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# A DSC and NMR-Relaxation Study of the Molecular Mobility of Water Protons Interacting with Chemically Modified Starches

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**Abstract**—Changes in the mobility of water protons in the chemically modified starches (CMS)–water system are studied by differential scanning calorimetry and NMR relaxation. The amounts of unfrozen water at negative temperatures and additional (after gelation) unfrozen for CMS are lower than those for native starch. The proton spin–spin relaxation time  $T_2$  for CMS samples, conventionally attributed to the water fraction in starch granules, decreases monotonically with increasing temperature, whereas for native starch, this dependence exhibits an extreme behavior. Studying the dispersion dependences for 7 wt % gels, which characterize the rate of chemical exchange of water protons with protons of hydroxyl groups of polysaccharides, showed the absence of this kind of dependence for the CMS studied when the instrument operated at a frequency of 20 MHz. This data indicate the significant destructive changes in the structure of the CMS.

*Keywords:* chemically modified starch, water, NMR relaxation, DSC

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At present, much attention is paid to studying the properties of chemically modified starches, which are prepared using a microwave irradiation effect on the reaction [1–4]. It was shown that microwave irradiation, providing a rapid and uniform heating of the reaction products, increases the reaction rate and selectivity, while decreasing the yield of the by-products of the esterification of starch with inorganic acids and their salts, anhydrides, and oxides [1]. Currently, modified starches produced under microwave irradiation are used to manufacture biodegradable materials. In particular, the introduction of silicates into starch biopolymers followed by microwave treatment enhances the functional properties of the resulting products, which

can serve as a component of biodegradable materials [3, 4]. One of the main characteristics of such materials is their interaction with water, which determines the functional properties of starch as a component of such materials.

The state of the starch–water system has been investigated by numerous experimental methods. In particular, differential scanning calorimetry (DSC) is widely used to study the processes of fusion, gelation, and phase transition [5–7]; X-ray diffraction is applied to investigate crystallization processes [8]; small-angle neutron scattering is used to examine the distribution of water in starch granules [9]. Along with high-resolution NMR, the NMR relaxation method has found a wide variety of applications [10–14] in studying this system.

A wide range of scientific techniques used by the authors of [3, 4] gives a clear picture of the properties of starch silicates. The molecular mobility of water in the interaction with such systems, the amount and properties of water unfrozen at subzero temperatures, which provide a more complete understanding of the changes in the properties of starch silicates, were the subject of our previous study [15]. The objectives of the present work were to increase the number of test objects and to use other methodological approaches and models in studying the molecular mobility of water protons interacting with starches modified by inorganic salts and subjected to microwave irradiation.

## MATERIALS AND METHODS

Samples of chemically modified starches were kindly provided by Gdansk University of Technology: (1) native potato starch (PS) ("Lomza," Poland);

(2) potato starch subjected to a convective heat treatment at  $t = 100^\circ\text{C}$  for 120 min (PSC);

(3) potato starch subjected to microwave irradiation at a power of  $w = 450\text{ W}$  for 30 min (PSW);

(4) a 1 : 1 wt mixture of potato starch and silicic acid subjected to a convective heat treatment at  $t = 100^\circ\text{C}$  for 120 min (PSCSi);

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(5) a 1 : 1 wt mixture of potato starch and silicic acid subjected to microwave irradiation at a power of  $w = 450\text{ W}$  for 30 min (PSWSi);

(6) a 1 : 1 wt mixture of potato starch and  $\text{Na}_2\text{ZnO}_2$  subjected to microwave irradiation at a power of  $w = 450\text{ W}$  for 30 min (PSWZn).

### DSC Study

The measurements were performed using DSC204F Phoenix calorimeter (Germany) provided with the Proteus software. The samples were mixed with distilled water in a weight proportion of 1 : 1, with allowance for the initial moisture content, which ranged within 10–12%, and held in a sealed aluminum capsule for 24 h. After the measurement, the capsule was opened, and the sample was dried at  $105^\circ\text{C}$  for 24 h to constant weight. Calorimetric measurements were carried out in several stages:

(1) cooling the sample to  $t = -40^\circ\text{C}$  at a rate of  $10^\circ\text{C}/\text{min}$ ;

(2) heating from  $-40$  to  $80^\circ\text{C}$  at  $10^\circ\text{C}/\text{min}$ ;

(3) cooling the sample again from  $80$  to  $-40^\circ\text{C}$  at  $10^\circ\text{C}/\text{min}$ ;

(4) reheating from  $-40$  to  $80^\circ\text{C}$  at  $10^\circ\text{C}/\text{min}$ .

The weight of the unfrozen water (UW) was determined from the relationship

$$M_{\text{UW}} = M_t - M_{\text{fw}},$$

where  $M_t$  is the total weight of water in the sample, determined by drying;  $M_{\text{fw}}$  is the weight of frozen water, determined from the endothermic peak of ice melting during the first heating, with regard for the specific heat of its melting.

The weight of additional unfrozen water (AUW) was found as the difference between the surface areas under the endothermic peaks of ice melting during the first heating and reheating. All the measurements were performed in triplicate.

Samples of 7% gels were prepared by heating starch in distilled water to  $t = 90^\circ\text{C}$  at a rate of  $10^\circ\text{C}/\text{min}$  under constant stirring. The sample was held at this temperature for 20 min, cooled to room temperature, sealed in an ampoule, and kept for 24 h at  $t = 5^\circ\text{C}$ .

### NMR Relaxation

The gelation of 1 : 1 wt starch–water samples was studied on a Minispec PC-120 instrument ("Bruker," Germany), operating at 20 MHz. The samples were placed in an ampoule 5 mm in diameter and hermetically sealed to prevent evaporation. The measurements were carried out at  $25$ – $95^\circ\text{C}$ , with the temperature maintained to within  $\pm 0.5^\circ\text{C}$  by a temperature control unit. At each temperature, sample was held for 5 min to reach thermal equilibrium. A further increase in the thermostating time did not affect the measurement results. The spin–spin relaxation time ( $T_2$ ) of protons was determined using the Carr–Purcell–Meiboom–Gill (CPMG) pulse sequence under the following conditions: the duration of the  $90^\circ$  pulse,  $2.3\ \mu\text{s}$ ; the time interval  $\tau$  between  $90^\circ$  and  $180^\circ$  pulses,  $20\ \mu\text{s}$ ; and the number  $n$  of points on the decay curve, 150. For each sample, three identical measurements were carried out, with accumulation of 16 scans at a delay between scans of 2 s.

The resulting transverse magnetization decay curves were analyzed using the MULTIT2 multiexponential expansion ("Bruker"). The relative error of relaxation measurements did not exceed 6%; in the following figures, the mean values of the relaxation parameters are presented.



The 7 wt % starch gels were studied on a Minispec PC 120 NMR relaxometer with a diffusion-type pulsed-gradient unit operating at a frequency of 20 MHz at  $t = 40^\circ\text{C}$ . The dispersion dependences of the spin–spin relaxation rate on the time between RF pulses were measured using the CPMG pulse sequence, with time  $\tau$  varied from 30 to 7500  $\mu\text{s}$ . The number of points on the decay curve was 150 (every tenth echo). The averaged curves were obtained by 16-fold accumulation of the signal with 10-s time intervals between the pulses. The dispersion curves were processed using the ORIGIN6 program.

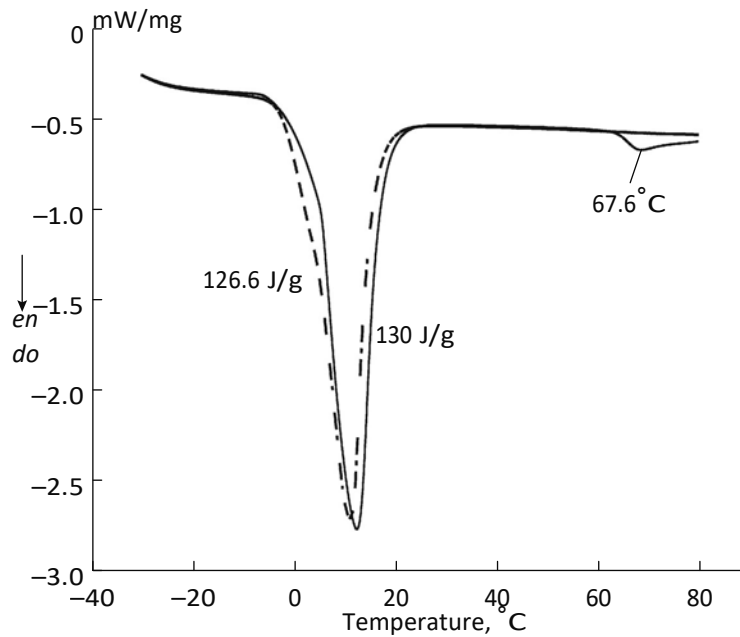
The diffusion coefficient  $D$  of water protons was determined by the pulsed gradient method with a twopulse sequence [16] by using the relationship

$D$  is the diffusion coefficient of water protons. The value of  $g$  ranged within 0.1–2.2 T.

## RESULTS AND DISCUSSION

### DSC Studies

Figure 1 shows typical DSC curves for ungelatinized and gelatinized starch–water samples. The results listed in Table 1 show that the content of unfrozen water before gelation is approximately the same for all the samples (0.3–0.4 g  $\text{H}_2\text{O}$  per g of dry weight). However, after gelation, a decrease in the UW content in all the chemically modified starches is observed, especially significant for PSWZn (almost twofold) as compared to PS. A similar reduction was



**Fig. 1.** Calorimetric curves of melting of ungelatinized (solid line) and gelatinized (dashed line) starch (PSC)–water samples. The gelation temperature and surface areas under the relevant peaks are shown.

$$\ln(A_n/A_0) = -\gamma^2 g^2 \delta^2 (\Delta - \delta/3) D,$$

where  $A_n$  and  $A_0$  are the echo amplitude with and without the pulsed gradient it,  $\gamma$  is the gyromagnetic ratio of the proton ( $26.75 \times 10^7 \text{ rad T}^{-1} \text{ s}^{-1}$ ),  $g$  and  $\delta$  are the amplitude and duration of the pulsed gradient,  $\Delta$  is the time between pulsed gradients, and

observed for AUW after gelation. Some of the data presented in Table 1, we published in [15] and them here for comparison. In the starch–water system, hydrated layer is located near the surface of the biopolymers. Due to the interaction with biopolymer macromolecules, the water molecules in this layer, can exist in the unfrozen state at subzero



temperatures. The degree of hydration is influenced by many factors, such as, for example, the distance between the water molecules and the interaction surface, surface charge, density of hydrogen bonds, and other. The amount of UW before gelation is largely determined by the degree of connectivity of the polymer chain, since the ability of water to migrate into void volume to form ice at subzero temperature involves a thermodynamic rearrangement of the polymer chain aimed at minimizing the energy of the system, and therefore, the amount of UW before gelation reflects the degree of water–biopolymer interactions. Additional unfrozen water arises as a result of gelation because of an increase (or a decrease for a negative AUW content) in the degree of interaction of starch macromolecules with water.

The authors of [10] observed an extreme dependence of the amount of AUW on the content of water in the starch–water system. The maximum was located near a 1 : 1 water-to-starch ratio (an observation that motivated us to select this ratio), which is due to the fact that the system in this state forms a saturated suspension, characterized by a uniform distribution of water over starch granules [17]; it was also pointed out that, in the interaction with water, amylopectin plays a more important role as compared to amylose. The structure of the gel after gelation was described [18] as an ensemble of tightly packed swollen granules with a thin layer of gel amylose in between. Such a structure presumably corresponds to the shortest distance of interaction between the water and macromolecule and the highest density of hydrogen bonds in a local volume.

Increasing the amount of water in the starch–water system leads to a change in these parameters (increase of the interaction distance) and to a decrease in the

amount of AUW. Thus, the content of AUW characterizes the additional hydration of the starch macromolecules during gelation. It should be noted that our results on the UW are similar to those for native starch obtained in [19] and [10], 0.38 and 0.43 g H<sub>2</sub>O per g of dry matter (d. m.), respectively. The content of UW in samples not subjected to chemical modification increases upon gelation (the AUW content is a positive quantity), reflecting an increase in the degree of hydration due to gelation. Convection heating has no effect on the AUW content, while microwave irradiation (MI) causes an almost twofold increase in the AUW content, probably, because of destruction processes in the starch structure under MI.

The destruction of starch granules under the action of MI produces additional hydroxy groups and increases the degree of interaction between starch polysaccharides and water [4]. On the other hand, the agglomeration of granules caused by MI leads to a reduction in the number of reaction centers. This can be accounted for by a decrease in the AUW content for PSCSi and PSWSi (for PSWZn, it is negative), as well as by the fact that a large number of hydroxyl groups of the starch is eliminated from the interaction with water because of esterification. That the temperature of gelation for the modified starch samples is lower than that for potato starch apparently reflects the destruction of the crystal structure of the latter during microwave treatment and chemical modification. Thus, these data confirm the results reported in [3, 4] on the destructive changes in the starch structure that cause a weakening of intramolecular and intermolecular hydrogen bonds.

#### NMR Relaxation

The relaxation curves of transverse magnetization decay were recorded by using a CPMG pulse sequence during heating of the samples from 25 to

**Table 1.** Fractions of unfrozen and additionally frozen water and the gelation temperatures of the starch samples tested and the limits the diffusion exchange rate constants ( $k_{exc}$ )

| Sample | Fraction of UW after gelation, g H <sub>2</sub> O/g d.m. | Fraction of AUW after gelation, g H <sub>2</sub> O/g d.m. | Gelation temperature, °C | $k_{exc}$ , s <sup>-1</sup> |
|--------|--|---|--------------------------|-----------------------------|
| PS     | 0.389 ± 0.009  | 0.021 ± 0.005   | 67.8 ± 0.2               | 87 ± 7                      |
| PSC    | 0.382 ± 0.010  | 0.021 ± 0.004   | 67.5 ± 0.3               | 103 ± 8                     |
| PSW    | 0.414 ± 0.012  | 0.039 ± 0.007   | 63.7 ± 0.8               | 93 ± 5                      |
| PSCSi  | 0.360 ± 0.011  | 0.003 ± 0.002   | 64.3 ± 1.0               | 106 ± 6                     |
| PSWSi  | 0.347 ± 0.012  | 0.013 ± 0.005   | 63.1 ± 0.7               | 155 ± 8                     |
| PSWZn  | 0.223 ± 0.011  | -0.103 ± 0.011  | 62.4 ± 1.1               | 393 ± 21                    |

95°C. For ungelatinized samples, two fractions of

protons were found, with a low and high mobility, the contents of which and characteristic relaxation times we denoted as  $W_a$ ,  $W_b$  and  $T_{2a}$ ,  $T_{2b}$ , respectively. It can be assumed that the less mobile protons of the aqueous fraction are located in intracellular structures of the starch granules. The fraction of more mobile protons, the relaxation time  $T_{2b}$  of which increases with the total water content [10], is located in the intercellular space. Similar models of the water fraction, based on the assumption that the time of diffusion exchange between the fractions is much longer than their relaxation times, were considered in [17]. It was found that, the ungelatinized potato starch–water system contains four different aqueous fractions, three of which belong, respectively, to the intercellular, amorphous, and semicrystalline lamellae regions, as well as a fraction located inside the hexagonal channels of the amylopectin crystals, which does not exchange protons with the other fractions. The relaxation time of the first fraction is  $\sim 50$  ms. The other two water fractions in the granules are in a state of rapid exchange with one another, characterized by a relaxation time of  $T_2 = 8$  ms. At temperatures below  $4^\circ\text{C}$ , the exchange slows down, and each fraction is characterized by its own time  $T_2$  [17]. Given that the conditions in [17] and present study are identical and that the results are similar give reason to consider our assumptions on the existence of the extracellular and intracellular fractions realistic. The presence of two phases is characteristic of regions with weak diffusion exchange, so the relaxation in these areas can be described by the expression [17]

$D/a^2 < |1/T_{2a} - 1/T_{2b}|$ , where  $a$  is the lower the size of the diffusion region. The limiting values of the diffusion exchange rate constant,  $k =$

$D/a^2$ , for the tested samples are presented in Table 1. Given that the diffusion coefficient for pure water at  $25^\circ\text{C}$  is  $D = 2.3 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ ,  $a$  was calculated to be 2–5  $\mu\text{m}$ , which corresponds to the lower size of the diffusion cells. The diffusion cell size can also be estimated using the formula  $\langle a^2 \rangle = 6Dt$  [20]. In this case, we set that the mean-square displacement of a freely diffusing water molecule occurs within a time of  $t = T_{2b}$ . Such calculations give  $a = 25\text{--}28 \mu\text{m}$ . Thus, for the ungelatinized samples, the size of areas with unrestricted diffusion lies within  $2 < a < 28 \mu\text{m}$ .

Figures 2–5 show how the water fractions and their relaxation times  $T_2$  change with increasing temperatures. As can be seen, from Fig. 2, with increasing temperature, the share of the fraction of less mobile water protons  $W_a$  in the PS, PSC, and PSW samples passes through an extremum.

During heating, the structure of the starch granules degrades, and consequently, the proportion of the intracellular water fraction  $W_a$  interacting with these structures before gelation increases. According to the authors of [12], this increase is largely a manifestation of the growing mobility of the starch polymer chains, the hydroxyl groups of which are involved in chemical exchange with the water, thereby characterizing the process of swelling of starch granules. Above the gelation temperature ( $62\text{--}67^\circ\text{C}$ ), this fraction decreases, which is a consequence of the formation of a gel structure, being characterized by a single value of  $T_2$  due to a rapid diffusion exchange between the fractions. That the values of  $W_a$  for PS, PSC, and PSW differ at the beginning of gelation can be apparently explained by a greater destructive influence of MI as compared to convective heating.

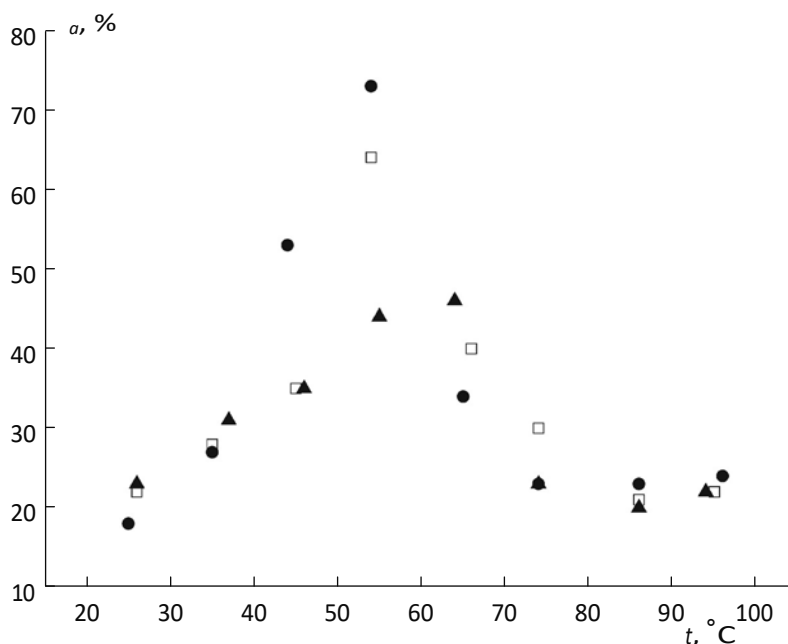
At  $t = 25^\circ\text{C}$ , for the chemically modified starch samples (Fig. 3), the value of  $W_a$  is three to four times higher than that for native starch due to destructive changes in the starch structure. Taking into account the DSC data on the reduction of the amount of unfrozen water in the chemically modified starches in comparison with PS, this fact can be explained by a

W

entire temperature range, which once again indicates a weak diffusion exchange.

To evaluate the rate of the chemical exchange of protons between water molecules and hydroxyl groups in gels of the starches studied, we investigated how the rate ( $1/T_2$ ) of spin–spin relaxation depends

**Fig. 2.** Time evolution of the content  $W_a$  of water protons with lower mobility during heating: (<sup>h</sup>) native starch (PS), (<sup>d</sup>) starch subjected to convective heat treatment (PSC), and (<sup>m</sup>) starch subjected to microwave irradiation (PSW).



decrease in the energy of water–starch interaction in this case due to a weakening of the hydrogen bonds in the polysaccharide chains [3, 4]. During heating,  $W_a$  decreases monotonically, without apparent changes in the gelation region. Apparently, in the modified structure of the samples under study, transitions in the gelation region are less pronounced. As can be seen from Figs. 4 and 5, the relaxation times  $T_{2b}$  increase with the temperature, which is indicative of the presence of free water in this fractions and the dominance of the dipole–dipole relaxation mechanism. That the time  $T_2$  decreases from that characteristic of free water (2–3 s) to the observed values of  $T_{2b} = 50$ –80 ms is apparently due to the chemical exchange of protons between water molecules and hydroxyl groups of polysaccharides on the surface of the granules. The values of  $T_{2a}$  for less mobile protons remain constant (4–8 ms) over the

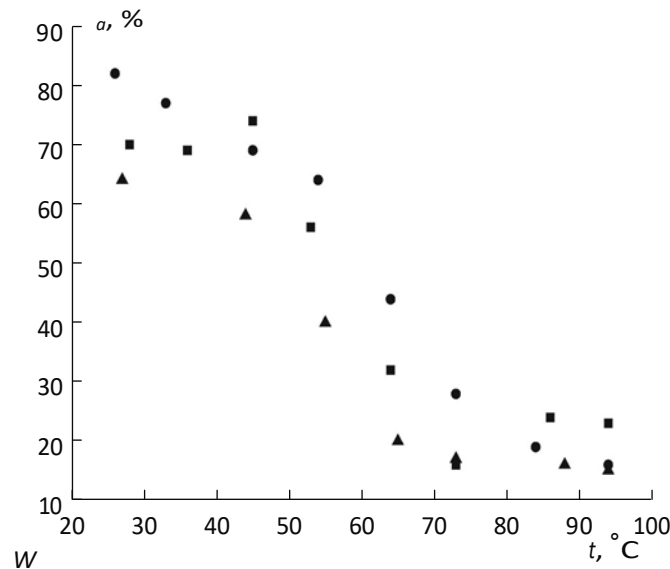
on the time interval  $\tau$  between the pulses in the CPMG sequence. According to the chemical exchange model [21], this dependence, known as dispersion, defines the rate constant of the chemical exchange of nuclei  $k_{\text{exc}}$  (in our case, protons) as a quantity inverse to the lifetime of the nucleus in a given state.

Typical dispersion dependences of the relaxation rate ( $1/T_2$ ) on the reciprocal of the time interval between the pulses ( $\tau^{-1}$ ) in the CPMG sequence are displayed in Fig. 6. The chemical exchange rate constant  $k_{\text{exc}}$  equals the value of  $\tau^{-1}$  for the mid-point of the dispersion curve. It should be noted that the spin–spin relaxation decay signal from all the samples of 7 wt % gels of the starches studied are described by a single exponential function, indicative of a rapid diffusion exchange.

As can be seen from Table 2, the chemical exchange rate constant  $k_{exc}$  for the samples of gels increases in the series PS, PSC, and PSW, characterizing a weakening of the water-polysaccharide interaction. For the PSCSi, PSWSi, and PSWZn gel samples, no dependence of the relaxation rate of water protons on the reciprocal of the time interval between the RF pulses  $\tau^{-1}$  was detected. This fact may be due to the low operating frequency of the measuring instrument (20 MHz). Dispersion dependences tend to flatten out with decreasing operation frequency, which was reported for measurements on devices with frequencies of 20,

100, and 300 MHz [22]. Table 2 shows that the spin-spin relaxation time  $T_2$  for the 7 wt % gels of the chemically modified starches differs from that for the native starch gel. A significant decrease in the values of  $T_2$  observed for the 7% wt gels of the CMS indicates an increased in the relaxation interaction. This decrease, like the increase of  $T_1$  in the same series, apparently reflects the destruction of starch granules under MI [4], which leads to a weakening of hydrogen bonds and an increase in the water-binding capacity of the starch.

According to the chemical exchange model, for short times  $\tau$  and low relative contents of hydroxyl



group protons, the process of relaxation is described by that the relaxation of water molecules far from the following simple expression [21]:

polysaccharide chains is similar to the relaxation in pure water ( $T \sim 2$  s), we obtained  $T \approx 5$  ms for all the

**Fig. 3.** Time evolution of the content  $W_o$  of more strongly bonded water protons during heating the chemically modified starches: (j) PSCSi, (d) PSWSi, and (m) PSWZn.

$$T_{2-1} = T_{2-a1} + P / T_b(2b + k - 1),$$

samples studied. In the first approximation, the spin- $2a$





- where  $T_2^{-1}$  is the measured spin-spin relaxation rate,

$T_{2a}^{-1}$  is the spin-spin relaxation rate of water protons far away from the polysaccharide chains,  $T_{2b}$  is the spin-spin relaxation time of protons of exchangeable groups of polysaccharides,  $P_b$  is relative concentration of exchangeable protons of polysaccharides, and  $k$  is the chemical exchange rate.

The relative content of exchangeable protons of polysaccharides in the 7 wt % gel of native starch was estimated from the known ratio between amylose and amylopectin in it and the relative contents of hydroxyl protons in them (3/162 for amylose and to 8/485 for amylopectin):  $P_b \approx 0.012$ . For the gel of the chemically modified starches, this ratio is even smaller because of a lesser number of hydroxyl groups. Assuming also

spin relaxation time of protons of starch hydroxyl groups equals the relaxation time of unexchangeable CH protons, so  $T_{2b}$  can be estimated from data on the starch-D<sub>2</sub>O system. In [12], for amylopectin protons in amorphous regions of semicrystalline lamellae in a starch gel with D<sub>2</sub>O,  $T_2 \approx 1$  ms, which is comparable in order of magnitude with our data, given their approximate nature, and confirms the applicability of the chemical exchange model.

The values of the diffusion coefficient of water protons in the 7 wt % starch gels are lower than the relevant diffusion coefficient for pure water ( $D_{H_2O} = 2.3 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ ). In studying the process of diffusion by the pulsed-gradient method, the uniformity of diffusion manifests itself through the linearity of the  $\ln(A_n/A_0) = F(g^2)$  dependence at a certain time interval  $\Delta$  between the

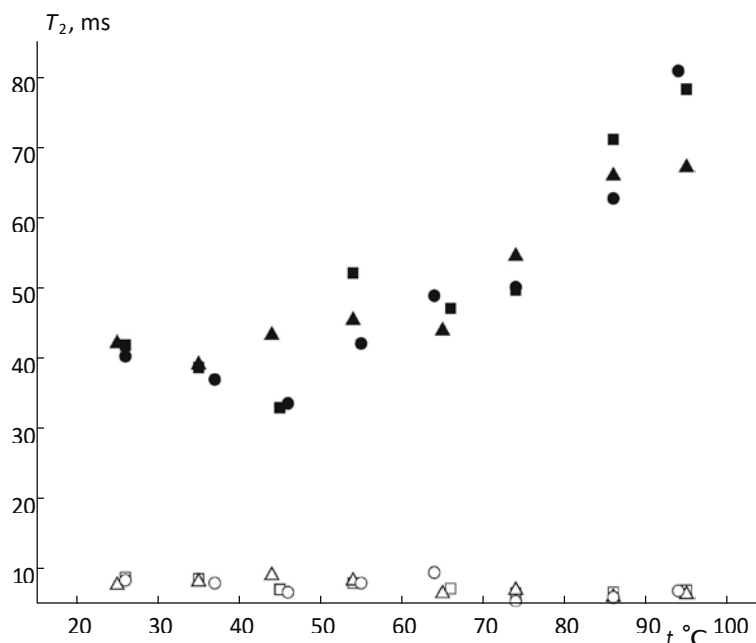
**Table 2.** Parameters of 7 wt % gels of the chemically modified starches

| Sample | $T_1$ , ms | $T_2$ , ms | $D \times 10^9$ , $\text{m}^2 \text{ s}^{-1}$ | $k_{\text{exc}}$ , $\text{s}^{-1}$ |
|--------|------------|------------|---|------------------------------------|
| PS     | 1312 ± 29  | 1169 ± 31  | 2.0 ± 0.2                                     | 417 ± 33                           |
| PSC    | 1174 ± 61  | 793 ± 24   | 1.57 ± 0.31                                   | 678 ± 48                           |
| PSW    | 1292 ± 48  | 784 ± 36   | 1.51 ± 0.15                                   | 885 ± 54                           |
| PSCSi  | 1618 ± 56  | 126 ± 6    | 1.66 ± 0.21                                   | –                                  |
| PSWSi  | 1581 ± 74  | 110 ± 7    | 1.61 ± 0.12                                   | –                                  |
| PSWZn  | 1594 ± 51  | 115 ± 5    | 1.59 ± 0.18                                   | –                                  |

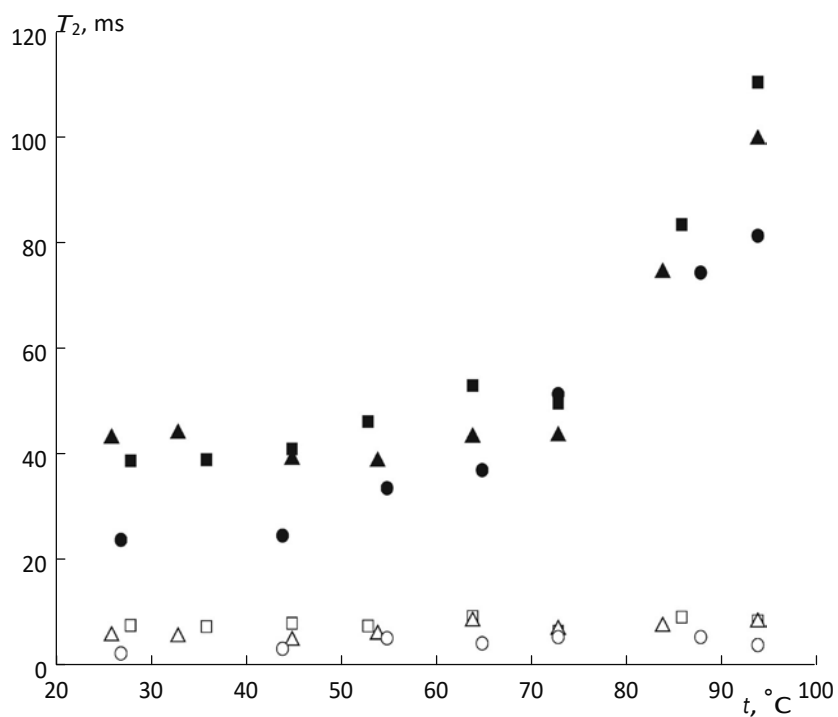
The time  $T_2$  in the CPMG pulse sequence was measured at  $T = 30$  ms; the diffusion coefficient  $D$  was measured at the following parameters of the  $90^\circ\text{-}\tau\text{-}180^\circ$  double-pulse sequence: diffusion time,  $\Delta = 7.5$  ms; pulsed gradient duration,  $\delta = 500$  ms.



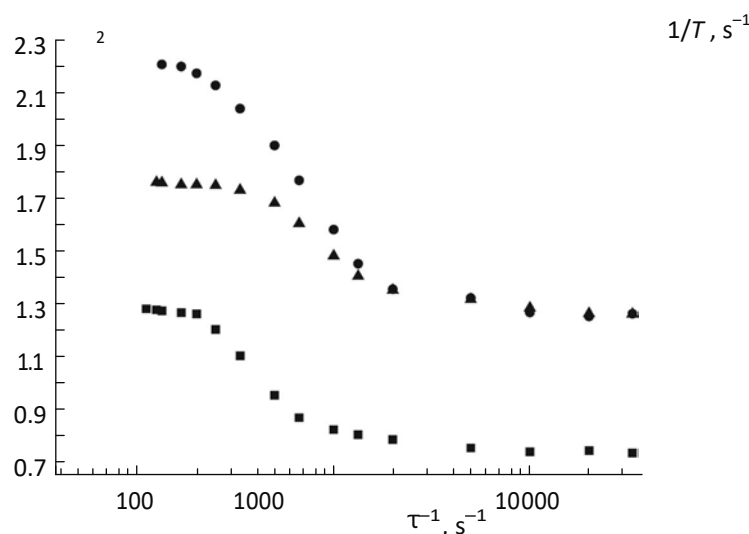




**Fig. 4.** Temperature dependence the components of the spin–spin relaxation time  $T_2$  of protons for water fractions with different mobilities in native starch samples: (<sup>h</sup>) short-time component  $T_{2s}$  for PS, (<sup>l</sup>) long-time component  $T_{2l}$  for PS, (<sup>n</sup>)  $T_{2s}$  for PSC, (<sup>m</sup>)  $T_{2l}$  for PSC, (<sup>s</sup>)  $T_{2s}$  for PSW, and (<sup>d</sup>)  $T_{2l}$  for PSW.



**Fig. 5.** Temperature dependence of the components of the spin–spin relaxation time  $T_2$  of protons for water fractions with different mobilities in chemically modified starch samples: (<sup>h</sup>) short-time component  $T_{2s}$  for PSCSi, (<sup>l</sup>) long-time component  $T_{2l}$  for PSCSi, (<sup>n</sup>)  $T_{2s}$  for PSWSi, (<sup>m</sup>)  $T_{2l}$  for PSWSi, (<sup>s</sup>)  $T_{2s}$  for PSWZn, and (<sup>d</sup>)  $T_{2l}$  for PSWZn.



**Fig. 6.** Dispersion dependences of the relaxation rate  $1/T_2$  on the reciprocal time interval  $\tau$  between  $90^\circ$  and  $180^\circ$  pulses for 7 wt % native

starch gels: (j) PS, (d) PSC, and (m) PSW.

pulsed gradients. A deviation from linearity is indicative of the heterogeneity of the diffusion process. For all the samples tested, the  $\ln(A_n/A_0)$  versus  $g^2$  dependence was linear for  $\Delta$  in the range from 4 to 65–70 ms. The lower limit was determined by the capabilities of the instrumentation, whereas the upper, by the influence of the gel structure on the diffusion process. Using the known values of  $D$  and  $\Delta$ , we estimated the size of the homogeneous diffusion region. According to the Einstein equation,  $\langle a^2 \rangle = 6D\Delta$ . The values obtained for all the samples lie within 8–9  $\mu\text{m}$ . In [23], the size of the pores in a starch gel pore was estimated as 10–20  $\mu\text{m}$ . The authors [11] determined the sizes of the homogeneous diffusion regions in the starch–water system, depending on the relaxation properties of the diffusion regions, were found to be 21 and 13  $\mu\text{m}$ . That the size  $\langle a^2 \rangle$  determined in our experiments is lower may be a result of the dependence of the diffusion coefficient of the gel concentration.

### CONCLUSIONS

The present study of chemically modified starches showed that they contain less unfrozen water as compared to native starch. The amount of additional unfrozen water arising because of gelation in these starches decreases. That the amount of unfrozen water in the chemically modified ungelatinized

starches decreases while the content of intracellular water  $W_o$  increases can be explained by a decrease in the intensity of interaction of the water with the starch biopolymers. The monotonic decrease of  $W_o$  with increasing temperature supports this assumption. Changes, such as a lowering of the gelation temperature, a significant decrease in the spin–spin relaxation time in the 7 wt % CMS gels, and an increase in the diffusion exchange rate constant for mixtures of these starches with water are manifestations of destructive rearrangements in the starch under the influence of physical and chemical factors.

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