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Spectrochemistry of Plasma-Induced Free Radicals in Cellulose Derivatives

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We report here the specific features of plasma-induced free radicals of cellulose derivatives such as ethylcellulose (EC) and hydroxyethylcellulose (HEC) on its comparison with those of cellulose. The electron spin resonance (ESR) spectra of Ar plasma-irradiated EC and HEC consist of three kinds of discrete spectral components, two isotropic spectra [doublets (I) and triplets (II), both being assigned to hydroxylalkyl radicals] and one anisotropic spectrum [doublet of doublets (IV) assigned to an acylalkyl radical], and a single broad line spectrum (III). The special feature here is the fact that the spectrum (III) is a major component, contrary to cellulose, which was assigned to an immobilized dangling-bond site (DBS) at the cross-linked region. The results suggest that plasma-induced cross-linking reactions are very predominant in EC and HEC relative to that of cellulose, due to the presence of alkyl substituents in EC and HEC.

Key words plasma-irradiation; solid state radical; ESR; ethylcellulose; dangling-bond site; computer simulation

In view of the fact that the surface reactions of plasma treatment are initiated by plasma-induced surface radicals, we have often emphasized that study of the radicals formed is of utmost importance for full understanding of the nature of plasma treatment. Thus, we reported a detailed electron spin resonance (ESR) study on plasma-induced radicals of several synthetic vinyl polymers[1] and fibrous polypeptides such as silk, wool and collagen.[2]

As part of our continuing work on the elucidation of plasma-induced surface radicals, we have recently reported an ESR study on a monocarbohydrate (*myo*-inositol)[3] and polycarbohydrates (cellulose and amylose),[4] because of their suitability as models for more complicated carbohydrates.

Several authors have reported on the plasma treatment of several polycarbohydrates such as cotton fibers (cellulose) and starch (amylose).[5] However, research has been directed mainly toward characterization of the surface properties of the plasma-treated materials. Detailed ESR studies on the elucidation of the plasma-induced surface radicals have not been worked out.

With a view to gaining insight into the nature of plasma treatment of cellulose derivatives, we have undertaken Ar plasma irradiation on ethylcellulose (EC) and hydroxyethylcellulose (HEC), known as pharmaceutical excipients, and the radicals formed were studied by ESR coupled with systematic computer simulations.

We report the detailed analyses of such ESR spectra and discuss the special features of the radical structures in comparison with those of cellulose.

Experimental

Materials Powdered EC (45—55 cps) and HEC (100—300 cps) were purchased from Tokyo Kasei Kogyo Co., Ltd. (Japan). It was screened with a 100—140 mesh sieve, and dried at 70 °C for 6 h *in vacuo*.

Method of Plasma Irradiation Powdered samples (100 mg) were placed in a specially designed ampule (30 mm i.d., 100 mm long) with a capillary tube (2 mm i.d.) at the uppermost part. The ampule was filled with argon gas for plasmolysis (0.3 Torr) and sealed. Then, the plasma state was sustained for the prescribed period of time with agitation of samples at room temperature by a radio frequency discharge of inductive coupling using a four-loop antenna at 13.56 MHz with the supplied power (50 W). The ESR measurements were performed while turning the ampule upside down after plasma irradiation at appropriate intervals, which is fundamentally the same procedure as that reported earlier.[1] The schematic representation is shown in Fig. 1.

ESR Spectral Measurement ESR spectra were recorded by a JES-RE1X (JEOL) spectrometer with an X-band and 100 kHz field modulation. Care was taken to ensure that no saturation occurred and that the line shape was not distorted by excessive modulation amplitude. From a plot of the square root of the microwave power *versus* the signal peak height, a microwave power level of 0.01 mW was chosen.

Computer Simulation of ESR Spectra Computer simulations were performed on a 32-bit microcomputer (NEC PC9801FA). The simulated spectra were obtained from Lorentzian functions by fitting iteratively the spectroscopic parameters (g-value, line width at half-height, hyperfine splitting constant (HSC), and relative intensity) with the observed digitized spectra using the nonlinear least squares method.[1] The simulation programs were fabricated so as to include the effect of g-factor anisotropy and/or α-hydrogen anisotropy on the line shape of powder spectra according to Kneubühl's equation[6a] and Cochran's equation,[6b] respectively.

Results and Discussion

Observed ESR Spectra of Plasma-Irradiated EC and HEC Figure 2 shows progressive changes in the observed ESR spectra of plasma-irradiated EC and HEC at various durations (A, B) and those of the plasma-irradiated samples (EC for 300 s duration and HEC for 60 s duration) on standing at room temperature under anaerobic conditions (C, D), together with those of plasma-irradiated cellulose at various durations for comparison purposes

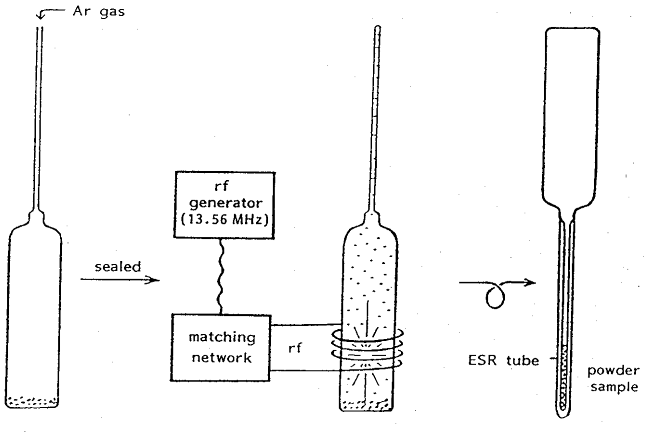

Fig. 1. Schematic Representation for Plasma Irradiation and ESR Spectral Measurement

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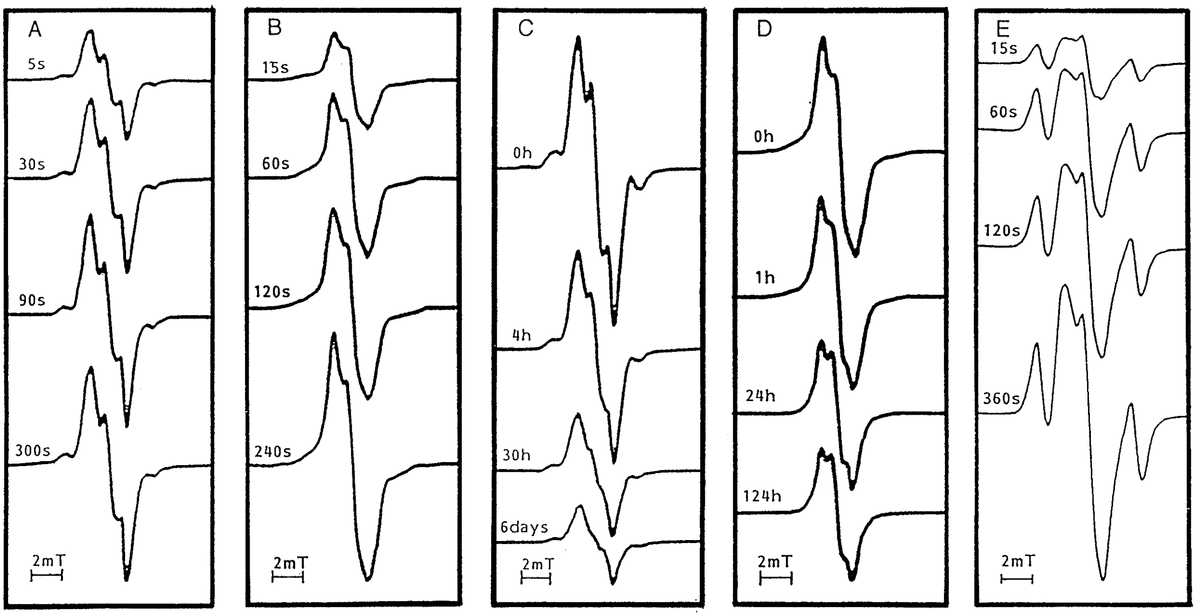

Fig. 2. Progressive Changes in Observed ESR Spectra of Plasma-Irradiated EC and HEC at Various Durations (A, B), Those of the Plasma-Irradiated Samples on Standing at Room Temperature under Anaerobic Conditions (C, D) and Plasma-Irradiated Cellulose at Various Durations (E)

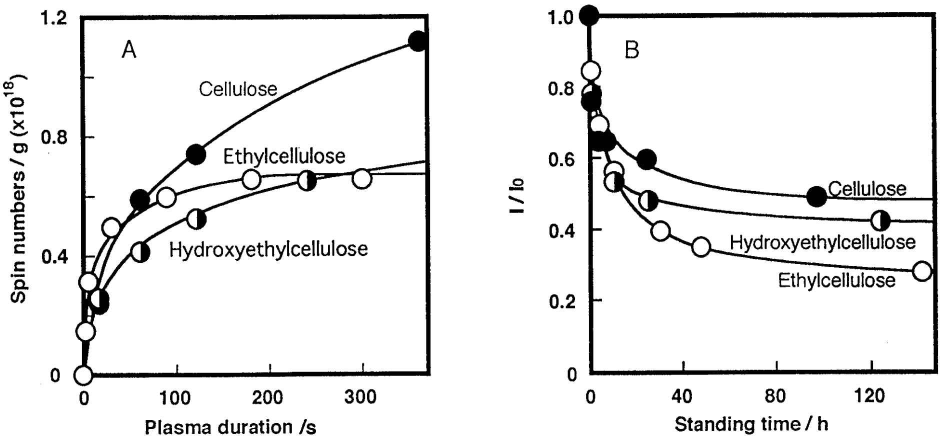

Fig. 3. Progressive Changes in Spectral Intensities Determined by Double Integration

A, on plasma-duration; B, on standing at room temperature.

(E).

It is seen from Figs. 2A and 2B that the spectral features vary with the materials, EC and HEC, but remain nearly unchanged in the course of plasma irradiation in each case. These spectra appear to represent multicomponent spectra and also apparently differ from those of cellulose, as shown in Fig. 2E.

In a series of spectra when the respective plasma-irradiated sample for 300 or 60 s was left to stand at room temperature under anaerobic conditions, the spectral pattern of EC and HEC did not appreciably change even on prolonged standing at room temperature, as shown in Figs. 2C and 2D.

Figure 3 shows the progressive changes in the total spectral intensities on plasma duration (A) and standing at room temperature (B) which were determined by double integration. It was shown that the spectral intensities of EC and HEC leveled off for a much shorter plasma duration and the decay rate of their radicals on standing at room temperature was higher than that of cellulose, indicating in them the presence of less-stable radicals.

Corresponding Simulated Spectra We have systematically conducted computer simulations of these progressive changes in the complicated spectra in an interrelated manner. The simulated spectra corresponding to the observed spectra in Fig. 2 are shown in Fig. 4. It can be seen that all the observed spectra have been satisfactorily reproduced by the simulated spectra. The computer simulations disclosed that in the observed spectra there exist as many as four component spectra in both EC and HEC, essentially identical to those of cellulose, and all the simulated spectra are obtained from admixtures of the component spectra with differing ratios.

Figure 5 shows the representative spectral components of the simulated spectra of EC as a representative example: three isotropic spectra [doublet (I), triplet (II) and a single broad line spectrum (III)], and one anisotropic spectrum [doublet of doublets (IV)].

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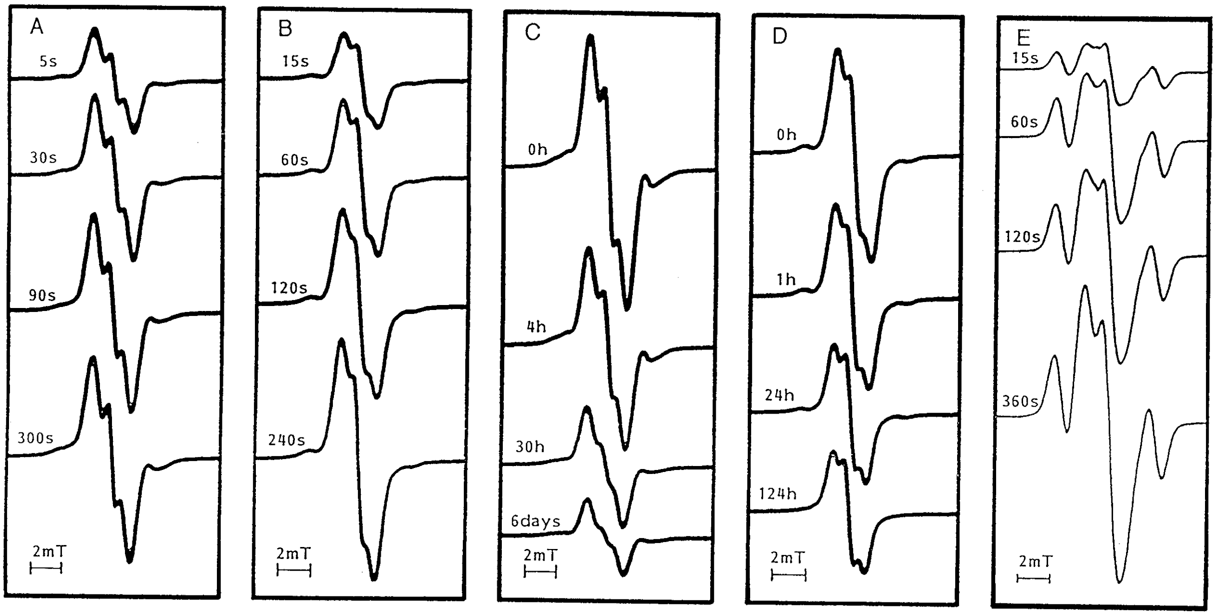

Fig. 4. Simulated Spectra Corresponding to the Observed Spectra in Fig. 2

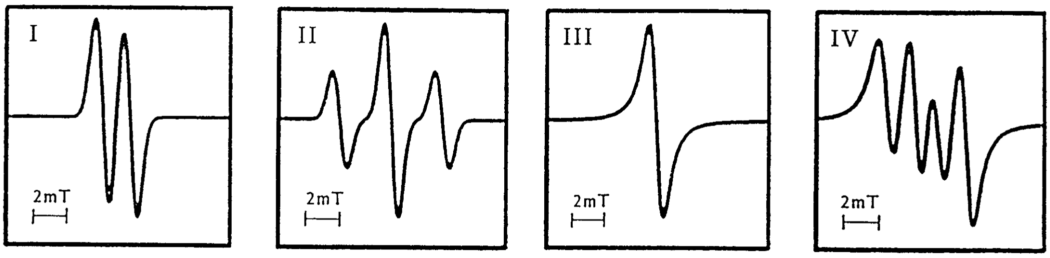

Fig. 5. Representative Selection of Component Spectra (I—IV) for the Simulated ESR Spectra of Plasma-Irradiated EC

Table 1. ESR Spectral Data for Component Radicals in Simulated Spectra of EC and HEC

	I	II	III	IV	
EC					
g	2.0033	2.0031	2.0026	$g=2.0051$	$g_1=2.0045$ $g_2=2.0048$ $g_3=2.0061$
A_α				$A_\alpha=1.63$	$A_1=1.40$ $A_2=1.55$ $A_3=1.95$
A_β (1)	1.61	3.00		$A_\beta=2.90$	$A_1=2.90$ $A_2=2.90$ $A_3=2.90$
A_β (2)	—	3.00			
HEC					
g	2.0039	2.0030	2.0038	$g=2.0045$	$g_1=2.0040$ $g_2=2.0040$ $g_3=2.0054$
A_α				$A_\alpha=1.65$	$A_1=1.45$ $A_2=1.60$ $A_3=1.90$
A_β (1)	1.60	3.00		$A_\beta=3.00$	$A_1=3.00$ $A_2=3.00$ $A_3=3.00$
A_β (2)	—	3.00			

Values of HSC are given in mT.

The ESR spectroscopic parameters for a representative selection of these component spectra deduced from the simulations are summarized in Table 1. The principal anisotropic parameters vary somewhat from the spectra so that their values are only of semiquantitative significance.

Progressive Changes in Component Spectra Figures 6 and 7 show the progressive changes in the spectral intensities of each component radical corresponding to the simulated spectra shown in Fig. 5. The total spectral intensities were very compatible with the intensities determined by double integration of the observed spectra. It is apparent that the rate of increase of each spectral intensity does not vary much from the component spectra (Fig. 6), accounting for rather small spectral changes in pattern in the course of plasma irradiation in both cases. On standing at room temperature, all the component spectra decayed with large initial rates in both cases, EC and HEC (Fig. 7).

Note that exposure to air caused a rapid dissipation of all the component radicals in both cases, indicating facile reactions with oxygen which result in the formation of oxidized nonradical species. This is in sharp contrast to the radicals of monocarbohydrates such as glucose and *myo*-inositol,$^{3)}$ where the radicals formed were very stable in a dry atmosphere at room temperature for a long period of time.

Structural Assignments Both simulated spectra, in EC and HEC, are primarily characterized by the presence of a large amount of the single broad line (III) as a major component. Although the g-value of III indicated that it is a carbon centered, not oxygen-centered, radical, we

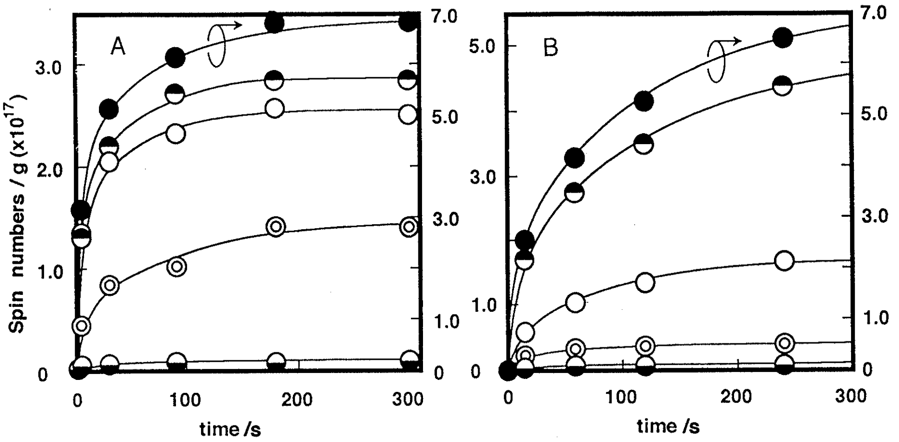

Fig. 6. Progressive Changes in Spectral Intensities of Component Spectra Corresponding to the Simulated Spectra of Plasma-Irradiated EC (A) and HEC (B) on Plasma-Duration

●, total; ○, I; ◒, II; ◓, III; ◎, IV.

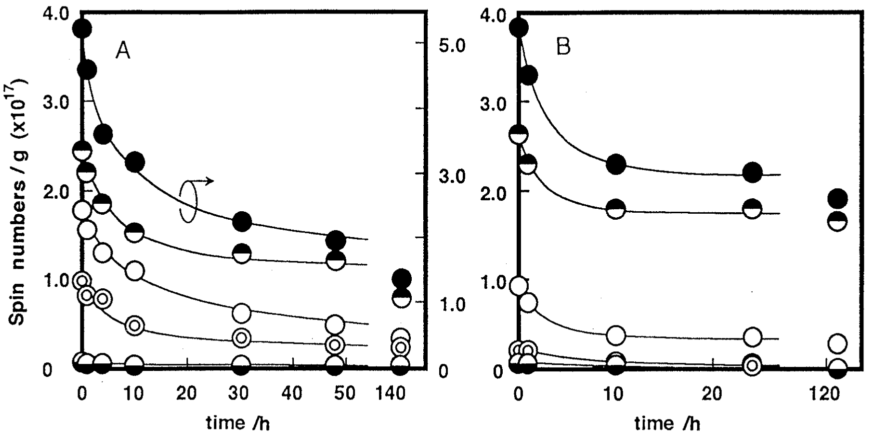

Fig. 7. Progressive Changes in Each Component Spectral Intensity in Simulated Spectra of Plasma-Irradiated EC (A) and HEC (B) Powders on Standing at Room Temperature

●, total; ○, I; ◒, II; ◓, III; ◎, IV.

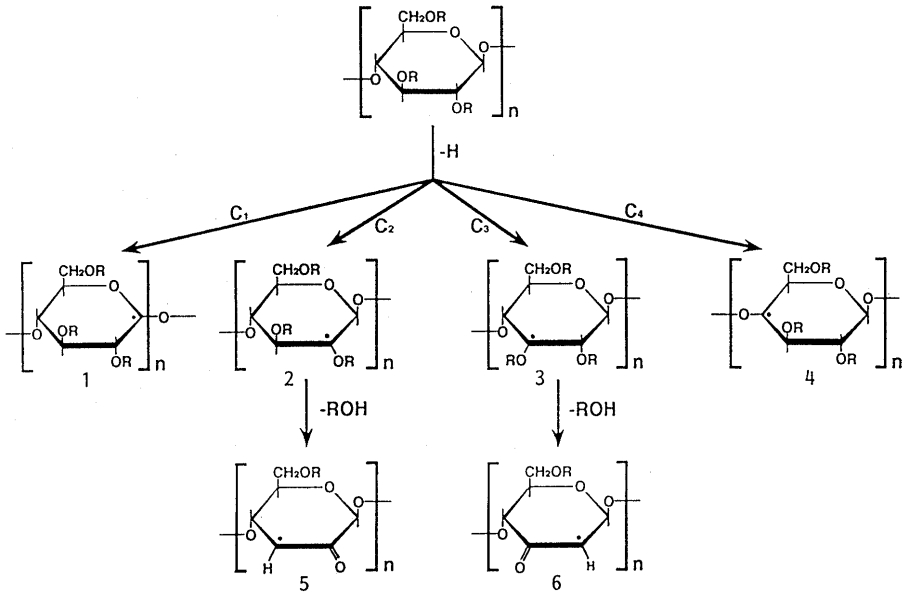

Fig. 8. Structures of Plasma-Induced Radicals in EC and HEC and the Reaction Sequence

cannot present any discrete radical structure, but assigned it to an immobilized dangling-bond site (DBS) mainly at the cross-linked region of side chain alkyl groups including a mixture of ring-opened and/or conjugated structures resulting from glucoside bond cleavages, and of no structural significance. A nearly isotropic doublet (I) can be assigned to an alkoxylalkyl radical at C_1 (**1**) of the glucose unit formed by a hydrogen abstraction. Based on the cosine square rule, the rather large g-values and smaller HSC of the doublet for axial β-hydrogen at C_2 may stem from the influence of the two oxygens bonded to the radical center. The isotropic triplet (II) is most reasonably assigned to an alkoxylalkyl radical at C_2 (**2**), C_3 (**3**) and/or C_4 (**4**) split by two axial β-hydrogens. However with the present ESR spectra we cannot discriminate these alternatives. Finally, we can assign a doublet of doublets (IV) with a g-factor and hyperfine anisotropy to the acylalkyl radical **2** and/or **3**, which has resulted from the facile dealkoxylation of the alkoxylalkyl radical at C_3 (**5**) and/or C_2 (**6**). All these radical structures and reaction sequences are summarized in Fig. 8.

Conclusion

We have presented a detailed analysis of plasma-induced radicals of EC and HEC based on ESR coupled with systematic computer simulations. From the present study, the radicals formed in plasma-irradiated EC and HEC were elucidated, and they involve a large amount of the single broad line (III) as a major component, assignable to the immobilized DBS. The most interesting contrast in the ESR spectra between cellulose and its alkyl derivatives, EC and HEC, is that the spectra of plasma-irradiated cellulose contain a large amount of isotropic triplets with 2.98 mT of HSC, while those of plasma-irradiated EC and HEC contain such triplets to a much lesser extent. The present results clearly indicated that alkyl and/or alkoxyl derivatization of cellulose would have a higher tendency to undergo cross-linking reactions due to the presence of alkyl (alkoxyl) groups, since the radicals formed in such side chains are of high reactivity.

The present finding provides a basis for future experimental design in the preparation of new pharmaceutically useful materials applicable for drug delivery systems (DDS)7) as well as plasma treatment with a variety of polycarbohydrates. Such applications will be the subject for a forthcoming paper and is reported elsewhere.

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