R. REZLER, H. M. BARANOWSKA, S. SURMA, S. POLISZKO

INVESTIGATION OF STARCH GELS BY MEANS OF THE RELAXATION METHOD

Abstract

Analysis of structural changes of starch gels of the polymer content from 0.05 g/cm^3 to 0.10 g/cm^3 has been performed on the basis of results of a study by the DMTA and ^{1}H NMR methods. For gels of starch concentration below 0.08 g/cm^3, the changes of the rigidity modulus are insignificant; a small increase is observed only in the first three hours of measurements. Gels of a higher starch content are characterised by much higher initial value of the rigidity modulus, which significantly increases with the time of measurements. The values of the rigidity modulus are determined by the density of network segments. In the systems with starch concentration up to 0.08 g/cm^3, the initial and the final concentrations of the network segments show insignificant differences, while for the gels of a higher starch content these concentrations differ significantly.

As follows from results of NMR relaxometry experiment, in the gels of a polymer concentration up to 0.08 g/cm^3 no changes in water dynamics in time have occurred. In those of starch concentration above 0.08 g/cm^3, the relaxation rate of water has changed in time. The maximum in the water relaxation rate observed after 3–4 hours of measurements indicates the process of water fixing in hydrates. A further monotonic decrease of the relaxation rate suggests that the water initially involved in the gel structure formation is evacuated from the starch network. This process should be related to respiralisation of amylopectin chains, whose participation in the gel structure formation increases with increasing polymer concentration. The results suggest that for the starch gels of polymer content lower than 0.08 g/cm^3 the gel structure formed on cooling is saved and not subject to development. In the time range studied no changes in the parameters studied which could suggest the occurrence of starch retrogradation have been observed, which has been interpreted as a result of a small contribution of amylopectin chains in formation of the gel spatial network.

Introduction

In food products polysaccharides may play the structure building role as thickeners, stabilisers, regulators of functional properties etc. [4, 6]. From the physical and chemical point of view the majority of food products are gels. Therefore, recognition

R. Rezler, H. M. Baranowska, S. Surma, S. Poliszko, Department of Physics, Agricultural University of Poznań, 60-637 Poznań, Wojska Polskiego 38/42, Poland.

of the mechanisms of gelation is of great importance. Amongst the gelating products starch obtained from potatoes as well as from grains has the greatest use in food industry. The gelating properties of starch or its isolated components as well as products containing starch have been used in production of deserts, fruit mousse sauces and baking bread. All the products are systems of different water content, which is decisive for spatial structure formation in starch gels. The widespread methods of structural investigation such as X-ray radiography analysis [10, 11], differential thermal and calorimetric analysis [7, 8, 21] and nuclear magnetic resonance [5] provide indirect data which are not sufficient for interpretation of structural conditions of mechanical and rheological properties of biopolymer systems.

Much more information on molecular conditions of mechanical and rheological properties of the structures investigated can be obtained with the use of methods of dynamic-mechanical analysis [9, 13, 14], which can be also used to investigate starch systems [12, 15, 19]. Moreover, in non-reticulated systems the density and stability of links determines mechanical and rheological properties of systems. In order to recognise the molecular processes accompanying the formation of spatial structures of starch, the kinetics of the structuring processes was analysed as a function of the concentration of solutions.

Investigation of starch gels with the NMR relaxometry methods was mainly performed for concentrated systems. For the starch concentrations up to ca. 45% a fast exchange of water, manifested as a monoexponential recovery of magnetization [17, 18] was observed.

This study reports an analysis of the process of spatial structuring of starch in time on the basis of results obtained by the DMTA and NMR methods.

Materials and methods

The study was carried out for samples of starch hydrogels obtained from solutions of starch from the wheat species *Triticum durum* (Sigma) prepared as paste on heating for 3/4 hours under constant stirring. A constant concentration of the mixture was maintained by continuous addition of water to compensate for its loss. The study was performed on the systems containing starch in the concentrations from 0.05 g/cm^3 to 0.10 g/cm^3. Immediately after preparation the solutions were placed in the measuring chamber of the rheometer and in the measuring tubes of the NMR spectrometer. Measurements were begun after stabilisation of the temperature of the gels (1 hour after the end of heating) and performed every 20 min by DMTA and every hour by NMR for 10 hours, at about +20°C.

Measurements of spin-lattice relaxation times $T_1 = (1/R_1)$ were carried out using an NMR pulse spectrometer operating at 30 MHz. The standard inversion-recovery pulse sequence was applied, recording 29 free induction decay (FID) signals for each

preset parameter of the sequence and from 60 to 90 points on the FID signal. The distances between RF pulses were changed from 0.001 to 3 s. The repetition time was 50 s. The relaxation times were calculated using the program Cracspin [20]. For all systems studied a monoexponential recovery of magnetisation was recorded.

In the conditions of sinusoidal variable mechanical interactions of frequency ω, the viscoelasticity of the materials investigated is manifested as a phase shift of the angle δ between strain and stress. So, the stress σ is described by:

$$\sigma = \sigma_o \exp(i\omega t + \delta) \tag{1}$$

while the strain by:

$$\gamma = \gamma_o \exp(i\omega t) \tag{2}$$

where ω is the angular part while δ is the angle of the phase shift.

The ratio of stress to strain is described by the complex shear modulus:

$$G^* = \frac{\sigma}{\gamma} = \frac{\sigma_o}{\gamma_o} e^{i\delta} = \frac{\sigma_o}{\gamma_o}(\cos\delta + i\sin\delta) = G_1 + iG_2 \tag{3}$$

where G_1 and G_2 are the real and the imaginary parts of the modulus, respectively.

The real part G_1 is called the dynamic modulus and it is related to that part of the potential energy of strain, which is saved during periodic deformations. The imaginary part G_2 of the modulus G^* is called the modulus of loss and is related to the part of energy which is dissipated in the form of heat. The values of G_1 characterising a gel network made of flexible macromolecules depend on the number of moles per a unit volume of the macromolecule segments n_s effectively transferring stresses in the network:

$$G_1 = n_s RT \tag{4}$$

The values of the loss modulus G_2 are determined by the local coefficient of viscosity:

$$G_2 = \omega\eta_L \tag{5}$$

The method of dynamical and mechanical analysis (DMA) consists in determination of variability of the modulus in a wide range of sinusoidally variable mechanical interactions.

The results presented in the paper were obtained on the basis of measurements made with an instrument working on the principle of free vibration (the inverse torsional pendulum). For measurements of low strength systems such as hydrated starch (hydrogels), the measuring cells used were in the form of coaxial cylinders. The gel

studied was placed between the walls of cylinders. The outer cylinder was fixed to the base of the instrument, while the inner cylinder was connected to an inertial element with a rod. The inertial element was made of a brazen cylinder hanged on an elastic string fixed to the upper wall of the casing. In the middle part of the stiff rod there was a measuring transducer recording angular displacements of the rod and thus also displacements of the sample investigated. The whole system was fully computer controlled. The mechanical system of the pendulum was fixed to a granite base mounted on a polystyrene table ensuring elimination of external interactions, such as vibrations of the base and other mechanical interactions [16].

The following parameters were measured: frequency of free vibrations f, logarithmic decrement of the system damping with a sample Δ, and without a sample. The values are denoted as f_o and Δ_o. The components of the complex modulus of rigidity were calculated from the following relationships:

$$G_1 = 4\pi^2 I F_g (f^2 F_{dk} - f_o^2) \tag{6}$$

$$G_2 = 4\pi^2 I F_g (f^2 \Delta - f_o^2 \Delta_o) \tag{7}$$

where:

$$F_{dk} = 1 - \frac{\Delta^2}{4\pi^2} \tag{8}$$

and F_g is a coefficient depending on geometric size and shape of a sample:

$$F_g = \frac{R_w^{-2} - R_z^{-2}}{4\pi l} \tag{9}$$

where R_w is the radius of the mobile inner cylinder linked to the pendulum, R_z is the radius of the outer fixed cylinder, l is the height of the gel layer.

Results and discussion

In order to recognise the processes accompanying the formation of spatial structures in starch solutions, taking place from the moment of reaching room temperature, analysis of the structure forming processes was made as a function of the concentration of solutions. The most suitable parameters characterising the kinetics of structure formation were assumed to be the number of macromolecular segments forming the spatial network per a unit volume of the forming gel n_s and a local viscosity coefficient η_L determined by the interaction of the network segments with the solvent and the rest of the polymer.

An increase in the values of the rigidity modulus with the time of crosslinking has been observed for the starch systems of different concentrations of the component (Fig. 1).

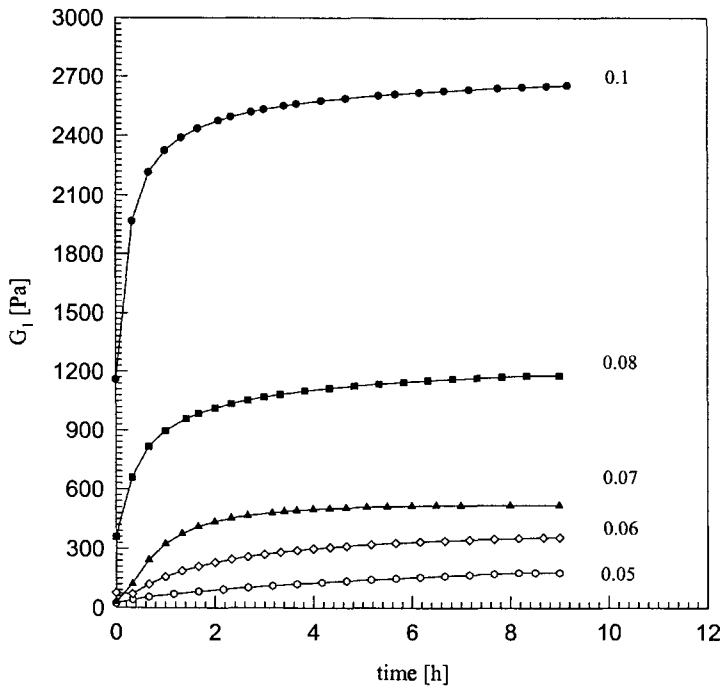

Fig. 1. Kinetics of changes of dynamic rigidity modulus during the process of starch gels formation at different starch concentrations.

As it can be observed in the range of concentrations from 0.07 g/cm^3 the initial values of the rigidity modulus vary very little with starch concentration. A small increase of its values was observed in the first 3 hours of the experiment. In the systems of the polymer concentration up to 0.08 g/cm^3, a significant increase in the initial values of the rigidity modulus was noted with increasing polymer concentration.

The relationship between the rigidity modulus of highly elastic polymer network and the concentration of segments in the network can be approximated by the expression (Ferry, 1970):

$$n_s \cong \frac{G_1}{RT} \tag{10}$$

An increase in the values of the rigidity modulus with the time of crosslinking has been observed for the starch systems. This fact indicates that the concentration of the effective segments in the network increases tending to the asymptotic values $n_{\infty s}(c)$. For the polymer systems the kinetics of crosslinking can be well described by the equation of the Avrami type [1, 2, 3], in which the time exponent is $m \cong 1$:

$$n_s(t) = n_{os} + [n_{\infty s} - n_{os}]\{1 - \exp[-(kt)^m]\} \qquad (11)$$

The value of this exponent means that recrystallisation in these systems runs at the initial stage of nucleation of the crystal forms that do not reach the critical size. Figure 2 presents the relationship between the initial and the final concentrations of segments in the network as a function of the square of the starch concentration.

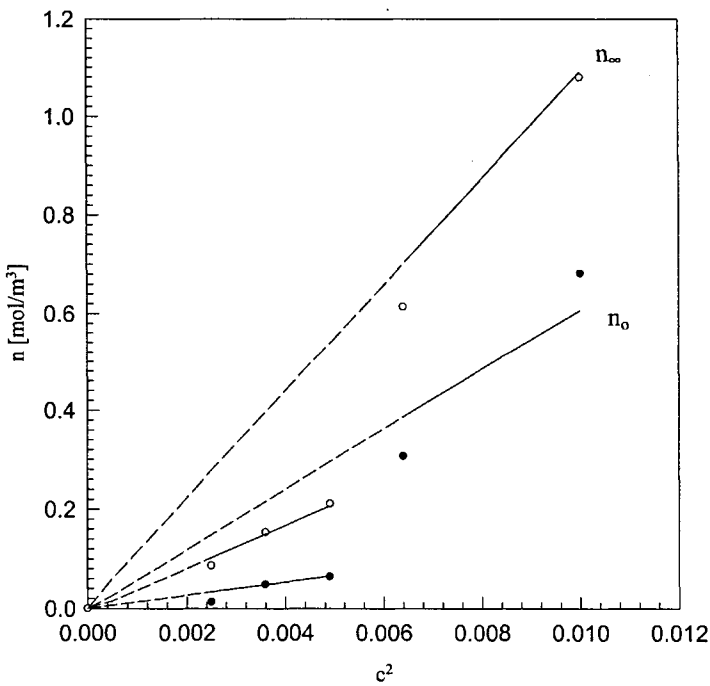

Fig. 2. The initial n_0 and the final n_∞ concentrations of the network segments as a function of the square of starch concentration in the system.

As follows from the plots presented in Fig. 2, the initial n_0 and the final n_∞ concentrations of the segments change linearly with c^2 (where c is a polymer content) and the slopes of the lines depend on the range of the starch concentration. The values of n_0 and n_∞ in starch gels of concentrations lower than 0.08 g/cm^3 show insignificant differ-

ences. For starch gels of higher concentrations the concentration of network segments increased in time. It means that with the ageing of gel, the fragments of macromolecules subsequently joining the network undergo adsorption on the nodes enhancing their functionality. Therefore, for the equilibrium network $n_\infty \sim c^2$, the inclination angle of anamorphoses, depending on the mean functionality of the network nodes $n_s = f(c^2)$, increases.

As follows from this dependence, at a given starch concentration in the system and at a constant temperature, an increase in the gel rigidity with time is a result of the development of the nodes realised by binding of new segments of macromolecules, which leads to an increase in the mean functionality of the nodes stabilising the network. The links between adjacent fragments of different macromolecules in a solution initiate a formation of the spatial network in the systems. The mechanism of the starch network formation involves spiralling of starch fragments and their association to bihelical forms characteristic of native and retrograded starch [22, 23].

For the systems of concentrations lower than 0.08 g/cm^3, long chains of amylose are responsible for formation of spatial structure of the network. With increasing concentration of the polymer in the system also short chains of amylopectin start to contribute in the formation of the spatial network, which is manifested as an increase of the initial concentration of segments in the network n_0. Therefore, the observed increase of the concentration of network segments in time and thus an increase in the rigidity modulus, are related to the formation of the network by chains of amylopectin.

DMTA measurements bring only the information on macroscopic changes in the biopolymer network dynamics. Analysis of the molecular dynamics of water in these systems was possible on the basis of NMR data.

The spin-lattice relaxation rate changes in time for the systems studied are shown in Fig. 3.

Changes of the spin lattice relaxation rates in time are only observed for the systems of the polymer concentration above 0.08 g/cm^3. The relaxation rates increased in the first 3–4 hours of the experiment and then monotonously decreased. The increase in the relaxation rates in the first hours recorded for starch gel suggests that water molecules are captured at the network nodes during the network formation. The later continuous decrease in the relaxation rate testifies to an increase in the water mobility in the systems studied as a result of evacuation of water from the network nodes. For systems with starch content below 0.09 g/cm^3 the relaxation rates are not time-dependent, which suggests that the dynamical state of the water does not change.

The results obtained by NMR and DMTA methods suggest that during the process of retrogradation, water molecules also participate in the initial formation of amylopectin network. The amylose network formed on cooling does not change in time, which explains no changes in the spin-lattice relaxation rate.

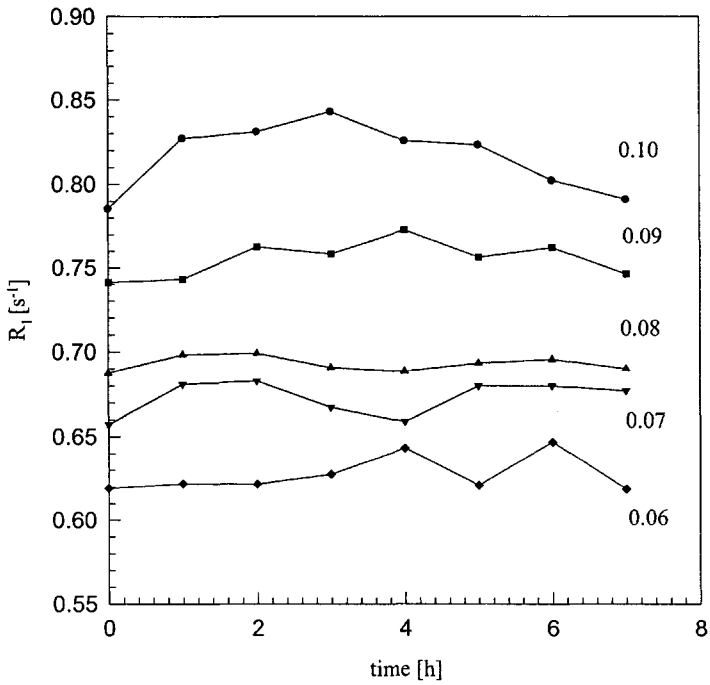

Fig. 3. Changes of the spin-lattice relaxation rates for starch gels in time.

Conclusions

1. Result of the relaxometric measurements of starch gels of the polymer content up to 0.10 g/cm^3 have shown that the process of retrogradation of the system leading to formation of a spatial network at a constant temperature can occur in the systems of a high polymer content (above 0,08 g/cm^3). The phenomenon involves association and spiralling of amylopectin chains into bihelical forms.
2. The process of retrogradation, leading to formation of the amylopectin network, takes place in the first 3–4 hours of the experiment.
3. In the systems studied, the process of amylose retrogradation on cooling leads to formation of a network whose structure does not change in time.

REFERENCES

[1] Avrami M.: J. Chem. Phys., 7, 1939, 1103.
[2] Avrami M.: J. Chem. Phys., 7, 1940, 212.

[3] Avrami M.: J. Chem. Phys., **9**, 1941, 177.
[4] Biliaderis C.G.: Can. J. Physiol. Pharmacol., **69**, 1991, 60.
[5] Cherian G., Chinachoti P.: Cereal Chem., **73**, 1996, 618.
[6] Clawson A., Taylor A.J.: Food Chem., **47**, 1993, 337.
[7] Erdogdu G., Czuchajowska Z., Pomeranz Y.: Cereal Chem., **72**, 1995a, 70.
[8] Erdogdu G., Czuchajowska Z., Pomeranz Y.: Cereal Chem., **72**, 1995b, 76.
[9] Ferry J.D.: Viscoelastic properties of polymers. Ed. J. Wiley and Sons, New York, 1970.
[10] Gidley M.J., Cooke D.: Biochem. Soc., **19**, 1991, 551.
[11] Liu H., Lelievre J.: Carbohydr. Res., **17**, 1991, 145.
[12] Morgenstern M.P., Newberry M.P., Holst S.E.: Cereal Chem., **73**, 1996, 478.
[13] Murayama T.: Dynamic mechanical analysis polymeric material. Eds.Elsevier, Amsterdam, 1978.
[14] Perepeczko J.: Acoustic Methods of Investigating Polymers. Mir. Publ., Moscov, 1975.
[15] Poliszko S., Lesiewicz Cz.: Dynamiczno-mechaniczne właściwości uwodnionych żeli skrobiowych. Sprawozd. Probl. 0509 CPBP, Poznań, 1986.
[16] Rezler R.: Dynamiczno-mechaniczna analiza termiczna kseroproduktów skrobiowych i zmian ich właściwości w warunkach rehydratacji. PhD. Thesis, AR Poznań, 1998.
[17] Richardson S. J., Baianu I. C., Steinberg M. P.: Starch, **39**, 6, 1987a, 79.
[18] Richardson S. J., Baianu I. C., Steinberg M. P.: Starch, **39**, 6, 1987b, 198.
[19] Vodovotz Y., Hallberg L., Chinachoti P.: Cereal Chem., **73**, 1996, 264.
[20] Węglarz W., Harańczyk H.: Mat. XXVI Ogólnopolskiego Seminarium na temat Magnetycznego Rezonansu Jądrowego i Jego Zastosowań, Kraków, 1994, 137.
[21] Zeleznak K.J., Hoseney R.C.: Cereal Chem., **64**, 1987, 121.
[22] Eliasson A.-C., Larsson K., Andersson S., Hyde S.T., Nesper R., Schnering H.G.: Starch, **39**, 1987, 147.
[23] Wu H.-C., Sarko A.: Carbohydr. Res., **61**, 1978, 7.

BADANIE ŻELI SKROBIOWYCH METODAMI RELAKSACYJNYMI

Streszczenie

W prezentowanej pracy podjęto próbę analizy zmian strukturalnych żeli skrobiowych o niskiej zawartości polimeru (od 0,05 g/cm^3 do 0,10 g/cm^3). Badania prowadzono w czasie do 10 godzin po osiągnięciu przez układ temperatury otoczenia.

Technikę DMTA wykorzystano do określenia zmieniających się w czasie parametrów reologicznych, określających stopień usztywnienia struktury żelu.

Stan dynamiczny wody w układzie, w czasie formowania struktury, analizowano wykorzystując technikę ^{1}H NMR.

Uzyskane rezultaty pozwoliły stwierdzić, że dla żeli o koncentracji skrobi poniżej 0,08 g/cm^3 zmiany modułu sztywności są niewielkie, a wzrost jego wartości obserwuje się przez trzy pierwsze godziny trwania eksperymentu. Po upływie tego czasu nie stwierdzono dalszych zmian wartości tego parametru. Żele o wyższej zawartości skrobi (powyżej 0,08 g/cm^3) charakteryzują się dużo wyższą wartością początkową modułu sztywności i obserwuje się znaczny wzrost wartości tego parametru w czasie.

Wartość modułu sztywności determinowana jest gęstością segmentów sieci. Stwierdzono, że w układach o koncentracji skrobi do 0,08 g/cm^3 początkowa i końcowa koncentracja segmentów sieci zmienia

się w niewielkim stopniu. Zróżnicowanie ich wartości można zaobserwować w układach o wyższej zawartości skrobi.

Pomiary relaksacyjne wykonane techniką NMR wskazują, że w żelach o koncentracji polimeru do 0,08 g/cm^3 woda nie zmienia swojego stanu dynamicznego w czasie. Jedynie układy o zawartości skrobi powyżej 0,08 g/cm^3 charakteryzują się zmiennymi w czasie wartościami szybkości relaksacji wody. Obserwowane po trzech pierwszych godzinach trwania eksperymentu maksimum wartości szybkości relaksacji wskazuje na proces uwięzienia wody w hydratach. Dalszy monotoniczny spadek wartości szybkości relaksacji pozwala wnioskować, że woda początkowo biorąca udział w formowaniu struktury żelu jest ewakuowana z sieci skrobiowej.

Uzyskane w badaniach rezultaty sugerują, że w przypadku żeli skrobiowych o zawartości polimeru nie przekraczającej 0,08 g/cm^3 struktura żelu, jaka powstała w procesie ochładzania, jest zachowana i nie ulega rozbudowie. Rozbudowa węzłów sieci w czasie, z udziałem wody obserwowana jest jedynie w układach o koncentracji polimeru przekraczającej 0,08 g/cm^3.