Effect of *n*-octyl acetate on the microstructure of corn starch sols studied by scanning tunneling microscopy

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The microstructure of a corn starch sol was studied by scanning tunneling microscopy. The influence of *n*-octyl acetate on the microstructure was found. The original starch sol contains compact anisodiametric particles 500—800 nm in size. The addition of *n*-octyl acetate produces friable oval associates consisting of fine spherical particles 50—20 nm in size.

Key words: scanning tunneling microscopy, sol, corn starch, clusters, *n*-octyl acetate.

In the previous[1,2] study of the sorption capability of cryotextures obtained from 3% starch sols, we have found that irreversible sorption is observed for compounds containing the *n*-octyl group. The XPES and scanning electron microscopy (SEM) studies of the surface of polysaccharide cryotextures[3] obtained from 3% corn starch sols with additives of *n*-octyl acetate, methyl *n*-octyl ketone, and *n*-octanol have revealed the influence of organic sorbates on the surface structure. Regions with a developed microrelief enriched in *n*-octyl acetate, methyl *n*-octyl ketone, or *n*-octanol are formed on the cryotexture surface. It was not clear whether these structures formed at the cryotexturation step during freezing—thawing out or this process began at the sol step in the starch polysaccharides—water system. In the last case, supramolecular associates of polysaccharides with *n*-octyl acetate spontaneously form due to numerous van der Waals interactions and hydrogen bonds. At the cryotexturation step, these supramolecular associates can additionally be strengthened due to noncovalent bonds between polymeric polysaccharides.

In this work, the system starch sol—water—*n*-octyl acetate was studied by scanning tunneling microscopy (STM).

Experimental

To study the surface structure of sols by scanning tunneling microscopy, we prepared samples of a 3% starch sol containing and not containing *n*-octyl acetate (0.65% with respect to the weight of starch in the sol). Sols were obtained by heating aqueous starch dispersions to 90 °C followed by cooling to 40 °C. *n*-Octyl acetate was added to one of the specimens, and then the specimens were exposed to 10 °C for 1 day.[1] Taking into account certain difficulties[4] that appear in STM study of biopolymeric systems that are related to the preparation of the conducting surface on which the specimen was placed, we pretested different methods for the preparation of starch sols. The best results were obtained as follows: sol samples in the form of microdrops were deposited on a freshly cleaved mica surface covered with a thin gold layer (5 nm). After drying of the plates in air for 1 min, gold layers (2—3 nm) were sputtered on the samples.

Experiments were carried out on an Omicron scanning tunneling microscope (UHV VT STM Omicron, Germany) under atmospheric pressure in the "direct current" mode. In this mode, the measured tunneling current between the tip and the specimen is maintained constant, and the variations of the current due to the roughness of the scanned region are detected by the transposition of the tip perpendicularly to the surface. The pattern of the surface relief (the measurement scale in nanometers) is the result of scanning. The parameters of the scanning of the sol specimens are the following: tunneling current 2.51 nA, bias voltage 60 mV, characteristic frame size 500×500 nm. After the end of detection, the obtained information was processed on a computer using a program that provides two- and three-dimensional images of the sample under study, "cuts" the surface in the vertical plane along an arbitrary direction, and mathematically processes data to improve the visual representation of the microstructure and obtain quantitative results.

Results and Discussion

The STM image of the corn starch sol clusters are presented in Fig. 1, *a*. The clusters are compact anisodiametric particles 500—800 nm in size. The cluster structure changes in the sol samples containing 0.65% *n*-octyl acetate. Oval friable clusters with sizes of 300—800 nm are observed (Fig. 1, *b*). It is seen that the cluster consists of spherical microparticles whose size is mainly 50 nm, but finer particles 20—30 nm in size are also observed.

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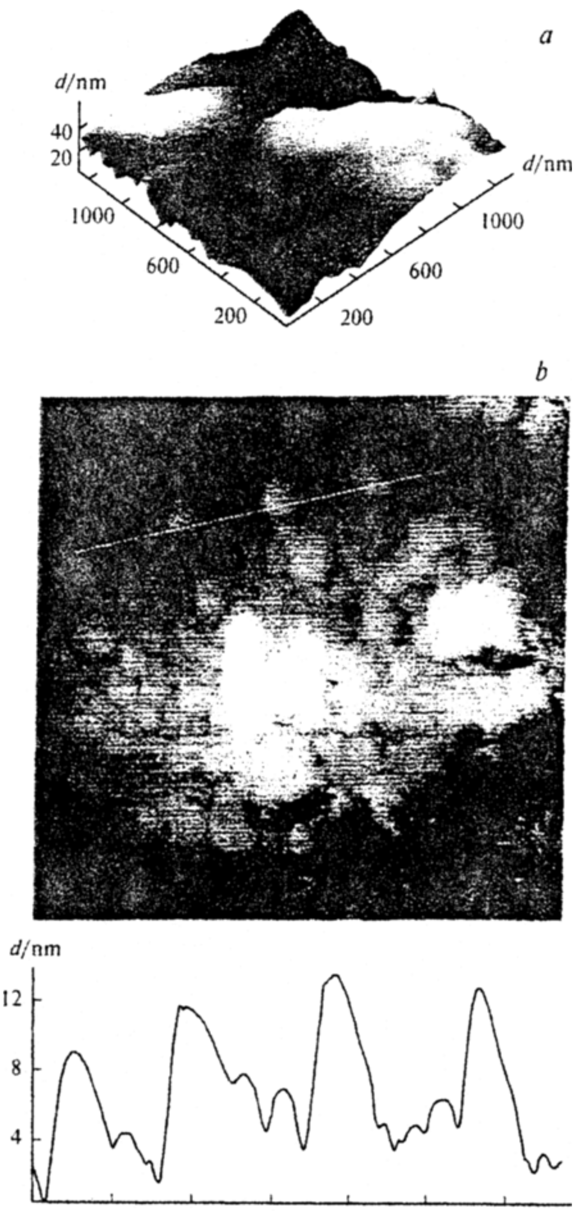

Fig. 1. STM image and the profile pattern of clusters of the corn starch sol: starting sample (*a*) and the sample containing *n*-octyl acetate (*b*); the results of measurements of the surface relief are presented in nm.

The results agree with the data obtained by us using SEM [3] and X-ray diffraction. The addition of *n*-octyl acetate to the starch sol results in the appearance of friable structures on the cryotexture surface. The degree of crystallinity calculated from the diffraction patterns, which were obtained on a DRON-3 diffractometer (Russia) using monochromatized Cu-Kα radiation, reaches 8% for the cryotexture without *n*-octyl acetate and decreases to 5% for that with *n*-octyl acetate. Therefore, the *n*-octyl acetate additive affects the structure formation of the cryotexture. The clusters with finite length have different structures, depending on the presence or absence of *n*-octyl acetate in the starting sol.

The results obtained by SEM and XPES,[3] X-ray diffraction, and STM indicate that molecular-organized systems of polysaccharides begin to form in the sol. These supramolecular structures undergo changes in the presence of *n*-octyl acetate. The clusters are formed at the sol phase, and the surface structure of the cryotexture obtained from the sol also changes.

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