

Preparation of Starch-Water-Probe Samples

The water-probe two-phase suspension was added to starch at a weight ratio of 1:2 of starch to water-probe suspension. The mixtures were then slurried for 24 hr at room temperature before transfer to 2-mm glass capillary tubes. ESR spectra were run on samples at room temperature. Other samples were heat treated for 4 min at 40, 45, 50, 55, 75, or 95°C with subsequent cooling to room temperature prior to obtaining ESR spectra.

ESR Spectra

Two ESR spectrometers were used in the study. Preliminary work was done using a Varian E-3 with an operating frequency of about 9.33 GHz with center field at 3.2 kG. The remainder of the study was done using an IBM ERO23M with an operating frequency of about 9.77 GHz with center field at 3.5 kG. Spectra were analyzed as described by Pearce et al (1985, 1987).

Mineral Analysis

Sodium and potassium were analyzed on an Applied Research Laboratories spectrometer (model QA137) by inductively coupled plasma (ICP). Samples (1–2 g) of dry starch were ashed overnight at 485°C, then dissolved in concentrated HCl and HNO₃ prior to analysis.

RESULTS

Probe Concentration and Spin Broadened Spectra

Figure 1a and b show the effect on the ESR spectra of doubling the concentration of 5-DOXYL-stearic acid from the 1:0.002 starch to probe ratio used by Pearce et al (1985, 1987) to 1:0.004 for waxy corn starch. Doubling the probe concentration of waxy corn starch resulted in a slightly spin broadened spectrum due to interaction broadening between paramagnetic electrons of adjacent probes. For regular corn starch (Fig. 1c), doubling the probe concentration did not change the spectra and it retained the dilute spin, broad-line, powder pattern observed at the lower probe concentration. The same differences in degree of spin broadening were not seen at this concentration ratio for 16-DOXYL-stearic acid. For comparison, the remaining spectra shown will be for the starch to 5-DOXYL-stearic acid ratio equal to 1:0.004.

Nonionic Hydrophilic Modification of Waxy Corn Starch

Figure 2 shows the room temperature spectra of the nonionic hydrophilic substitutions of the commercially modified ACW and HPW corn starch. The two spectra are very similar, with both

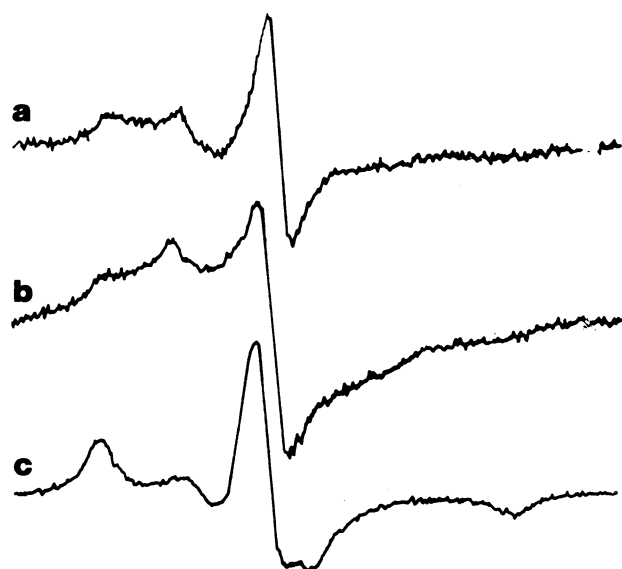


Fig. 1. Electronic spin resonance spectra (Varian) of starch and 5-DOXYL-stearic acid: waxy corn starch at a ratio of 1:0.002 (a), waxy corn starch at a ratio of 1:0.004 (b), regular corn starch at a ratio of 1:0.004 (c).

showing more spin broadening than unmodified waxy corn starch (Fig. 1b), an indication of impeded penetration of the probe into the granule. Figure 3 further illustrates the effect of hydroxypropyl substitution for the series of laboratory-prepared modifications of waxy corn starch at increasing DS levels. Progressively increased spin broadening from that of waxy corn starch (Fig. 3a) occurs when increasing the DS from 0.055 to 0.085 to 0.133 (Fig. 3b–d). The commercially modified HPW at an unknown DS appears to have a high level of DS when Figure 2b is compared with Figure 3.

Spectra of Modified Regular Corn Starch

Figure 4 shows native unmodified and a series of hydroxypropyl substitutions of regular corn starch. The spectra for the substituted starches, like those of native unmodified regular corn starch, show

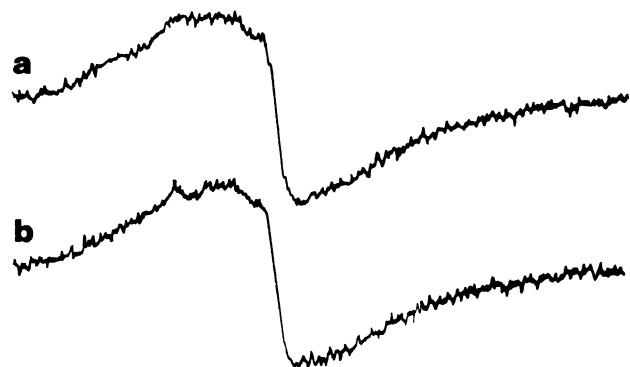


Fig. 2. Electronic spin resonance spectra (Varian) of commercially modified waxy corn starch and 5-DOXYL-stearic acid at a ratio of 1:0.004: acetylated (a), hydroxypropyl (b).

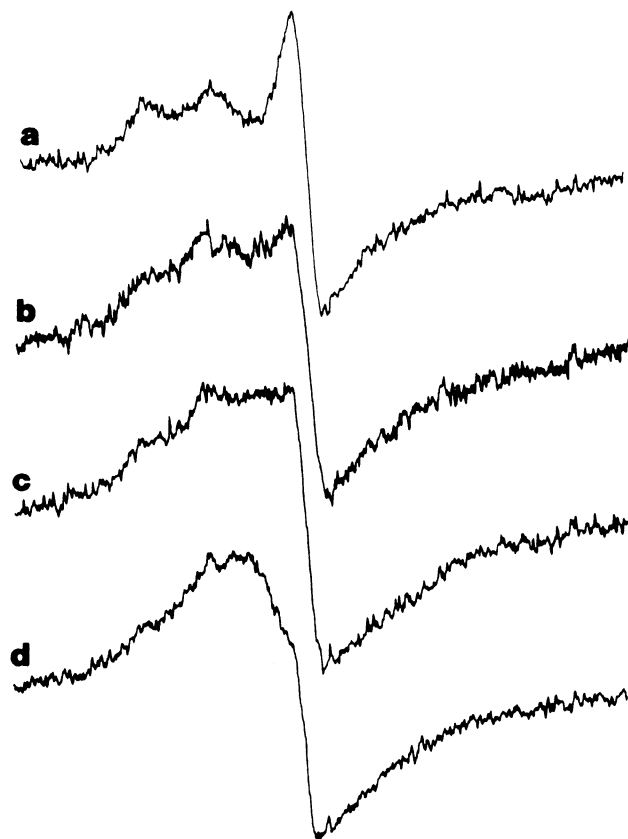


Fig. 3. Electronic spin resonance spectra (IBM) of native unmodified waxy corn starch and of laboratory prepared modifications of hydroxypropyl waxy corn starch and 5-DOXYL-stearic acid at a ratio of 1:0.004: native unmodified (a), DS 0.055 (b), DS 0.085 (c), DS 0.148 (d).

no spin broadening. As the levels of DS increase from 0.055 to 0.098 to 0.148, there is a progressive decrease in the slow motion component with a corresponding increase in the fast motion component in the low-field region of the spectra. Correspondingly, progressive changes are also noted in the high-field region of the spectra.

Ionic Substituions of Waxy Corn Starch

The cationic substitutions studied, a quaternary ammonium derivative of waxy corn starch at DS 0.036 and 0.052 had spectra identical to that of the unmodified waxy corn starch (Fig. 3a);

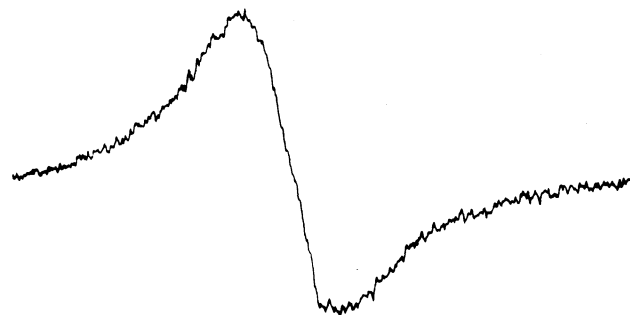


Fig. 6. Electronic spin resonance spectra (IBM) of a laboratory prepared modification of waxy corn starch octenylsuccinate at DS 0.015 and 5-DOXYL-stearic acid at a ratio of 1:0.004.

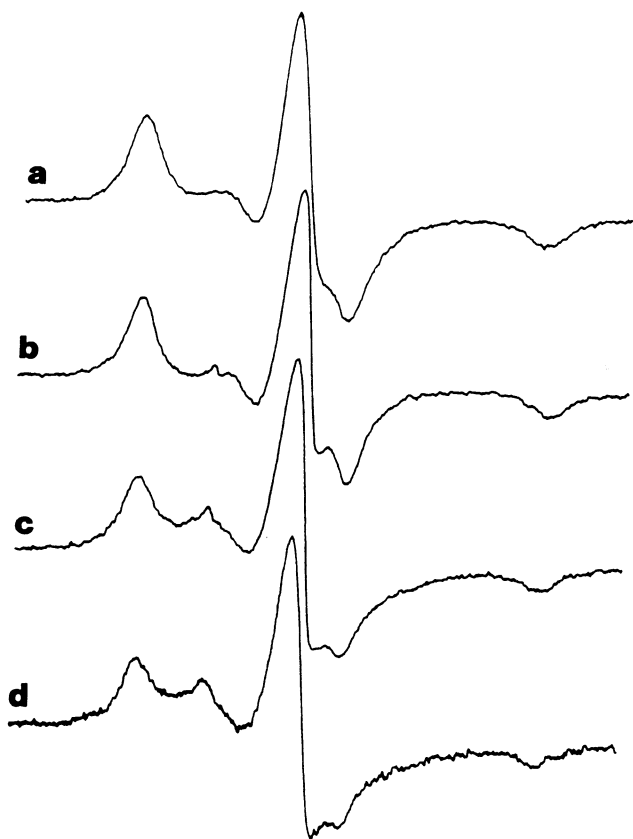


Fig. 4. Electronic spin resonance spectra (IBM) of native unmodified regular corn starch and of laboratory prepared modifications of hydroxypropyl regular corn starch and 5-DOXYL-stearic acid at a ratio of 1:0.004: native unmodified (a); DS 0.055 (b); DS 0.098 (c); DS 0.148 (d).

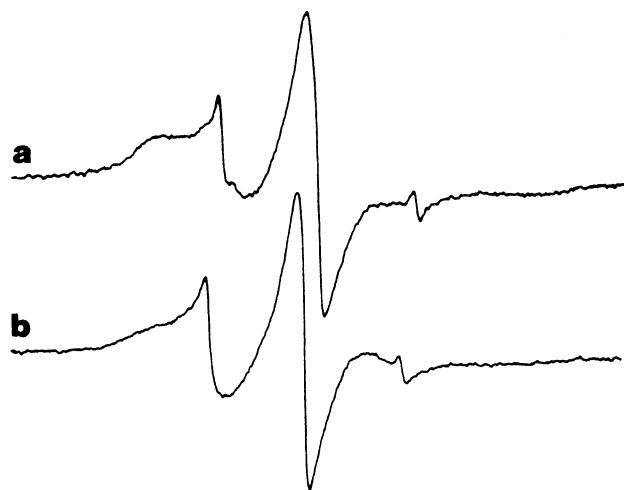


Fig. 5. Electronic spin resonance spectra (IBM) of laboratory prepared modifications of waxy corn starch phosphate monoester and 5-DOXYL-stearic acid at a ratio of 1:0.004: DS 0.0087 (a), DS 0.026 (b).

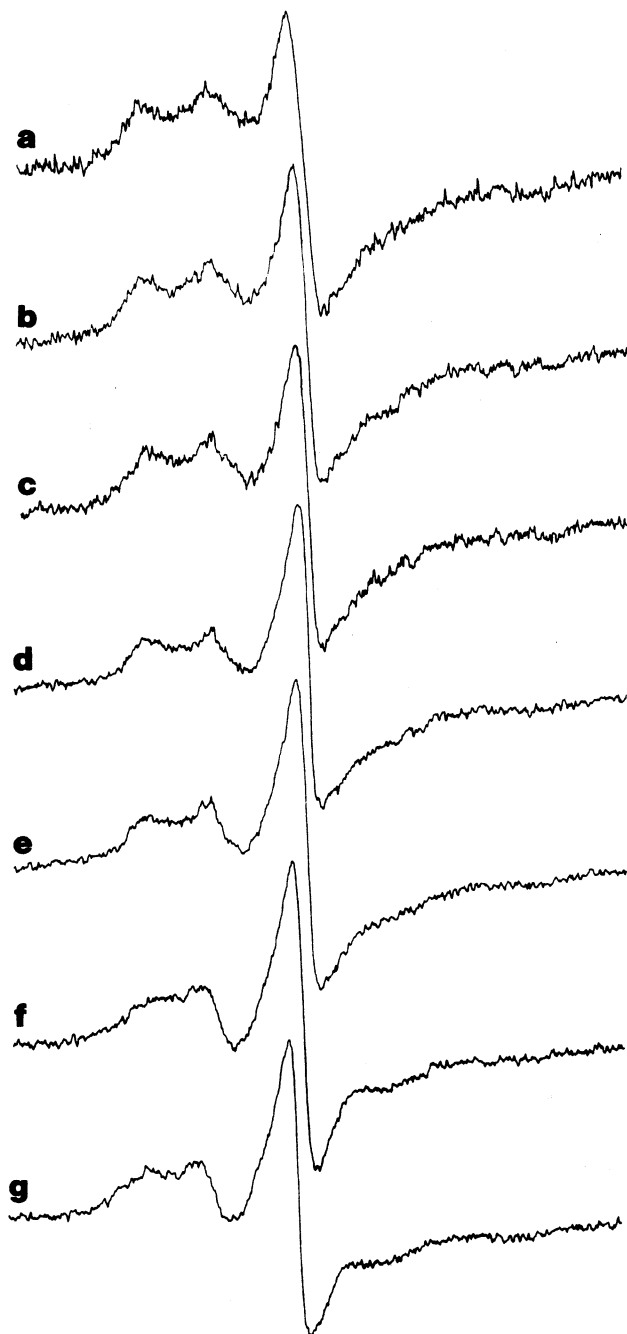


Fig. 7. Electronic spin resonance spectra (IBM) of native waxy corn starch and 5-DOXYL-stearic acid at a ratio of 1:0.004 at varying degrees of heat treatment: none (a), 40 (b), 45 (c), 50 (d), 55 (e), 75 (f), and 95°C (g).

thus the spectra are not shown. The anionic substitutions studied, a waxy corn starch phosphate monoester at DS of 0.0087 and 0.026, are shown in Figure 5. Conversely, this modification had spectra very dissimilar to that of the unmodified waxy corn starch. The spectra were neither like the powder pattern nor spin broadened spectra but appeared to show the three-line components of rapid isotropic motion of the nitroxide, which was superimposed on a slight powder pattern. This is an indication of a very little binding of the fatty acid probe.

Hydrophobic Substitution of Waxy Corn Starch

Figure 6 shows the unheated spectrum of the octenylsuccinate derivative of waxy corn starch with a DS of 0.015. The spectrum shows extreme spin broadening at very low DS when compared with the spin broadening for the nonionic hydrophilic substitutions.

Spectra of Heat Treated Native and Modified Waxy Corn Starch

Figure 7 shows gradual reduction in spin broadening from room temperature spectra of native waxy corn starch after heating to several different temperatures. Reduction in spin broadening was found to correspond to the amount of heating given.

Modified waxy corn starch also showed reduced spin broadening with heating. Figure 8 shows the spectra after heating at 95°C for the highest DS levels studied of hydroxypropyl waxy corn starch, quaternary ammonium waxy corn starch, waxy corn starch phosphate monoester, and the octenylsuccinate of waxy corn starch. For the spin broadened spectra of the hydroxypropyl and quaternary ammonium derivative there is a reduction in the amount of spin broadening (Fig. 8a and b). The phosphate monoester (Fig. 8c) showed reduction in the motionally narrow three-line component with replacement of a powder pattern that still showed much mobility. For the octenylsuccinate there was very little reduction in spin broadening (Fig. 8d).

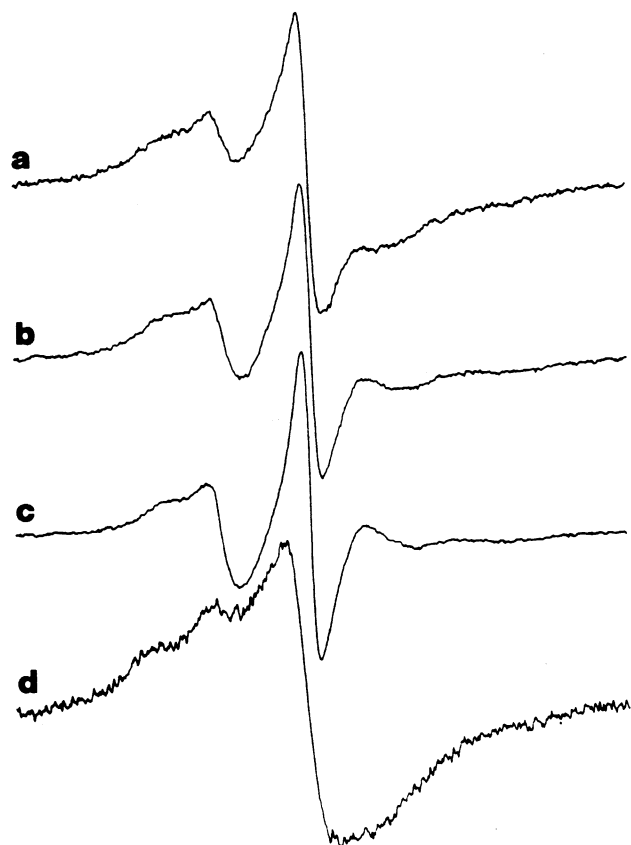


Fig. 8. Electronic spin resonance spectra (IBM) of modified waxy corn starches after heating at 95°C: hydroxypropyl, DS 0.085 (a); quaternary ammonium, DS 0.052 (b), phosphate monoester, DS 0.026 (c), octenylsuccinate, DS 0.015 (d).

ESR Spectra Affected by Salts

Figure 9 shows a series of starch samples (waxy corn starch and the laboratory-prepared modifications of hydroxypropyl waxy corn starch at increasing levels of DS) that were not washed with distilled water before probe addition. The same series of starches that were washed before probe addition (shown in Fig. 3) are quite dissimilar to those of Figure 9 in every case. Mineral analysis by ICP for washed and unwashed samples showed that the levels of sodium were reduced from 250 to 20 ppm, and the levels of potassium were reduced from 50 to <10 ppm after washing of the waxy corn starch. Sodium was reduced from 970 to 50 ppm and potassium from 20 to <10 ppm for the DS 0.133 hydroxypropyl waxy corn starch. The waxy corn starch was more spin broadened in the presence of salts, whereas the hydroxypropyl waxy corn starches showed elements of the three-line, motionally narrowed spectrum (which increased in the presence of salts) superimposed on a spin broadened type spectrum.

DISCUSSION

Three types of interactions of the fatty acid probe with the granular starch could be distinguished from the ESR spectra. The first type, when a powder pattern was obtained, was the relative strength of the complex seen by comparing fast and slow motion components of the ESR spectral line shape. Powder pattern spectra were obtained for regular and modified regular corn starch and for waxy and some modified waxy corn starches after heat treatment. In general, chemical modification led to more mobile powder pattern type spectra.

The second type of interaction seen when spin broadened spectra were obtained was the amount of surface absorption rather than granular penetration of the probe. This was noted by the degree of spin broadening, which for all modified starches differed from waxy corn starch. The nonionic hydrophilic substitutions inhibited

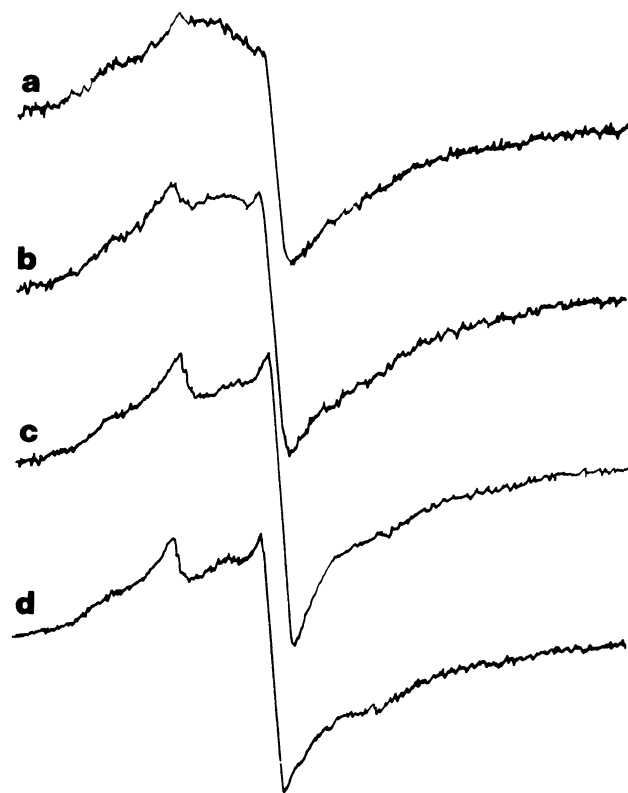


Fig. 9. Electronic spin resonance spectra (Varian) of unwashed native unmodified and unwashed laboratory prepared hydroxypropyl modifications of waxy corn starch with 5-DOXYL-stearic acid at a ratio of 1:0.004: native unmodified (a), DS 0.055 (b), DS 0.085 (c), DS 0.133 (d).

