Journal of Thermal Analysis and Calorimetry, Vol. 93 (2008) 2, 605–610

THERMAL ANALYSIS OF THE INFLUENCE OF WATER CONTENT ON GLASS TRANSITIONS

Heat capacities of starches from different origins

W. Louaer[1], *A-H. Meniai*[1] *and J.-P. E. Grolier*[2,*]

[1]Laboratoire de L'Ingénierie des Procédés de L'Environnement (LIPE), Département de Chimie Industrielle, Université Mentouri, Constantine, Algérie
[2]Laboratoire de Thermodynamique des Solutions et des Polymères, Université Blaise Pascal, 63177, Aubière, France

Starch is an important natural substance in which the water content has a significant influence on its structure and properties. In the present study, the effect of the water content on glass transition temperatures T_g and heat capacities C_p of wheat, maize and potato starches were investigated by high-sensitivity differential scanning calorimetry (temperature modulated TMDSC and conventional DSC). Thermal analysis measurements were performed on starch samples with different water contents. The exact water mass percentage of each sample was determined using the Karl–Fischer method.

The obtained results show that the water content does influence the starch thermal properties in a systematic and measurable trend, the higher the water% the lower the glass transition temperature, and the higher the heat capacity jump during gelatinisation. At this stage possible interpretations of the results are just put forward and should be confirmed through complementary measurements.

Keywords: *glass transition temperature, heat capacity, maize, potato, starch, TMDSC, water content, wheat*

Introduction

As a natural biopolymer used in multiple industrial processes dealing essentially with food, pharmacy and packaging to cite a few major applications, starch is the object of intensive research activities. The starch intrinsic properties which are typically exploited depending on specific purposes, do have a strong influence on processing methods as well as on the thermomechanical behaviour of the end products, including their aging capabilities and life cycles. The localization of the domains of gelatinization (or melting) and of glass transition by their respective (T_m and T_g) temperatures is certainly the main characteristic to be properly documented. Numerous investigations have been carried in the wide field of thermal properties and thermodynamic equilibria in relation with food characteristics and quality; a large amount of data concerns starch-water systems. Exhaustive literature compilation and publications are due to Roos *et al*. [1, 2]. The specific aspect of water content influence on the glass transition of starch was examined by Zeleznak and Hoseney [3]. Furthermore, heat capacity (C_p) plays also a major role in the sense that this thermodynamic property is the one directly reflecting the molecular structure; in addition, the estimation of the heat capacity jump during state changes is of practical interest for process engineering. Wunderlich *et al*., Pyda *et al*. have produced in recent years authoritative publications on using thermal methods to investigate in depth heat capacities of biomacromolecules emphasizing either the experimental techniques and methods [4–6] or the relation with molecular structures and the influence of the water content [7–9]. The native structure of starch, in particular, the liquid crystal approach, has received much attention from Waigh *et al*. [10–12]. The structural analogy with a chiral side-chain polymeric liquid crystal where the double (amylopectin) helices are disposed side by side strongly supports the possible changes observed during gelatinization which are largely favoured in presence of water. We have recently [13] initiated a re-examination of phase transformations in starch-water systems; from high sensitivity temperature-controlled DSC measurements at very low heating rate, we have [13] generated differential (with respect to completely dried starch) calorimetric curves of wheat starch samples having different water contents. This careful experimental study has permitted to revise the understanding of phase transformations during starch gelatinisation and the influence of water on the observed thermal effects over the temperature range from 283–383 K under atmospheric pressure. The present investigation is focused on the comparison of starch samples from three different origins, i.e. wheat, maize and potato, in

---

[*] Author for correspondence: j-pierre.grolier@univ-bpclermont.fr

1388–6150/$20.00

Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands

order to document the influence of the water content on their thermal properties. Relations between starch structures, i.e., amylose content or lipid-amylose ratio and physical, particularly thermodynamic, properties, have also been investigated. To this end, several physico-chemical techniques have been used to investigate such relations like light microscopy (LM), scanning electron microscopy (SEM), wide angle X-ray diffraction (WAXS), and high sensitivity DSC. Most recent studies by Bocharnikova *et al.* [14] and Kozlov *et al.* [15] do not show significant correlation; in particular no simple correlation appears between structural composition and thermodynamic properties. It seems that the increase of amylose content would induce the decrease of melting temperature, in fact of the gelatinization temperature. Similar course of transition was observed irrespective of starch types (and formulations) [16]. Furthermore, it has been observed that in most cases despite slight difference in composition the glass transition temperature occurs after the onset of gelatinization temperature and that the heat capacity change occurs within the gelatinization main endothermic peak. As a matter of fact, the glass transition domain overlaps with the gelatinization region. For the three types of starch investigated in this work it has been reported slight differences in the overall gelatinization/melting domains which for two of them (maize and potato) almost coincide whereas for wheat this domain appears in a lower temperature range, namely: 319–333 K for wheat [13], 335–350 K for maize [16, 17] and 327–348 K for potato [17], respectively. Nevertheless, the simultaneous occurrence of the glass transition and of the gelatinization/melting makes the determination of thermal properties T_g and C_p difficult to determine unambiguously. In this context, temperature modulation added by Reading [18] to (conventional) differential scanning calorimetry to yield temperature modulated differential scanning calorimetry (TMDSC) [19] has been a major contribution to polymer science [5, 19, 20].

As regards the influence of water on the thermal behaviour of starch, different recent publications document the accepted observations/conclusions. Systematic and very careful experimental measurements by high sensitivity (conventional) DSC [13] have shown that the melting peak or gelatinization domain for wheat starch appears over the temperature range from 319 to 333 K practically independently of water content. At the same time, Santos de Souza *et al.* have reached the same conclusion by means of (conventional) DSC coupled with photovisual system [21]. In the present study the comparison between the three types of starch was made through the determination of their respective glass transition temperature domains and of their gelatinisation/melting heat capacities jumps, depending on their water contents.

Experimental

Chemicals

Three different native starch powders from maize and from wheat (provided by Fluka, Switzerland) and from potato (provided by Roquette, France) having respectively water mass percentages of 10.65, 10.18 and 2.63 were used to prepare the different samples used in calorimetric measurements. The contents of water in the native starches were determined on the basis of mass losses after heating weighted samples in a vacuum oven at 393 K for 110 h, to obtain the dehydrated starches. The water dispersions or pastes were prepared from weighted samples of native starches by adding known amounts of bidistilled and demineralised water in order to obtain different final water contents, taking into account the respective initial water percentages of native starched. The exact weight percentages of the different samples were determined by the Karl–Fischer method.

Instrumentation

Thermal analysis was conducted by differential scanning calorimetry either in TMDSC or in the conventional (no temperature modulation) mode (DSC), using a Mettler Toledo DSC 821 calorimeter. As indicated in the Introduction, due to the glass transition/melting overlapping, the TMDSC mode has been used to separate through the heat flux reversible[**] component the glass transition domain [5, 19, 20]. The variations of heat capacities have been determined in separate runs using the conventional DSC mode which directly yields the heat flux corresponding to heat capacity change. The DSC 821 calorimeter was equipped with a cryostat (LabPlant RP 100 model) allowing measurements down to 200 K. A dry nitrogen flow was used to purge the cells; for this, a gas flow of 10 mL min^{-1} was monitored and adjusted with a gas flow controller. For the investigation of the glass transition temperature domains, samples were encapsulated in 40 μL standard aluminium sealed pans with pierced cover lids. The reference pan, used for each experiment, was empty and identical to the one used on the measuring side. Temperature scans were conducted over the temperature range from 273 to 493 K using op-

---

[**] The terms ‘reversible’ and ‘non-reversible’ currently used are not used in the proper thermodynamic sense. They should be instead ‘reversing’ and ‘non-reversing’, respectively. This nomenclature recommendation should appear in Guidelines for TMDSC in preparation by a IUPAC task group coordinated by one of the authors (JPEG)

timized parameters [20], namely: modulation amplitude A_T=0.398, with a period p=30 s and average heating rate q=5 K min^{-1}. Heat capacities were determined against standard (artificial) sapphire reference discs (ref. ME-51140818 No. 3784111; rhombohedral hexagonal Al_2O_3 single crystal) provided by Mettler Toledo. The classical three-step procedure [22] was followed: that is, on the measuring and reference captors respectively, a) empty pan and empty pan run, b) empty pan and reference containing pan run and c) sample containing pan and reference containing pan run. Samples and reference were placed in 40 μL standard aluminium not sealed pans, with not pierced cover lids. Temperature scans were performed over the temperature range from 273 to 423 K with 5 K min^{-1} heating rates. All samples investigated had masses between 15 and 20 mg. Temperature calibration was made using two reference standards, indium (ME-119442 No. WE2767) and zinc (ref. ME-119441 No. WE1240), provided by Mettler-Toledo.

Results and discussion

Glass transition temperature domain

For the three different native starch samples the differential scanning calorimetric traces obtained by TMDSC were typically similar, as illustrated in Fig 1a in the case of maize starch, characterized by the three curves corresponding respectively to the total heat flux and its non reversible and reversible components. The present observation is in agreement with previous results reported in literature as indicated in the Introduction. As expected from very close melting temperatures the corresponding overall heat fluxes are then of similar shape and amplitude.

The calorimetric traces of the three dehydrated starches exhibit also similar shapes, as illustrated in Fig. 1b in the case of maize starch, for the three different corresponding heat flux curves (total, non reversible and reversible). Interestingly, comparison of the respective groups of the three graphs on Figs 1a and b for dehydrated and native (water containing) starches, shows that the water percentage content has clearly an influence on the endothermal gelatinization/melting peak: the corresponding transition heat flux is practically twice as large for the native samples which contain water compared to the corresponding dehydrated samples. In this respect water, acting like a ‘lubricant’ between the double (amylopectin) helices, facilitates gelatinization lowering consequently at the same time the glass transition temperature. This is corroborated by the observed glass transition domains. However, the glass transition domain essentially overlaps with the endothermic peak of gelatinization, and then the reversible heat flux component which inflection graphically shows the characteristic glass transition domain is retained to compare the three different starches. These characteristic inflexions are visible on the reversible heat flux components on Figs 2a–c for both native and dehydrated starches. As indicated above the reversible heat flux components unambiguously permit to determine the glass transition temperature despite its overlap with the endothermic peak of gelatinization.

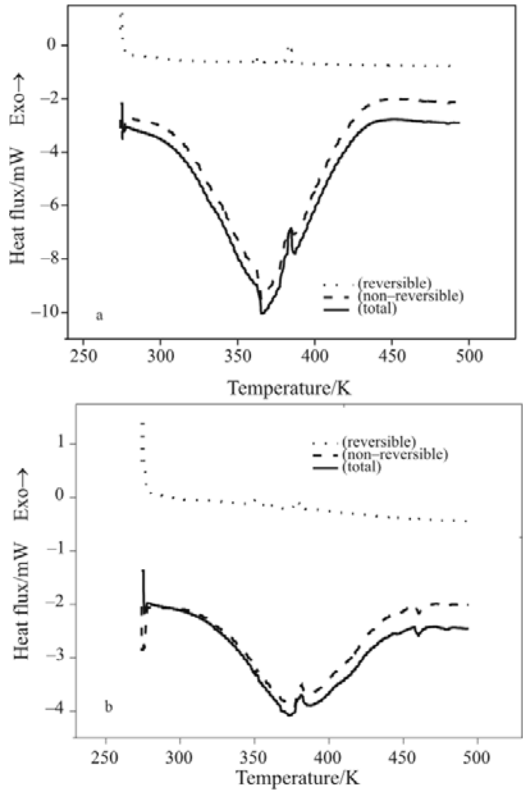

Fig. 1 Heat flux three-component (reversible, non reversible and total) curves obtained by TMDSC for maize starch a – native and b – dehydrated, respectively

From the reversible heat flux curve the glass transition temperature can be determined as either the transition onset or the transition midpoint. Although the former, i.e. the onset, is often considered the most appropriate temperature, midpoint values which are easier to locate represent the central temperature of the glass transition region. For this, two different treatments can be applied to the reversible heat flux curve *vs*. temperature: *i*) a plot of the first derivative of the polynomial fit of this curve shows a peak which corresponds to the inflexion point, i.e. the midpoint, of the glass transition; *ii*) the graphical construction of appropriate tangents to this curve (see example of graphical representation on Fig. 2b) permits to locate the inflection point or midpoint. The last method was adopted in the present work, as illustrated for example in the case of native maize starch where the obtained value for the glass transition temperature is 375 K.

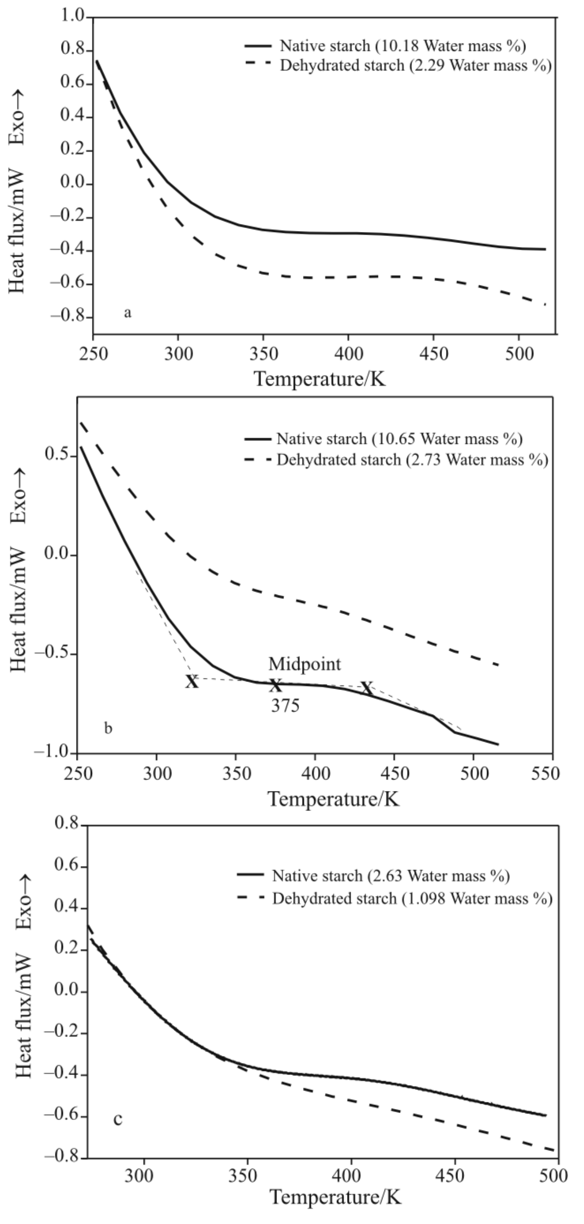

Fig. 2 Smooth reversible component curves for native and dehydrated starches, from a – wheat, b – maize and c – potato, respectively. The glass transition domain is identified by the observed inflexion; the temperature T_g corresponds to the inflexion point (or midpoint).

Alternatively, to confirm the results obtained graphically, a numerical method was also used in this work. It was based on the determination of the polynomial fit of the reversible heat flux curve *vs*. temperature and then the calculation of the root of the second derivative. It was applied to the same reversible curve of native maize starch. The obtained polynomial function giving the heat flux Q (mW) *vs*. temperature was expressed by the following relation (1):

$$\begin{aligned}Q(\mathrm{mW})={}&-191.40181+3.15407T-0.02072T^2+\\&+6.99815\cdot10^{-5}T^3-1.28907\cdot10^{-7}T^4+\\&+1.23243\cdot10^{-10}T^5-4.78993\cdot10^{-14}T^6\end{aligned}\qquad(1)$$

The root of the second derivative function d^2Q/dT^2 numerically calculated yielded for the inflection temperature 377 K, a value which is close enough to the value of 375 K obtained graphically (Fig. 2b).

Table 1 shows the (midpoint) values of the different transition temperatures (T_g), obtained from the corresponding reversible heat flux curves by means of the graphical method described above (Fig. 2b). The values agree qualitatively with most of the results reported in [7, 8, 12, 14]: accordingly, as moisture content increases, there is a concomitant decrease in T_g. Consequently, the transition temperatures of the dehydrated starches are higher than those of native starches, and this for the three types considered. In fact water lowers the transition temperature and acts as a plasticizer. The small molecules of water make chain movements easier. Therefore water has a great impact on materials containing more amylopectin. The effect can be explained by the fact that the glass transition temperatures of amylopectin and water are more different from each other than those of amylose and water. However water can also act as a solvent in which amylose and amylopectin dissolve, forming a more homogeneous mixture, reducing the existing heterogeneity between them.

Beside the water content of a given starch, as mentioned before, its chemical composition does also influence its behaviour. Generally, products containing higher amount of amylopectin have higher glass transition

Table 1 Glass transition temperatures T_g of the different, native and dehydrated starches, depending on the actual water content (in mass%)

Starch	Native		Dehydrated	
	Water content/mass%	Transition temperature/K	Water content/mass%	Transition temperature/K
Wheat	10.18	364	2.29	373
Maize	10.65	374	2.73	382
Potato	2.63	374	1.098	381

temperature values, than materials with less amylopectin which then are more flexible. Also the lower molar mass of amylose and its lack of branches results in a greater free volume so that parts of the chains can move easily. This explains the lower glass transition temperature of amylose compared to the branched amylopectin. Therefore, the amylose/amylopectin ratio should be as important as the water content for a given starch, whatever its origin. Also these two parameters (water content and amylose/amylopectin ratio) may have combined or mutual counterbalancing effects. For the present study, and according to information from starch suppliers, maize starch has the lowest amylose/amylopectin ratio of 1:99, followed by wheat and potato starches which have very close equal ratios around 1:4. From Table 1, native potato starch has a glass transition temperature equal to 374 K, very close to that of the native maize starch (373 K), although the latter has the lowest amylose/amylopectin ratio. This can be explained by the large difference in the water mass%, 10.65 and 2.63, for maize and potato starches, respectively. It can be concluded that the water content effect is predominant and has completely counterbalanced the amylose/amylopectin ratio effect. Remarkably, dehydrated wheat starch and native potato starch which have practically identical water mass%, 2.29 and 2.63, respectively, show very close glass transition temperature values, 375 and 374 K respectively. These values are reasonable since both potato and wheat starches have the same amylose/amylopectin ratio.

Heat capacities

As indicated above, the heat capacities were measured on the same starches. Measurements were taken over a slightly smaller temperature range (from 273 to 423 K) including the glass transition temperature domain as well as the gelatinization domain. Additional hydrated samples with different water contents were prepared. The water content contributes to shift the characteristic heat capacity jump occurring at the onset of the gelatinization towards lower temperatures in the same trend observed with the glass transition temperature T_g. This is clearly shown by all types of starches native, 'dehydrated' or 'hydrated'. For a given starch, Figs 3a–c demonstrate that the shift of the inflection point of the temperature jump is qualitatively proportional (the higher the water mass% the lower the inflection point T) to the water contents, namely for wheat starch (2.29 and 10.18%), for maize starch (2.73, 10.65, 18.04 and 26.7%) and potato starch (1.098 and 2.63%), respectively. Figure 4a allows a comparison of the heat capacity jumps for the different native starches in agreement with the trend observed with the values for the associated glass transition temperatures given in Table 1. Similarly, Fig. 4b shows the same agreement with associated T_g values in Table 1 for the corresponding dehydrated starches. Remarkably, in complete agreement with literature reports [5, 7], not only the water content lowers the temperature at which the C_p-jump appears, but also the amplitude of the increase follows the increase of the water content. This amplitude results both from the increase of the quantity of water having higher heat capacity (than that of starch) involved and from the 'activation' of

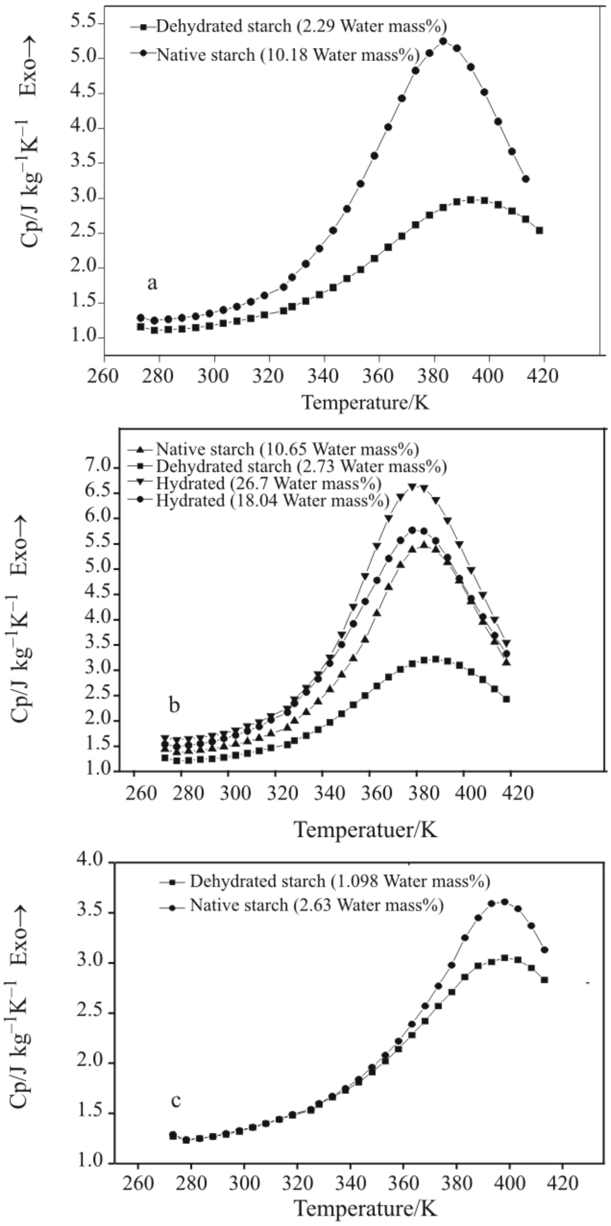

Fig. 3 Heat capacity jumps obtained for the three starches with different water contents in water mass percentages: a – wheat, b – maize and c – potato, respectively

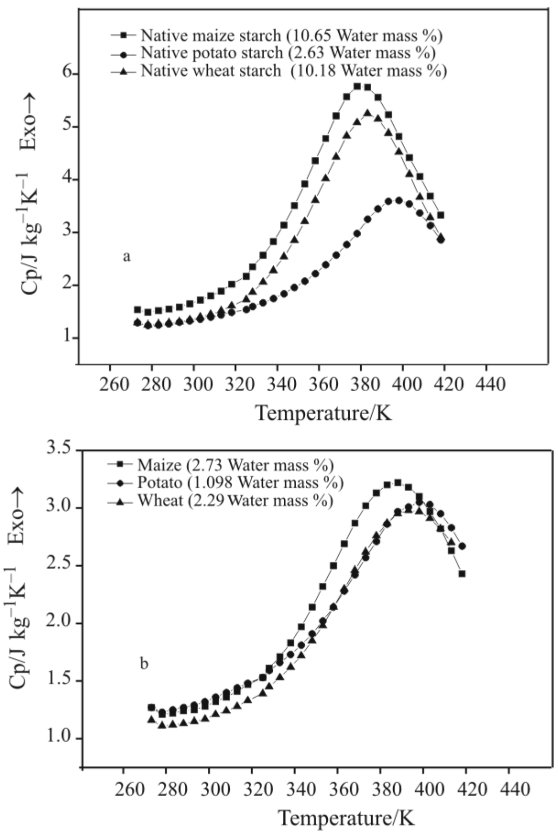

Fig. 4 Comparison of the heat capacity jumps observed for a – the three native starches and for hydrated samples of the three starches with b – similar low water contents

the gelatinization phenomenon by water molecules (cf. Figs 1a and b).

Conclusions

In accord with numerous structural investigations of starches and on the strong influence of the presence of water on their global properties, the present investigation based on thermal analysis shows that rather very small quantities of water do modify the thermal behaviour of this very important type of biopolymer. High sensitivity differential scanning calorimetry, in the temperature modulated (TMDSC) mode or in the conventional (DSC) mode, can be adequately used to monitor the water content and there from qualitatively adjust the thermophysical properties of starch systems for different major applications. Ongoing investigation of starch systems with much higher water contents should permit to follow the evolution of these properties over extended ranges of water content depending on the starch from different natural origins.

References

1 Y. H. Roos, 'Phase Transitions of Foods', Academic Press, New York 1995; see also "Thermodynamics and non/equilibrium criteria for development and application of supplemented phase diagrams", IUPAC Project 2003-036-2-100.
2 Y. H. Roos, J. Therm. Anal. Cal., 71 (2003) 197.
3 K. J. Zeleznak and R. C. Hoseney, Cereal Chem., 64 (1987) 121.
4 J. Pak, W. Qiu, M. Pyda, E. Novak-Pyda and B. Wunderlich, J. Therm. Anal. Cal., 82 (2005) 565.
5 B. Wunderlich, in "Thermal Analysis of Polymeric Materials", Springer, Berlin 2005.
6 B. Wunderlich, J. Therm. Anal. Cal., 82 (2005) 565.
7 M. Pyda, J. Polym. Sci., Part B. Polym. Phys., 39 (2001) 3038.
8 M. Pyda, Macromolecules, 35 (2002) 4009.
9 M. Pyda, R. C. Bopp and B. Wunderlich, J. Chem. Thermodyn., 36 (2004) 731.
10 T. A. Waigh, P. J. Jenkins and A. M. Donald, Faraday Discuss., 103 (1996) 325.
11 T. A. Waigh, A. M. Donald, F. Heidelbach, C. Riekel and M. J. Gidley, Biopolymers, 49 (1999) 91.
12 T. A. Waigh, M. J. Gidley, B. U. Komanshek and A. M. Donald, Carbohydr. Res., 328 (2000) 165.
13 S. L. Randzio, I. Flis-Kabulska and J.-P. E. Grolier, Macromolecules, 35 (2002) 8852.
14 I. Bocharnikova, L. A. Wasserman, A. V. Krivandin, J. Fornal, W. Blaszcak, V. Ya. Chernykh, A. Schiraldi and V. P. Yuryev, J. Therm. Anal. Cal., 74 (2003) 681.
15 S. S. Kozlov, A. V. Krivandin, O. V. Shatalova, T. Noda, E. Bertoft, J. Fornal and V. P. Yuryev, J. Therm. Anal. Cal., 87 (2007) 575.
16 I. Tan, C. C. Wee, P. A. Sopade and P. J. Halley, Carbohydr. Polym., 58 (2004) 191.
17 T. R. Noel and S. G. Ring, Carbohydr. Res., 227 (1992) 203.
18 M. Reading, D. Elliot and V. L. Hill, J. Thermal Anal., 40 (1993) 949.
19 M. Reading, A. Luget and R. Wilson, Thermochim. Acta, 238 (1994) 295.
20 M. Ribeiro and J.-P. E. Grolier, J. Therm. Anal. Cal., 57 (1999) 253.
21 F. Santos de Souza, A. P. Gomes Barreto and R. O. Macêdo, J. Therm. Anal. Cal., 64 (2001) 739.
22 G. W. H. Höne, W. Hemminger and H.-J. Flammersheim, 'Differential Scanning Calorimetry. An Introduction for Practitioners', Springer, Berlin 1996.

Received: February 25, 2008
Accepted: April 3, 2008

DOI: 10.1007/s10973-008-9071-6