

¹Chair and Department of Applied Pharmacy,

²Chair and Department of Synthesis and Chemical Technology of Pharmaceutical Substances,
Medical University of Lublin

PIOTR BELNIAK¹, DARIUSZ MATOSIUK², WIKTOR CZARNECKI¹

*The influence of starch hydrolysates on rheological properties
of mucilage solutions and the ability of tablets for water sorption*

Wpływ hydrolizatów skrobiowych na właściwości reologiczne kleików i podatność tabletek
na sorpcję wody

In literature there are many ways of modification of starch. One of them is enzymatic hydrolyze which is often used in food system. There are low-particles substances (glucose, maltose syrup) and high-particles substances (maltodextrin) with good rheological properties. Maltodextrin is used as a gelling agent, stabilizator of emulsion, filler and it increases viscosity and density of food products [4]. Starch can also be modified by chemical hydrolyze. Hydrocolloids obtained from polysaccharides such as starch, derivatives of cellulose, pectin, gum arabic or protein (gelatin) are widely used in food system and for pharmaceutical purposes. These polymers interact strongly with water. Their caloric value is quite low and makes them useful, particularly in the development of diet foods [3]. Nagano et al. [5] tested a combination of starches and non-starches hydrocolloids to modify rheological properties of mucilages. Addition of guar gum to corn starch changed the viscosity of hydrocolloid [2]. Touvien L. et al. [7] examined natural starch and product of acetylating of starch. They obtained coatings of tablets with better control of release and a possibility of slowing down the release of timolol as model drug.

In the literature there are no data on mucilage solutions or tablets with starch hydrolysates received according to our prescription. Therefore, the influence of starch hydrolysates on rheological and physical proprieties of mucilage solutions and tablets was tested.

MATERIALS AND METHODS

Starch hydrolysates were prepared at the Chair and Department of Synthesis and Chemical Technology of Pharmaceutical Substances, Medical University of Lublin, according to Dariusz Matosiuk's prescriptions by chemical hydrolyze of potato starch (Nowamyl S.A. Łobez Poland) with solutions of several acids. Molecular weight of obtained hydrolysates was estimated in a crioscope (Trtident 800 CL) on the ground of the freezing point determination. Hydrolysates were

used for obtaining aqueous mucilage solutions in the first part of the test, and for producing tablets in the second part. All hydrolysates were powdered and passed through a sieve (500 μm), then each sample equivalent to 100 mg was pressed into a flat tablet on a single punch of the eccentric tableting machine (Korch EK0, Berlin, Germany).

The obtained hydrolysates with their molecular weights, time of hydrolyze of acids and properties of obtained tablets are presented in Table 1.

Table 1. Absolute density of starch hydrolysates' tablets obtained at high compaction pressure (n=20)

Symbol	Acid used and time of hydrolyze (h)	Molecular weight (Da)	Tablets				
			High (mm)	Diameter (mm)	Weight (mg)	Hardness (kg/mm ²)	Absolute density (g/cm ³)
SH-1	Chloroacetic acid (1.5)	785.7	2.14±0.94%	7.00±0.29%	96.7±6.5%	0.58	1.15
SH-2	Chloroacetic acid (2)	496	2.17±2.3%	7.00±0.29%	97.48±4.74%	0.35	1.14
SH-3	Tartaric acid (1.5)	788.6	2.17±1.38%	7.00±0.14%	83.62±2.61%	0.21	0.98
SH-4	Tartaric acid (2)	856.6	2.17±2.30%	7.00±0.14%	100±5.8%	0.59	1.18
SH-5	Apple acid (1.5)	941.5	2.25±2.23%	7.00±0.14%	102.8±5.06%	0.40	1.14
SH-6	Apple acid (2)	877.3	2.23±1.79%	7.00±0.14%	104.30±6.1%	0.32	1.18

Preparation of solutions. Aqueous mucilage solutions at different concentrations ranging from 1 to 10% (w/v) were prepared by agitation and dissolving dry hydrolysates at room temperature. The obtained mucilage solutions were examined for density and viscosity.

Density and viscosity tests. The relative density of mucilage [6] can be estimated by pycnometric technique and calculated from equation 1:

$$d_m = \left(\frac{m}{w} \cdot 0,997 + 0,0012 \right) [\text{g} / \text{cm}^3], \quad \text{Eq. 1}$$

where d_m – relative density of tested mucilage at 20 °C, m – weight of tested substance in pycnometer, w – weight of water in the same volume, 0.997 – density of water at 20 °C, 0.0012 – correction of weighing in air atmosphere.

The dynamic viscosity of the substance can be assayed in a viscosimeter of Höppler, and calculated from equation 2:

$$\eta = K \cdot t \cdot (d_k - d_m) [\text{mPa} \times \text{s}], \quad \text{Eq. 2}$$

where: η – dynamic viscosity, K – coefficient of apparatus ball, t – time of falling of ball in sec., d_k – density of ball, d_m – relative density of tested mucilage.

The influence of concentration of products of hydrolyze in mucilage solutions on its dynamic viscosity is shown in Fig. 1 (n = 6).

Water sorption. Tablets were tested using a climatic test chamber (Wamed KBK-65W, Poland)

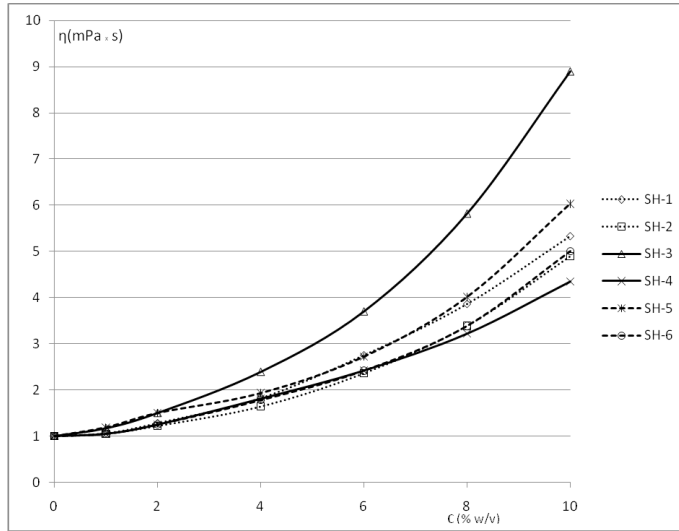


Fig. 1. The effect of conditions of hydrolyze and concentration of starch hydrolysate in mucilage solutions on its dynamic viscosity (n=6)

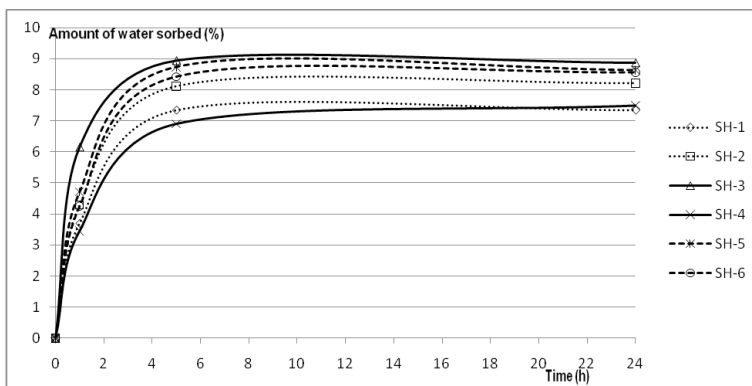


Fig. 2. Water sorption of tablets at 22 °C and 90 % humidity (n=6)

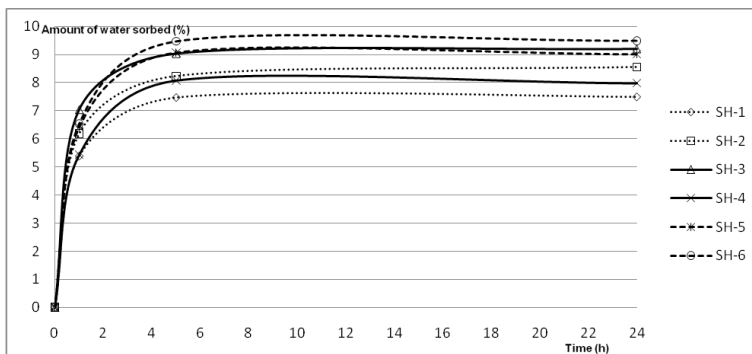


Fig. 3. Water sorption of tablets at 35 °C and 90 % humidity (n=6)

in which relative humidity can be varied within the range of 5–95% and temperature from + 5 to + 70°C.

Each tablet was dried in a dryer at 40 °C and 5 % of humidity for 24 h before the test. Then the tablet was put on a small sieve (1000 µm) attached to a perforated plastic dish and put into the climatic test chamber at the temperature of 22 °C and 35°C and humidity of 90 % for each test. The water sorption of tablets is shown in Fig. 2 and 3.

RESULTS AND DISCUSSION

Albert Einstein developed the equation of flow (Eq.3) applicable to dilute colloidal dispersions of spherical particles:

$$\eta = \eta_0(1+2,5 \phi) \text{ [mPa x s]} \quad \text{Eq.3}$$

where η – viscosity of suspension, η_0 – viscosity of dispersion medium, ϕ – fraction of the total volume of suspension which is occupied by the particles [1].

Theoretically, if η is plotted against ϕ , a straight line will result. In actual practice, the line will deviate from straight line as the volume concentration of the dispersed phase is increased (Fig. 1).

Density of mucilage solutions is the same for each hydrolyze products and it increases in a linear way according to increasing its concentrations. However, increase of dynamic viscosity is nonlinear with different values for each hydrolysate. But the dependence between the concentration of starch hydrolysate in mucilage solutions and its dynamic viscosity can be shown as

$$\ln(\eta) = f(c) \text{ (fig. 4)} \quad \text{and described by equation 4:}$$

$$\ln(\eta) = a \cdot c - \ln(b) \quad \text{[mPa x s] Eq.4}$$

where a – directional coefficient, b – calculated viscosity of dispersion medium.

Density (d_m), dynamic viscosity measured (η), dynamic viscosity calculated according to eq. 4 (η^*), with estimated directional coefficients (a) and viscosity of dispersion medium (b), η/η^* , and their correlation coefficients (r), and standard deviation (sd) are shown in table 2.

Theoretically, if values of viscosity of dispersion medium (b) amount to 1.00 mPa x s, it will be viscosity of pure water. In actual practice, values of b coefficient amount to 1.03–1.05 mPa x s, which probably means presence of impurity of dispersion medium.

Mucilage solutions with starch hydrolysates (10 % w/v) obtained with any acid hydrolyze for 2 h (SH-2, SH-4, SH-6) with directional coefficient (a) ranging from 0.142518 to 0.159411, reach the lowest values of dynamic viscosity from 4.35 to 5.01 mPa x s. A shorter time of hydrolyze of starch hydrolysates gives mucilage solution (10 % w/v) with a higher directional coefficient (a) 0.170124 – SH-1, and 0.182412 for SH-5 and proportionally higher values of dynamic viscosity – 5.33 mPa x s and 6.03 mPa x s. In the case of starch hydrolysate obtained with tartaric acid's hydrolyze for 1.5 h (SH-3), the highest directional coefficient (a) – 0.219044 gives the highest dynamic viscosity of 10 % (w/v) mucilage solution – 8.9 mPa x s.

The water sorption test conducted in the maximum value of humidity – 90 % – shows that the weight of tablets obtained from hydrolysates slightly increases for each kind of series and it amounts up to 9.49 % for tablets with hydrolysates obtained with apple acid hydrolyze (for 2 h),

Table 2. Comparison of viscosity measured (η), viscosity calculated (η^*) at various concentration risen to second power ($n = 6$)

	C % (w/v)	1	2	4	6	8	10
SH-1	dm (g/cm ³)	1.002	1.005	1.012	1.019	1.025	1.032
	η (mPa * s)	1.06	1.28	1.82	2.75	3.86	5.33
	sd	0.9573	0.3758	0.7156	0.1686	0.1650	0.22.65
	η^* (mPa* s)	1.1509	1.3644	1.9173	2.6944	3.7865	5.3211
	η^*/η	1.0858	1.0659	1.0535	0.9798	0.9809	0.99.83
	$r = 0.9994; \bar{a} = 0.1701; \bar{b} = 1.03$						
SH-2	dm (g/cm ³)	1.002	1.005	1.012	1.019	1.026	1.032
	η (mPa * s)	1.05	1.22	1.64	2.36	3.39	4.9
	sd	0.4796	0.9109	1.2955	0.1350	0.0289	0.4309
	η^* (mPa* s)	1.1247	1.3156	1.7999	2.4627	3.3694	4.610
	η^*/η	1.0712	1.0783	1.0975	1.0435	0.9939	0.9408
	$r = 0.9986; \bar{a} = 0.1567; \bar{b} = 1.04$						
SH-3	dm (g/cm ³)	1.001	1.005	1.012	1.019	1.026	1.033
	η (mPa * s)	1.17	1.5	2.39	3.7	5.82	8.9
	sd	0.7275	1.6590	0.2754	0.3043	1.1594	0.9489
	η^* (mPa* s)	1.1993	1.4930	2.3138	3.5857	5.5570	8.6119
	η^*/η	1.0250	0.9953	0.9681	0.9691	0.9548	0.9676
	$r = 0.9999; \bar{a} = 0.2190; \bar{b} = 1.038$						
SH-4	dm (g/cm ³)	1.002	1.005	1.012	1.019	1.026	1.033
	η (mPa * s)	1.05	1.25	1.81	2.42	3.22	4.35
	sd	1.0353	0.6483	0.0666	0.0665	0.0929	0.2491
	η^* (mPa* s)	1.0975	1.2656	2.2381	2.2381	2.9763	3.9579
	η^*/η	1.0453	1.0125	0.9249	0.9249	0.9243	0.9099
	$r = 0.9996; \bar{a} = 0.1425; \bar{b} = 1.0507$						
SH-5	dm (g/cm ³)	1.002	1.055	1.012	1.019	1.025	1.032
	η (mPa * s)	1.19	1.5	1.93	2.72	4.01	6.03
	sd	1.3929	1.5106	0.2608	0.2367	0.7061	0.6976
	η^* (mPa* s)	1.1429	1.3716	1.9755	2.8451	4.0976	5.9015
	η^*/η	0.9605	0.9144	1.0236	1.0460	1.0219	0.9787
	$r = 0.9982; \bar{a} = 0.1824; \bar{b} = 1.05$						
SH-6	dm (g/cm ³)	1.001	1.005	1.012	1.018	1.026	1.032
	η (mPa * s)	1.05	1.25	1.78	2.42	3.39	5.01
	sd	0.8641	0.7616	0.1039	0.3161	0.1210	1.1607
	η^* (mPa* s)	1.1393	1.3362	1.8379	2.5276	3.4771	4.7827
	η^*/η	1.0850	1.0689	1.0325	1.0446	1.0257	0.9546
	$r = 0.9985; \bar{a} = 0.1594; \bar{b} = 1.03$						

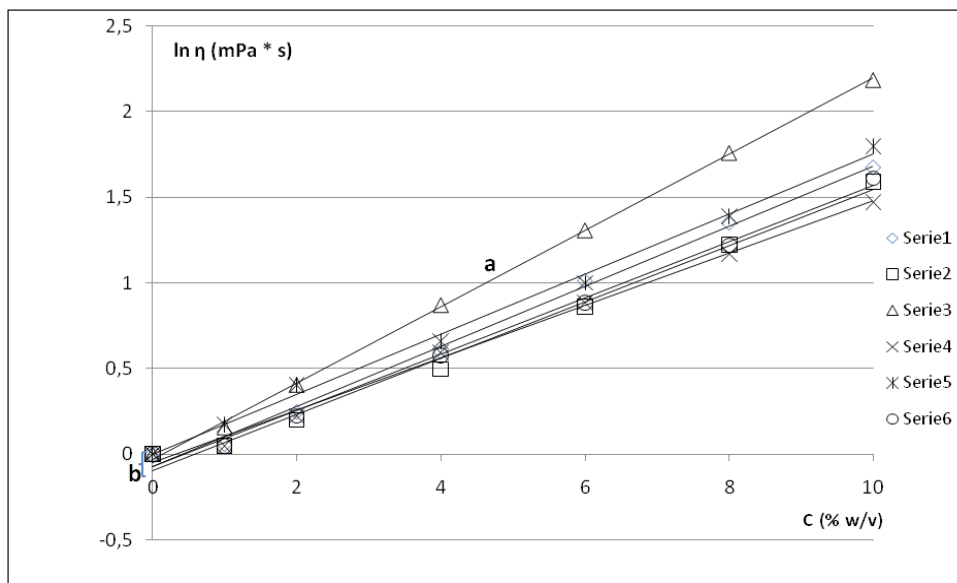


Fig. 4. The effect of concentration of starch hydrolysate in mucilage solutions on natural logarithm of its dynamic viscosity ($n=6$)

after 24 h of test, at temperature of 35 °C. It was observed that weight does not increase after 6 h of test. Tablets absorb more water in higher temperature, but the differences are not significant.

Concluding, low ability for water sorption of starch hydrolysates, slow dissolving process, high concentrations and significant density of solutions gives possibilities of using them for preparation of mucilage solutions or suspensions.

Tabletting process of hydrolysates and physical properties of tablets showed that they may be used as fillers in tablet production. They have a nonadhesive property and they do not cause jam of punches with wall of die.

Slow dissolving and significant values of density of prepared solutions also give possibilities of using these hydrolysates for a sustained release of dosage forms, like granules or tablets.

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SUMMARY

The purpose of this study was to investigate the influence of starch hydrolysates on the dynamic viscosity of mucilage solutions and on the ability of water sorption of tablets with the above hydrolysates. Aqueous mucilage solutions at different concentrations ranging from 1 to 10 % (w/v) were prepared. The obtained mucilage solutions were examined for density and viscosity.

Tablets with the weight of 83.62–104.30 mg, having hardness ranging from 0.21 to 0.59 kg/mm², absolute density from 0.98 to 1.18 g/cm³, were pressed on a single punch eccentric tableting machine (Korch EK0, Berlin, Germany). Tablets were tested for water sorption using the climatic test chamber (Wamed KBK-65W, Poland).

STRESZCZENIE

Celem pracy było zbadanie wpływu hydrolizatów skrobiowych na lepkość dynamiczną kleików i na zdolność wiązania wody przez tabletki zrobione z tych hydrolizatów. Przygotowano kleiki o stężeniu od 1 % do 10 %, a następnie zbadano ich gęstość i lepkość dynamiczną. Tabletki otrzymane w tabletkarce uderzeniowej (Korch EK0, Berlin, Germany) o wadze 83,62–104,30 mg, mające twardość od 0,21 do 0,59 kg/mm² i gęstość rzeczywistą 0,98–1,18 g/cm³, przebadano na zdolność wiązania wody przy użyciu komory klimatycznej (Wamed KBK-65W, Poland).