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Interactions of potato starch with selected polysaccharide hydrocolloids as measured by low-field NMR

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Abstract

Relaxation times of water molecules in binary potato starch gels with Arabic, carob, guar, karaya, and xanthan gums as well as ι and κ-carrageenans were measured. On heating 5% aqueous suspension of potato starch up to 55 °C, relaxation times T_1 and T_2 increased, that is, molecular dynamics of water molecules rose as the consequence of producing disorder in solution on elevating temperature. However, beginning from 55 °C T_1 decreased as a consequence of gelation and, hence, immobilization of water molecules in the gel formed. After passing the point of gelation, T_1 almost monotonously rose up to the end of the measurement range (96 °C). Admixture of plant gums qualitatively and quantitatively perturbed these tendencies but did not reverse them. Gelation of starch in aqueous gum solution first involved conformational changes in polysaccharides. They proceeded until temperature of gelation was achieved. After that, formation of polymeric network took place. The course of gelation was controlled by water availability. The latter depended not only on the ability of particular gums to hold water molecules but also on their conformational changes and inhibition of gelation resulting from the interactions between gums and starch granules.

Keywords: Binary hydrocolloid gels; Starch gelatinization; Water activity; Water relaxation

1. Introduction

Blends of starch with nonstarchy hydrocolloids have been studied as structure providers in food production, as they influence gelatinization, modify viscosity, flow properties, and retrogradation of resulting binary gels (Alloncle and Doublier, 1991; Alloncle, Lefebvre, Llamas, & Doublier, 1989; Closs, Conde-Petit, Roberts, Tolstoguzov, & Escher, 1999; Eidam, Kulicke, Kuhn, & Stute, 1995; Kowalski, Sikora, & Tomasik, 2006; Kulicke, Eidam, Kath, Kix, & Kull, 1996; Sikora & Kowalski, 2003; Sikora, Kowalski, & Tomasik, 2006a, 2006b; Tolstoguzov, 2003).

Alloncle et al. (1989) characterized starch–nonstarchy hydrocolloid systems as suspensions of swollen starch granules in a solution of hydrocolloid and dissolved amylose. In such solutions thermodynamic incompatibility of components might be a controlling factor (Alloncle & Doublier, 1991; Kulicke et al., 1996; Tolstoguzov, 2003).

In our previous projects, rheological properties of the blends of cereal starches with guar gum, xanthan gum, and κ-carrageenan were described (Kowalski et al., 2006). Relatively less attention has been paid to potato starch systems blended with other hydrocolloids (Mandala & Palogou, 2003; Sikora & Kowalski, 2006). Among the effects considered as essential in controlling formation and properties of such binary gels, molecular weight of the partners, their polydispersity, and level of amylose in starch were crucial. The role of molecular weight and polydispersity should be understood as that influencing thermodynamic compatibility of the interacting polysaccharide partners and, in part, a factor influencing water activity in solution. Water activity has been considered essential in mutual interactions of dextrans

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and low-molecular saccharides in aqueous solutions (Mazurkiewicz, Rębilas, & Tomasik, 2006). It could play a particular role, in case of karaya gum which, among plant gums under study, had relatively low molecular weight and high polydispersity (Kowalski et al., 2006).

In this paper the relaxation time measurements of starch and of the blends of starch with other polysaccharide hydrocolloids were carried out, in a wide temperature range, and the changes of relaxation parameters were analyzed during heating and cooling of the systems.

A low-field NMR technique was used for observation and analysis of water molecular dynamics in biopolymer systems (Chatakanonda et al., 2003; Choi & Kerr, 2003a, 2003b; Kim, Yoo, Cornillon, & Lim, 2004; Rugraff, Desbois, & Le Botlan, 1996). Relaxation time spin–lattice (T_1) describes the interaction of nuclear spins with an environment, while relaxation time spin–spin (T_2) describes the mobility of interacting spins. In this kind of research the results of relaxation time, spin–spin (T_2) measurements or analysis of free induction decay, (FID)'s shape are used. The measurements are conducted at determined temperature.

The theoretical analysis of water molecular dynamics during gelling, based on relaxation time spin–spin (T_2) measurements was previously presented in the work of Zhang, Matsukawa, and Watanabe (2004).

Relaxation rate, that is, reciprocal of the relaxation time, is related to the precession frequency and correlation time, τ_c, describing the time required for the change of the orientation of a molecule by one radian. In the system with a low viscosity, in one period of the precession of spins the molecule changes its orientation several times. Under such circumstances, value of both relaxations are close to one another and proportional to a value of τ_c and independent of the precession frequency. Temperature dependence of τ_c can be presented with a fairly good approximation by Arrhenius equation. (1)

$$\tau_c = \tau_0 \exp\left(\frac{\Delta E_a}{RT}\right), \quad (1)$$

where R, T, and ΔE_a are the gas constant, temperature in Kelvins and energy barrier of the reorientation of molecules, respectively, and τ_0 is a constant (Bloembergen, Purcell, & Pound 1948; Janik, 1989).

Changes in the energy barrier of the water molecules in the system are available from the temperature effects upon the spin–network relaxation. Temperature-dependent changes of T_1 were associated with changes in molecular dynamics of water molecules due to developing polymeric network which inhibited water mobility.

2. Materials and methods

2.1. Materials

Potato starch—"Superior" was purchased from PPH Kupiec Enterprise in Krzymow, Poland.

Table 1
Ash and nitrogen content in polysaccharides and their polydispersity

Polysaccharide	Ash (%)	Nitrogen (%)	Polydispersity Pd
Starch	0.37	0.33	21.05
Arabic gum	3.38	None	2.45
ι-Carageenan	24.53	None	
κ-Carageenan	32.97	None	11.00
Carob gum	0.90	None	7.21
Guar gum	0.76	None	9.70
Karaya gum	6.92	None	339.70
Xanthan gum	13.17	None	9.70

Carob, guar, Arabic, xanthan, karaya gums, κ- and ι-carrageenans were purchased from Sigma Co., St. Louis, MO., USA. Ash content in those polysaccharides and their polydispersity are presented in Table 1. Qualitative test of fusion with metallic sodium showed that gums under study we are entirely free from nitrogen. Ash content approximately corresponded to that calculated for pure potassium salts of gums. Residual nitrogen in granular starch is common (Sychowska & Tomasik, 1997)

2.2. Methods

2.2.1. ^{1}HNMR relaxation time measurements

The measurements of relaxation time spin–lattice (T_1) and spin–spin (T_2) were conducted by the use of impulse spectrometer ^{1}HNMR (WLElectronic, Poznań, Poland), at 30 MHz, equipped with temperature control system (Bruker B-VT-1000, Rheinstetten, Germany).

Aqueous suspensions of starch and nonstarchy hydrocolloids (0.8 mL) were placed in sealed tubes. The measurements were conducted at increasing temperatures from 20 to 90 °C, and then at decreasing temperatures to 20 °C, every 10 °C. The measurements were carried out at each temperature after 20 min of stabilization. After measurement at 90 °C, the system was kept at this temperature for 60 min, after the next measurement was done.

For measurements of relaxation times spin–lattice (T_1) the inversion-recovery impulse sequence was used: 180x-TI-90x-TR (Fukushima and Roeder, 1981). The distance between TI impulses was dependent on low temperature: at 20 °C—in the range 50–6000 ms, and at high temperature (50–60 °C)—in the range of 125–16500 ms. The repetition time TR was 35 s. During each measurement of relaxation time (T_1) 32 signals of FID, and 119 points on each FID were collected. For calculations of T_1 values the program CracSpin was used (Węglarz & Harańczyk, 2000). With the use of distribution of the relaxation time, that program certified the mono-exponential escalation of magnetization in each analyzed sample. That set a quick proton exchange.

For the measurements of relaxation times spin–spin (T_2), the series of impulses CPMG: 90x-(TE/2-180y-TE)$_n$ (Carr & Purcell, 1954; Meiboom & Gill, 1958) were used. The distance between spin echoes TE was 6 ms. Each time