TEMPERATURE CHANGES OF THE MECHANICAL AND DYNAMIC PARAMETERS IN THE WATER-FAT-STARCH SYSTEMS

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Abstract. Rheological properties and water-binding ability in the water-fat-starch systems have been studied by the DMTA and NMR methods. The addition of fat into the starch-water system results in a decrease in the density of the intermolecular bonds in the gel network, determining the components of the complex elasticity modulus, and a decrease in the energy of the interactions, leading to the shift of the relaxation transitions towards lower temperatures. The shift amounts to about 10°C. The formation of fat complexes with amylose blocks the accessibility of water to the sorption centres, which imposes restrictions on the network nodes development. Consequently, the mean density of the network segments, and hence also the elasticity modulus, are much lower in the systems with fat than in the pure starch gel. Analysis of the molecular dynamics of water leads to a conclusion that the presence of fat in starch gel partly blocks the accessibility of water to the starch systems. For reorientation, the water molecules displaced from the nodes of the polymer network need to go over an energy barrier much lower than in the pure gel. The differences in the spin-spin relaxation processes in systems containing different type fats reflect the differences in the mechanisms of spin exchange. When bovine fat is added, the interactions between the water protons and protons of the acid residues dominate. In the presence of pork fat in the system, an additional mechanism of internal spin interactions within the methyl groups plays a role.

Keywords: starch gel, fat, NMR, DMTA

INTRODUCTION

Potato starch is often used as a functional addition in many food products. In the presence of water, starch forms permanent structures responsible for mechano-rheological properties of the food products. Many authors have been interested in improvement of the structure of fat-containing food products [5,7,8,15]. However, the majority of them have studied the interactions of starch with fat of plant origin

[13,14,23], while the mechanisms of interactions between starch gel chains and animal fat are poorly recognised. Preliminary studies performed with pork fat have shown that starch is an effective stabiliser of fat-in-water type emulsions [17]. Fat plays an important role in the formation of the rheological properties of final food products, mainly influencing their texture and consistency [16,18].

The aim of the study reported was to investigate the effect of animal fat on structuralization and water binding in model systems containing potato starch and water. The fat-induced changes in the structure of starch gel were analyzed. The effect of fat on mechano-rheological properties of model systems was determined. The mechanisms of interactions on the molecular level were resolved. The study was conducted in a wide range of temperatures, which permitted a detailed analysis of changes in the mechanical parameters taking place in the presence of fat and the effect of fat on binding of water.

MATERIALS AND METHODS

The study was performed on systems containing water, potato starch and fats of animal origin. The control system did not contain fat. The ingredients were: unmodified potato starch, bovine fat (saturated fatty acids – 38.9%, monounsaturated fatty acids – 43.8%, polyunsaturated fatty acids – 4.2%) or pork fat (saturated fatty acids – 34.4%, monounsaturated fatty acids – 45%, polyunsaturated fatty acids – 10.4%) [11].

Into a 10% starch suspension in water, an amount of 10% of fat (either bovine or pork) (relative to the mass of the suspension) was added and the mixtures was heated for 30 minutes at $+85^{o}C$. For the same sample the NMR and DMTA measurements were performed at $+85^{o}C$. The control sample was pure 10% starch gel. The fat to be studied was preliminary heated to $+85^{o}C$. The study was performed in the range from $+85^{o}C$ to $+10^{o}C$ with the system cooled in the measuring cell.

The components of the complex elasticity modulus G_1 and G_2 were measured by a mechanical DMTA spectrometer described by Rezler and Poliszko [19]. The free vibrations frequency was 0.11 Hz.

The spin-lattice T_1 and spin-spin T_2 relaxation times were measured on an NMR pulse spectrometer working at 15 MHz, equipped with a temperature stabilization system. The measurements of T_1 relaxation times were made using the sequence ($\pi-\tau-\pi/2$), while the measurements of T_2 – using a sequence of *CPMG* pulses. The systems studied were characterized by a single spin-lattice relaxation time and a single spin-spin relaxation time.

RESULTS AND DISCUSSION

The components of the complex elasticity modulus G_1 and G_2 measured by the DMTA method for the samples of starch gels with and without fat undergo changes with sample cooling (figures 1 and 2). The changes suggest the formation of a spatial network of the concentration of starch chain segments depending on temperature [1-3]. The formation of a spatial network in such systems is initiated by the bonds appearing between the neighbouring fragments of different macromolecules. The mechanism of the formation of such bonds in starch involves helix formation of the macromolecular fragments and their association to bihelical associates characteristic of native and retrograded starch [12,22]. The occurrence of these phenomena is confirmed by the temperature dependencies of the elasticity modulus and tangent of loss obtained for starch gel sample without fat. These dependencies reveal a region of the elasticity modulus dispersion typical of the sol-gel transitions and a maximum of loss occurring at about +35°C (fig. 1 and 2). The coil-helix transition observed in a relatively low temperature testifies to the formation of network segments with nodes showing low functionality. This effect is a consequence of a fast cooling of the system – the thermal stabilization took about 15 minutes.
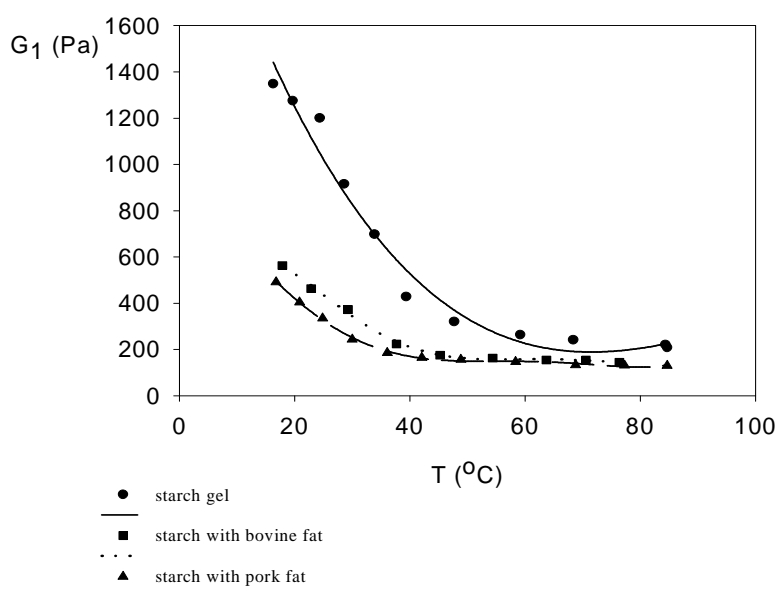

Fig. 1. Temperature dependence of the elasticity modulus for the system of starch-water-fat
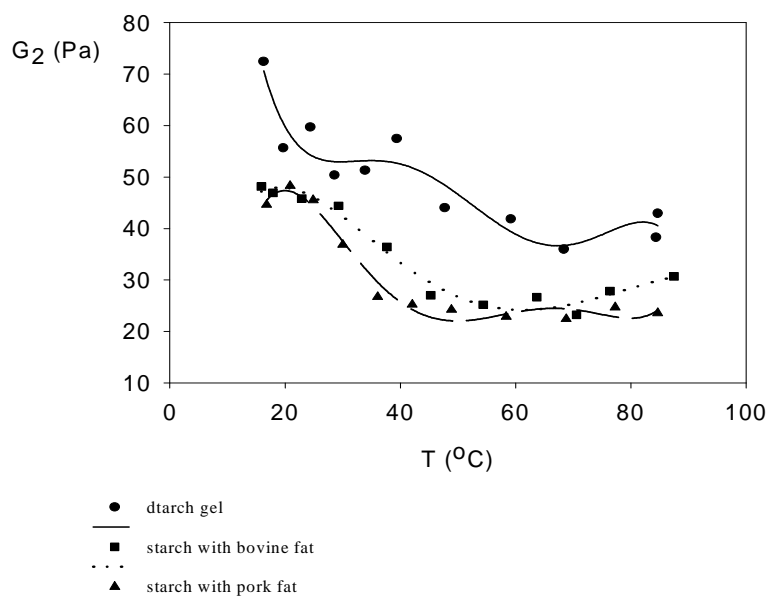
Fig.2. Temperature dependence of the loss modulus for the system of starch-water-fat

In the range of high temperatures the elasticity modulus and the loss modulus take similar values although slightly higher for the sample with bovine fat. For the sample of pure starch gel, the values of these parameters are considerably higher. With temperature decreased below $+45^oC$, the values of both moduli, G_1 and G_2, monotonously increase. Again the corresponding values of these parameters are much higher for the sample of pure starch gel. The temperature dependencies and the values of the G_1 and G_2 moduli change as a result of the addition of fat (either bovine or pork) into the system. Their course reveals differences in the rate of the network development processes and the 10° C shift of the starting point of the cross-linking process in the samples with fat towards lower temperatures relative to that in pure starch gel.

Significant differences in the thermo-rheological properties between the systems with bovine and pork fat follow from different temperatures of solidification of these two types of fat. These differences are a consequence of different contents of saturated fatty acids and length of their carbon chains, so a different capability of complex formation with amylose. In pork fat, dominant are the saturated fatty acids of carbon chain lengths much shorter than in bovine fat. Thus, the presence of pork fat seems to favour the formation of lipid amylose complexes to a greater

degree than bovine fat [9,15,16,20,21]. The complexes of fat with amylose block the centres of interchain association, hence restricting the development of the network. The blocked nodes are not able to attach new segments of the macromolecules. Consequently, the mean functionality of the nodes stabilizing the spatial network increases and the mean density of the network segments is much lower in the systems with fat [any type of fat] than in the system with pure starch gel. These phenomena are reflected by a significantly lower level of the elasticity modulus G_1 (Fig.1) and by a shift of the relaxational transition of starch gel towards lower temperatures, to about $+25^{\mathrm{o}}$C in the systems with bovine fat, indicating a lower energy of the polymer bonding at the network nodes.

A similar shift of the relaxational transition is observed for the system with pork fat. However, this effect is masked by an increase in the rheological parameters of the system as a result of the pork fat solidification in the network of starch gel already present.

The differences in the elasticity modulus and loss modulus appearing below 50°C between the systems with bovine and pork fat are a result of the fact that the former type of fat solidifies in higher temperatures than the latter. Therefore, with temperature decreasing below the value at which bovine fat solidifies, the phenomenon of the fat phase separation can take place, which affects the final elasticity of the system.

Measurements of the spin-lattice and spin-spin relaxation times permit analysis of the interactions on the molecular level. The T_1 time describes the process of reaching equilibrium as a result of exchanging the nuclear spin energy with the lattice. This time (T_1) can be expressed through microscopic parameters describing the interactions of the nuclear spin with the environment and the parameters describing the reorientational movements of the molecules in a given system. The T_2 time describes the process of reaching the equilibrium state through the exchange of energy among the spins. This time can be related to the parameters characterizing the molecular motion in the systems and those describing the interaction of nuclear spins within the same molecule.

The spin-lattice relaxation rate $(1/T_1)=R_1$ and spin-spin relaxation rate $(1/T_2)=R_2$ are described by the equations of Bloembergen, Purcell and Pound [4]. For the systems studied, in good approximation, the two relaxation rates are interrelated through a single expression [12]:

$$R_1 = R_2 = A \cdot \tau_c \tag{1}$$

where: A is a constant depending on the properties of the nucleus and τ_c is the correlation time.

On the basis of the measured temperature dependencies of the relaxation times, it is possible to derive a temperature dependence of the correlation time which can be described by the Arrhenius equation:

$$\tau_c = \tau_0 \exp\left(\frac{E_a}{RT}\right) \qquad (2)$$

where: τ_0 is a constant, and E_a is the energy barrier for reorientation of a whole molecule or a group of molecules.

The measurements performed in a wide range of temperatures permitted analysis of molecular motion, inter- and intra-molecular interactions.

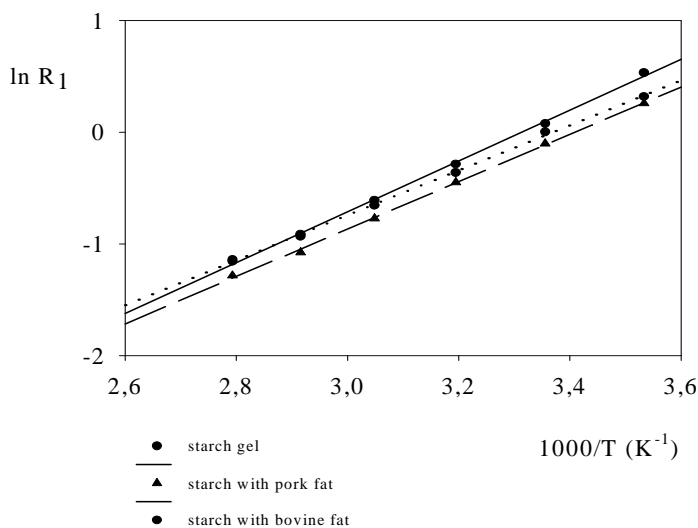Figure 3 presents temperature dependence of the spin-lattice relaxation rate R_1.

Fig. 3. Temperature dependencies of the spin-lattice relaxation time for starch gel, starch gel with bovine fat, and starch gel with pork fat

On the basis of the temperature dependencies of the relaxation times, the values of the reorientation energy E_a of the molecules in the starch gel and starch gel with the two types of fat have been calculated. In pure starch gel, E_a is 18.91 kJ mol^{-1}. Addition of fat in general decreases the activation barrier. The values of the energy differed for the systems containing bovine and pork fat, although the analogous values obtained for pure fat of these two types did not differ much. The addition of pork fat causes a decrease of this activation energy to 17.6 kJ mol^{-1}, while the addition of bovine fat to 16.94 kJ mol^{-1}.

The decrease of the energy barrier as a result of fat addition is a result of a specific interaction of fat with the biopolymer chain. Fatty acids form complexes with amylose and block the accessibility of water to the sorption centres, preventing the formation of bonds among the starch chains. Water molecules removed from the polymer network have to go over a lower energy barrier of reorientations.

The differences between the particular systems become more pronounced in analysis of the temperature dependencies of spin-spin relaxation rates (Fig. 4).
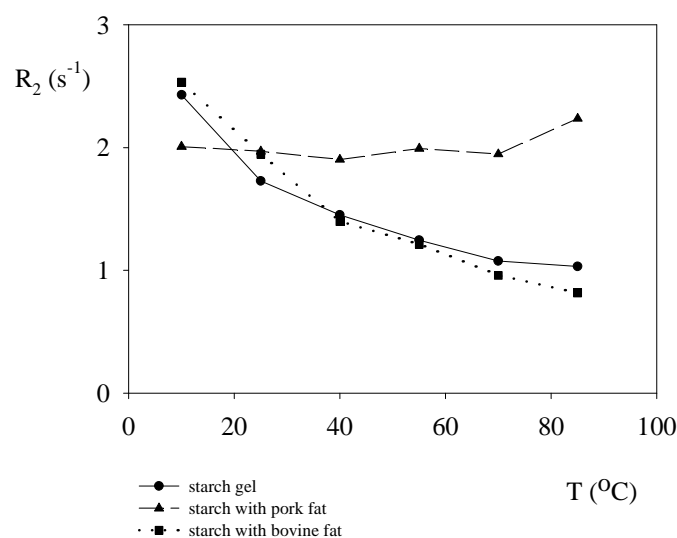

Fig. 4. Temperature dependencies of the spin-spin relaxation rate R_2 for starch gel, starch gel with pork fat, and starch gel with bovine fat

The relaxation time T_2 describes the molecular mechanism of energy transfer between the spins in the nearest neighbourhood, first of all within the same molecule. The temperature dependencies of R_2 in the samples of pure starch gel and starch gel with bovine fat have similar character. In high temperatures, the addition of fat increases the relaxation rate because of the presence of the liquid phase. The spins of the fatty acid groups interact between one another and with the protons of water molecules displaced from the network nodes. In the process of preliminary heating, water molecules are squeezed in between the bimolecular layers formed by fat chains. A temperature decrease causes a decrease in the relaxation rate because of reduced mobility of the fat chains, which increases the rate of the spin exchange process. The processes of relaxation in the systems of

starch gel with bovine fat on cooling take place with a rate comparable to that in pure starch gel. However, the activation energy of the molecules reorientation determined from equation (2) is higher in the system with bovine fat and equals 12.8 kJ mol^{-1}, while for the pure gel it is 9.52 kJ mol^{-1}.

No similar temperature changes in the spin-spin relaxation rate were observed for the system of starch gel with pork fat. For this system, no changes in the relaxation rate R_2 were noted with decreasing temperature. The effect observed is probably related to the competition between the interactions of the water molecule protons with the fatty acid protons and the intramolecular interactions of protons within the methyl groups. The interactions of the water protons with those of the fatty acids in this system are compensated by the interactions of protons of the methyl groups. Such interactions are more pronounced in the systems of starch gel and pork fat than with bovine fat.

The differences between the systems with bovine and pork fat can suggest that the thickness of the layer of water in the fat emulsion separating fat chains does not change with decreasing temperature in the system with pork fat in which fat chains get poorer solidified or do not solidify as a result of a decrease in temperature. In the system with bovine fat, in high temperatures the carbon chains are elastic and with decreasing temperature they solidify forming a quasi-crystalline structure.

CONCLUSIONS

1. The coil-helix transition observed in the starch-water system in a relatively low temperature indicates the formation of segments of a network made up of nodes characterized with low functionality, depending on the conditions of measurements.

2. Addition of animal fat to the starch-water system leads to a decrease in the density of the intermolecular bonds in the gel network, determining the elasticity modulus value, and in the energy of the interactions, shifting the relaxation transition point towards temperatures lower by about 10°C.

3. Analysis of the molecular dynamics has shown that the presence of fat in the starch gel partly blocks the access of water to starch chains. The water molecules displaced from the nodes of the polymer network have a lower barrier of reorientation than those in pure starch gel.

4. The differences in the spin-spin relaxation rates in the systems with different types of fat indicate different mechanisms of spin exchange in these systems. In the systems with bovine fat, the dominant are the interactions between the water protons and the protons of the acid residues. In the systems with pork fat, a mechanism of internal spin interactions within the methyl groups is revealed.

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TEMPERATUROWE ZALEŻNOŚCI PARAMETRÓW MECHANICZNYCH I DYNAMICZNYCH W UKŁADACH WODA-TŁUSZCZ-SKROBIA

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S t r e s z c z e n i e . Właściwości reologiczne i zdolność wiązania wody w układach skrobia-woda-tłuszcz zbadano metodami DMTA i NMR. Dodanie tłuszczu do układu skrobia-woda prowadzi zarówno do obniżenia gęstości wiązań międzymolekularnych w sieci żelu, określających wartości składowych zespolonego modułu sztywności, jak i do obniżenia energii oddziaływań, co przejawia się przesunięciem przejść relaksacyjnych w kierunku niższych temperatur. Przesunięcie to wynosi około $10^{o}C$. Kompleksy tłuszczu z amylozą powodują blokowanie dostępu wody do centrów sorpcji. Ogranicza to rozbudowę węzłów. W rezultacie średnia gęstość segmentów sieci jest znacznie niższa w układach z dodanym tłuszczem w porównaniu do czystego żelu. Znajduje to swoje odbicie w niższym poziomie wartości modułu sztywności w układach z dodanym tłuszczem. Analiza dynamiki molekularnej wody pozwala stwierdzić, że obecność tłuszczu w żelu skrobi ziemniaczanej częściowo blokuje dostęp wody do łańcuchów skrobi. Molekuły wody usunięte z węzłów sieci polimerowej pokonują mniejszą, w porównaniu do czystego żelu, barierę e02nergetyczną reorientacji. Ujawnione różnice w procesach relaksacji spinowo-spinowej dla układów zawierających różne tłuszcze wskazują, że mechanizmy wymiany spinów są różne dla tych układów. W przypadku tłuszczu wołowego przeważają oddziaływania protonów wody i protonów reszt kwasowych między sobą. W tłuszczu wieprzowym ujawnia się dodatkowo mechanizm wewnętrznych oddziaływań spinowych w obrębie grup metylowych.

S ł o w a k l u c z o w e : żel skrobiowy, tłuszcz, NMR, DMTA