MAŁGORZATA BĄCZKOWICZ
PIOTR TOMASIK

SOLVENT EFFECT ON STARCH MATRIX

Department of Chemistry and Physics
The Hugon Kołłątaj Academy of Agriculture, Cracow, Poland

Potato starch was heated in various solvents followed by conditioning of starch in the air. The effect of the treatment was characterized by means of water uptake, aqueous solubility, characteristics of gelation and thermal behavior (TG, DTA, DTG) of processed samples.

Amylose and amylopectin as the components of starch form pretty compact structure of starch grains. Therefore merely well penetrating reagents provide effective reactions on native starch. These kinds of reagents are responsible for side reactions such as depolimerization of starch and for this sake their use suffers several limitations. Hence, the tendency of the turn to less effective reagents is obvious. Their use requires loosening of the compact structure of starch matrix prior to the proper reaction. There are several physical methods proposed for this puropse. They are thermal pretreatment with heat and/or steaming, extrusion, radiation, the solvent effect and so on. Also chemical methods may be involved. They are mainly partial, mild hydrolysis either by acids or bases. The solvent effect may provide subtle and easily controlled changes of starch matrix. Several mechanisms may be involved in the loosening of matrix and, therefore, a variety of modifications are offered by the use of this effect. The theory of the solvent effect is well developed [1] and may deliver a convevient way of prediction of the results of the modifications by the solvent.

MATERIALS AND METHODS

The experiments were carried out on the potato starch manufectured in Głowno in 1988. Both air-dried, native starch as well as oven-dried (130°C, 2h) starch were subject to the investigations.

Starch (50 g) was heated in a given solvent (250 mL) for 3h at $78° + 0.5°C$. Then the suspension was filtered through the sintered glass filter (G3) an left to stand in the air for couple days. Air-dried samples were sieved (0.2 mm).

The estimation of the day mass content, solubility and water binding capacity were carried out according to [2]. The characteristics of gelation of 3.2% aqueous starch suspensions was run in the standard manner using the Rheotest-2 (GDR) apparatus.

Thermal analysis was run using Paulik-Paulik-Erdey apparatus (made in Hungary). The procedure has been described in our earlier paper [3].

RESULTS

T a b l e 1. The dry mass content (DMC) of air-dried starch after processing in solvents. Their water binding capacity (WBC) and aqueous solubility (AS). The data are quoted for air-dried starch (ADS) and Oven-dried starch (ODS).

Solvent used	DMC [%]		WBC [g/gl]		AS [%]	
	ADS	ODS	ADS	ODS	ADS	ODS
None	79.7	99.3	5.41		9.89	
Ethanol abs.	86.8	99.6	21.20	20.80	10.85	7.56
Ethanol 99.6%	87.0	87.4	11.20	17.34	7.46	5.88
Ethanol 90%	86.2	87.3	12.16	18.61	7.06	8.04
1-propanol	91.1	89.0	15.65	12.59	7.87	6.34
1-pentanol	90.9	87.6	18.01	14.87	9.52	6.10
Nitrobenzene	88.9	87.6	8.54	10.47	4.08	5.47
Benzene	88.1	87.0	16.82	13.79	7.88	3.05
Acetonitrile	88.6	88.6	12.72	15.28	7.79	5.36
2-butanone	89.3	87.1	16.27	16.82	9.02	6.76
Dimethyloformamide	86.1	87.3	12.25	22.17	6.41	8.60
1.4-dioxane	88.7	90.3	14.58	16.86	7.14	5.17
Pyridine	84.2	87.7	14.44	15.19	6.01	4.86

Table 1 presents the results of estimations of dry mass, water binding capacity and aqueous solubility of original and solvent processed starch. Table 2 reports the characteristics of gelation of 3.2% starch gels.

DISCUSSION

In our former paper [4] we have presented the results of the modification of starch involving the solvent effect of a series of solvents. The extent of the damage of starch grains was shown using the microscopic observations of processed material in the polarized light. Also some unusual characteristics of gelation were run for starch after modification by heating in a majority of tested solvents. This result was ascribed to the residual amount of the solvents used trapped in the starch matrix. This amount of the solvent could not be evacuated. We have also shown in another our paper [5] that drying of native starch their in the oven or

T a b l e 2. The characteristics of gelation of 3.2% aqueous starch suspensions*

Solvent used	T_g^a [°C]	η_{max}^b [mPs]	T_η^c [°C]	η_{96}^d [mPs]	$\eta_{96}^{l\,e}$ [mPs]	η_{50}^f [mPs]
None	66.5	335-425	78-80	25-35	25-35	1195
	65.0	190	80-82	25	25	480
Ethanol abs.	66.0	265-300	79-80	25	25	1090
	65.0	185	80-85	25	25-60	500
Ethanol 96%	67.5	160-215	88-90	25	150-25	850
	66.0	180	77-81	<25	25	360
Ethanol 90%	79.5	?	?	145-180	105-145	610
	64.5	130	81-84	25-240	25-240	440
1-propanol	66.5	330-390	89-92	25	25	910
	66.0	370	84	0	0	0
1-pentanol	67.5	180-220	91	70-80	70-80	740
	65.0	200	79-82	12-25	12-25	470
Nitrobenzene	75.0	?	?	145	275	480
	64.0	190	78-80	<25	25	490
Benzene	68.0	90-150	90-92	25	25	760
	67.0	130	81-83	<25	25	730
Acetonitrile	66.5	265-420	83-88	25	25	1090
	65.5	240	77-85	25	25	490
2-butanone	68.0	140-215	84-88	10-25	10-25	325
	66.0	150	78	<25	10-25	360
DMF^g	81.5	?	?	55-75	130-200	400
	64.5	215	77-83	<25	25-50	455
1,4-dioxane	79.0	?	?	85-105	160-190	310
	65.5	175	78-79	<25	12-25	480
Pyridine	83.0	?	?	50-85	115-120	145
	65.0	190	78-80	25	12	490

* The upper values are for air-dried starch and the lower values for oven-dried starch. The question mark in some columns means that the given property was not observed.
^{a} The temperature of gelation. ^{b} The maximum of viscosity. ^{c} The temperature of the maximum of viscosity. ^{d} The viscosity at 96°C. ^{e} The viscosity at 96°C after 20 min. ^{f} The viscosity after cooling to 50°C. ^{g} Dimethylformamide.

azeotropically with benzene produces some changes of the starch matrix. Therefore we focused our attention on the possibility of subsequent modification of thermally premodified starch matrix as well as on the possibliltiy of removal of residual solvent from the solvent modified starach.

The insight in the dry mass content after solvent treatment of air- and oven dried-starch points that in majority of tested cases the oven-dried matrix trapps slightly less solvent molecules than native starch does. However, 1-propanol, 1-pentanol, 2-butanone as well as benzene and nitrobenzene seem to be trapped more effectively by the thermally damaged starch matrix. It is known that long

chain molecules more willingly form inclusion complexes with amylose by entering inside of its helix. Thus the thermally damaged amylopectin shell of the starch grain may open the access for these molecules to the helix. The status of benzene and nitrobeznene in the starch matrix is not well perceived. Possibly, it is the result of the rate of the substitution of these molecules with water molecules. This proccess will be documented in a subsequent part of this discussion.

The water binding capacity of starch after modification with solvent significantly increases in comparison with original starch. It confirms the deterioration of the matrix by the solvent effect. This capacity is different for different solvents and it is in no relation to the solvent parameters specified in our recent paper [3]. The comparison of discussed index for air- and oven-dried starch shows in a majority of cases that the damage of the grain increases the water binding capacity of starch. The opposite tendency is observed in starch modified with anhydrous 1-propanol, 1-pentanol and benzene. This fact confirms to a certain extent the formation of inclusion complexes of these molecules with the amylose helix. The aqueous solubility of solvent modified starch varies within the group of preparations made by processing in solvents air- and oven-dried starch. The effect of a given solvent on both kinds of investigated starch is different. Generally, preparations obtained from native starch by processing in various solvents spread into three groups. The first group is constituted by original starch as well as this processed in absolute ethanol, 1-pentanol and 2-butanon. The solubility of all these preparations reaches approximately 9–10%. The second group includes starch preparations from the modification with aqueous ethanol, 1-propanol, benzene, dimethylformamide, 1.4-dioxane and pyridine. The solubility of these preparations is lower than that of original starch and reaches from about 6 to 7.5%. The third group contains starch preparation after modification in nitrobenzene. The lowest solubility of preparations from oven-dried starch is noted when benzene and pyridine are used for modification.

The effect of particular solvents on the parameters of the characteristics of gelation is also irregular. The temperature of gelation of native starch before and after processing in solvents does not change in a majority of cases. The solvent processing of oven-dried starch does not change this prameter at all. It suggests that the solvent trapping by oven-dried starch occurs within the amylose helix. Contrary to it the increase of the temperature of gelation in the case of air-dried starch processed in aq. ethanol, nitrobenzene, dimethyloformamide, 1.4-dioxane and pyridine may result from the adsorption of the molecules of these solvents on the surface and capillaries of the grains. The variation of other parameters of the gelation characteristics is clear but their reason is not well understood. Anyway the affinity of particular preparations toward retrogradation is different from one processing to anther. However, the drying of starch in the oven has more pronounced effect on it than the solvent processing.

The solvent processing preparations were left for several days for wittering to equilibrate the humidity content with the atmosphere. Even after such long

equilibration some preparations save the subtle odour of the solvents used. It was particularly true for starch processed in pyridine, nitrobenzene and dimethyloformamide. The thermal examination (TG, DTA, DTG) of all preparations brought the following results: all preparations with the odour of solvents contain minute, possibly surface adsorbed amount of solvent molecules. Their thermograms usually do not exhibit any any effect of the mass loss and accompanying thermal effects than that belonging to the evolution of humidity. In few cases there is a small thermal effect showing the leavings of small amount of the component of the sample before the humidity departures. The amount of leaving mass is so negligible that it is registered neither on the TG nor DTA curves. (see Fig. 1).
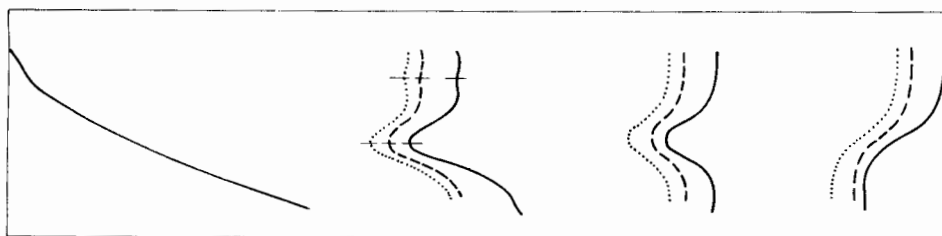

Fig. 1. Thermograms of starch processed by heating in benzene (Sold line); 1 — propanol (dotted line), and 1 — butanol (pointed line). Solvent processed samples of starch were conditioned in the prior to the analysis
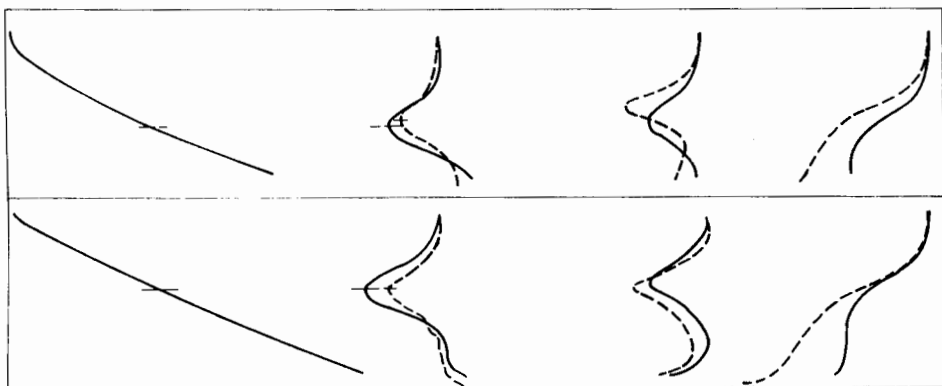

Fig. 2. Thermograms of starach processed in pyridine (left) and in dimethylformamide (right). Oven-dried samples — solid lines and air-dried somples — dried lines. The samples were conditioned in the air prior to the analysis

Fig. 1 presents a typical pattern of the TG, DTA and DTG curves for almost all samples studied independently of their thermal pretreatment prior to the processing in solvents. It may be seen that the solvent processed starch looses practically all solvent molecules trapped in some manners. They are replaced by

water molecules. Their number in the case of air-dried starch is approximately the same as in the original starch before processing. The oven-dried starch traps to the matrix 1–5% humidity less than the matrix of native air dried starch does. The other parameters of thermograms are practically identical within the range of accuracy of the method. In two cases the pattern of thermograms is different. Some essential changes of the starch matrix are noted in the samples of air-dried starch processed in pyridine and in dimethylformamide (see Fig. 2).

Since such changes are absent from the samples of oven-dried starch processed in the same solvents one may assume that some basic hydrolysis has taken place in both mentioned solvents well known as basis compounds.

In conclusion inclusion complexes and adducts of starch with investigated solvents are pretty unstable and undergo transcomplexation by water molecules from the environment as the relevant water — starch complex in more stable. Such transcomplexation from starch — water into starch — solvent compounds seems to be fully reversible from the quantitative point of view.

LITERATURE

1. Reichhardt C.: Solvent Effects in Organic Chemistry. Verlag Chemie, Weinheim 1979.
2. Richter M., Augustat S., Schierbaum F.: Ausgewaehlte Methoden der Staerkcchemie, VEB Fachbuch Verlag, Leipzig 1968.
3. Kudła E., Tomasik P.; Effect of High Pressure on Starch Matrix. Part. 1.: Starch/Staerke, 1990 in the press.
4. Bączkowicz M., Tomasik P.: Solvent effect on Starch Matrix. Part. 1.: Starch'Staerke, 1989: **41,** 449.
5. Bączkowicz M., Tomasik P.: On Water in Potato Starch, Starch/Staerke, 1986, **38,** 339.

Author address: 30-059 Cracow, Mickiewicz Ave., 24/28, Poland.

M. Bączkowicz, P. Tomasik

EFEKT ROZPUSZCZALNIKOWY NA MATRYCĘ SKROBIOWĄ

Katedra Chemii i Fizyki, Akademia Rolnicza im. Hugona Kołłątaja, Kraków

Streszczenie

    Pokazano, że ogrzewanie skrobi w różnych rozpuszczalnikach do pewnego stopnia modyfikuje matrycę skrobiową. Tego rodzaju modyfikacja jest na ogół wyraźniejsza w przypadku skrobi powietrznie suchej. Suszenie skrobi w suszarce (130°C, 2h) samo przez się ma wpływ na matrycę skrobiową. Skrobia suszona w piecu łatwiej tworzy kompleksy inkluzyjne z amylozą, szczególnie, gdy rozpuszczalnik zawiera dłuższy łańcuch. Zastępowanie wody w matrycy skrobiowej cząsteczkami rozpuszczalnika ma charakter odwracalny. Ogrzewanie wilgotnej skrobi z pirydyną lub dimetyloformamidem powoduje katalizowane tymi zasadami przekształcenie matrycy.