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MOLECULAR DYNAMICS IN DEHYDRATED STARCH GELS

S u m m a r y

We have recently developed a transformation method for representation of different relaxation proc-
esses data (DMTA, DETA and 1H-NMR) as a function of free energy of activation in freeze-dried wheat
starch gel. In our previous paper [12] the method of transformation was applied for freeze-dried wheat
starch gel of density of 0.13 g/cm^3, while in this paper we present results of a similar analysis of relaxation
parameters measured in a wide temperature range in dehydrated wheat starch gel of a twice lower density.
In the system studied, we observed a decreasing value of the complex rigidity modulus, due to much lower
degree of crosslinking. Similar courses of dispersion profile obtained with 1H-NMR relaxation method
and DMTA method, at temperature ranging from 100 to 380 K, point to a correlation between the nuclear
and mechanical relaxation processes, confirming the results of our previous work, which are related to the
dynamics of hydroxymethylene groups in freeze-dried starch gel.

Introduction

Dehydrated starch gels have been commonly met as components of many food
products based on starch and obtained in a form of glassy-crystalline extrudates such
as corn flakes, crackers or chips. Molecular mobility and physical state of these bio-
polymers in freeze-drying starch products posses important and informative aspects
related to food stability. Characterisation of the structure of freeze-dried product, tex-
ture, mechanical and thermal properties might help in understanding of the structure
and behaviour of the corresponding frozen food. Several techniques such as DSC,
SEM, X-ray diffraction, are used to study food in a glassy state [3-6, 8, 15]. Relaxation
methods, DMTA (dynamic-mechanical thermal analysis) [4-6, 8, 10], NMR relaxation
[2, 12], DETA (dielectric-thermal analysis) [11] are one of the most powerful tool to
probe the structure of such material for determining changes in molecular mobility and
dynamic biopolymer interactions. Each technique involves a type of external force

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under specified and controlled conditions in order to elicit a response from the material during measurements, thus probing the property of interest. It is expected that a comparison of different relaxation processes will serve to identify and characterise the specific motions responsible for the observed relaxation. The main purpose of this work is to verify formerly described transformation procedure, used for comparison of different relaxation experiments, applied to freeze-dried wheat starch gel of the density of 0.065 g/cm^3.

Theory

The spin-lattice proton relaxation rate (R_1) is a sensitive parameter describing molecular dynamics in a macromolecular system. In order to compare molecular response of a system to an external perturbation of mechanical, magnetic, and dielectric character, a transformation procedure was applied based on the theory of the absolute reaction rate. In the first step temperature changes of R_1 are transformed into its changes as a function of the magnetic field frequency. A NMR dispersion profile was obtained, which could be fitted to an adequate distribution function. As shown by Koenig [7], in a macromolecular system, spin-lattice magnetic relaxation experimental data can be fitted to the Cole-Cole [1] dispersion formula (1):

$$R_1 = A \frac{1+(\omega/\omega_c)^{\beta/2}\cos(\pi\beta/4)}{1+2(\omega/\omega_c)^{\beta/2}\cos(\pi\beta/4)+(\omega/\omega_c)^{\beta}} \qquad (1)$$

where A, ω_c, and β are the degree of dispersion, inflection frequency, and steepness of the inflection, respectively.

The distribution parameters obtained by a computer fitting, enabled determination of the course of NMR relaxation time spectrum, using the formula (2) [14]:

$$\Phi(\ln\tau/\tau_c) = \frac{1}{2\pi} \frac{\sin(1-\beta/2)\pi}{ch[(\beta/2)(\ln\tau/\tau_c)]-\cos(1-\beta/2)\pi} \qquad (2)$$

where τ and τ_c are the nuclear correlation time and mean correlation time at the maximum of the relaxation rate, respectively.

In the subsequent step the transformation eliminated effect of the difference in the frequency of the measuring force fields used in experiments, on the localisation of dispersion regions. In the case of local relaxation processes, relaxation as well as the correlation times satisfied the relation following from the theory of absolute reaction rate (3):

$$\tau = (\hbar/kT)\exp(\Delta F/RT) \qquad (3)$$

where ΔF is the free energy of activation of relaxation process, $\hbar$, k, R are Planck, Boltzmann and gas constants, respectively, and T is a temperature.

Taking into account that angular frequency, $\omega = 1/\tau$, the free energy of activation of the relaxation process can be expressed by (4):

$$\Delta F = - RT \ln (\hbar\omega / kT) \qquad (4)$$

This analysis provided normalised curves describing temperature or frequency changes in the relaxation parameters: complex rigidity modulus in mechanical relaxation, complex dielectric permitivity in dielectric relaxation, and function of nuclear correlation in NMR, and representing the spectrum of relaxation as a function of free energy of activation.

Materials and methods

Freeze-dried starch gel was prepared from solutions of *Triticum durum* wheat starch (Int. Grain Products, Canada) gelated on cooking for 1h on continuous stirring and maintaining constant concentration by addition of water. The solutions of the starch concentration of 0.05 g/cm^3 were used to fill cylindrical tubes stored in a dessicator for 24 h in the atmosphere of saturated water vapour at 298 K. After this time the cross-linked starch gel was subjected to sublimation drying in the lyophiliser (the LGA 05 type manufactured by MLW, Leipzig, Germany) at 284 K. As a result of 10% reduction of the sample volume the xerogel of the density of 0.065 g/cm^3 was obtained. The samples for measurements were in the form of rods (11 cm length, 0.55 cm diameter). Measurements were carried out in the temperature range of 100–380 K under nitrogen.

Dynamic mechanical - thermal analysis (DMTA) measurements

DMTA measurements were performed in the free vibration system (Spectra-Spin Poznań, Poland) based on the inverted torsion pendulum. One side of a cylindrical rod in the system was rigidly mounted and the other was attached to an inertia disk providing its free oscillation. The successive oscillation amplitudes decreased in time because of damping. It gradually converted the elastic energy of the system into heat. The mechanical system of the pendulum was fixed on the granite base mounted on a polystyrene table ensuring elimination of external interactions as vibrations of the base and other mechanical interactions. The measuring unit was equipped in an optical-electronic set for vibration periods and vibrating amplitudes reading. The dynamic mechanical technique was based on the analysis of the sinusoidal signals related to the applied stress and resulting strain of the sample. The frequencies of free vibrations and logarithmic decrements of damping were measured in the system with and without the sample. From the displacement – time curve, one could determine both the dynamic shear or torsion modulus G_1 and logarithmic decrement δ. The shear modulus G_1 (real

part of the complex shear modulus G) for a cylindrical rod was given by equation (5) [9]:

$$G_1 = (8 \pi I L / \gamma^4)(1/P^2) \tag{5}$$

where L. I, γ, and P were the length of specimen, moment of inertia of the inertial member, the cylinder radius, and period of oscillation in seconds, respectively. The logarithmic decrement Λ was calculated from the logarithm of the ratio of the amplitudes of two successive oscillations (6):

$$\Lambda = \ln \frac{A_1}{A_2} \tag{6}$$

where A_1 and A_2 were the amplitude of the first and the second oscillation, respectively.

It was related to the dissipation factor, tan δ by the relation: $\Lambda = \pi \tan \delta = \pi (G_2/G_1)$.

The data provided calculation of two components of the complex rigidity modulus, real part (G_1), and imaginary part (G_2) of the studied material. The real part G_1 of the complex modulus reflected the capability of the examined material to storage mechanical energy of the strain. The imaginary part G_2 was related to the energy dissipation processes and reflected a capability for exchange of mechanical energy into the heat. The mean frequency of mechanical perturbation was 0.1 Hz.

1HNMR spin-lattice relaxation measurements

The measurements of spin-lattice proton relaxation rate R_1, in freeze-dried wheat starch gel were carried out on the pulse, laboratory made solid-state NMR spectrometer (Institute of Physics, Adam Mickiewicz University, Poznań, Poland) operating at 25 MHz. The sequences of pulses composed of a saturating series were used, which nullifies the transversal component of magnetisation and a $\pi/2$ pulse measuring the recovery of the magnetisation vector. All magnetisation recovery curves were one-exponential functions of time.

Results and discussion

Temperature changes of complex rigidity modulus (both, real G_1 and imaginary part, G_2) and the spin-lattice proton relaxation rate, R_1 in freeze-dried starch gel of the density of 0.065 g/cm^3 are presented in Fig.1 and 2, respectively. Over 6-fold decrease in storage rigidity modulus with temperature increasing from 100 K to 300 K was observed. It is interesting to note that the lowest storage modulus obtained for the freeze-dried wheat starch gel of the density of 0.065 g/cm^3 at 300 K was exactly half of that observed for the freeze-dried starch gel of the density of 0.13 g/cm^3. This concentra-

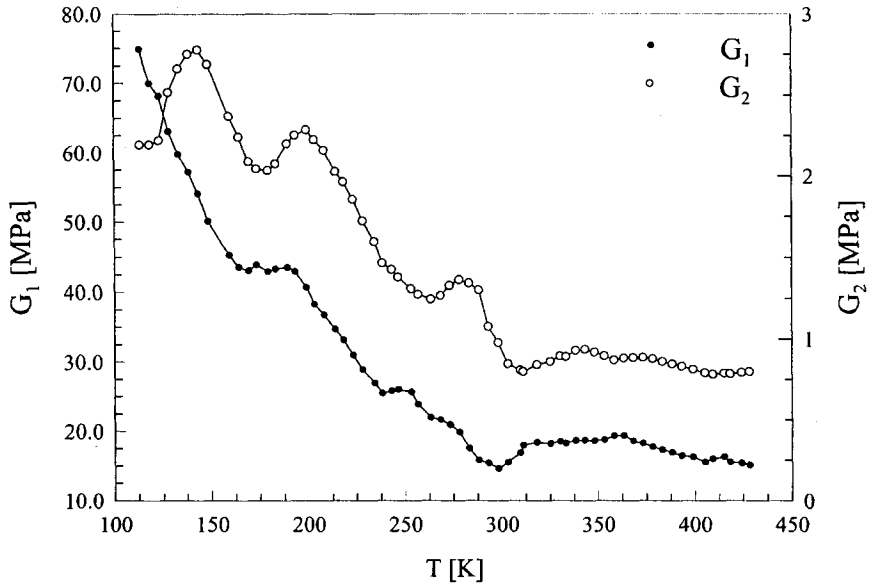tion dependence of the storage modulus pointed to a relation between the polymer

Fig. 1.   Temperature dependence of the storage component (G_1) and loss component (G_2) of the complex rigidity modulus in freeze-dried wheat starch gels of the density of 0.065 g/cm^3.
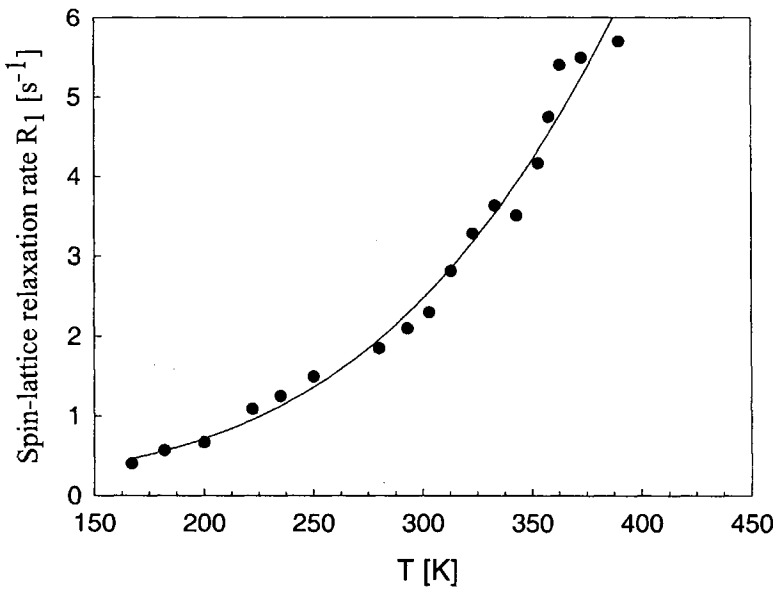

Fig. 2.   Temperature course of spin-lattice proton relaxation rate R_1 in freeze-dried wheat starch gel of the density of 0.065 g/cm^3.

concentration in solution and the concentration of the network segments determining mechanical properties of the system after freeze-drying. The freeze-drying of starch gel resulted in fixing of the three-dimensional network of cross-links, forming a starch gel on cooling. The concentration of the network segments determined the mechanical properties of the product and the values of dynamic modulus of hydrogels formed [11].
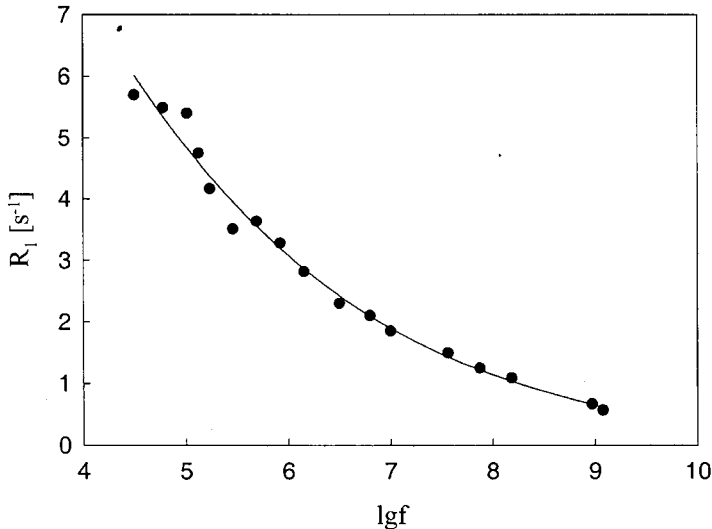

Fig. 3.   1HNMR dispersion profile for the freeze-dried wheat starch gel of the density of 0.065 g/cm^3. The solid line was calculated from the Cole - Cole Eq. (1).
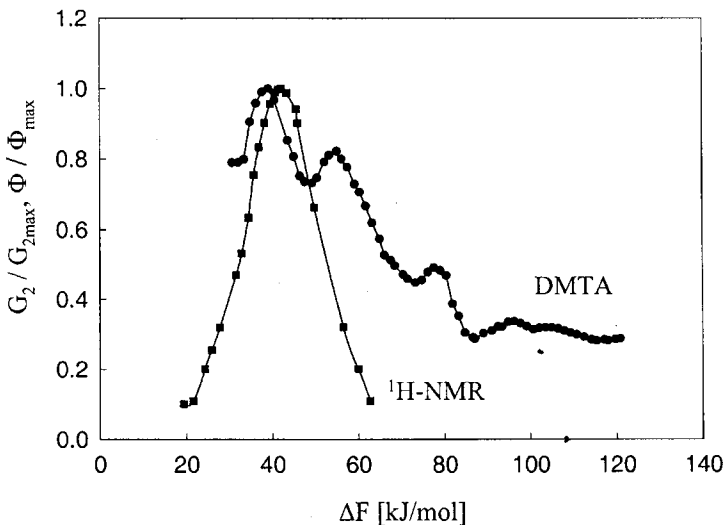

Fig. 4.   The normalised curves of mechanical loss, G_2/G_{2max} and 1HNMR relaxation spectrum, $\Phi(\Delta F)/\Phi_{max}$ as a function of the free energy of activation of relaxation in freeze-dried wheat starch gel of the density of 0.065 g/cm^3.

As it is known from earlier study [13], for a given starch concentration, mechanical-rheological properties of freeze-dried starch in amorphous xerogel form were determined by the rigidity of macromolecule chains rather then by the network density. Moreover, the results have shown that complete dehydration of starch chains resulted in an increase of its rigidity by about 10^5. According to the theoretical assumptions, the temperature changes in R_1 were transformed into its changes as a function of the magnetic field frequency. An NMR dispersion profile shown in Fig. 3 was obtained, which was fitted to Eq. (1). The fitting procedure gave the following parameters of distribution: degree of dispersion $A = 8.80$ s^{-1}, inflection frequency $\omega_c = 0.65$ MHz and steepness of the inflection $\beta = 0.71$. These parameters provided determination of the spectrum of correlation times from Eqs. (2) and (3) as a function of the free energy of activation of the relaxation process. The results of this transformation are shown in Fig. 4. The NMR relaxation spectrum was compared to the normalised curve of mechanical loss G_2/G_{2max}, representing the spectrum of mechanical relaxation. The position of the most intense maximum of mechanical relaxation was close to the pattern of the spectrum of magnetic relaxation. This maximum was characterised by the activation energy ΔF of about 40 kJ/mol. Because the proton magnetic relaxation method was sensitive to the dynamics of groups rich in protons, one could assume that the relaxation transition observed is attributed to the polar hydroxymethylene groups in starch polymer chains. The intrachain bonds of hydroxymethylene groups were responsible for the high rigidity of starch chains in the range of low temperatures. With increasing temperature, dissociation of these bonds induces an increase in the flexibility of starch polymer chains. The results of the temperature analysis of the relaxation phenomena in the glassy state of wheat starch gel of the density of 0.065 g/cm^3 showed the same character of the relaxation transitions recorded at 150 K by DMTA and at 320 K by 1HNMR, as in the previously studied freeze-dried starch gel of the density of 0.13 g/cm^3 with the same value of energy of activation.

The results indicated that the proposed method of reduction of the data obtained by different relaxation techniques to the functions of free activation energy could be considered as a very efficient tool in studying molecular dynamics in local dispersion regions of macromolecular system.

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BADANIE DYNAMIKI MOLEKULARNEJ ODWODNIONYCH ŻELÓW SKROBIOWYCH

S t r e s z c z e n i e

W pracy przedstawiono wyniki temperaturowych badań relaksacji mechanicznej (DMTA) i magnetycznej (1H-NMR) w liofilizowanym żelu skrobi pszenicy, otrzymanym w wyniku liofilizacji 5% kleiku skrobiowego. Do analizy danych, modułu sztywności (G_1 i G_2) i szybkości relaksacji spin-sieć protonów (R_1) zastosowano procedurę transformacji, testowaną wcześniej na układach o większej koncentracji sieci, eliminującą efekt różnicy częstości zewnętrznego pola zaburzającego. Procedura ta polega na przekształceniu zależności temperaturowych parametrów dynamiki mechanicznej i jądrowej na zależność od energii swobodnej aktywacji badanego procesu. Spośród trzech przejść relaksacyjnych obserwowanych w temperaturze 150, 210 i 280 K za pomocą zmian modułu sztywności kserożelu skrobi, jedno z nich, zachodzące w temperaturze 150 K związane jest z dynamiką molekularną tych samych grup, które odpowiadają za przejście relaksacyjne obserwowane w widmie 1H-NMR w temperaturze 320 K. Energia swobodna aktywacji tych procesów jest rzędu 40 kJ/mol. Są to najprawdopodobniej grupy hydroksymetylenowe łańcuchów skrobiowych, które jak wskazują wyniki, są także odpowiedzialne za wysoką sztywność sieci dehydratowanego żelu w niskiej temperaturze. ▨