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Gelatinization of industrial starches studied by DSC and TG

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The microstructure and thermal behaviour of industrial starches with different origin were characterized by X-ray diffraction and thermal analyses (DSC, TG). Some of the studied starches revealed crystalline structure (type A and type B), while others were predominantly amorphous, having only about 15 % crystallinity. The moisture content of the pristine starches correlated with their microstructure: starches with a higher amount of amorphous phase showed larger water content. The thermal behaviour of the starches with different amount of additional water was also studied by DSC. In a starch-water paste at higher water content the gelatinization started earlier and gelatinization enthalpy change was greater, than what was observed at lower water content. At certain starch to water ratio two distinguished endothermic peaks denoted the gelatinization and melting processes. The determined enthalpies of gelatinization were in the range of 5-15 J/g and did not correlate with the initial crystallinity of the starches. The activation energies of gelatinization in the range 40-100 kJ/mol, obtained by the Kissinger method, were found not to depend on the initial crystallinity of the starch either. At starch concentrations of 20-35% after the gelatinization endothermic peaks a clear exothermic effect could also be observed, which could be described by the formation of internal hydrogen-bonded associations.

Keywords: gelatinization, heat-moisture treatment, starches

INTRODUCTION

Starch is a natural biopolymer, produced and stored in plants as partially crystalline granules, consisting mainly of two components: predominantly linear amylose and highly branched amylopectin [1]. It is commonly used in food, chemical, textile, papermaking, medicine and many other industries [2]. Depending on the botanical source starch granules may vary in size (from <1 to 100μm), shape (including spherical, lenticular, oval, elongated) with alternating semi-crystalline and amorphous layers (growth rings) [3, 4]. Granules may also have different type of crystallites and crystal fraction [5]. The crystallinity of the granules is often assigned to the double helix formed by the branches of amylopectin [6]. Wide-angle X-ray diffraction can be used to determine if starches have A-, B-, or C-type crystallinity, as well as the contribution of the amorphous and the crystalline regions to the overall X-ray pattern. In general, cereal starches generate A-type X-ray diffraction patterns; tuber and high amylose starches are of the B-type; and legume, root and some fruit and stem starches, are of C-type, which is a combination of A- and B-type polymorphs [7,8]. The hilum, which is the core of the granule and the starting point from which the granule grows, is usually less organized than the rest of the granule and could be situated either near the middle or towards one end of granules [9].

Starch granules are insoluble in cold water. During heat treatment of starch in presence of sufficient amount of water, starch gelatinization occurs, where amylose is leached into the outside solution, while bulk water penetrates into the granules, which leads to swelling, destabilization of the crystalline structure, resulting in granule fragmentation and a loss of birefringence. The kinetics of this process depends on the temperature and on the ratio crystalline to amorphous regions, since the latter tend to absorb water more easily. It is believed that there is a certain amount of bound water in the native starch granule, specific to different starches, which is crucial for their gelatinization behaviour and which depends on the ratio of crystalline vs. amorphous regions.

Since starch is the major source of energy in human nutrition, providing more than 50% of the caloric value, and the properties of starch foods strongly depend on the processing, obtaining a better understanding of gelatinization is essential not only from a scientific, but also from an industrial point of view, as well. Many methods have been suggested for investigating the gelatinization process of starches, including electron microscopy, optical microscopy, X-ray diffraction, differential scanning calorimetry, viscosity measurement and more. Stevens and Elton (1971) first reported the

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application of DSC for measuring the heat of gelatinization of the starch/water system [10]. Two distinct endotherms can be observed during heating of starch in a low- water content system. Donovan (1979) reported that these endotherms were determined by the degree of hydration of ordered regions within the starch granules and the high-temperature transition disappears in presence of excess water [11]. In most starches these order-disorder transitions may follow two different mechanisms of melting and gelatinization. Melting usually takes place at low water contents (less than 30%) and corresponds to the high temperature endotherm, while gelatinization occurs in the presence of excess water (more than 70% for most starches) and corresponds to the low temperature endotherm on the thermogram [12]. Both processes can be observed if heating is done at an intermediate moisture content [13]. Evans and Heisman (1982) proposed the so-called "Cooperative melting theory" which explained the bi-phasic endotherm as a result of different crystallite stability within the granules [12]. Water absorption by the granules lowers the melting points of crystallites resulting in quick melting. This reduces the constraints of still remaining crystallites to lower their melting points. This process of cooperative melting happens quickly in sufficient amount of water and leads to a single DSC endotherm. When the available water is not sufficient for the cooperative melting to occur a distinct second endotherm or a "shoulder" appears on the thermogram representing melting of remaining crystallites at a higher temperature. Biliaderis et al. suggested that gelatinization process involves partial melting, recrystallization, and final melting of the crystallites, while Fukuoka et al. reported that enthalpic transitions during heat-moisture treatment represent a number of different simultaneously occurring processes [14,15]. Some authors reported that in the presence of more than 70% water in the system only one endothermic peak was visible in the DSC curve, while at 50% water content, two distinct peaks were observed [16].

Although many starch gelatinization theories have been suggested, none of them is able to thoroughly explain the mechanism of structural changes that granules undergo during heating in the presence of water, therefore further research is needed [17]. It is commonly accepted that depending on the starch nature and the conditions of the thermal experiments (amount of water, heating rate, quality of the DSC baseline, accounting of specific heat, C_p, variation) serious differences in the thermal behaviour of the examined starch can be observed. Additionally, due to the different rate of the phase transformations occurring during gelatinization, routine DSC does not always give an adequate explanation of these processes. Therefore, the present work aims at studying the gelatinization process in a series of starches of industrial interest from different sources and different pre-treatments at various experimental conditions (amount of additional water, heating rate), combining carefully performed thermal (DSC,TG) and X-ray diffraction (XRD) analyses.

MATERIALS AND METHODS

Materials

Modified starches with different origin were the objects of the present study. Information about their origin and modification treatment is presented in table 1.

Thermflo was obtained from Ingredion (UK), Merigel 100 and Merigel 340 starches were provided by Tate & Lyle (UK). Eliane 100 and Eliane SC 160 starches were supplied by AVEBE (Netherlands).

Optical and Scanning Electron Microscopy (SEM)

The morphology of the starches was characterized by optical and scanning electron microscopy (SEM-JEOL 5510). For the electron microscopy starch granules were dispersed on a holder, coated with a thin golden layer, and used for observation.

Table 1. List of the starches used in the study, their origin and modification.

Trade name	Origin and modification
Thermflo	Maize starch, with high amylopectin content (> 95%)
Merigel 100	Maize, pre-gelatinized
Merigel 340	Maize, pre-gelatinized, with high amylopectin content (>95%)
Eliane 100	Native waxy potato starch
Eliane SC 160	Waxy potato starch, pre-gelatinized, acetylated

X-Ray Diffractometry (XRD)

The structure and microstructure of the dry starch powder samples were studied by X-ray diffraction (XRD) with Cu-Ka radiation. The time per step was 5 sec, the step was 0.03°, operating voltage of 30kV and current of 15mA.

Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA)

DSC (Perkin Elmer DSC7) and DTA/TG (Perkin Elmer Pyris) were used to study the thermal behavior of the dry starches as well as of the starch-water suspensions (pastes) varying the starch concentration. The DSC experiments with the starch-water pastes were carried out in sealed sample pans at a scanning rate of 10 K/min. All samples were scanned one hour after sealing, in order to equilibrate. For the enthalpies of starch gelatinization the arithmetic average of 3 independent measurements was taken.

Kissinger analysis

DSC curves, used for Kissinger analysis were obtained by preparing three samples for each starch and scanning them with three different heating rates. Samples were prepared by placing the same amount of starch and water in sealed sample pans, so that 10% w/w was obtained. All the samples were given one hour to equilibrate before scanning. The used scanning rates (2.5 K/min, 5K/min, and 10K/min) were selected so as to ensure actual heating rates of the samples.

RESULTS AND DISCUSSION

The morphology and the microstructure of starches with different origin were characterized by electron microscopy (fig.1) and X-ray diffraction (fig.2). Typical morphology of starch granules with an irregular shape is presented in fig.1. The granule size did not differ very much for the different starches, as it ranged from about 10 to 50 μm. The granule surface was rough; pores and holes could also be observed at higher magnification. Formation of granule agglomerations was seen, as well. One of the studied starches (Thermflo) showed A-type crystalline structure with characteristic diffraction peaks at 15°, 17°, 18° and 23°, while Eliane 100 revealed diffraction peaks typical for crystal structure type B (intensive peak at 17° and less intensive ones at 15°, 20°, 22° and 24°). Merigel 100, Merigel 340 and Eliane SC160 could be considered as mainly amorphous, which was expected because these three starches had been pre-gelatinized, fig.2. The degree of starch crystallinity, determined from the X-ray diffraction patterns, according to the method described in [18], ranged from about 15% to 75%, Table 2.

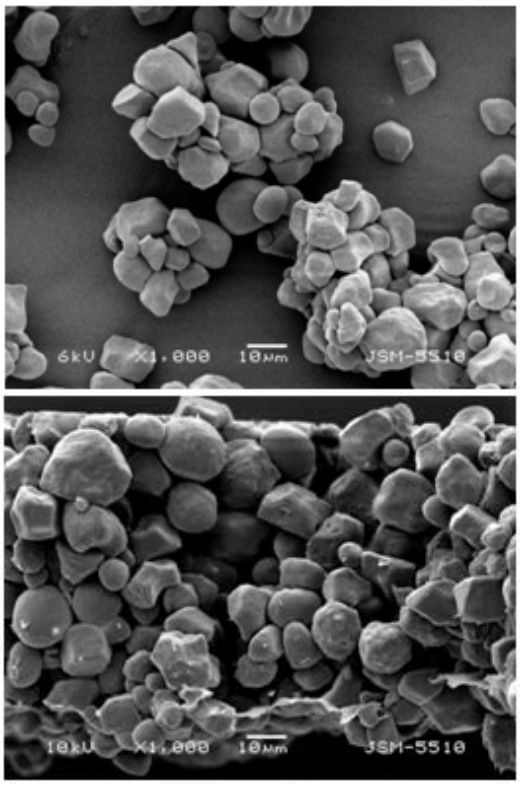

Fig. 1. SEM micrographs of Thermflo starch.

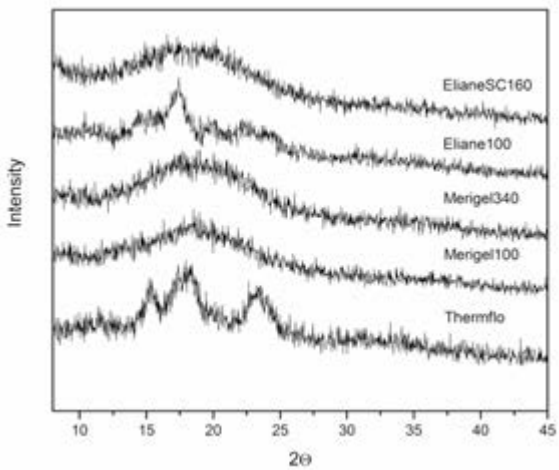

Fig. 2. XRD patterns of the untreated starch powders.

Table 2. Moisture content, relative crystallinity and heat effect, measured for the used starches.

Starch	Moisture content (%)	Relative crystallinity (%)	Heat effect (J/g)
Thermflo	11.4	74	88.5
Merigel 100	8.6	34	62.5
Merigel 340	7.2	23	51.9
Eliane 100	13.8	58	151.7
Eliane SC160	6.8	17	55.2

The native moisture content and the thermal behaviour of the initial starches were studied by TG and DSC, fig.3 and fig. 4, respectively. The thermogravimetric curves of all starches had identical shape, but differed in the height of the first step (weight decrease), fig.3. Water is the only volatile component of the dry starches (containing only native moisture) and during heating it is released in the temperature range of 60-120ºC; at higher temperatures (250-300ºC) starches undergo thermal degradation and lose between 60% and 80% of their weight for only few degrees.

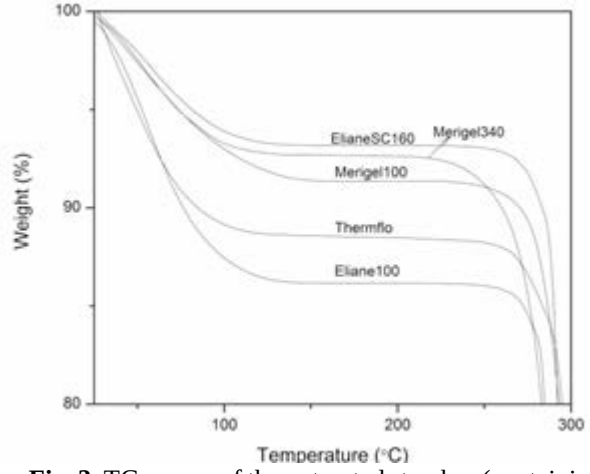

Fig. 3. TG curves of the untreated starches (containing only the native moisture).

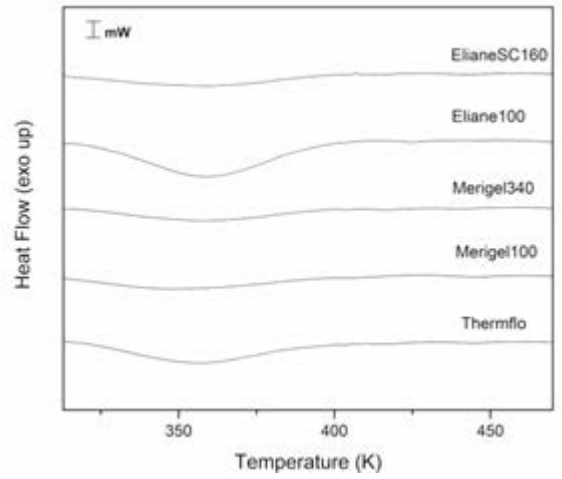

Fig. 4. DSC curves of the untreated starches (containing only the native moisture).

The observed differences in the moisture content and in the thermal stability of the studied starches were also expected due to their different origin, crystal type, relative crystallinity and different starch modification. The starches moisture content varied between 7 and 14 wt.% and for the non-pregelatinized starches showed obvious correlation with the degree of crystallinity. The starches with lower crystallinity had larger amount of included moisture, which confirmed available results for other starches [19,20].

The DSC results corresponded entirely to the TG analysis and correlated with those of the XRD. The single endothermic peaks observed by DSC in the temperature range 30-130ºC (fig.4) had to be obviously related to the release of moisture from the starches, which process was also detected by the themogravimetric analysis. The temperatures and enthalpies (heat effects) of the DSC peaks, connected with the moisture release, are also presented in Table 3.

It is possible the larger heat absorbed (endothermic heat effect) observed for starches with larger crystallinity to be due not only to the water release, but also to the melting of parts of the crystalline starch granule regions. However, typical crystallite melting endotherms were not seen in the DSC curves of the dry samples, which confirmed that the presence, quantity, and type of plastisizer play significant role in the process of gelatinization [21, 22]. It is necessary to be mentioned that good quality DSC curves of dry starch samples (containing only native moisture) are not frequently seen in the literature.

Studying the starches gelatinization when using the same amount of additional water (10 wt.% starch in water suspension; heating rate 10 K/min) revealed identical DSC curves for all samples – a broad endothermic peak was observed. However, the starches thermal scans differed in the peak area, as well as in the temperature range of the gelatinization peak. DSC curves of two of the investigated starches having different structure are presented in fig.5.

Table 3. Enthalpy change and activation energy of the gelatinization process for all studied starches.

Starch	T_{max} [K]	Activation energy [kJ/mol]	Gelatinization enthalpy [J/g]
Thermflo	336	62.4±16.1	5.67
Merigel100	339	105.6±23.3	36.65
Merigel340	336	74.5±4.7	4.52
Eliane100	341	58.2±4.2	12.36
ElianeSC160	341	49.1±10.6	13.05

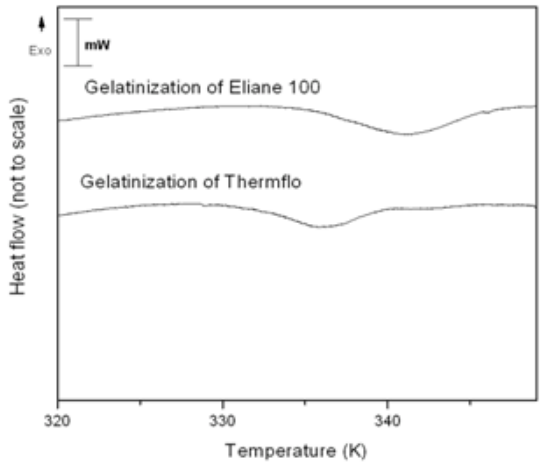

Fig. 5. DSC curves of Thermflo and Eliane 100.

Both, the thermal effects (enthalpy change) and the activation energy of the gelatinization process were determined, Table 3, for all studied starches. For the apparent activation energy of gelatinization, E_a, Kissinger's analysis was applied [23]:

$$ln\frac{q}{T_{max}^2} = -\frac{E_a}{RT_{max}} + const., \quad (1)$$

where q is the heating rate, T_{max} is the temperature of the maximum of the endothermic DSC peak and E_a is the activation energy of the thermally activated process (in this case gelatinization). According to the Kissinger's method, the activation energy can be obtained by plotting $ln(q/T_{max}^2)$ *vs.* $1000/T_{max}$. Fig.6a shows the DSC data in Kissinger coordinates for the two crystalline starches and in fig.6b the data for the pre-gelatinized amorphous starches are presented. The values for the activation energies ranged from about 40 to 105 kJ/mol, and the highest value applied for Merigel100, which is also the starch with the highest gelatinization enthalpy. Both the activation energies and heat effects of gelatinization were close to those available in the literature for similar systems [24-28]. Furthermore, two different methods for obtaining activation energies (thermal and rheological) seem to produce consistent results, indicating, that both are suitable for investigating the gelatinization process [29].

To understand the influence of the gelatinization on the structure of the starch granules XRD analysis was applied to a sample obtained after gelatinization of Thermflo. The X-ray diffractograms of the initial starch and of the corresponding gel are shown in fig.7. Drastic reduction in the intensity of the crystalline peaks could clearly be seen, revealing that the gelatinization took place in a large degree, and resulted in an amorphous granule structure according to the XRD data.

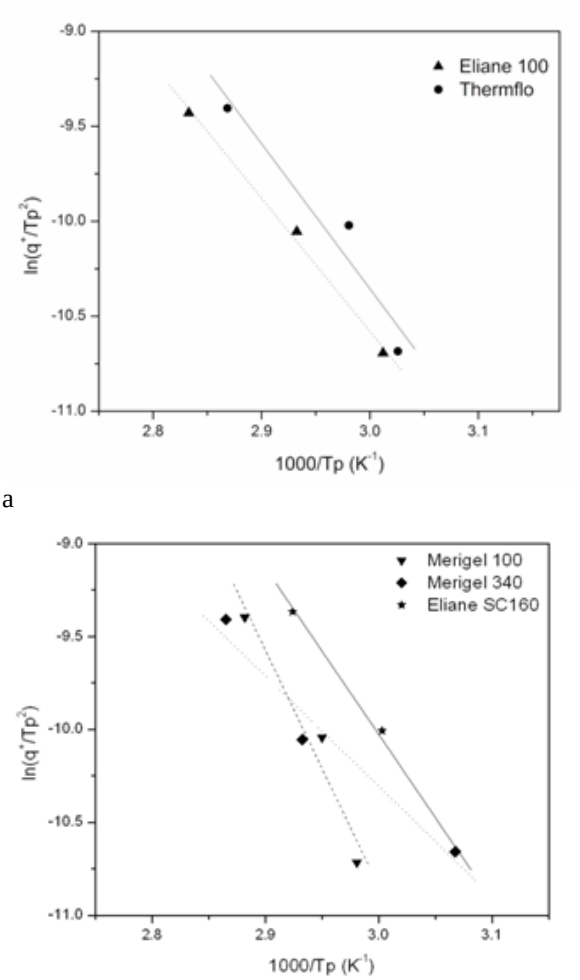

Fig. 6. a) DSC data in Kissinger coordinates for the two crystalline starches given in the legend; b) DSC data in Kissinger coordinates for the three pre-gelatinized amorphous starches.

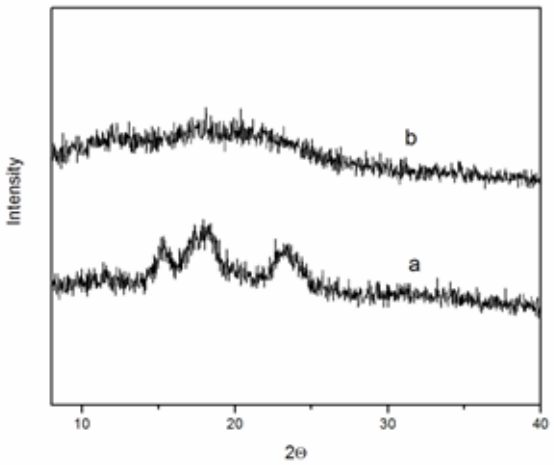

Fig. 7. XRD patterns of the untreated Thermflo, a, and of the corresponding gel, b.

It is known, however, that except gelatinization a process of melting is also possible in starch-water suspensions with insufficient amount of water.

Moreover, although carefully studied, these processes still need further understanding due to the great diversity of the results available in the literature, as well as to the big importance of the gelatinization for the cooking properties of the starches with different origin. To separate both processes (gelatinization and melting) a series of DSC measurements on a starch-water system (paste) at different concentrations were performed. DSC plots of gelatinization of Thermflo with different concentrations are shown in fig.8, as the weight percentage of the starch was varied between 5% and 90%. At large amount of water (5% starch) the gelatinization process started at lower temperatures, and a big complex endothermic peak was observed, which might be due to the fact that the peaks of gelatinization and melting were strongly overlapped. With the increase of the starch concentration the endothermic peaks became more separated and the two processes (gelatinization and melting) became distinguishable. Besides, the peaks were shifted to lower temperatures. At concentrations 20-30% two clearly separated peaks were observed, as the low temperature one corresponded to starch gelatinization and the high-temperature peak – to the melting of the non-gelatinized crystalline parts of the starch granule. Although both processes are extremely sensitive to the amount of additional water, the heat (enthalpy change) determined from the low-temperature DSC peak showed a very good correspondence to the heat effects of gelatinization determined in excess water.

This result is inconsistent with the available report in the literature [16], revealing that in the presence of more than 70% water in the system only one endothermic peak was visible in the DSC curve, while at 50% water content, two distinct peaks were observed.

Exactly in the same range of 20-35% starch concentration after the endothermic DSC peaks a clear exothermic effect (peak) could also be seen, which could be described by possible formation of hydrogen-bond associations between the free ends of the unwound helixes of amylopectin and parts of amylopectin molecules other than their original helix partner [30]. Another possible explanation of the exothermic DSC effect is based on the association of the amylose molecules extracted from the granule into the surrounding water or formation of amylose-lipid complexes [31].

As it could be expected, at insufficient amount of water in the system not all of the starch granules and crystalline parts participated in the gelatinization process and the heat effect gradually decreased with

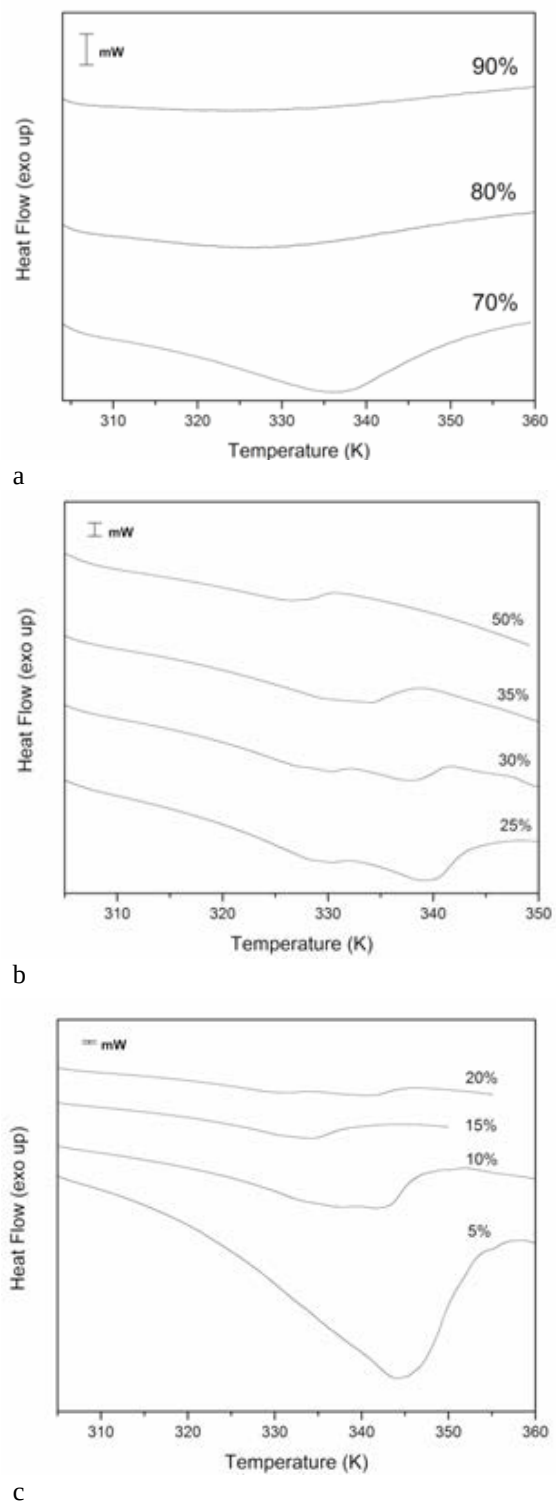

Fig. 8. DSC curves of gelatinization of Thermflo at different concentrations.

the starch concentration increase. At the same time the intensity of the high-temperature peak increased,which corresponded to the melting of larger amount of ordered starch zones. At further increase of the starch concentration the two endothermic peaks gradually transformed to a single peak. At these concentrations the water in the system was not enough for the gelatinization to take place.

This result shows that by precise control of these processes (gelatinization and melting) it is possible to obtain starch gelatinization preserving some of the ordered granules zones, which may result in materials and food products with interesting mechanical and digestive properties.

CONCLUSIONS

The microstructure and thermal behaviour of starches with different origin were investigated. It was found that the starches structure ranges from predominantly crystalline (type A or type B) to almost amorphous (15% crystallinity) and their moisture content correlated with their microstructure. The starches revealed different thermal behaviour when varying the amount of water added to the starch before the DSC experiments, which is consistent with the results of similar experiments available [33]. At larger water content the gelatinization started at lower temperatures and the gelatinization enthalpy change was larger as observed by other authors as well [34]. At starch concentrations in the range 20-30% two distinguished endothermic DSC peaks denoted the gelatinization and the melting processes [35]. A clear exothermic thermal peak was also seen, which could be explained by the formation of internal hydrogen bonds. Both the enthalpies and the activation energy of gelatinization were determined and it was found that they did not depend on the initial crystallinity of the starches.

Our results indicate that by adjusting the ratio of water vs. starch and gelatinisation temperature one can control granule melting and gelatinisation independently, allowing to obtain gelatinized starches where parts of the ordered granule zones are preserved, which in turn can result in materials and food products with interesting mechanical and digestive properties.

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REFERENCES

1. D.J. Gallant, B. Bouchet, P.M. Baldwin, *Carbohyd. Polym.* **32**, 177 (1997).
2. R. Hoover, T. Hughes, H.J. Chung, Q. Liu, *Food Res. Int.* **43,** 399 (2010).
3. J.L. Jane, J. In BeMiller, R. Whistler (Eds.). Structural features of starch granules II. Starch: Chemistry and technology, 3rd ed., Academic Press, Amsterdam, 2009, p. 193.
4. J.L. Jane, T. Kasemsuwan, S. Leas, H. Zobel, J.F. Robyt, *StarchStärke*, **46**, 121 (1994).
5. M.G. Sajilata, R.S. Singhal, P.R. Kulkarni, *Compr. Rev. Food Sci. F.*, **5**, 1 (2006).
6. R. Hoover, *Carbohyd. Polym.* **45,** 253 (2001).
7. R.F. Tester, J. Karkalas, X. Qi, Starch, *J. Cereal Sci.*, **39,** 151 (2004).
8. A. Sarko, H.-CH. Wu, *Starch/Stärke*, **30,** 73 (1978).
9. A. Gott, H. Barton, D. Samuel, R. Torrence, in: Biology of starch. Ancient starch research, R. Torrence, H. Barton (eds.), Left Coast Press, Walnut Creek, CA, 2006, p. 35.
10. D.J. Stevens, G.A.H. Elton, *Starch/Stärke*, **23**, 8 (1971).
11. J.W. Donovan, *Biopolymers,***18**, 263 (1979).
12. I.D. Evans, D.R. Haisman, *Starch/ Stärke*, **34**, 224 (1982).
13. A.-C. Eliasson, *Starch/Stärke*, **32**, 270 (1980).
14. C.G. Biliaderis, C.M. Page, T.J. Maurice, B.O. Juliano, *J. Agr. Food Chem*., **34**, 6 (1986).
15. M. Fukuoka, K. Ohta, H. Watanabe, *J. Food Eng*., **53**, 39 (2002).
16. F. Nakazawa, S. Noguchi, J. Takahashi, *Agr. Biol. Chem. Tokyo*, **48**, 2647 (1984).
17. W.S. Ratnayake, D.S. Jackson, Advances in Food and Nutrition Research, Chapter 5 Starch Gelatinization, Elsevier, 2008.
18. A. Lopez-Rubio, B.M. Flanagan, E.P. Gilbert, M.J. Gidley, *Biopolymers*, **89**, 761 (2008).
19. M. Schirmer, A. Höchstötter, M. Jekle, E. Arendt, T. Becker, *Food Hydrocolloid*., **32**, 52 (2013).
20. H. Liu, L. Yu, F. Xie, L. Chen, *Carbohyd. Polym*., **65**, 357 (2006).
21. H. Jacobs, J.A. Delcour, *J. Agr. Food Chem*., **46**, 2895 (1998).
22. T.A. Waigh, K.L. Kato, A.M. Donald, M.J. Gildey, C.J. Clarke, C. Riekel, *Starch/Starke*, **52**, 450 (2000).
23. H.E. Kissinger, *Anal. Chem.* **29**, 1702 (1957).
24. W.S. Ratnayake, D.S. Jackson, *Carbohyd. Polym.* **67**, 511 (2007).
25. R.B. Campanha, C.M.L. Franco, *J. Therm. Ana.l Calorim*., **106**, 799 (2011).
26. H. Liu, L. Yu, G. Simon, K. Dean, L. Chen, *Carbohyd. Polym*., **77**, 662 (2009).
27. W. Jiranuntakul, C. Puttanlek, V. Rungsardthong, S. Puncha-arnon, D. Uttapap, *J. Food Eng*., **104**, 246 (2011).
28. S.S. Sablani, S. Kasapis, Z.H. Al-Tarqe, I. Al-Marhubi, M. Al-Khuseibi, T. Al-Khabori, *J. Food Eng.*, **82**, 443 (2007).
29. F. Teyssandiera, P. Cassagnaua, J.F. Gérardb, N. Mignardc, *Carbohyd. Polym.* **83**, 400 (2011).
30. T.A. Waigh, M.J. Gidley, B.U. Komanshek, A.M. Donald, *Carbohyd. Res.*, **328**, 165 (2000).
31. P. Le Bail, H. Bizot, M. Ollivon, G. Keller, C. Bourgaux, A. Buléon, *Biopolym.*, **50**, 99 (1999).
32. D. Bajer, H. Kaczmarek, K. Bajer, *Carbohyd Polym.*, **98**, 477 (2013).
33. S. Wang, L. Copeland, *J. Agric. Food Chem.*, **60**, 6439 (2012).
34. L. Zhaofeng, L. Wenjing, G. Zhengbiao, L. Caiming, H. Yan, C. Li, *Food Hydrocolloid.*, **48**, 189 (2015).
35. Z. Fu, L. Wang, H. Zou, D. Li, B. Adhikari, *Carbohyd. Polym*., **101**, 727 (2014)

ГЕЛИРАНЕ НА ИНДУСТРИАЛНИ НИШЕСТЕТА, ИЗСЛЕДВАНО С ДСК И ТГ

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(Резюме)

Микроструктурата и термичните свойства на индустриални нишестета с различен произход бяха изследвани с помощта на рентгенова дифракция и термичен анализ (ДСК, ТГ). Някои от изследваните нишестета демонстрираха кристална структура (тип А и тип Б), а други бяха предимно аморфни, с около 15% степен на кристалност. Влагосъдържанието на чистите нишестета корелираше с тяхната микроструктура: нишестета с по-голямо количество аморфна фаза имаха по-високо влагосъдържание. Термичното поведение на нишестетата с добавено различно количество вода също беше изследвано с помощта на ДСК. В сместа нишесте-вода при по-големи количества вода гелирането започваше по-рано и енталпията на гелиране беше по-висока от наблюдаваната при по-малки количества вода. При определено съотношение нишесте-вода два отделни ендотермични пика показват процесите на гелиране и топене. Определените енталпии на гелиране бяха в рамките 5-15 Дж/г и не корелираха с първоначалната степен на кристалност на нишестетата. Не беше открита зависимост между активиращите енергии на гелиране в рамките на 40-100 КДж/мол, получени по метода на Кисинджер, и степента на кристалност. При концентрации на нишесте между 20% и 35% след ендотермичния пик на гелиране се наблюдава екзотермичен ефект, който би могъл да се обясни с формиране на вътрешни водородни връзки.