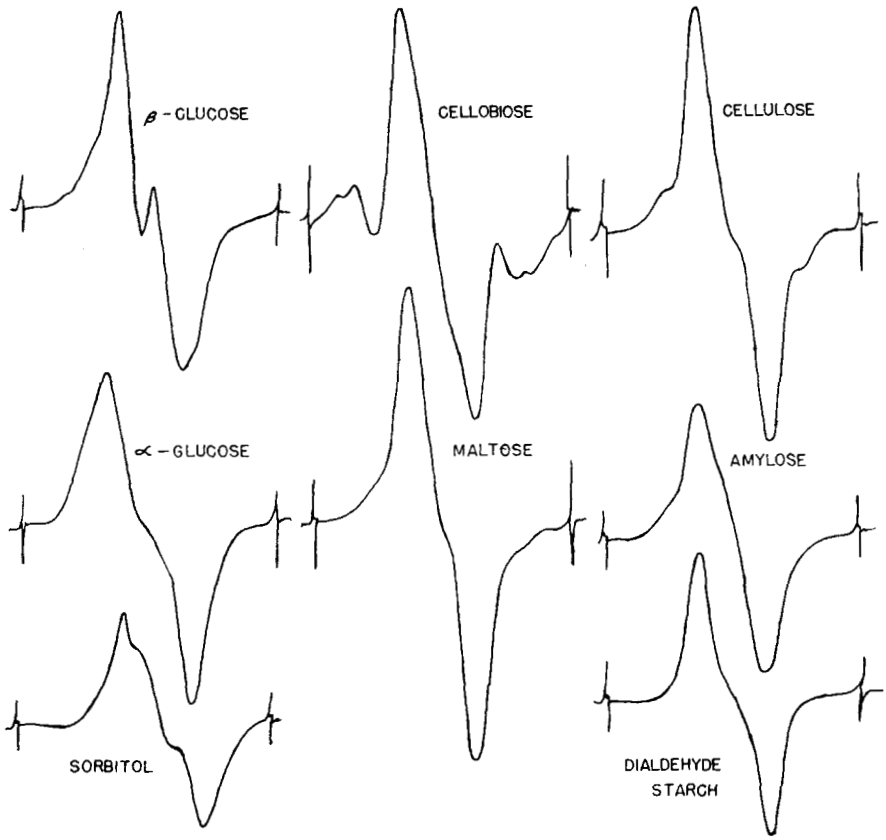

Fig. 1. ESR spectra for eight model compounds activated in rf plasma of argon (30 min, 40 W, 100 mtorr); 100-G scan.

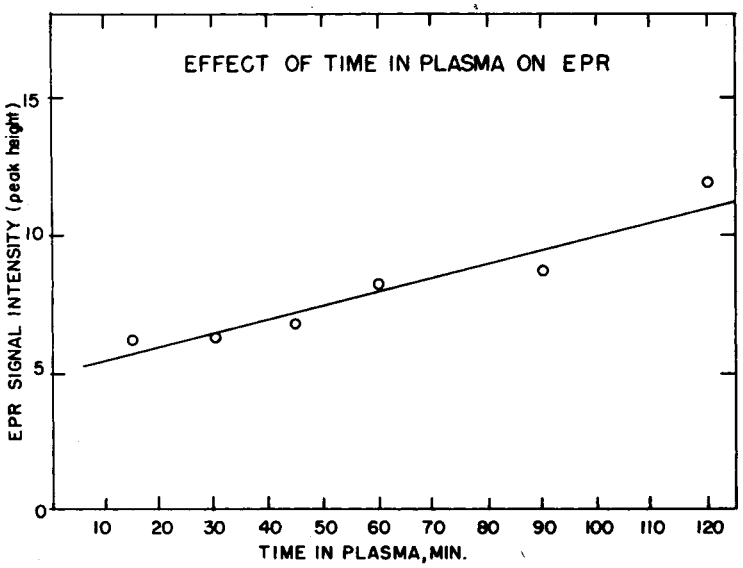

Fig. 2. Change of ESR signal with time of activation of a purified cellulose in rf plasma of argon (40 W, 100 mtorr).

downstream from the electrodes. In each plasma treatment, the system was evacuated to a pressure of 25 mtorr before argon was introduced into the reactor at a flow rate of 6.5 cm^3/min. After a 5-min interval of argon flow, the rf generator was turned on to give 40 W of continuous power. After activation, rf power was turned off and the system was returned to atmospheric pressure by bleeding argon into the reactor. Samples were kept in an argon atmosphere while being removed from the reactor and transported for testing. All samples were loaded and transported in a dry box and inert atmosphere.

Tests

Samples were examined by ESR, ESCA, IR, and multiple internal reflectance spectroscopy as described previously.[6]

Chemiluminescence was measured with a Packard 3255 liquid scintillation spectrometer equipped with low dark-noise photomultiplier tubes (RCA 4501/4V) and a Packard 585 linear recorder.

Redox properties of the activated samples were indicated by application of the following conventional spot tests: reduction of Ag^+, oxidation of Fe^{2+}, and oxidation of hydroxylamine to nitrite.[9] Reduction of nitroblue tetrazolium (NBT) was carried out in a 2:1 v/v mixture of $CHCl_3$ in CH_3OH to which CN was added; in reduced form it becomes blue. The reducing power of activated cotton cellulose was measured with 535-nm light in a 2400 Beckman DU spectrophotometer as the intensity of the color in NBT solution.

RESULTS AND DISCUSSION

The ESR spectra in Figure 1 show that plasma activation produces free radicals in all compounds. With the exception of sorbitol, spectra exhibit main peaks having similar linewidths. Spectra of the β materials are more complicated than

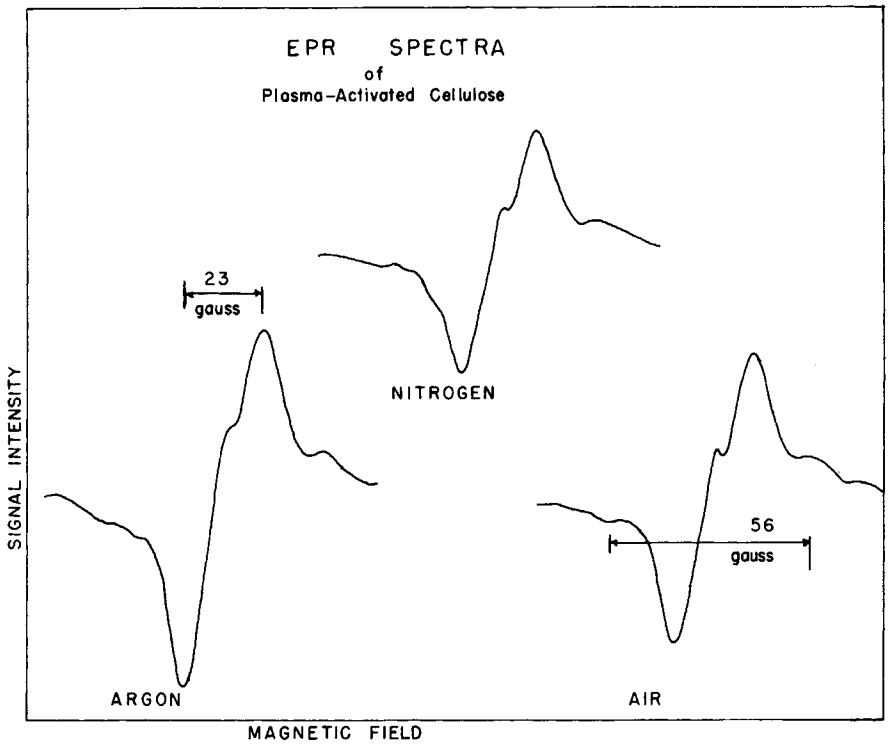

Fig. 3. Purified cellulose activated in rf plasma of argon, nitrogen, or air (30 min, 40 W, 100 mtorr); 100-G scan.

those of their α analogs. These differences are greater with the monomers and dimers than with amylose and cellulose, the more polymeric materials. Similar radicals that produce a singlet are formed in all compounds except sorbitol, and different radicals must be responsible for secondary peaks visible in many spectra.

Comparison of the ESR spectra for activated α- and β-glucose shows that each isomer has some of the other in it. Comparison of the α series with the β series shows that the β compounds have more secondary peak structures than do the α compounds. Spectra of amylose (α) and cellulose (β) have main peaks with the same linewidths, but that of cellulose has extra shoulders.

Plasma-treated dialdehyde starch gives a pure singlet ESR spectrum with the same linewidth as the singlet in the spectra of the compounds with the glucose rings. Thus, the secondary peaks for the other compounds must be associated with the number 2 and 3 carbon atoms since they represent the only real difference between dialdehyde starch and the ring compounds. These carbons have aldehyde groups in dialdehyde starch, whereas they have hydroxyl groups in the other materials.

The ESR spectrum of acyclic sorbitol consists of two singlets having g factors, linewidths, and intensities that differ from those of the other compounds. This indicates that the radicals formed in the other compounds are not at CH_2OH positions.

The increase in free radicals in cellulose is a linear function of duration of exposure to the plasma (Fig. 2). This effect is true for all model compounds.

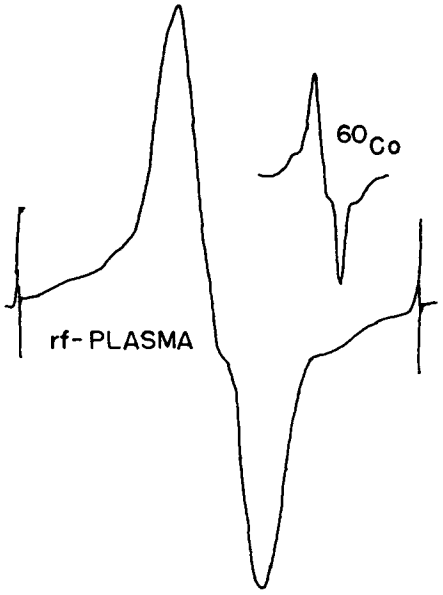

Fig. 4. ESR spectra to show similarities of cellulose activated by rf plasma of argon or by ^{60}Co; 100-G scan.

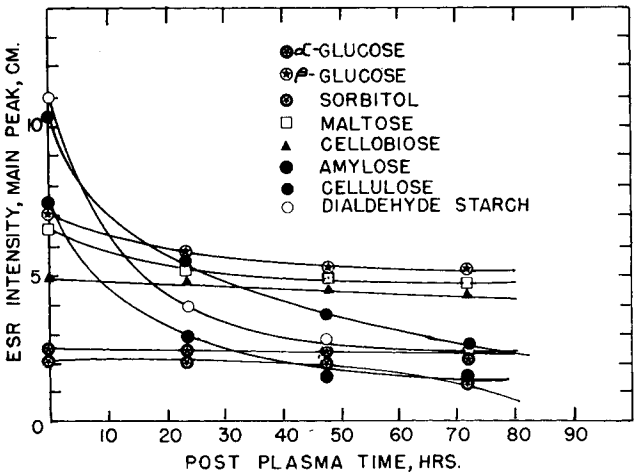

Fig. 5. Loss of ESR signal for eight model compounds activated in rf plasma of argon (30 min, 40 W, 100 mtorr). Stored in dry N_2, 26°C.

Plasmas of argon, nitrogen, or air produced similar free radicals in purified cellulose (Fig. 3). Argon plasma has a slight tendency to form more of the singlet radical (main peak) than the radical represented by the lesser peaks and shoulders.

Although rf plasmas are not as energetic as irradiation from ^{60}Co, which has previously been used to irradiate cotton cellulose,[8] the two sources produce free radicals in cellulose that have almost identical ESR spectra. Each spectrum consists of a large singlet and a lesser triplet, with the central peak of the triplet somewhat obscured by the singlet peak (Fig. 4).

TABLE I
ESR Intensity[a]

Compound	Immediately after plasma	After storage[b]	
		In N_2	In air
β-1,4-			
Glucose	7.09	6.19	5.09
Cellobiose	5.40	5.00	3.70
Cellulose	11.02	6.37	0.30
α-1,4-			
Glucose	2.57	2.57	2.00
Maltose	4.24	3.04	3.22
Amylose	7.49	2.85	1.53
Open Chain			
Dialdehyde starch	10.45	8.15	1.36
Sorbitol	2.36	1.61	1.96

[a] Main peak height, in cm; argon rf plasma, 30 min.
[b] In ESR quartz tubes, in dry N_2 or in air of 75% relative humidity at 25°C.

Free radicals produced by plasma decay at different speeds, depending on the compound treated and storage conditions. When stored in dry nitrogen, free radicals of polymeric cellulose, amylose, and dialdehyde starch decay much more rapidly than do those of smaller molecules (Fig. 5).

Data in Table I show changes in ESR intensities for activated samples stored 24 hr. Except for sorbitol and maltose, moist air induces more rapid decay than does dry nitrogen, and the effect of moist air is greatest with cellulose and dialdehyde starch.

To see whether the decay of the free radicals is due to oxygen or moisture, equal weights of argon plasma-activated cellulose were kept in either dry nitrogen, dry oxygen, or nitrogen saturated with water vapor, and the ESR spectra were ob-

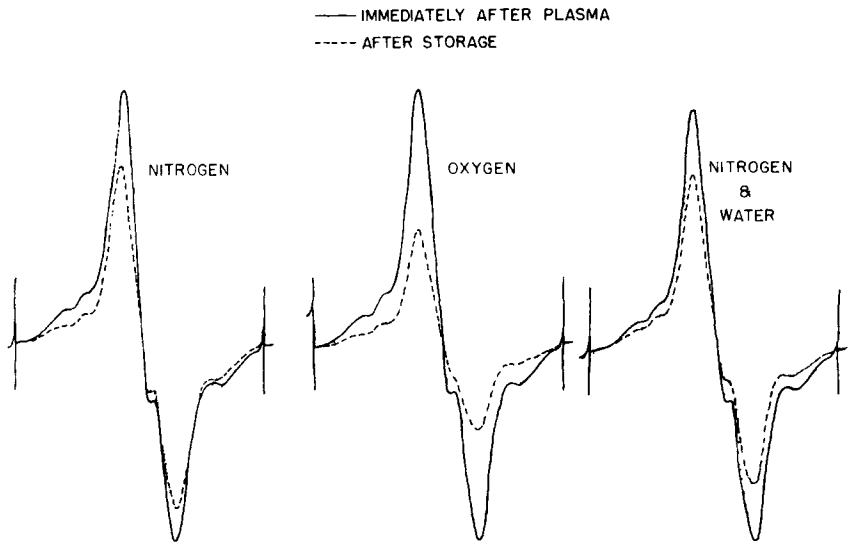

Fig. 6. ESR Spectra for purified cellulose activated in rf plasma of argon (30 min, 40 W, 100 mtorr). Stored in dry N_2, O_2, or N_2 saturated with H_2O: (—) immediately after activation; (- - - -) after storage for 6 hr.

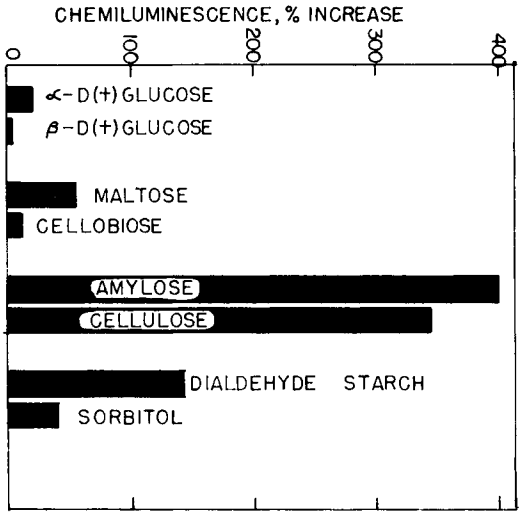

Fig. 7. Increase in chemiluminescence (CL) of eight model compounds after activation in rf plasma of argon (30 min, 40 W, 100 mtorr). CL measured on material neat immediately after activation.

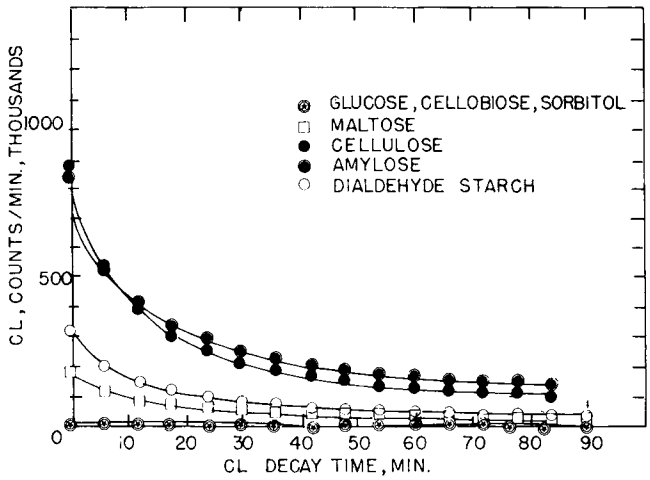

Fig. 8. Chemiluminescence decay in dry N_2 of eight model compounds activated in rf plasma of argon (30 min, 40 W, 100 mtorr).

tained after 6 hr. Figure 6 contains the spectra both before and after storage. Moisture in nitrogen caused no more decay than did dry nitrogen, but the decay caused by oxygen was almost twice as great. We also observed that all of the ESR spectral structure decays at the same relative speed, showing that the different radicals formed are equally susceptible to oxygen, nitrogen, or moisture.

The plasma-treated polymers also chemiluminesce. Simple sugars and disaccharides had little chemiluminescence (Fig. 7).

When cellulose activated with argon plasma is added to a mixture of 2 parts $CHCl_3$ and 1 part CH_3OH, a threefold increase in chemiluminescence (CL) results. Addition of KCN to this system raised the light emission 60-fold. CL is quenched by flushing the system with dry nitrogen but is regenerated to about half the original value when the nitrogen is replaced by oxygen. These same

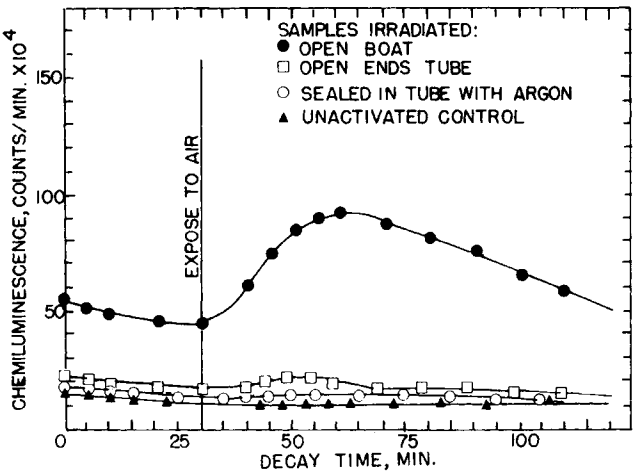

Fig. 9. Chemiluminescence decay for purified cellulose activated in rf plasma of argon (30 min, 40 W, 100 mtorr). Activated and stored in the indicated sample containers. All samples exposed to ambient air after 26 min of storage.

materials activated with rf plasma of nitrogen or air also exhibit CL, but the intensity is less than after argon activation. These data suggest transfer of energy or of unpaired electrons from active sites in the activated material to the added reagent and/or possible creation of new reactive species within the solvent system.

The amount of initial CL of cellulose varies linearly with its residence time in the argon plasma up to as long as 120 min. However, 30 min of plasma treatments were sufficient to differentiate degrees of activation of the various compounds. Cellulose and amylose that have the most CL lose it most rapidly as shown in Figure 8. Dialdehyde starch and maltose, with intermediate amounts of CL, lose it more slowly. Cellobiose, sorbitol, and α- and β-glucoses gave identical results and are plotted as one line.

Effects of shielding a cellulose sample during plasma irradiation are illustrated by the decay curves in Figure 9. Cellulose sealed in a quartz tube containing argon gas and placed in the plasma shows little more CL than the unactivated control. Cellulose contained in a quartz tube open at both ends displays only a slight increase in CL. Only when irradiated in an open boat does the cellulose

TABLE II
Relation of Chemiluminescence to ESR[a]

Compound	CL, counts/min	ESR[b]
Cellulose	111,899	4.65
Amylose	105,775	4.64
Dialdehyde starch	33,349	2.30
Maltose	15,041	1.20
Sorbitol	9,196	0.75
Cellobiose	2,299	0.40
β-Glucose	235	0.90
α-Glucose	4,770	0

[a] Argon rf plasma, 30 min, 40 W, 100 mtorr.
[b] Change in main peak height (in cm) after storage of 24 hr in dry N_2.

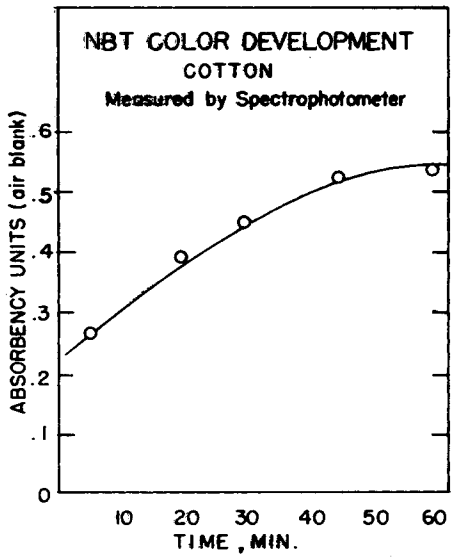

Fig. 10. Change in reducing power of purified cotton cellulose, activated in rf plasma of argon (30 min, 40 W, 100 mtorr), with time in NBT solution.

produce CL significantly greater than that of the control. The UV radiations of argon plasma are of too short wavelengths to be transmitted by quartz. With the open-ended tube, the plasma flowing downstream from the electrodes toward the vacuum source resists entering small openings. After exposure to air, the CL of the sample in the open boat increased over the ensuing 30 min; that in the open-ended tube showed a slight increase in CL.

Data in Table II show the CL immediately after activation and the change in ESR intensity during storage in nitrogen. There is no clear-cut relationship between the intensity of ESR and CL, but a rapid decay of the ESR signal is associated with CL.

Plasma-treated natural polymers undergo chemical reactions of α-hydroxyperoxides[10] or their precursors.[11,12] They oxidized Fe^{2+} to Fe^{3+} and hydroxylamine to nitrite, and reduced Ag^{+} and NBT in the presence of CN^{-}. Typical reducing power of a plasma activated cotton on NBT is shown in Figure 10. Test solutions were kept in the dark, and all transfers were made in the dark. Solutions containing activated materials were tested against empty cuvets as well as against solution blanks with no activated material. There is some very slow color development in the blank solutions. Color develops rapidly when activated cellulose is present and reaches a maximum after about 45 min.

In UV degradation of cellulosic materials, the scission of glycosidic bonds resulted in the formation of carbonyl compounds observable in the IR spectra.[13] The IR absorption spectrum obtained by the usual procedure with KBr disks of pulverized argon-activated cotton cellulose does not show a carbonyl band, probably because that procedure reflects "bulk" changes and plasma has most effect on the material surface. Hence, IR spectra were obtained with the multiple internal reflectance technique, which measures only the surface property. An additional peak in the 5.8-μm region (Fig. 11) indicates carbonyl. The location is that usually associated with either keto or aldehyde structure. The 6.1-μm

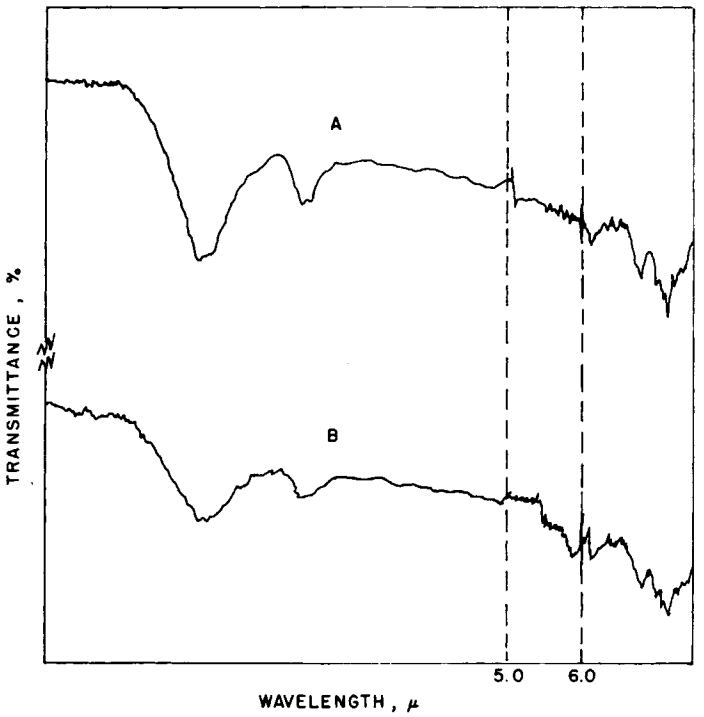

Fig. 11. Infrared spectra of purified cotton cellulose obtained by multiple internal reflectance: (A) unactivated; (B) argon plasma-activated (30 min, 40 W, 100 mtorr).

band associated with bound water in cellulose is present with unactivated and activated cottons.

ESCA can give information regarding both the location and oxidation state of atoms. The similar effects of argon, nitrogen, or air plasmas on cotton are evident in Figure 12. For each gas, ESCA spectra shows peaks of higher electron binding energies ($E_{b.e.}$) for the C_{1s} electron indicating more electropositive carbon atoms after plasma activation. The C_{1s} spectra can be deconvoluted into three parts. The largest peak, that of the lowest $E_{b.e.}$, is like that of the unactivated control. The peak intermediate $E_{b.e.}$ is similar to that of carbonyl carbons and that of even higher $E_{b.e.}$ could be that of carbon-free radicals. There is also a slight shift of the O_{1s} peak toward lower $E_{b.e.}$, indicating an increase in electron density of some oxygen atoms. In addition to these shifts, the oxygen-to-carbon ratio (calculated from peak areas) increased as a result of plasma activation, indicating that oxygen concentration on the cotton surfaces was higher after activation than before.

Ions and electrons in the plasma are effective only in the surface of the natural polymers, but the far UV can penetrate deep within the material. Since ESCA analyzes only the surface, activated cotton fabric was ball milled in a CO_2 atmosphere. This procedure has been found to be effective in ESCA analyses of chemically modified cottons in the absence of oxygen.[14] Comparison of ESCA spectra before and after ball milling (Fig. 13) shows that the C_{1s} peak of highest $E_{b.e.}$ is absent after ball milling, so those carbon atoms are only on the surface of the activated material and were diluted in the bulk by ball milling. However,

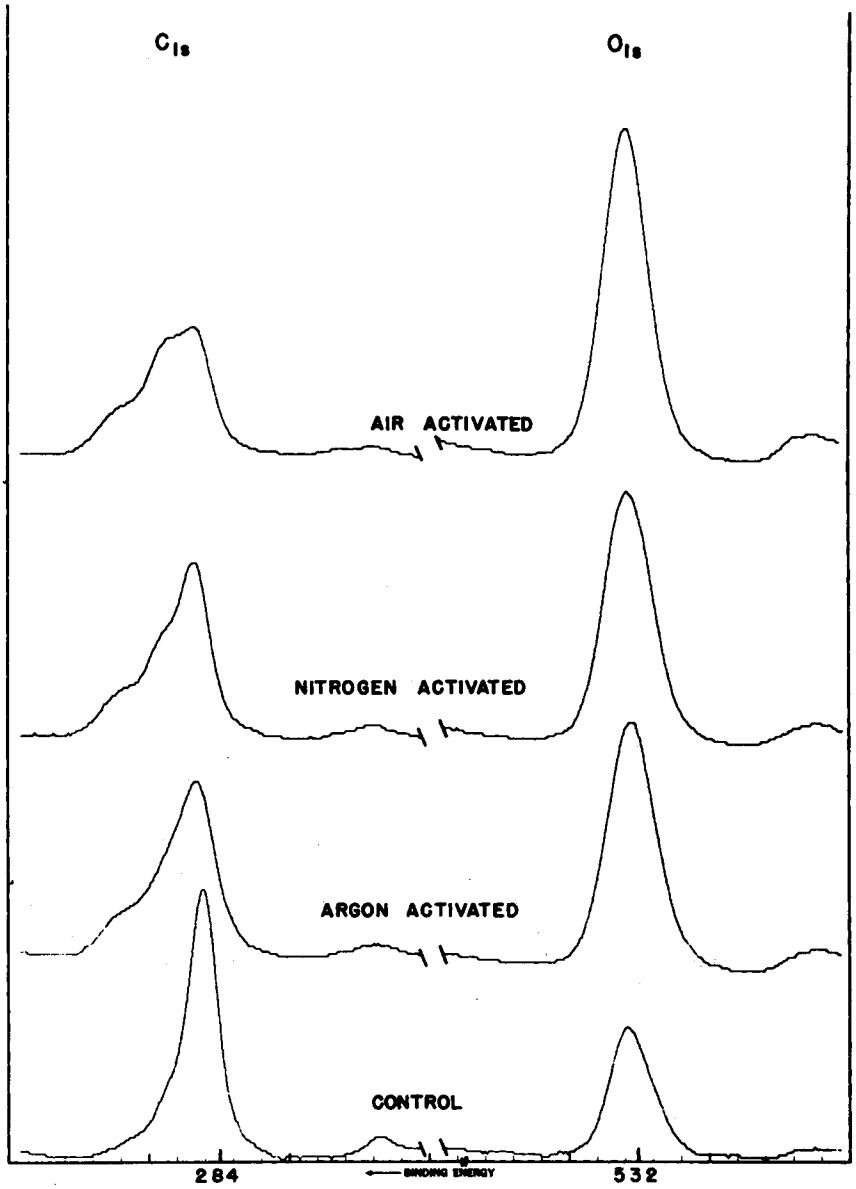

Fig. 12. ESCA Spectra for C_{1s} and O_{1s} of purified cellulose activated in rf plasma of argon, nitrogen, or air (30 min, 40 W, 100 mtorr).

the peak corresponding to carbonyl carbons is still present in the pulverized sample.

The C_{1s} peak of highest $E_{b.e.}$ is still present after 24 hr of exposure to ambient air but is destroyed by immersion in water (Fig. 14). This peak is probably associated with the radical that was shown by ESR to be destroyed by moist air.

Bubbles emanate from all activated natural polymers when they are immersed in water. An oxygen electrode in the water showed that the oxygen content did not change, pointing toward either entrapment of gas or production of either hydrogen or CO_2 gas.

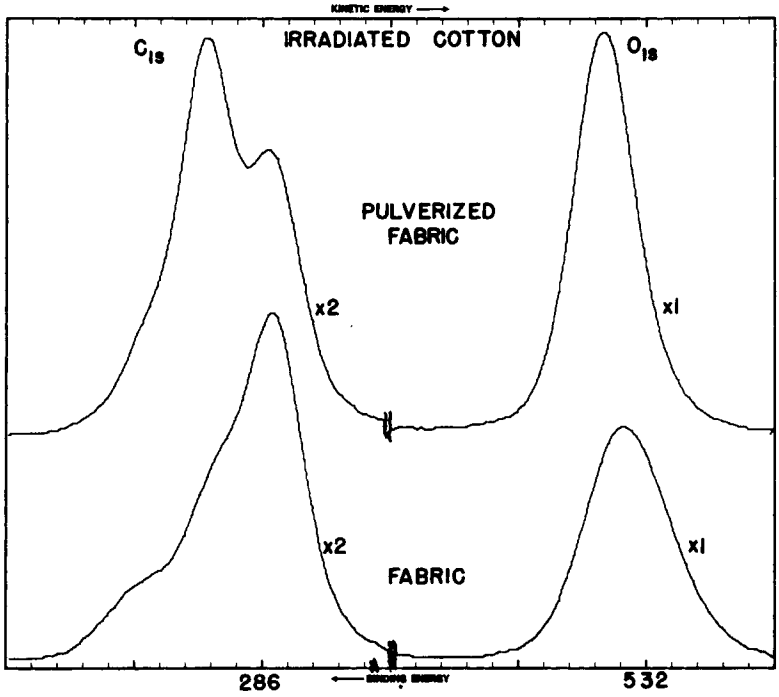

Fig. 13. ESCA Spectra for C_{1s} and O_{1s} of pulverized and unpulverized cotton cellulose fabric that was activated in rf plasma of argon (30 min, 40 W, 100 mtorr).

Both the ESR decay rate and the CL are strongly related to the presence of glycosidic bonds in the model compounds. Thus, formation of radicals at the glycosidic bond would be expected. Breakage around C_1 (Fig. 15) in the glucose units would be expected because that is the only carbon bonded to two oxygens. Dehydrogenation of C_1 would give a singlet (as observed), but this would provide no mechanism for CL nor would it cause breakage of glycosidic bonds needed to lower the degree of polymerization to account for increased solubility.[6,13] Other possibilities at C_1 include breakage of either the ring oxygen bond or the glycosidic bond (Fig. 16). Although the plasma is energetic enough to break either bond and either could give the ESR singlet observed, breakage of the glycosidic bond would explain why amylose and cellulose with many such bonds gave a more intense ESR singlet than did maltose or cellobiose, which have fewer glycosidic bonds. Broken chains would increase the hydrophilicities of the materials and their solubilities.[6,7] The oxygen radical shown on C_4 in Figure 16(D) could easily rearrange to a carbonyl, accounting for the IR spectra, and perhaps form an excited carbonyl capable of producing luminescence. The carbon radical shown in Figure 16(C) could pick up oxygen from air, moisture, or the ruptured molecular structure to form a peroxide. Either an excited carbonyl, a cyclic peroxide, or a dioxetane could account for the observed CL. Nitrogen could link to the oxygen to suppress the CL, which could be revived by flushing with oxygen. The peroxide or dioxetane would also be an obvious explanation for the increased O/C ratio observed by ESCA. The described radical structure would also result in the more electropositive carbon observed by ESCA.

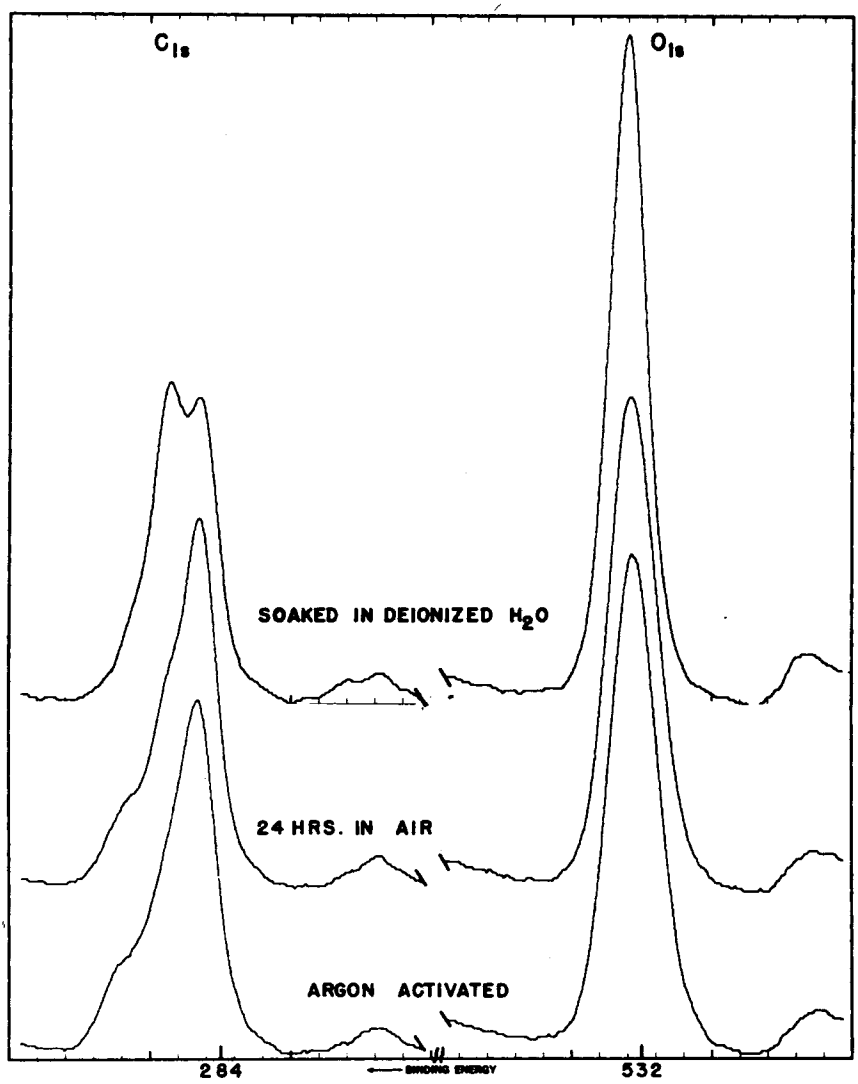

Fig. 14. ESCA Spectra for C_{1s} and O_{1s} of purified cellulose activated in rf plasma of argon (30 min, 40 W, 100 mtorr). Activated control and activated cellulose immersed in deionized H_2O or stored in ambient air for 24 hr.

Dialdehyde starch [Fig. 17(B)] results from cleavage of the C_2 to C_3 bonds of the glucose rings and oxidation of the C_2 and C_3 groups to aldehydic ones. Since the ESR spectrum for this compound is a pure singlet, the secondary peaks for the other materials are probably associated with those groups. They are the only locations for triplets that are present in the other materials but not in the dialdehyde starch. Dehydrogenation at the C_2 or C_3 of the glucose ring would yield a radical with triplet ESR spectrum. Comparison of plasma-activated dialdehyde starch structure with that of the compounds that have glucose rings shows that dehydrogenation at the C_5 carbon, the mechanism proposed[8] for cellulose irradiated with ^{60}Co, is unlikely after activation in rf plasma since it would result in an ESR triplet in the spectra of all of the compounds, and all did not show this type of spectrum.

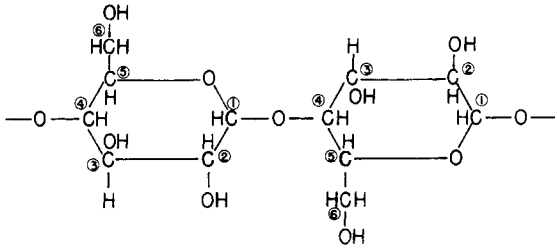

Fig. 15. Anhydroglucose units linked by glycosidic bonds as in cellulose, amylose, cellobiose, and maltose.

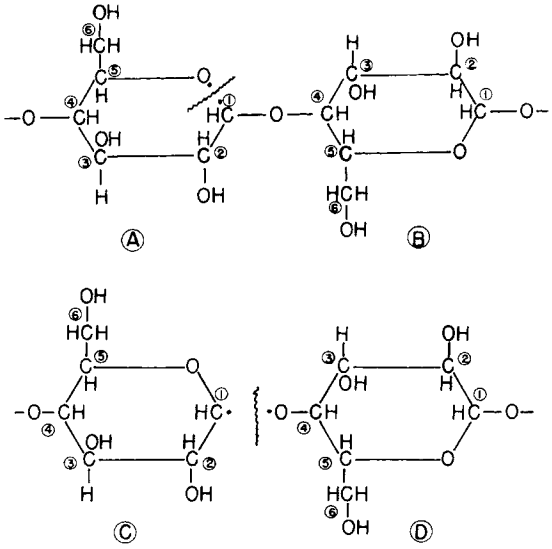

Fig. 16. Diagrams showing free radicals formed by cleavage of bond between C_1 and ring oxygen (A, B), or between C_1 and glycosidic bond oxygen (C, D).

Thus far, we have found experimentally that thin polymeric films on cotton can most easily be formed in our reactor[6] when the fabric is in a horizontal position downstream from the external electrodes and the monomer is allowed to enter above the fabric. Other plasma conditions easily cause polymerization but not as films on the substrate. Typical data for such polymerizations are shown in Table III. Finished fabrics showed little, if any, weight change. Losses in weight, despite film formation, are probably due to prevention of reentry of moisture lost during plasma treatment. Most treated materials showed water repellency, which was measured as the time required for a drop of water to completely diffuse into the treated surface. With HCHO, only unmodified cellulose treated with air plasma failed to result in a water-repellent finish. In most cases, conditioned wrinkle recovery was improved, but wet recovery was adversely affected.

Exploratory investigations into the use of plasma-activated natural polymer substrates to initiate polymerization outside of the reactor have met with limited success (Table IV). It does appear that reaction will occur for free radical-ini-

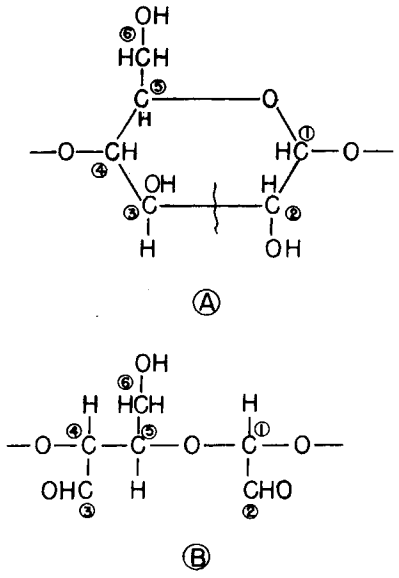

Fig. 17. Diagram showing cleavage of anhydroglucose unit (A) and oxidation of hydroxyl groups on C_2 and C_3 to form dialdehyde starch (B).

tiated polymerizations if all oxygen is removed from the system of monomer and solvent before the activated substrate is introduced. Since the activated materials have redox character, other reactions are possible; and this approach is being investigated.

TABLE III
Polymerization on Cellulose Fabric in Plasma[a]

Plasma Monomer	Gas	Wt. change, %	Wetting, min.	W.R.[b] change, % Cond.	W.R.[b] change, % Wet
		Unmodified Cellulose			
Benzene	air	−0.08	5	+6.6	−26.9
Benzene	Ar	+0.85	60	+1.7	−16.5
Styrene	Ar	+1.40	60	+8.0	−12.0
Formaldehyde	Ar	−4.43	5	−2.0	−25.3
Formaldehyde	air	−3.71	0	0	−24.2
Formaldehyde	N_2	−1.69	5	−1.1	−20.6
β-Butyrolactone	Ar	−3.53	5	+1.7	−17.0
		Diethylaminoethyl Cellulose			
Formaldehyde	Ar	−2.95	5	+29.8	−25.5
Formaldehyde	air	−1.83	5	+31.6	−24.0
		Diethylaminoethyl Cellulose (HCl)			
Formaldehyde	air	−1.38	5	+10.5	−23.5
		Carboxymethyl Cellulose			
Formaldehyde	Ar	−2.48	5	+20.4	+4.6
Formaldehyde	air	−2.03	5	+21.7	−6.4

[a] Thin films formed on indicated fabrics while in rf plasma of argon, nitrogen, or air; monomer introduced at 1 std cm^3/min, 30 min, 40 W, 150 mtorr.

[b] W.R. stands for wrinkle recovery.

TABLE IV
Postactivation Polymerization[a]

Monomer	Solvent, %	Flush, N_2	Wt. change, %	Hand
Acrylonitrile				
100%	—	no	−0.03	same
15%	DMF, 85	no	−0.03	same
15%	DMF, 85	yes	+3.00	stiffer
15%	DMF, 75; H_2O, 10	no	−0.03	same
15%	DMF, 75; styrene, 10	no	−0.03	same

[a] Cotton fabric activated in rf plasma of argon (30 min, 40 W, 100 mtorr) and then treated with solutions of acrylonitrile.

SUMMARY

Use of rf plasmas of argon, nitrogen, or air to treat natural polymers such as cellulose, amylose, or dialdehyde starch produces free radicals that decay slowly in nitrogen but rapidly in oxygen. The decay results in chemiluminescence. The activated materials exhibit chemical reactivity characteristic of α-hydroxyperoxides. ESCA spectra show some carbon atoms have been oxidized to two higher states, and some oxygen atoms have been reduced by plasma activation. IR spectra indicate the presence of either keto or aldehyde groups. Like the ESR signal, the ESCA signal of highest binding energy for the C_{1s} electrons disappears in the presence of air or moisture. Comparison of compounds in the series leads to the conclusion that free radicals are formed by the breakage of glycosidic bonds as well as by either dehydrogenation or dehydroxylation of the number 2 or 3 carbons in glucose rings, and that the chemiluminescence is due to formation of cyclic peroxides, dioxetanes, or excited carbonyls formed by rearrangement or by addition of oxygen at these sites. Monomers introduced in the plasma reactor above the fabric that is located in a horizontal position downstream from the external electrodes polymerize as thin films on the surface of the activated material.

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