STEFAN POLISZKO
GRZEGORZ HOFFMANN
RYSZARD REZLER

DYNAMIC MECHANICAL- AND DIELECTRIC-THERMAL ANALYSIS OF FREEZE-DRIED STARCH GELS

Department of Physics, Agricultural University, Poznań, Poland

Temperature dependences of components of the complex modulus of rigidity and complex electric permittivity of freeze-dried starch gel were obtained for the temperature interval from about 100 to 500 K. At low-temperature region relaxation process with free energy of activation of about 38 kJ/mol related with release of reorientational degrees of freedom of the polar hydroxymethylol groups was observed in DETA as well as in DMTA tests. Secondary relaxation processes with activation energies of 48 and 67 kJ/mol found in mechanical spectra only were ascribed to the local conformational mobilities of polymeric chains.

INTRODUCTION

In many food products the formely gelatinized and then retrograded starch occurs in form of a matrix determining mechanical-rheological properties of these products. As far as hydrated starch systems are concerned (2,3,8, 12-14), the results of the investigation of their mechanical properties have been correlated with the results of structural analysis carried out by differential scanning calorimetry, magnetic nuclear resonance and other methods. The observations of kinetics of the dispersive structure formation in the studied polymers were interpreted in therms of the theory of the crystallization [1]. In many cases, to enhance the durability of starch products they are dehydrated or directly produced in the low-hydrated form with the application of extrusion technique. Molecular and structural conditioning of mechanical properties of low-hydrated starch products have not been well known mainly due to the lack of reliable methods for instrumental analysis of these substances. The methods considered the most promising are dynamic mechanical-thermal analysis (DMTA) and dielectric-thermal analysis (DETA), which popularity in the studies polymer systems are growing. They both are belived to provide the information on molecular dynamics and the state as well as the changes in structure of the studied substances, directly related to their macroscopic properties [5, 9, 10]. With regard to all of that we undertook the experimental studies of model starch systems aiming at making grounds for relaxational spectroscopy of starch products.

MATERIALS AND METHODS

The investigations were carried out on the samples of xerogel obtained by sublimative drying of starch hydrogel of polymer concentration of 0.10 g/cm^3. The hydrogels were prepared from wheat starch paste boiled for 0.5 h under continuous stirring, then cooled down to 25°C and subjected to ageing for 100 h in the conditions preventing them from drying up. Before freeze drying the samples were initially frozen at $-$ 25°C and the dehydrating process was programmed to end at tk $\leqslant$ 0°C. Dried hydrogels were put into cyllindrical tubes of internal diameters 6 and 22 mm, so finally, the freeze-dried samples to be studied by DMTA method were in the form of cyllindrical rods of 80 mm in lenght and 5.5 mm in diameter whereas the samples studied by DETA method were formed into discs of 20 mm in diameter and 1.5 mm in thickness.

DMTA METHOD

Dynamic mechanical thermal analysis method is based on the fundamental hypothesis of molecular rheology claiming the relation between macroscopic viscoelasticity of materials and the intensity and character of mechanical relaxation processes in the materials [4].

In the DMTA method the changeabilities of real G_1 (T) and imaginary G_2 (T) parts of complex modulus of elasticity:

$$G^{*)+} = G_1 + i G_2 \tag{1}$$

are determined in wide ranges of temperature for one or a few frequencies of mechanical action of sinusoidal character.

Despite great interest in and growing popularity of studies of dynamic mechanical properties of materials there is still lack of the unification and standarization of relevant measuring techniques. In our work the dynamic mechanical properties of the studied starch gels were measured in the free vibration system based on the application of an inverted torsion pendulum [11]. This system makes us use of an optic-electronic set for period reading with a photoelectronic detector and a milisecond clock FPM-14 ELWRO. The system also provides the possibility of visual reading of vibration amplitudes and ensures a high accuracy of measurements by eliminating the errors introduced by mechanical to electric converters and signal recorders. Both the movable and fixed sampleholders of the pendulum together with the tested sample were placed in a chamber providing the possibility of carrying the measurements in the temperature range from 100 to 500 K in the atmosphere of liquid nitrogen vapors, redusing in this way the kinetics of thermal destruction of the material studied in high temperatures.

Directly we measured the frequency of free vibrations (f) and the logarythmic decrement of damping (L) of the system with and without sample (in the latter case the corresponding values are f_0 and L_0). The components of the complex

rigidity modulus of the investigated material were calculated from the following expresions: [10]

$$G_1 = 4\pi^2 \, IF \, (f^2 \, (1-0.25 \, L^2/\pi^2) - f_0^2 \tag{2}$$

and

$$G^2 = 4\pi^2 \, IF \, (f^2 \, L - f_0^2 \, L_0) \tag{3}$$

where I is the moment of inertia of the pendulum vibrator, and F is the shape parameter of the tested sample.
Our samples of freeze-dried gels were made in the form of cylindrical rods of a diameter R and heigh H, so their appropriate shape parameter is: $F = 2 \, H/(\pi R^4)$.

DETA METHOD

In dielectric-thermal analysis method we determine temperature dependences of the real (ε') and imaginary (ε'') parts of the complex dielectric permittivity:

$$\varepsilon^* = \varepsilon' - i\varepsilon'' \tag{4}$$

of a given material at different frequences of the measuring electric field. The real part of the so defined permittivity is measured as a ratio of the capacity (C_x) of measuring capacitor with a studied material between its plates to the capacity of the same capacitor with the dielectric replaced by vacuum (C_0):

$$\varepsilon'(\omega, T) = C_x(\omega, T)/C_0$$

The value of the imaginary part of permittivity $\varepsilon''(\omega, T)$ known as a coefficient of dielectric losses corresponding to the same experimental conditions is found as function of a tangent of the angle, σ, of phase shift between the voltage and current in the circuit of the measuring capacitor containing the studied sample, and the following relation holds:

$$\varepsilon''(\omega, T) = \varepsilon'(\omega, T) \, tg\sigma$$

The construction of the DETA spectrometer used in our measurements of freeze dried starch gels is described in Ref. [6]. The experimental setup was made of a capacity bridge and a measuring capacitor which was placed in a variable temperature chamber with liquid nitrogen vapors as a working medium. The required temperature chosen from the range of about 80 to over 500 K was maintained within 0.1 K.

RESULTS AND CONCLUSIONS

Exemplary temperature dependences of the components G_1 (T) and G_2 (T) of the complex rigidity modulus determined at the frequency of about 0.25 Hz for freeze-dried starch gel of a density of 0.13 g/cm³, are presented in Figs. 1 and 2.

As follows from a comparison of dynamic modulus of a dehydrated gel at a temperature e.g. 300 K when $G_1 \simeq 35$ MPa with the value of the same modulus of a fully hydrated gel of the same polymer concentration and the same temperature but with $G_1 \simeq 350$ Pa [12], mechanical properties of dehydrated starch systems are not determined by the density of spatial network but by the
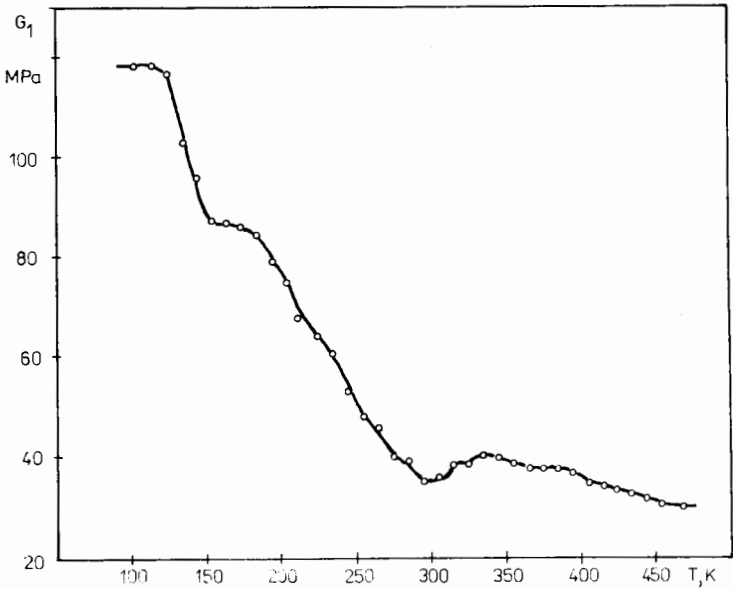

Fig. 1. Temperature dependence of G_1 at frequence 0.25 Hz for freeze-dried starch gel
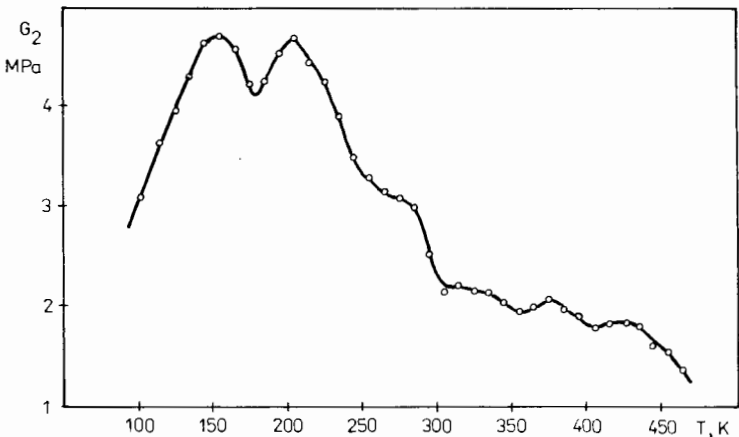

Fig. 2. Temperature dependence of G_2 at frequence 0.25 Hz for freeze-dried starch gel

rigidity of macromolecular segments of this network. These exemplary values given above illustrate that total dehydration of starch chains increases their rigididy by about 10^5 times. Further increase in rigidity, by over 3 times, which occurs with the temperature of xerogel decreasing from 20°C to -170°C proves an additional increase in energy of intramolecular barriers stiffening the chains of high-molecular starch components proceeding with decreasing gel temperature. According to these data the changes in configuration of polymer chains in low temperature range induced by mechanical action are elestic in character, so the mechanical energy of deformation is stored without the possibility of its dissipation in the form of heat. In the high temperature range a part of rotational barriers and hydrogen bonds stabilizing the chain configuration gets defrosted and does not contribute into the elastic reaction of the chain segments. It is the origin of a decrease in rigidity modulus of the studied gels with the temperature increasing from 100 to 300 K, which is illustrated in Fig. 1. The impossibility of mechanical energy storage eliminates the possibility of its dissipation which leads to a decrease in the loss modulus outside the transition zone. In the transition zone a decrease in rigidity of starch polymer chains is accompanied by three overlapping maxima of the mechanical loss modulus, which can be seen in Fig. 2. The appeerence of three transition processes in freeze-dried starch gels in low-tempereature range proves a complex molecular mechanizm of confor- mational transitions controlling the phenomena of mechanical relaxation. Some insight into this mechanism, we can get from the analysis of dielectric relaxation phenomena in the same material.

Temperature dependencies of real part of dielectric permittivity $\varepsilon'(T)$ and dielectric loss coefficient $\varepsilon''(T)$ determined for fully dehydrated freeze-dried starch gel at the measuring electric field frequencies of 0.4, 2.0 and 10 kHz are shown in Fig. 3 and 4.

In the range of very low temperatures the components of complex dielectric permitivity take the values $\varepsilon'' = 1$ and $\varepsilon' = 0$ characteristic of vacuum and
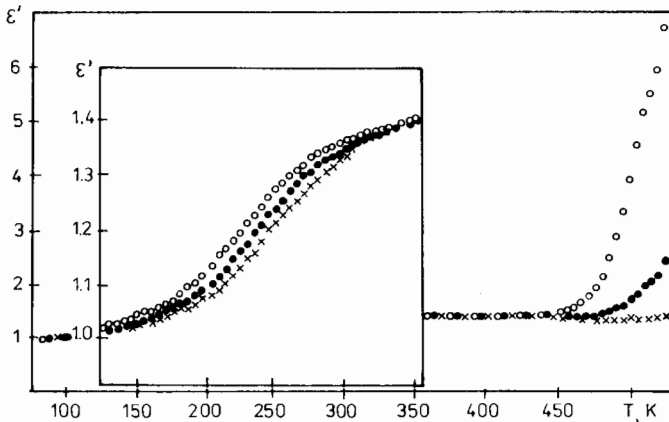

Fig. 3. Temperature dependence of ε' at various frequencies for freeze-dried starch gel: (○) 0.4 kHz, (●) 2 kHz, (x) 10 kHz
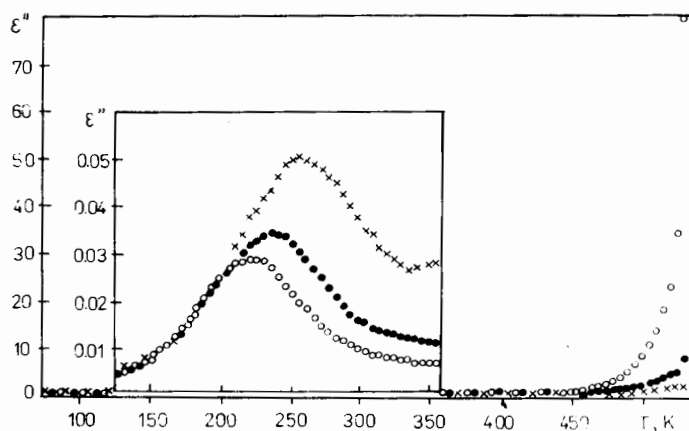
Fig. 4. Temperature dependence of ε'' at various frequencies for freeze-dried starch gel: (○) 0.4 kHz, (●) 2 kHz, (x) 10 kHz

proving the total freezing of electric dipols reorientation. Above 100 K we observe a dispersions of the real part ε' and the maxima on the imaginary part ε" of the complex dielectric permittivity. The recorded shift of the curves on the temperature scale with changing frequency of measuring field is characteristic of relaxational phenomena which, in the case of polysaccharides, are identified as the processes related with release of reorientational degrees of freedom of a polar hydroxymethylol groups [7]. The next great increase in ε' and ε" is observed above 450 K in result of the release in polar hydroxyl group rotations most probably due to the dissociation of intrachain hydrogen bonds as well as the possibility of reorientation of polar segments of flexible polymer chains.

A comparison of the results obtained by DMTA and DETA methods requires the application of a procedure allowing us to eliminate the effect of different frequences of measuring filds on the localization of dispersion regions [9]. As far as local relaxational processes revealing in low temperatures are concerned, their relaxation times obey the relation predicted in the theory of absolute reaction rates:

$$\gamma = (h/kT) \exp (F/RT) \tag{5}$$

where h, k, and R are Planck, Boltzmann, and gas constants, respectively, F is the free energy of activation of relaxation process.

This fact, taking into account that angular frequency $\omega = 1/\gamma$ makes it possible to drow a few curves obtained for the same process as a function of temperature for different frequences into one curve showing the results as a function of free energy of activation of relaxations:

$$F = RT \ln (h\omega/kT) \tag{6}$$

Fig. 5 presents the mechanical and electric loss curve reduced in the above described way and normalized to unity at the maxima.
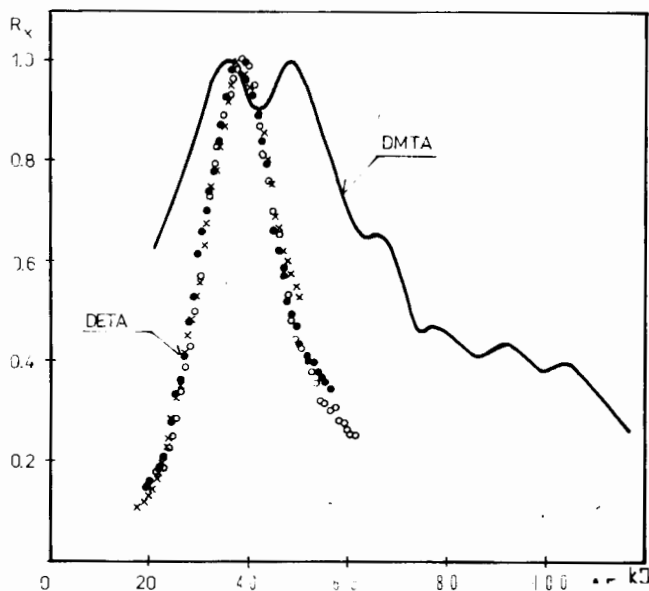
Fig. 5. Normalized curves of mechanical (DMTA) and dielectric (DETA) losses plotted as the function of ΔF

The appropriate character of the above reduction method is proved by the fact that the results of dielectric measurements from the insert in Fig. 4 could be presented as a single curve, $R\varepsilon\,(F) = \varepsilon''(F)/\varepsilon''_{max}$, which gives a relatively narrow distribution of activation energy of relaxational processes with the most probable value of 38 kJ/mol. The same figure presents also the normalized curve $R_M(F) = G_2(F)/G_{2\,max}$ describing the mechanical losses, which displays much more complex character. As it can be concluded from the latter figure, the dissociation of interactions releasing the rotation of hydroxymethylol groups is accompanied by a reduction in the rigidity of the chains and the appearance of mechanical relaxation processes of the activation energy close to that of dielectric relaxation. Mechanical action is, however, less selective and thus can induce reorientations of not only polar elements. In the considered gels this leads to the onset of additional relaxation processes of activation energies of 48, 67 kJ/mol and higher. These processes can be supposed to be associated with a release of conformational mobility of short range controlled by the height of barriers limiting the rotation of monomer units around the glycoside bonds α-1-4'.

Local flexibility of chains favours the helix-coil conformational transitions characteristic of starch polymers. The effect of this kind probably occurs in the temperature range between 40 and 60°C where a temperature increase induces an increase in rigidity modulus of freeze-dried starch gels.

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Authors address: 60-637 Poznań, Wojska Polskiego 38/42

S. Poliszko, G. Hoffmann, R. Rezler

DYNAMICZNA MECHANICZNO- I DIELEKTRYCZNO-TERMICZNA ANALIZA LIOFI-
LIZOWANYCH ŻELI SKROBIOWYCH

Katedra Fizyki, Akademia Rolnicza, Poznań

Streszczenie

W celu przeprowadzenia molekularnej interpretacji mechanicznych właściwości odwodnionych układów skrobiowych, uzyskano temperaturowe zależności składowych złożonego modułu sprężystości poprzecznej i złożonej przenikalności elektrycznej dla liofilizowanego żelu skrobiowego w zakresie temperatur od 100 do ponad 500 K. Porównanie wskaźnika dynamicznego odwodnionego żelu ze wskaźnikiem całkowicie uwodnionego żelu dla tych samych stężeń polimeru wskazuje na to, że odwodnienie łańcuchów skrobiowych powoduje wzrost aktywności ok. 10^5 razy. Mechaniczne właściwości odwodnionych systemów skrobiowych nie są zdeterminowane przez gęstość makromolekularnych segmentów sieci. Lepkosprężystość segmentów w liofilizowanym żelu skrobiowym przejawia się w temperaturowej zależności rzeczywistej i urojonej części złożonego modułu sprężystości. Pojawienie się wielopośrednich procesów potwierdza złożony cząsteczkowy mechanizm przejść konformacyjnych kontrolujący zjawisko mechanicznych relaksacji w odwodnionych łańcuchach polisacharydowych. Proces relaksacji o energii swobodnej równej 38 kJ/mol

obserwowany w niskotemperaturowym zakresie testów analizy dielektryczno-termicznej (DETA), a także w testach dynamicznej analizy mechaniczno-termicznej (DMTA) może być związany z uwodnieniem reorientacyjnych stopni swobody polarnych grup hydroksymetylowych ($HOCH_2-$).

Drugie przejścia mają energię aktywacji 48, 67 kJ/mol i wyższe wartości znalezione w spektrach mechanicznych, zostały przypisane lokalnej, konformacyjnej ruchliwości łańcucha polimerycznego. Szczegółowy, molekularny opis tych procesów wymaga dodatkowych badań, które będą prowadzone.