SPECTROCHEMISTRY OF PLASMA-INDUCED FREE RADICALS IN GLUCOSE-BASED POLYCARBOHYDRATES

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ABSTRACT

We report here 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 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 a 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-link reactions are very predominant in EC and HEC relative to that of cellulose, due to the presence of alkyl substituents in EC and HEC.

INTRODUCTION

In view of the fact that 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 elucidation of plasma-induced surface radicals, we have recently reported ESR study on monocarbohydrate (*myo*-inositol) /3/ and polycarbohydrates (cellulose and amylose) /4/, because of the suitability as a model for more complicated carbohydrates.

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

In this paper, we report the special features of plasma-induced free radicals of cellulose derivatives such as EC and HEC, on its comparison with those of cellulose studied by ESR coupled with the systematic computer simulations.

EXPERIMENTAL SECTION

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

ESR Spectral Measurement ESR spectra were recorded by a JES-RE1X (JEOL) spectrometer with 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 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 1 shows progressive changes in the observed ESR spectra of plasma-irradiated EC and HEC at various durations (A and B) and those of the plasma-irradiated samples (EC for 300s duration and HEC for 60s duration) on standing at room temperature under anaerobic conditions (C and D), together with those of plasma-irradiated cellulose at various duration for a comparison purpose (E).

It is seen from Figure 1A and 1B that the spectral features vary with materials, EC and HEC, but remain nearly unchanged in the course of plasma irradiation in each case. These spectra appear to be an outline of multicomponent spectra and also apparently differ from those of cellulose shown in Figure 1E.

In a series of spectra when the respective sample plasma-irradiated for 300s or 60s 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 Figure 1C and 1D.

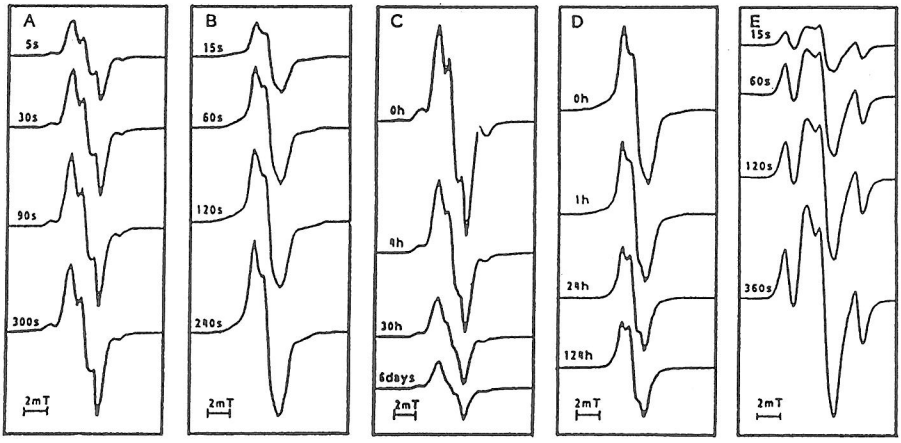

Fig. 1 Progressive changes of observed ESR spectra of plasma-irradiated EC and HEC at various durations (A and B), those of the plasma-irradiated samples on standing at room temperature under anaerobic conditions (C and D) and plasma-irradiated cellulose at various duration (E).

Figure 2 shows the progressive changes of 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 were leveled off for much shorter plasma duration and the decay rate of their radicals on standing at room temperature was higher than that of cellulose, indicating the presence of less-stable radicals in them.

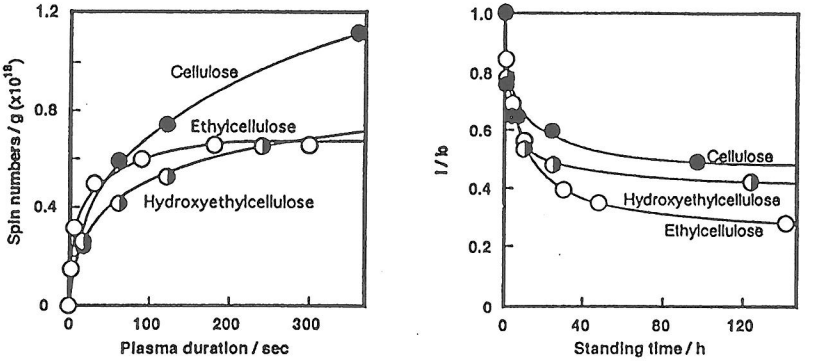

Fig. 2 Progressive changes in spectral intensities determined by double integration : (A) on plasma-duration, (B) on standing at room temperature.

Corresponding Simulated Spectra We have systematically conducted the computer simulations of these progressive changes of the complicated spectra in an interrelated manner. The simulated spectra corresponding to the observed spectra in Figure 1 are shown in Figure 3. 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.

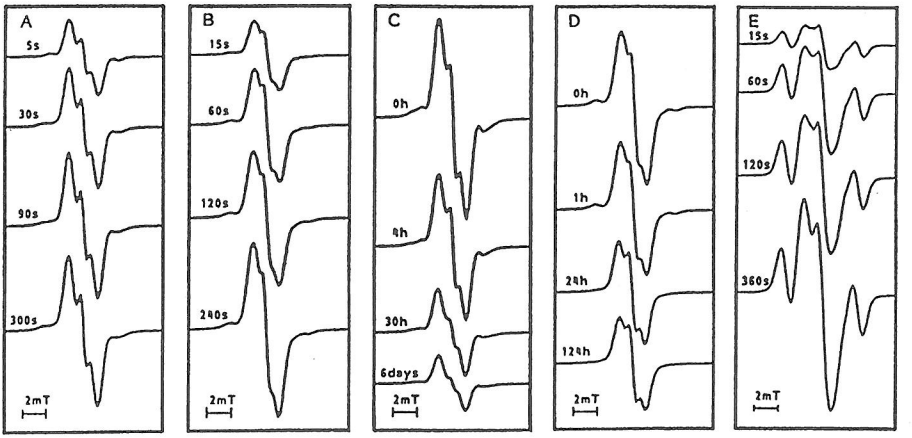

Fig. 3 Simulated spectra corresponding to the observed spectra in Fig. 1.

Figure 4 shows the representative spectral components of the simulated spectra of EC as a presentative example; three isotropic spectra [doublet (I) of g=2.0033 with 1.61 mT of HSC, triplet (II) of g=2.0031 with 3.00 mT of HSC and a single broad line spectrum (III) of g=2.0031], and one anisotropic spectrum [doublet of doublets (IV) of $\bar{g}$=2.0051 (g_1=2.0045, g_2=2.0048, g_3=2.0061) with $\bar{A}_\alpha$=1.63 mT (A_1=1.40 mT, A_2=1.55 mT, A_3=1.95 mT), and A_β=2.90 mT of HSC].

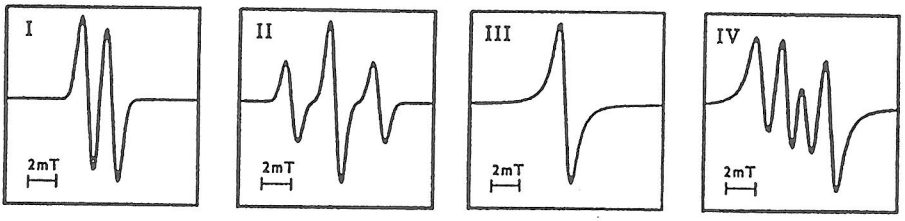

Fig. 4 Representative selection of component spectra (I-IV) for the simulated ESR spectra of plasma-irradiated EC.

Progressive Changes in Component Spectra Figures 5 and 6 show the progressive changes in the spectral intensity of each component radical corresponding to the simulated spectra shown in Figure 3.

It is apparent that the rate of increase in each spectral intensity does not vary much with component spectra (Fig. 5), 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 decay with large initial rates in both cases, EC and HEC (Fig. 6).

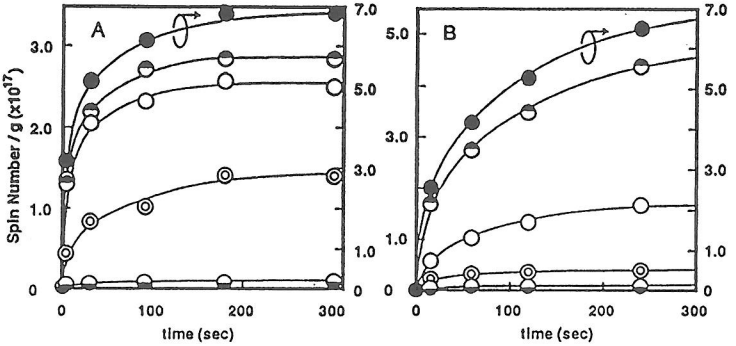

Fig. 5 Progressive changes of spectral intensities of component spectra corresponding to the simulated spectra of plasma-irradiated EC (A) and HEC (B) on plasma-duration : (●) total; (○) I; (◒) II; (◓) III; (◎) IV.

Note that exposure to air has caused a rapid dissipation of all the component radicals in both cases, indicating the facile reactions with oxygen to 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 dry atmosphere at room temperature for a long period of time.

Structural Assignments Both simulated spectra, in EC and HEC, are most characterized by the presence of a large amount of the single broad line (III) as a major component, which was assigned to an immobilized dangling-bond site (DBS) at the cross-linked region. 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 a alkoxylalkyl radical at C_2, C_3 and/or C_4 split by two axial β-hydrogens. But, the present ESR spectra can not discriminate these alternatives. Finally, we can assign a doublet of doublets (IV) with g-factor and hyperfine anisotropy to the acylalkyl radical at C_2 and/or C_3, which have resulted from the facile dealkoxylation of alkoxylalkyl radical at C_3 and/or C_2. All these radical structures and reaction sequence are summarized in Figure 7.

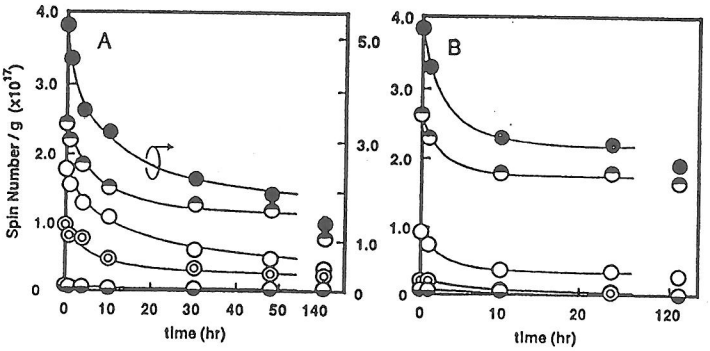

Fig. 6 Progressive changes of each component spectral intensity in simulated spectra of plasma-irradiated EC (A) and HEC (B) powders on standing at room temperature : (●) total; (○) I; (◒) II; (◓) III; (◎) IV.

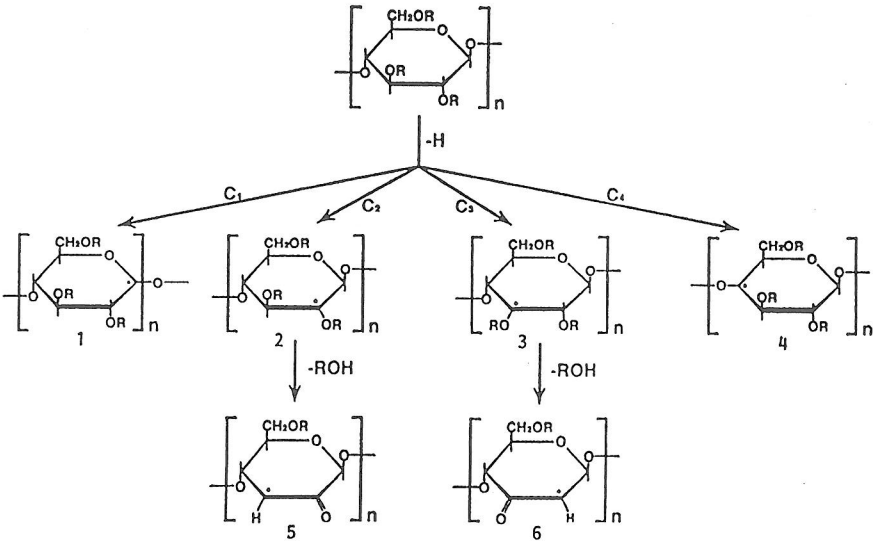

Fig. 7 Structures of plasma-induced radicals in EC and HEC and the reaction sequence.

CONCLUSION

We have presented the detailed analysis of plasma-induced radicals of EC and HEC based on the ESR coupled with systematic computer simulations. From the present study, the radicals formed in plasma-irradiated EC and HEC were elucidated, which involve a large amount of the single broad line (III) as a major component, assignable to the immobilized dangling bond site. 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 triplet with 2.98 mT of HSC, while those of plasma-irradiated EC and HEC contain such a triplet to a much lesser extent. The present result clearly indicated that alkyl derivatizaton of cellulose would have higher tendency to undergo the cross-linked reactions. This type of finding provides a basis for the future experimental design on plasma treatment of a variety of polycarbohydrates.

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