ROLF STUTE

DSC INVESTIGATIONS ON STARCHES. III HEAT-MOISTURE TREATMENT AND TREATMENTS IN WATER CONTAINING ORGANIC SOLVENTS

CPC Europe Consumer Foods Ltd. Research and Development Center, Germany

The DSC technique applied upon the structure and property changes which occur during the controlled application of heat and moisture (either in aqueous suspensions,, in semidry systems or in water miscible solvents) always delivers valuable information as to what happens to the granule, and on the state of the reaction etc. Therefore, it can be used not only for controlling such treatments, e.g. excluding an inhomogenous treatment, but also for the optimization with respect to certain properties (e.g. granular cold swelling starches).

INTRODUCTION

The differential-scanning-calorimetry is, in the meanwhile, being widely used within the investigation of starches, in most cases, in the presence of excess water, but also systems of low water content have been investigated [1–13]. The latter is of interest, e.g. under the background of using starch as a natural polymer resp. in combination with synthetic polymers for packaging materials etc. [20].

In the following, only systems with excess water will be stressed. In such a system, it is important that optimal conditions are used with respect to the starch/water ratio, the heating rate etc. These conditions have previously been described [7]. From these investigations a water concentration of 85% and a heating rate of 2°C/min. is recommended for a sample size of 150 μl. If these conditions are used with respect to the gelatinization temperature (beginning, maximum, end), identical results compared to the microscopic determination can be obtained. Furthermore, these conditions have been used for the investigation of starch-lipid-complexes and their desintegration resp. transformation of amorphous into crystalline complexes [8]. Also, other researcher groups [14–17] investigated lipid complexes with the DSC.

The DSC-method can furthermore be applied for the determination of the starch content in plant tissue [18], the degree of mechanical damage [8], the increase of crystallinity during the preparation of Nageli-dextrins [4, 8], (in all cases via the enthalpy changes) and also for the detection of starch mixtures,

which is helpful in those cases where the microscopic appearance of the granules is identical and also staining techniques (like the blue vs. violett iodine staining which allows the differentiation between normal corn/waxy corn starch mixtures) do not allow a differentiation between different granules. Such examples are show in Fig. 1 and 2 for a bean starch and a rice flour which for unknown reasons are mixtures.
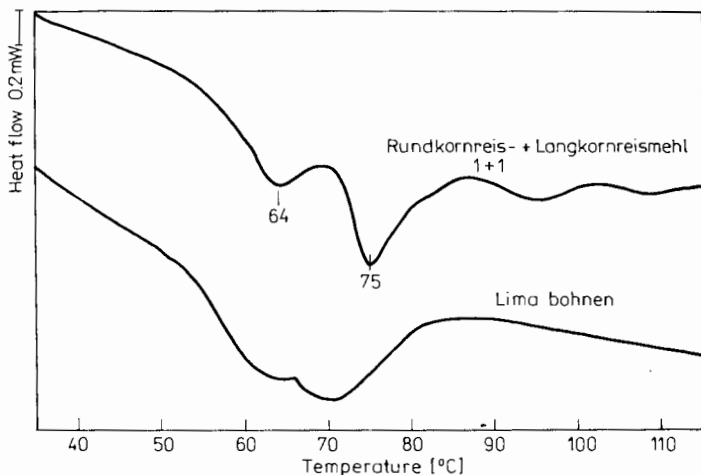

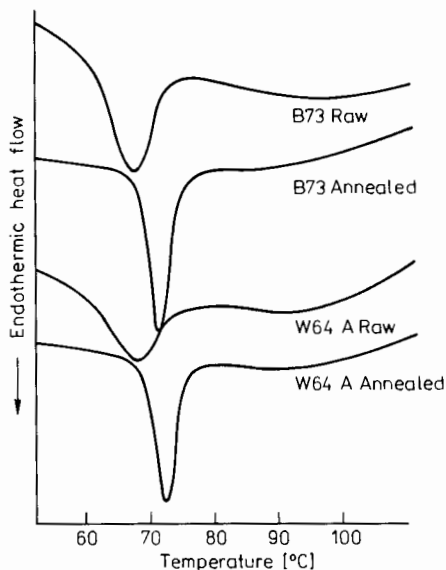Fig. 1. DSC-Curves of rice flour and lima bean starch which for unknown reasons are abviously mixtures

Fig. 2. Raw and annealed corn starch [22]

INVESTIGATION OF THE HEAT-MOISTURE-TREATMENT EFFECTS VIA DSC

Since structure and property modifications, which are obtained via the controlled application of the three parameters:
— temperature (heat)
— moisture
— time,
can also include a complete desintegration of the starch granules (e.g. during gelatinization or dextrinization), the term 'heat-moisture-treatment' has, first of all, to be defined as a modification of the internal structure.

Such a structure modification goes, of course, in line with property changes, but the granule appearance (size, shape etc.) remains absolutely unchanged.

The classical heat-moisture-treatment (sometimes also called 'hydrothermal modification') is the heating of starches [19] under semi-dry conditions (moisture below 40%) with temperatures between 60°C and 130°C.

But also treatments in aqueous suspensions just below the gelatinization temperature have been named 'heatmoisture treatment' [19]. Due to this fact, there is a clear overlapping with what is called 'annealing', which describes the changes of the starch in the plant tissue after harvesting, during the starch isolation, or upon a heat treatment in aqueous suspension, which is seen in correlation with the glass transition resp. rearrangement of growth of the crystallites in the granule [24]. Also here the effect again depends upon the three parameters heat, moisture and time and therefore can be seen as a heat-moisture-treatment [21–24].

Last, but not lease, also ageing may be defined as a special type of heat-moisture-treatment [25, 26] because the ageing effect also depends upon these three parameters, but in this special case, the dominating factor is 'time', while 'moisture' and 'temperature' also have a high influence but, of course, are kept constant in this case. The three parameters temperature, moisture and time are obviously not enough to differentiate between 'annealing' and what is normally called 'heat-moisture-treatment'. As shown in Table there are overlapping areas. Nevertheless, there are typical differences between 'annealing' and 'heat-moisture-treatment' and the DSC technique can be helpful to detect these differences.

First of all, annealing can be observed for all starches (cereal, tuber, root etc.) when they are heated below the gelatinization temperature (in the plant tissue, direct after isolation etc.). Annealing effects are most pronoucend for fresh isolated native starches (Fig. 2), but can be observed also in industrial starches. (For corn starch in Fig. 3 the effect is, of course, much smaller since the steeping process is conducted in the factory at elevated temperatures up to 48 h which means under annealing conditions). Annealing can also be observed for waxy and high-amylose starches (amylo corn see Fig. 4) and is therefore independent upon the amylose content, where obviously no correlation to the X-ray structure exists.

Table

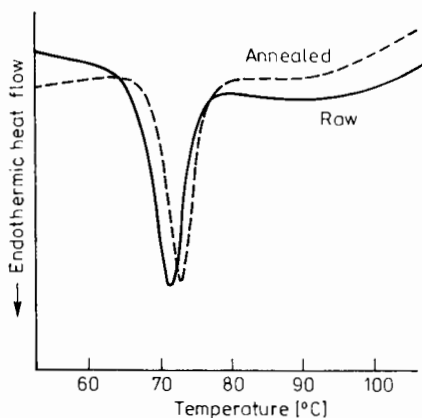|		ANNEALING	HEAT/MOISTURE-TREATMENT
treatment conditions	T (°C)	> 42° g.t	60-130°C
	t (h)	0.5-48	0.1-18
	H$_2$O (%)	> 25%	10-40
	Starches	cereal ≫ tuber, root	root, tuber ≫ cereal
effects	Gelatinization temperature	increase	increase
	Gelatinization enthalpy	inrease	decrease
	Peak Shape	narrower	broader

Fig. 3. Commercial (raw and annealed) corn starch [22]

In contrast, the heat-moisture-treatment is always closely correlated with the X-ray structure of starches, and the most characteristic criteria for a successful heat-moisture-treatment is the shift in the X-ray spectrum from a B-type spectrum in the direction A-type. With respect to the structural changes this seems to be very important because there is always a clear order with respect to the response of the starches upon such a treatment and this goes parallel with the X-ray structure $(B > A > A)$. The most effective heat-moisture-treatment can therefore be made with B-type starches (potato etc.), while starches with a C-type X-ray spectrum are much less sensitive. If in A-type starches changes can be observed, which are caused by a heat-moisture-treatment (e.g. under much harder conditions than for potato starch), then these changes have to be explained in a different way, e.g. via the migration of lipids.

Both annealing and heat-moisture-treatment cause an increase in the gelatinization temperature, but, while within the annealing a sharpening of the DSC peaks and an increase in the gelatinization enthalpy can be observed, the heat- moisture treatment usually goes parallel with a decrease in the gelatiniza-tion enthalpy and a broadening of the peaks (Fig. 5).
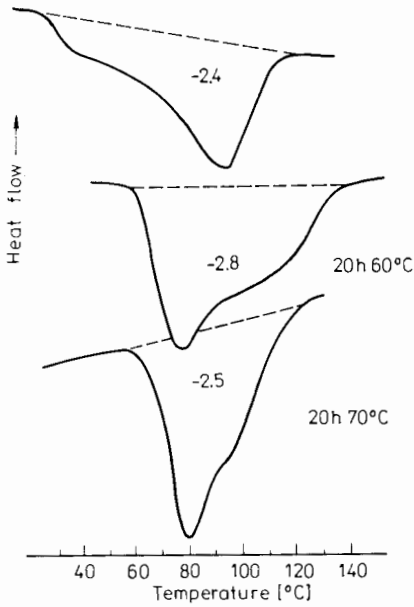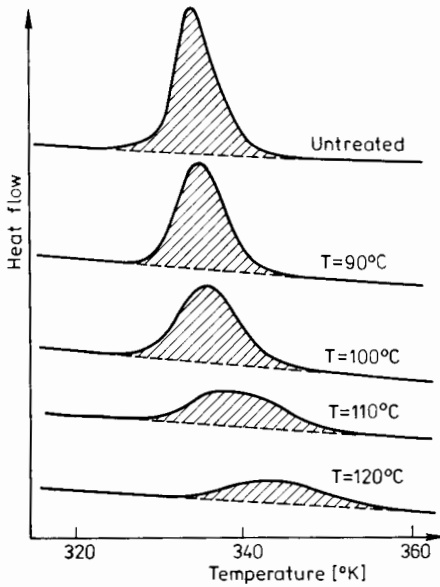
Fig. 4

Fig. 5

Therefore, the DSC technique can be used to differentiate between annealing and a heat-moisture-treatment (ageing, which needs investigations over decades, had not bęen sufficiently investigated to draw any conclusions). Nevertheless, there are many open questions with respect to a clear differentiation between annealing and what is normally called heat-moisture-treatment.

For the annealing the increase in crystallinity is seen in correlation with the glass transition, whille for the heat-moisture-treatment, the crystallinity changes seem to be closely correlated with the allocation of the water molecules. Since detailed X-ray studies have only been made with heat-moisture-treated starches, more detailed and systematic X-ray investigations seem necessary, especially for overlapping conditions.

TREATMENTS OF STARCH IN WATER-CONTAINING ORGANIC SOLVENTS

The heating of starches in water-miscible organic solvents is a special technique to modify the starch properties. It is not only the solvent-water-ratio which guarantees an exact control and absolute homogeneous distribution of the water, but also the temperature can be controlled much better than within semi-dry processes; therefore the heat transfer is identical for all granules (in semi-dry processes this is very often a problem). For food starches the preferred organic solvent is ethanol.

If the conditions are chosen properly with this technique a complete gelatinization can be obtained without any changes in shape or size of the starch granules (Fig 6a, b). In Fig. 6b, the granules are absolutely intact and only some holes can be seen which are formed when some granules stick together. Such starches are called granular cold-swelling starches and have been developed for instant puddings [27. 28].
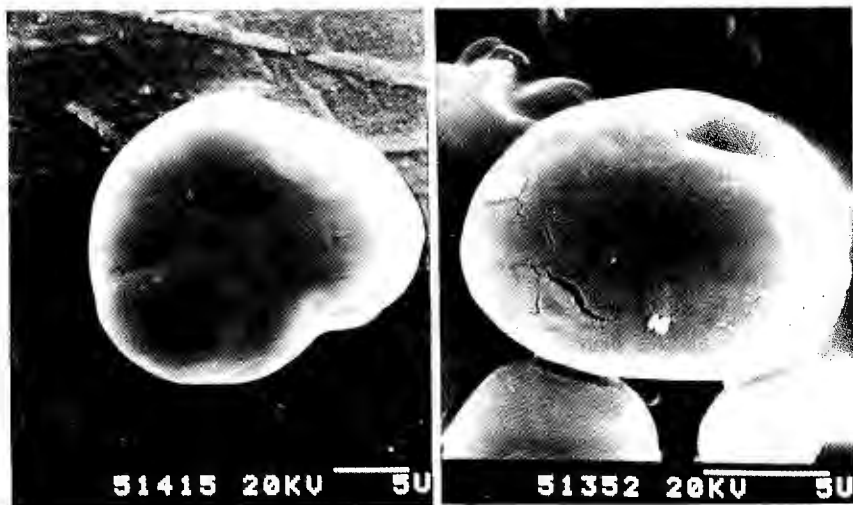

Fig. 6. Corn starch before (a) and after (b) a solvent treatment

Via DSC measurement, the conditions can be defined as to which starches can be obtained with the above properties. Fig. 7 shows the behavior of corn starch in water-ethanol-mixtures indicating that what happens to the starch granules is quite different at varying ethanol concentrations.
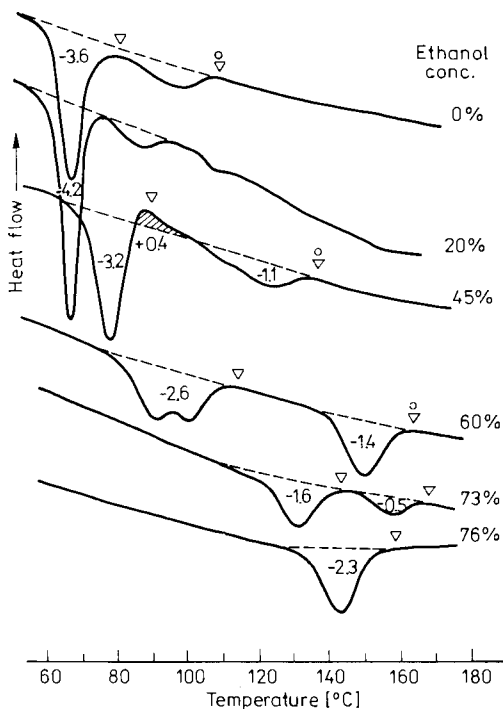

Fig. 7

At low concentrations (20%) there are little changes in the DSC curves. The gelatinization temperature remains constant, only the gelatinization enthalpy increases by about 15% which may be explained by the restricted availability of the water in the presence of ethanol. At higher alcohol concentrations a completely different DSC pattern can be observed. At 45% ethanol there is an exothermic part, at 60% there is something which, at least, looks like a double peak and, a second peak at higher tempertures occurs. Finally, there is only one peak. Via microscopic investigations, it can be shown that up to 60% ethanol the first peaks always represents the gelatinization of the granules (loss of birefringence). The point is indicated in the curves by ▽. The second peak represents the total desintegration of the granules (indicated by V̇). At high alcohol concentration only the birefringence is lost, but the size, shape etc. of the granule remains unchanged as shown in Fig. 6b. What is furthermore typical for such water-solvent systems is that the gelatinization (loss of birefringence) starts from the center of the granules, which is quite opposite to what happens in water.

Corn resp. cereal starches show the most complicated DSC pattern in water-solvent systems. Waxy starches (corn, rice, barley) show only one peak at all concentrations (waxy corn, Fig. 8). There is only the enthalpy increase at low alcohol concentrations and then a continuous shift to higher temperatures.

Tuber, root and legume starches show two peaks at the typical range of 50-60% ethanol (Fig. 9), at higher concentration also only one peak.
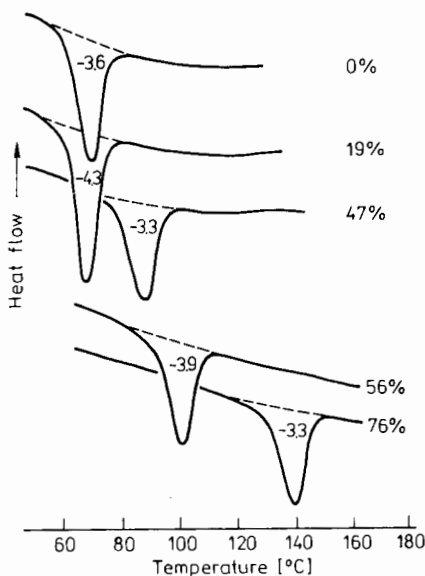

Fig. 8

Comparing the DSC-pattern of the different starches, it can be concluded that there seems to be a correlation between the number of peaks, the amylose and the lipid content.

1. No amylose and only amylopectin-containing starches (waxy starches) show one peak.

2. Amylose-containing starches (tuber, root, legume starches) show two peaks.

3. Amylose and lipid complexes contaning starches show the most complicated DSC pattern including an exothermic part. From these findings, it can be concluded that the amylose as well as the lipids are of importance with respect to the DSC curves, the lipids especially for the exothermic reaction which can be confirmed via the DSC-curves of oat starch. Oat starch has the highest lipid content of all cereal starches and, it can be shown that after the removal of the main part of the lipids by extraction, the exothermic peak disappears and only a shoulder remains. [Fig. 10].

The exothermic reaction therefore has to be brought into correlation with the lipid complex. What remains is the question upon the role of the amylose. Up to
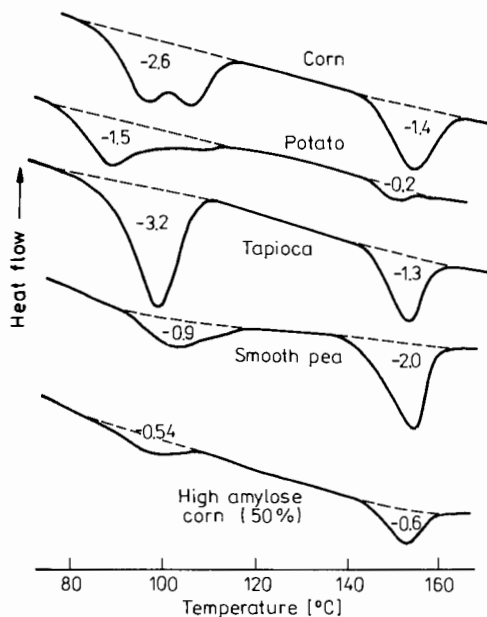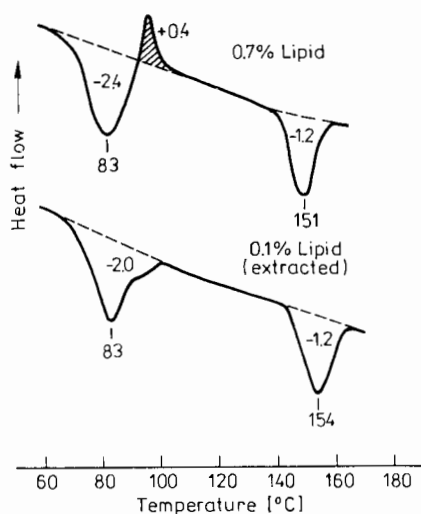
Fig. 9

Fig. 10

now, no final answer can be given, but the following explanation seems to be realistic in spite of the fact that it has to be proved by further experiments.

1. An alcohol-amylose complex is formed in all amylose-containing starches during or directly after the gelatinization and, this complex is destroyed in line with the complete desintegration of the granules (2nd peak).

2. In the presence of a lipid complex as in cereal starches, the overall reaction: formation of the alcohol complex, destruction (or restructuration) of the lipid complex is a strong exothermic reaction which either can be detected as an exothermic peak or (because of the overlapping of an endothermic and an exothermic reaction) can also simulate a double peak (as found in corn starch Fig. 8).

Up to now, this is the best hypothesis to explain the different behavior of the different starches in alcoholwater systems. This explanation would, at least, fit into the present understanding as to what happens during gelatinization — which is seen as a multiple thermal process and represents an exothermic melting of crystallites — granule swelling and denaturation, an exothermic hydration of the starch molecules and, the formations of an amylose-lipid complex [15].

Other alcohols like methanol, propanol (butanol is not sufficiently miscible with water) show an almost identical behavior to ethanol.

A completely differnet DSC-pattern is obtained in glycerol (Fig. 11). This goes in line with the complete desintegration of the granules in glycerol, which has been detected already by Zulkowski [29], who used this technique for the production of water-soluble starches.
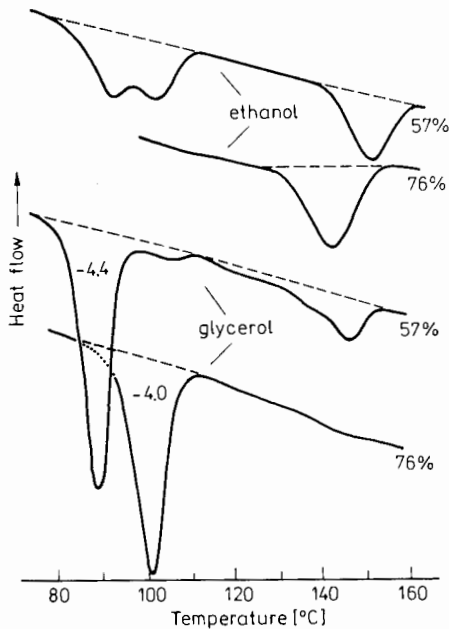

Fig. 11

Acknowledgement

LITERATURE

1. Stevens D.J., Elton G.A.: Thermal properties of the Starch Water System I Measurement of the Heat of Gelatinization by DSC. Stärke 1971, **23**, 8.
2. Donovan J.W.: Phase Transition of the Starch-Water System. Biopolymers 1979, **18**, 363.
3. Donovan J.W., Lorenz K., Kulp K.: DSC of Heat/Moistrue-Treated Wheat and Potato Starches. Cereal Chem., 1983, **60** (5), 381.
4. Donovan J.W., Mapes C.J.: Multiple Phase Transitions of Starches and Nägeli Amylodextrins. Stärke 1980, **32**, 190.
5. Eliasson A.C., Karlsson R.: Gelatinization Properties of Different Size Classes of Wheat Starch. Granules Measured with Differential Scanning Calorimetry. Stärke 1983, **35**, 130.
6. Eliasson A.C.: Wirkung des Wassegehaltes auf die Verkleisterung von Weizenstärke. Stärke, 1980, **32**, 270.
7. Eberstein K., Höpcke R., Konieczny-Janda G., Stute R.: DSC-Untersuchungen an Stärken. Teil I: Möglichkeiten thermoanalytischer Methoden zur Stärkecharakterisierung. Stärke 1980, **32**, 397.
8. Ghaisi K., Hoseney R.R., Varriano E.: Gelatinization of Wheat Starch. III: Comparison od DSC and Light Microscopy. Cereal Chem., 1982, **59**, 258.
9. Wooton M., Bamunuarchi A.: Application of DSC to Starch Gelatinization. I: Commercial Native and Modified Starches. Stärke 1979, **31**, 201; II: Effect of Heating Rate and Moisture Level. Stärke 1979, **31**, 262; III: Effect of Sucrose and Sodium Chloride. Stärke 1980, **32**, 126.
10. Biliaderis C.G., Maurice T.J., Vose J.R.: Starch Gelatinization Phenomena Studied by DSC. J. Food Sci., 1980, **45**, 1669.
11. Hollinger G., Kuniak L., Marchessault R.H.: Thermodynamic Aspects of the Gelatinization and Swelling of Cross-linked Starch. Biopolymers 1974, **13**, 879.
12. Wada K., Takahashi K., Shirai K., Kawamura A.: DTA Appied to Gelatinization of Starches in Foods. J. Food Sci., 1979, **44**, 1366.
13. Lund D.: Influences of time, temperature, moisture, ingedrients and processing conditions of Starch Gelatinization. Crit. Review 1984, **20** (4), 249.
14. Stute R., Konieczny-Janda G.: DSC-Untersuchungen an Stärken. Teil II: Untersuchungen an Stärke-Lipid-Komplexen. Stärke 1983, **35**, 340.
15. Kugimiya M., Donovan J.W., Wong R.Y.: Phase Transitions of Amylose Lipid Complexes in Starches A Calorimetric Study. Stärke 1980, **32**, 265.
16. Kugimiya M., Donovan J.W.: Colorimetric Determination of the Amylose Content of Starches Based on Formation and Melting of the Amylose-Lysolectithin Complex, vol. 46. Journal of Food Science 1981.
17. Eliasson A.C.: Part II: Effect of Gluten and Sodium Stearoyl Lactylate on Starch Gelatinization. J. Cereal Sci., 1983, 1, 207.
18. Stute R.: Unpublished results.
19. Stute R.: See references of the lecture "New Bibding Systems via the Heat/Moisture Treatment of Starches" within these proceedings.
20. Tomka J.: Stärke als Werkstoff lecture given 42st Starch convention, Detmold, April 25-27, 1990.

21. Münzing K., Bolling H.: Mikro-kalorimetrische Darstellung von Phasenumwanlungen uns Strukturveränderungen bei Getriedestärken Voröff. Nr 5802 der Bundesforschungsanstalt für Getreideforschung, Detmold 1989.
22. Krueger B.R., Knutson C.A., Inglett G.E., Walker C.E.: A Differential Scanning Calorimetry Study on the Effect of Annealing on Gelatinization Behaviour of Starch. Journal of Food Science 1987, **52** (3), 715.
23. Krueger B.R., Walker C.E., Knutson C.A., Inglett G.E.: Differential Scanning Calorimetry of Raw and Annealed Starch Isolated from Normal and Mutant Maize Genotypes. Cereal Chem., 1987, **64** (3), 187.
24. Yost D.A.,Hoseney R.C.: Annealing and Glass Transition of Starch. Starch/Stärke 1986, **38** (9), 289.
25. Pałasiński M., Bukowska W., Kujawski M., Norek H.: Roczniki Technologii i Chemii Żywności 1965, **11**, 91.
26. Schierbaum F.: Zur Veränderlichkeit der physikalischen und chemischen Eigenschaften der Stärke. Stärke 1966, **18**, 110.
27. Eastman J.E., Moore C.O.: Cold Water-Soluble Granular Starch EP 110 549; US Pat. 438088.
28. Germino F., Golik R.S.: Novel Instant Pudding Starch and Process for Preparing Same.
29. Zulkowski K.: Soluble. Starch Ber., 1990, **23**, 3295.

Authors address: 71100 Heilbronn, Germany, CPC Europe, Consumer Foods Ltd. Res & Dev. Center

R. Stute

BADANIE SKROBI TECHNIKĄ KALORYMETRII RÓŻNICOWEJ

Centrum Badawczo-Rozwojowe, CPC Europe, Consumer Foods Ltd. Heilbronn, Niemcy

Streszczenie

Technika różnicowej kalorymetrii scanningowej (DSC) stosowana do badań struktury i zmian właściwości zachodzących podczas kontrolowanego ogrzewania i nawilgocenia skrobi (zarówno w zawiesinach wodnych, czy w warunkach obniżonej wilgotności, jak i w rozpuszczalnikach mieszających się z wodą) zawsze dostarcza wartościowych informacji dotyczących zmian w obrębie ziarna, postępu reakcji itd. Dzięki temu może być ona używana nie tylko do kontroli takich oddziaływań (np. z wykluczeniem oddziaływań w układzie niejednorodnym), ale również do uzyskania najkorzystniejszych parametrów obróbki w celu otrzymania szczególnych właściwości (np. „skrobie spulchniane na zimno" używane do przygotowywania błyskawicznych budyni).