Microstructure and surface composition of corn starch cryogels with sorbed organic flavoring agents

*A. G. Filatova,[a] I. O. Volkov,[b] N. I. Krikunova,[a] T. A. Misharina,[a] and R. V. Golovnya[a]**

[a]*N. M. Emanuel Institute of Biochemical Physics, Russian Academy of Sciences, 4 ul. Kosygina, 117977 Moscow, Russian Federation. Fax: +7 (095) 137 4101*

[b]*A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 28 ul. Vavilova, 117813 Moscow, Russian Federation. Fax: +7 (095) 135 5085*

The surface composition and surface microtopography of corn starch cryogels obtained from a 3% starch sol containing organic flavoring agents were studied by X-ray photoelectron spectroscopy and scanning electron microscopy. The cryogels with *n*-octanol, *n*-octyl methyl ketone, and *n*-octyl acetate have a well-developed microtopography and their surface layer (5—20 nm) is enriched in sorbed compounds. *n*-Octyl acetate, unlike *n*-butyl acetate, influences the composition and microstructure of the cryogel surface. The sorbed *n*-octyl acetate occupies 20—25% of the surface, which has a well-developed topography and a porous structure. Drying and evacuation do not change the concentration of the organic sorbates having a C_8 alkyl group in the surface layer.

Key words: corn starch cryogel with sorbates, *n*-octanol, *n*-octyl acetate, butyl acetate, *n*-octyl methyl ketone, surface, scanning electron microscopy, X-ray photoelectron spectroscopy.

Study of the sorption properties of starch and starch gels toward organic components of food flavoring agents is of interest for both theoretical and practical purposes.

It was shown previously[1] that cycles of freezing and thawing of starch sols can give cryogels with porous structures. In the studies devoted to the structure and physicochemical properties of synthetic polymeric systems,[2,3] these specific features have been explained by accumulation of the solvent during crystallization. The structure of starch cryogels has not been studied. The sorption capacity of corn starch cryogels toward alkyl acetates or alcohols was first studied in previous publications.[4,5] This work is devoted to the influence of a sorbed low-molecular-weight compound on the surface composition and structure of corn starch cryogels.

Experimental

The corn starch cryogels used in the work were prepared by freezing of 40 mL of a 3% sol at −18 °C for 24 h and subsequent thawing for 16 h in order to attain equilibrium in the water—cryogel system.[4,5] Five samples were studied, the initial cryogel and four cryogel samples obtained from sols containing 1 mmol L^{-1} of an organic sorbate. *n*-Butyl acetate, *n*-octyl acetate, *n*-octyl methyl ketone, and *n*-octanol were used as the sorbates. The three last-mentioned compounds containing the *n*-C_8 alkyl group attached to a functional group are capable mainly of hydrophobic interactions with cryogels.[4]

The amounts of flavoring compounds sorbed by cryogels (in percent of the amount introduced) determined by capillary gas chromatography were 88% for *n*-octanol, 95% for *n*-octyl acetate, 96% for methyl octyl ketone, and 38% for *n*-butyl acetate.[4,5]

The samples of cryogels were studied by scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS), which provide information on the microstructure and composition of a 5—20-nm thick surface layer. The cryogel microstructure was studied using an S-2500 Hitachi scanning electron microscope (Japan) at an accelerating voltage of 15 kV in the secondary electron mode. The materials were prepared by the freezing—drying procedure.[3] A thin layer of a cryogel was frozen in liquid nitrogen, dried lyophilically at −80 to −90 °C. The cryogenic preparation conditions were determined by thermal analysis using an ISK instrument (the "Elektron" association, Ukraine), which allows detection of ice crystals on freezing of a water-containing sample.[6] The resulting thermograms were analyzed in order to choose the best conditions for the cryogenic preparation of samples, which were freezing at a rate of 100 K s^{-1} followed by drying *in vacuo* at −80 to −90 °C; this made it possible to avoid artefacts associated with crystallization or recrystallization of ice. A thin layer of gold was applied *in vacuo* onto the surface of a lyophilically dried sample to form a conducting surface.

The surface composition of the cryogels was determined by XPS[7] using a Kratos XSAM-800 instrument (UK) in a vacuum of about 10^{-7} Pa. The spectra were excited by the characteristic emission of magnesium ($h\nu$ = 1253.6 eV). The power of the X-ray gun in the experiments did not exceed 60 W (15 kV, 4 mA); no radiation-induced destruction of samples was observed under these conditions. The X-ray photoelectron spectra were processed using the DS-800 program package. The starch and sorbate concentrations in the 5—20-nm thick surface layers of cryogel were determined from the ratio of the integral intensities of individual carbon components using a known procedure.[7]

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 2, pp. 312—314, February, 2000.

1066-5285/00/4902-0314 $25.00

Results and Discussion

Based on the electron-microscopic study, the corn starch cryogels show porous structure. Two types of pores, with narrow (1—15 μm) and wide (60—70 μm) dimensions, were detected in each sample. No grains of the initial starch were found inside the pores; apparently, all polysaccharides form the cryogel walls during cryostructuring. The nature of supramolecular organization of the porous structure found in the five samples is similar, probably due to identical conditions of cryostructuring.

It should be noted that the surface topography of the cryogel walls in the samples is different. According to an SEM examination, the cryogel of the initial corn starch has a poorly developed surface topography (Fig. 1, *a*) compared to those prepared in the presence of organic sorbates. The initial cryogel is characterized by a uniform surface structure comprising uniform spherical particles. The surface of the cryogel formed in the presence of *n*-butyl acetate almost does not differ from that of the cryogel prepared without the addition of a sorbate. This might be due to the fact that *n*-butyl acetate is adsorbed on the surface and removed during evacuation when the sample is prepared for the investigation.

The surface of the starch cryogel containing *n*-octyl acetate shows heterogeneous structure. In addition to the uniform areas typical of the sorbate-free cryogel, areas with a well-developed topography with large particles of up to 2—3 μm can be distinguished (see Fig. 1, *b*). These particles, aggregated in clusters, cover 30—50-μm areas adjacent to more uniform and smoother surfaces.

The particle size in the cryogel prepared from the octyl methyl ketone-containing sol ranges from 0.5 to 4 μm.

In the case of *n*-octanol, most particles on the cryogel surface are smaller (0.5—1 μm) but larger particles can also be found occasionally. The areas with well-developed surface topography are inferior to those in the starch cryogel with *n*-octyl acetate. The structures with a well-developed topography cover, on the average, 20—25% of the surface of the starch cryogel with *n*-octyl acetate and 10—13% of the surface of the cryogels containing *n*-octyl methyl ketone or *n*-octanol. Probably, the formation of the cryogel surface layer is due to the introduction of a low-molecular weight organic compound into the strarch sol before cryostructuring.

According to the XPS data, the surface of the starch cryogel is enriched in the sorbate. The C1s line of the X-ray photoelectron spectrum of the initial starch cryogel is presented in Fig. 2, *a*. By resolving the experimental carbon line into the contributions of individual chemical groups, one can distinguish the components caused by the carbon atoms not linked to oxygen atoms (CC, bond energy — E_b = 285.0 eV), those bonded to one oxygen (CO, E_b = 286.5 eV), and those connected to two oxygens (COO, E_b = 288.0 eV). Since all C atoms in starch are bonded to O atoms, the presence of the component with E_b = 285.0 eV in the X-ray photoelectron spectra of the cryogel is due to the possible admixtures.

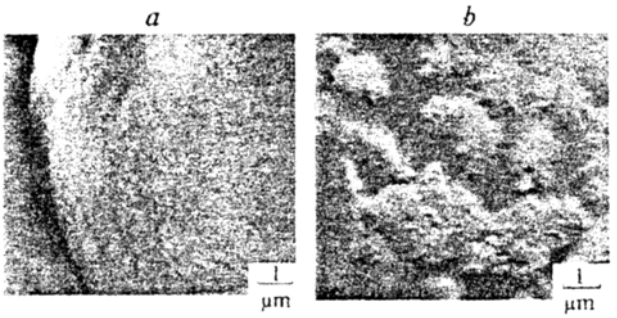

Fig. 1. Electron photomicrographs of the wall surface of the corn starch cryogel prepared from the 3% initial sol (*a*) and from a sol containing *n*-octyl acetate (*b*).

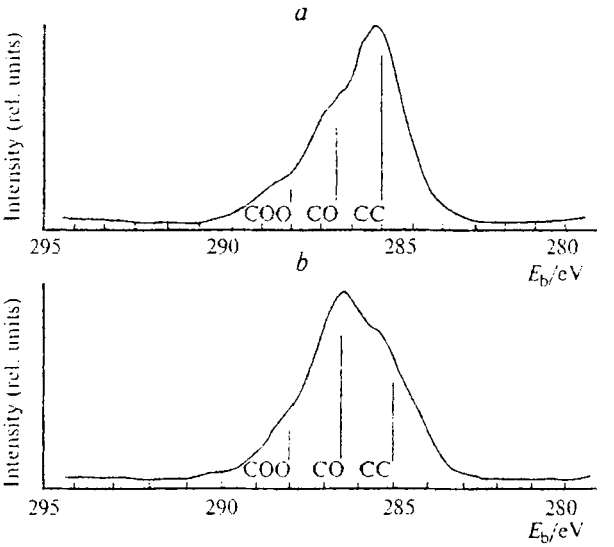

Fig. 2. C1s XPS line of the initial corn starch cryogel (*a*) and that containing *n*-octyl acetate (*b*).

The C1s line in the spectrum of the cryogel prepared from the sol containing *n*-octyl acetate has a greater contribution of the CC component (E_b = 285.0 eV), whereas the intensity of the starch components is markedly lower (see Fig. 2, *b*). Since *n*-octyl acetate consists mainly of C atoms that are not linked to O atoms, the observed changes might be due to the sorption of this compound by cryotexturate. Quantitative analysis shows that the intensity of the CC component (E_b = 285.0 eV) in the sample with *n*-octyl acetate increases by ~20—25% with respect to that in the initial sample (see Fig. 2, *a*), which is due to the sorption of *n*-octyl acetate by the surface layer.

Comparison of the results of quantitative XPS analysis with the SEM examination data suggests that the areas with a well-developed topography on the photomicrographs match the regions enriched in the low-molecular-weight sorbate. Verification showed that the substance sorbed by the cryogel is not evaporated from the

surface in a high vaccum or on prolonged storage. On heating in water, the low-molecular-weight sorbate passes into the aqueous medium and the cryogel structure is destroyed. Thus, it was shown for the first time that flavoring agents are bound noncovalently by the polysaccharides of a starch cryogel.

This work was financially supported by the Russian Foundation for Basic Research (Project No. 97-03-33109a).

References

1. M. Rikhter, Z. Augustat, and F. Shirbaum, *Izbrannye metody issledovaniya krakhmala* [*Selected Methods for the Investigation of Starch*], Pishchevaya Promyshlennost', Moscow, 1975, 356 (in Russian).
2. V. J. Lozinsky, E. S. Vainerman, E. F. Titova, E. M. Belavtseva, and S. V. Rogozhin, *Colloid Polym. Sci.*, 1984, **262**, 769.
3. E. M. Belavtseva, E. F. Titova, V. I. Lozinsky, E. S. Vainerman, and S. V. Rogozhin, *Colloid Polym. Sci.*, 1984, **262**, 775.
4. R. V. Golovnya and T. A. Misharina, *Nahrung*, 1998, **6**, 380.
5. M. B. Terenina, T. A. Misharina, and R. V. Golovnya, *Izv. Akad. Nauk, Ser. Khim.*, 1999, 734 [*Russ. Chem. Bull.*, 1999, **48**, 730 (Engl. Transl.)].
6. E. M. Belavtseva, I. I. Chemeris, T. A. Kabanova, and L. G. Radchenko, *Biofizika*, 1983, **28**, 958 [*Biophysics*, 1983, **28** (Engl. Transl.)].
7. A. I. Pertsin, M. M. Gorelova, V. Ju. Levin, and L. I. Makarova, *J. Appl. Polym. Sci.*, 1992, **45**, 1195.

Received March 30, 1999;
in revised form August 2, 1999