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STUDIES ON THE MECHANICAL PROPERTIES OF GELS OF CHEMICALLY MODIFIED PROTEINS

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Key words: chemical modification of proteins, physico-chemical properties of modified proteins, Tolstoj apparatus, dialdehyde starch, protein gelation.

Casein forms gels after modification by dialdehyde starch (DAS). The creep behavior of gels was studied with the Tolstoj apparatus. The total shear compliance and the plastic and elastic components there of were determined as a function of time. The influences of concentrations of casein and DAS, of pH, and of storage time were studied. Free amino groups and available lysine were determined, too. The processes of crosslinking of protein and of blocking of amino groups show different kinetics. At least two polypeptide chains of casein corresponds with one crosslink. This means that the crosslinking process is a supermolecular one.

Dialdehyde starch (DAS) reacts with casein and other proteins by blocking the basic amino acid residues and by crosslinking the polypeptide chain [1, 2]. This crosslinking enables to form casein gels in neutral and weak basic medium [3]. Pure casein shows no gelation under similar conditions. The main parameters for gel formation are: concentrations of casein and DAS, pH, and storage time.

The gels properties were studied using the Tolstoj apparatus [4, 5]. On the one hand this apparatus und method enable to determine the simple mechanical properties of all gel systems, e.g. shear strain, shear modulus, and shear compliance. On the other hand, it is also possible to discriminate the plastic and elastic components of total compliance.

PRINCIPLE OF MEASURING METHOD

The mixture of 10% casein and 1% DAS is poured rapidly into a Plexiglass form (Fig. 1) between two parallel rifled plates of 3×5 cm [5]. The forms are put into an exiccator, which, in order to avoid drying of the gel layer, contains some water, and stored in a refrigerator. About 24 hours later the gel layers are taken out of the form together with the ground and upper plate and stored cool until the measurement in

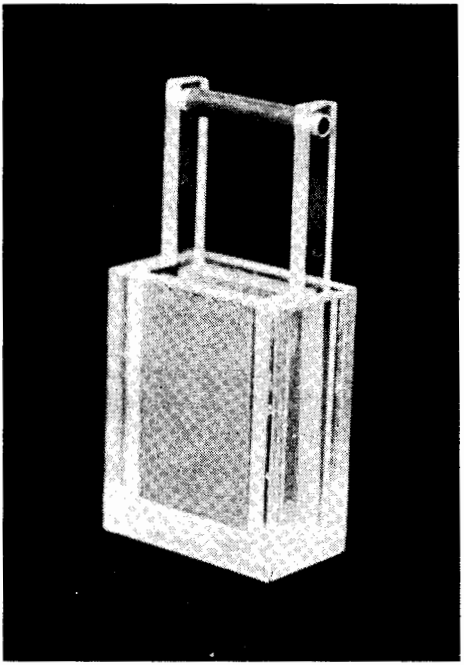

Fig. 1. Form for preparing gel layers

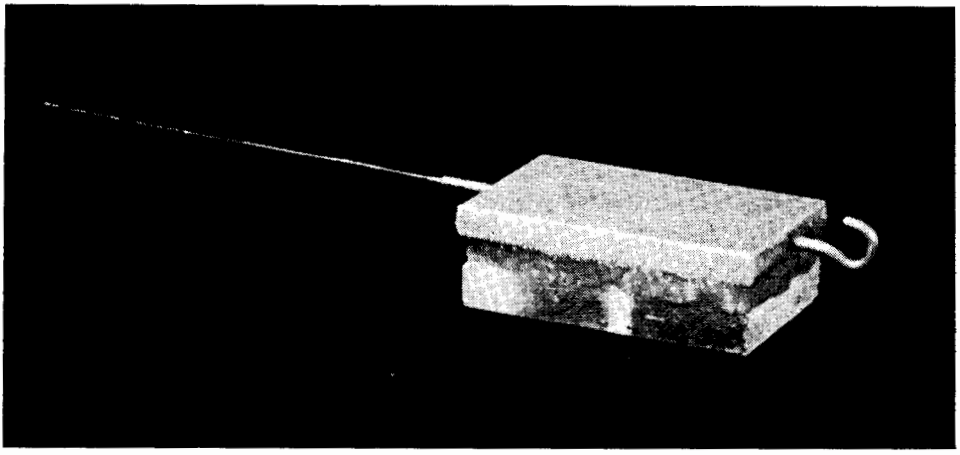

Fig. 2. Gel layer in the middle of the ground plate and the upper one with hook and needle

an atmosphere of 100% relative humidity. A hook and on the opposite side a long needle are screwed after this into the upper plate (Fig. 2). The hoock is to hold a thread with a weight. At the other end the needle indicates the deformation of the gel layer which is observed by a microscop and measured by an ocular micrometer. The gel layer is kept in a measuring cell in water saturated atmosphare during measuring time and kept at constant temperature by an ultra thermostate (Fig. 3). After

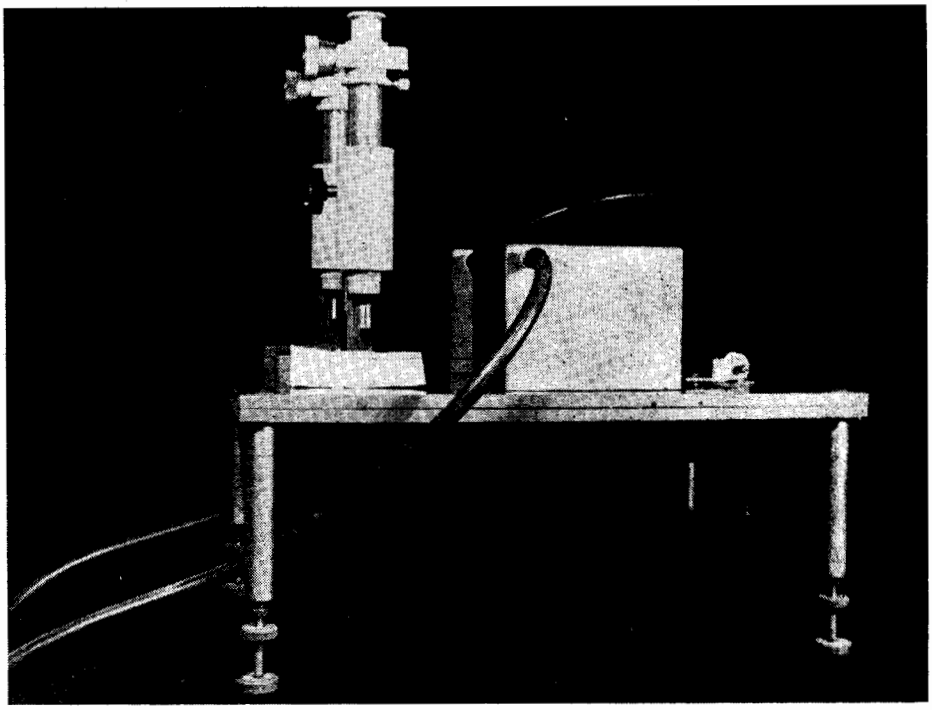

Fig. 3. Complete Tolstoj apparatus

adjusting the end of the needle to zero point of ocular micrometer or after recording the position of needle end the experiment can be started by putting the thread with weight onto the pulley. The deformation is read at the ocular micrometer practically at the same time and next to this in short intervals, e.g. 2, 5, 7, 10 minutes, and later on up to 24 hours in longer intervals of about 30 minutes. After these measurements in the stress phase the weight and thread are taken of and now the release phase is measured as described before. The equilibrium plastic deformation value is determined after thoroughly accomplished relaxation process. With these results it is possible to calculate the percentage of plastic and elastic deformation of the gel studied as, for example, is shown in [5].

Fig. 4 represents the curves of an extremely elastic and of one rather plastic gel.

RESULTS

In Fig. 5 is shown the creep of gels at three pH values after a storage time of 8 days. Table 1 contains all the values of the total shear compliance and the elastic and plastic components thereof as well as the quotient of the plastic component to the total shear compliance. With increasing pH all values of the compliance are decreasing, whilst the quotient of plastic to total deformation is constant above pH 8. In this tab. is also to be seen that the pH in the reaction mixture decreases up to one (and more) pH unit during 24 hours.

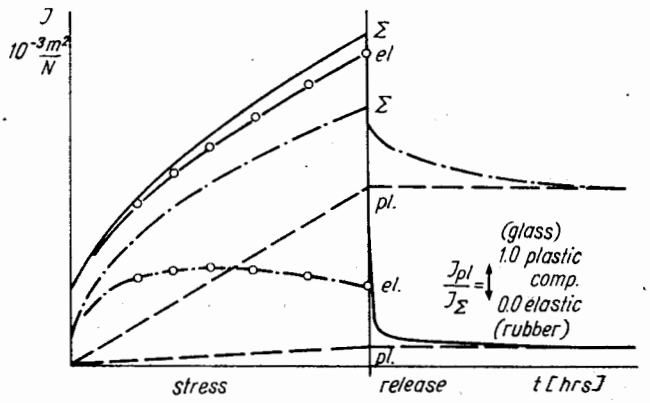

Fig. 4. Creep behaviour of an extremely elastic gel and a rather plastic one

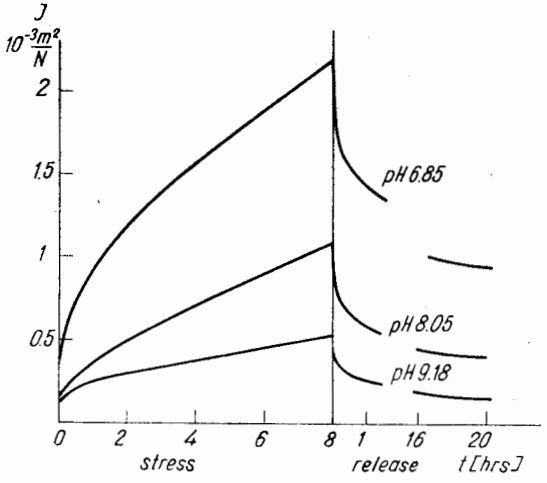

Fig. 5. Creep behaviour of gels at different pH values; storage time 8 days

Fig. 6 shows the creep of one gel at pH 8.37 and a casein : DAS-ratio of 1 : 0.1 after a storage time of 1 to 15 days. The deformation decreases in this time; this means an increase of firmness and on the other hand

T a b l e 1. Total shear compliance (I_Σ), elastic (Iel) and plastic (I_{pl}) components thereof, and the ratio of plastic to total compliance of casein DAS gels (1:0.1) at different pH values; stress phase 8 hours

pH		I_Σ	I_{el}^{8h}	I_{pl}	$\frac{I_{pl}}{I_\Sigma}$
start	end				
6.20		5.3	2.7	2.6	0.49
6.85	6.62	2.2	1.2	1.1	0.45
7.50	6.96	2.2	1.4	0.8	0.37
8.05	7.17	1.2	0.8	0.4	0.33
8.60	7.40	0.74	0.52	0.22	0.31
9.18	8.25	0.54	0.37	0.17	0.31

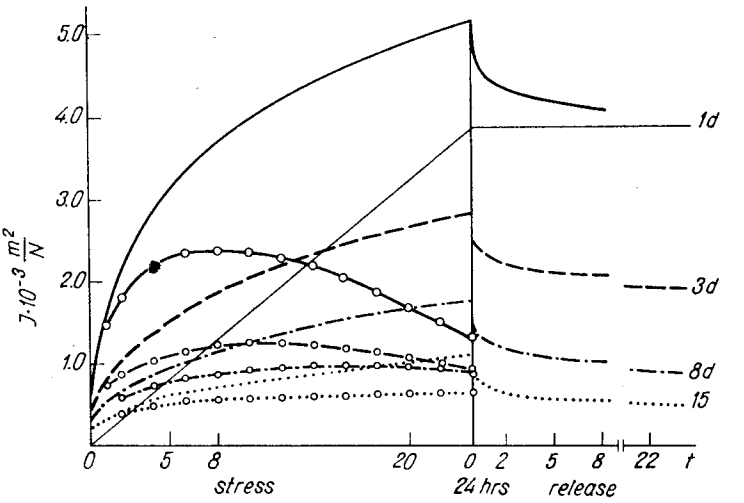

Fig. 6. Creep behaviour of a casein DAS gel 1 : 0.1 after different storage times; pH 8.37

an increase of elastic (rubbery) deformation of the gel, as shown in Table 2.

The curves in Fig. 7 of the elastic part of shear compliance plotted against the time on logarithmic scale according to Ferry [6] show a normal rubber elastic state only for the 15 days old gels. The form of the curves after a storage time of 1 and 3 days points to an increase of firmness of gels apparently by crosslinking of polypeptide chains during the measuring time. Fig. 8 showing the curves of 15 days old gels indicats that crosslinking has been completed. These results are confirmed impressively by the ultramicroscopic fotographs [2].

Calculating the number of crosslinks per volume unit according to Flory [7], we found that at least 2 polypeptide chains of casein correspond with one crosslink. It means that crosslinking process is a super-

Table 2. Total shear compliance (I_Σ), elastic (I_{el}) and plastic (I_{pl}) components thereof, and the ratio of plastic to total compliance at different pH values and storage times; stress phase 24 hours

Casein: DAS	pH start	pH end	Storage time (d)	I_Σ	I_{el}^{24h}	I_{pl}	$\frac{I_{pl}}{I_\Sigma}$
1:0.25	7.40	6.35	1	0.77	0.29	0.48	0.62
			3	0.46	0.25	0.21	0.46
			8	0.31	0.23	0.08	0.26
			15	0.21	0.18	0.03	0.14
1:0.1	8.37	7.30	1	5.2	1.3	3.9	0.75
			3	2.8	0.9	1.9	0.68
			8	1.8	0.9	0.9	0.49
			15	1.1	0.6	0.47	0.43

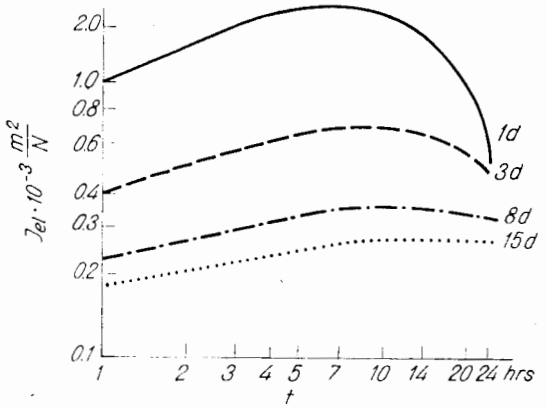

Fig. 7. Curves of elastic component of shear compliance of a casein DAS gel 1 : 0.25 after different storage times; pH 6.52

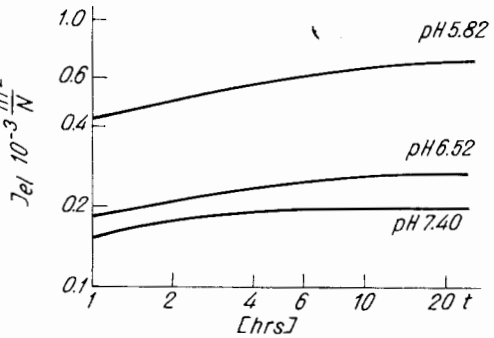

Fig. 8. Curves of elastic component of shear compliance of a casein DAS gel 1 : 0.25 at different pH values; storage time 15 days

molecular one, because by molecular crosslinking one polypeptide chain must correspond at least one crosslink [7]. Contrarily to that, the number of blocked amino groups of a protein is higher than the number of crosslinks. Taking into account these results and the different speeds of crosslinks of protein and blocking of amino groups, we can suppose that both processes follow different kinetics.

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STUDIA NAD MECHANICZNYMI WŁAŚCIWOŚCIAMI ŻELÓW BIAŁEK CHEMICZNIE ZMODYFIKOWANYCH

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Streszczenie

Badane żele tworzono przez reakcję kazeiny z modyfikowaną skrobią (dwualdehyd skrobi). Właściwości pełzające badano przy użyciu aparatu Tołstoja (rys. 3). Określano ogólną charakterystykę ścinania, jak również składowe elementy plastyczne i elastyczne w funkcji czasu (rys. 4). Przebadano wpływ stężenia kazeiny i dwualdehydu skrobi (rys. 6, 7), pH i czasu składowania. Określono również zawartość wolnych grup aminowych i dostępnej lizyny. Wykazano różną kinetykę tworzenia wiązań poprzecznych w białkach i blokowania grup aminowych. Wypada najmniej 2 łańcuchy polipeptydowe kazeiny na jedno wiązanie poprzeczne. Wskazuje to supermolekularny charakter procesu tworzenia wiązań poprzecznych.