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Influence of glycerol on the melting of potato starch

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Abstract

The gelatinization and melting of granular and recrystallized starch have been studied in the presence of low and high levels of glycerol or water by differential scanning calorimetry. The gelatinization onset temperature is increased in the presence of glycerol, whereas the excess gelatinization enthalpy is not affected. A broadening of the transition or change in shape is observed by lowering the amount of plasticizer. The increase of the melting onset temperature by the addition of glycerol is explained by an increase in the activation energy of the melting of the starch crystallites. The rise in activation energy is the result of the higher glass transition temperature of the amorphous phase and by the higher interaction forces of glycerol with the starch polymers. The changes in the shape of the endotherm at low plasticizer content is interpreted as an entropic effect. With less plasticizer the change in entropy during melting is low as a result of the lower mobility and viscosity of the starch polymers and the diluent molecules leading to less conformational freedom.

Keywords: Starch; Melting; Glycerol; Water; Differential scanning calorimetry

1. Introduction

There is an increasing interest in biodegradable plastic materials based on thermoplastic starch (TPS). In order to be able to process native starch to form a bioplastic material, it is necessary to disrupt and melt the semicrystalline granular structure of native starches (Banks and Greenwood, 1975; French, 1984). Several methods have been developed to make thermoplastic starch. The stability, transformation and the physical properties of the starch materials depend on the nature of amorphous and crystalline zones present in the granule structure. The transformation of granular starch into TPS is influenced by the processing conditions such as temperature and plasticizer content. Water and glycerol are the most commonly used plasticizers in TPS materials. The influence of water and glycerol on the disruption of the native starch granule is therefore of great importance.

Previous studies on the gelatinization and melting of granular starch have been made at high and intermediate water contents (Bean and Yamazaki, 1973; Biliaderis, 1991, 1992; Biliaderis and Vaughan, 1987; Biliaderis et al., 1986; Burt and Russell, 1983; Cheer and Lelievre, 1983; Donovan, 1979; Eliasson, 1990, 1992; Evans and Haisman, 1982; Gerlsma, 1970; Ghiasi et al., 1983; Glover et al., 1986; Kim and Walker, 1992; Kohyama and Nishinari, 1991; Maurice et al., 1985; Oosten, 1984; Sears and Darby, 1982; Slade and Levine, 1988; Zeleznak and Ho-

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seney, 1987). TPS can be obtained during extrusion processing or injection moulding, with low water content, usually below the excess of water (i.e. less than 66%). Therefore, it is necessary to get insight into the melting of starch at low water contents. In this study the influence of glycerol on the gelatinization and melting of potato starch has been studied with Differential Scanning Calorimetry (DSC) at low (less than 50%) and medium (between 50% and 66%) water content. The results are compared with the influence of sucrose on the gelatinization and melting of potato starch. Sucrose is a well-known additive in food products and is known to effect the gelatinization of starch during food processing. The product properties of starch-containing baked foods are, analogous to those of the TPS materials, highly depending on the degree of starch gelatinization and melting (Bean and Yamazaki, 1973; Evans and Haisman, 1982).

In previous studies the melting of the granular starches with high levels of water and the influence of a wide range of additives used in starch processing, have been studied by various techniques. The results have been explained in several, sometimes contradictory, ways. The purpose of this study is to investigate the influence of glycerol and water on the gelatinization and melting of potato starch over a wide range of compositions.

2. Materials and methods

2.1. Materials

Potato starch was a commercial product (Farina; Avebe, The Netherlands) consisting of 79% amylopectin and 21% amylose [on a dry basis (d.b.)]. Waxy corn starch (Amioca; Cerestar, Belgium) was essentially free of amylose (<0.5%). Glycerol, glycol and sucrose were obtained from Boom B.V. (p.a.; water-free). Recrystallized starch was prepared by heating granular starch in deionized water (10% w/w) for 3 h at 95°C. As preservative, 0.1% sodium azide was added. The mixture was stored at room temperature for approximately one year. Then, the gels were allowed to dry by evaporation until the water content was 13.5%. Dried starches (with less than 1% water) were obtained by drying granular and recrystallized starch in vacuo.

2.2. Methods

The DSC measurements on granular starches were carried out with a SEIKO DSC 120C, cooled with liquid nitrogen and flushed with a constant flow of nitrogen (40 ml/min) to obtain an inert atmosphere. An empty pan was used as a reference. The measurements on the recrystallized and dried starch were performed with a Perkin-Elmer DSC-7. The heating rate was 10°C/min. The instrument calibration was done with indium (ΔH_{fusion} = 28.59 J/g, melting point (T_{onset}) = 156.60°C) and gallium (ΔH_{fusion} = 79.91 J/g, melting point (T_{onset}) = 29.78°C). The enthalpy of the endothermic peaks were calculated from the peak areas and expressed on the basis of dry material (J/g starch).

Sample preparation

The DSC samples were measured directly or mixed with an accurately preweighed amount of plasticizer, i.e. water, sucrose or glycerol. The mixtures were premixed and equilibrated overnight under parafilm at room temperature. The mixtures containing approximately 10 mg starch were weighed into silver or stainless steel pans. The pans were sealed hermetically.

Wide-angle X-ray diffractograms were recorded with a Philips powder diffractometer (model PW 3710) operated at the CuK$_\alpha$ wavelength of 1.542 Å and 2000 mW at ambient temperature.

3. Results

The influence of water, glycerol and sucrose has been measured with DSC. Typical thermograms are shown in Fig. 1. The two endothermic transitions are assigned to the gelatinization endotherm, denoted as G, and the melting endotherms, denoted as M_1 and M_2.

3.1. Gelatinization of native potato starch

When increasing the amount of water (Fig. 1) the shape of the transition changes from a single endotherm at high water contents (>66%) to a asymmetrical double endotherm at low water contents. The onset temperature, T_o, the peak temperature, T_p, and the conclusion temperature, T_c, shift to higher

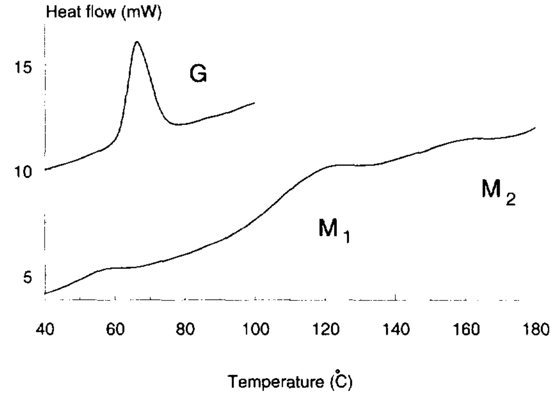


Fig. 1. The thermograms of the gelatinization (top, with 17% water) and melting (bottom, with 87% water) of granular potato starch.

Table 1
Effect of water on the gelatinization and melting parameters of potato starches differing in water content

Water[a] (%)	ΔH (J/g starch)	T_o (°C)	T_p (°C)	T_c (°C)	ΔT ($T_c - T_o$)
17	0.5	105	148	170	65
18	1.5	105	125	160	55
24	2.5	100	135	160	60
31	8	80	97	108	28
41	17	60	90	97	37
49	15	64	80	104	40
56	16	57	62	81	24
66	16	57	63	75	18
87	16	57	64	70	13

[a] On the basis of total mass.

values. The value of ΔT ($T_c - T_o$) increases with decreasing water content. The ΔH increases from about 0.5 J/g to 18 J/g with increasing water content. These effects are shown in Fig. 2 and summarized in Table 1. These findings are in agreement with previous reports (Biliaderis et al., 1986; Biliaderis, 1992; Burt and Russell, 1983; Donovan, 1979; Eliasson, 1990, 1992; Evans and Haisman, 1982).

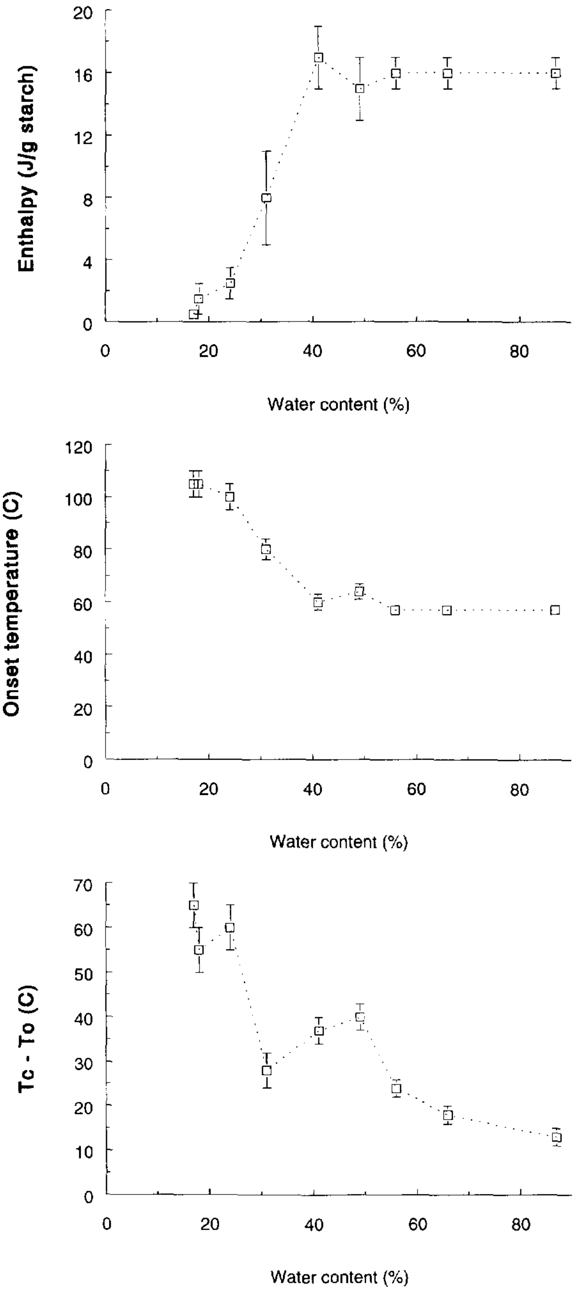


Fig. 2. The melting parameters of granular potato starch as a function of water content.

3.2. Effects of glycerol and sucrose

Glycerol and sucrose each have an influence on the melting of potato starch depending on the water content. The thermograms of the mixtures with glycerol and sucrose added are similar in appearance to those of the starch–water mixtures. Both the endothermic transitions G and M are observed. A typical thermogram of the melting of potato starch in the presence of glycerol is shown in Fig. 3.

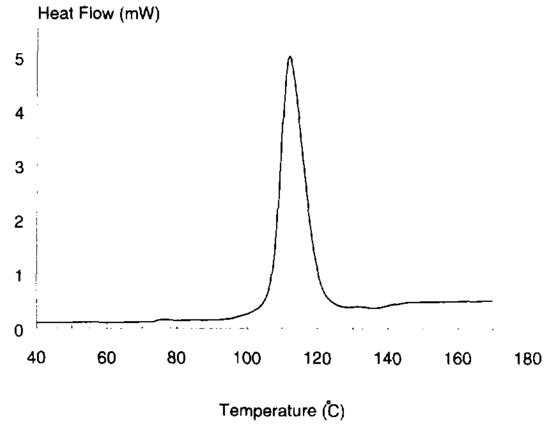


Fig. 3. Thermograms of the gelatinization of granular potato starch with an excess of glycerol.

(1) Low water [i.e. <50% (w/w)]. At low water–starch ratios, the effects of glycerol on the melting of potato starch are very pronounced as shown in Fig. 4. At low water and glycerol contents there is no G endotherm visible. Only a broad melting endotherm is visible. At high glycerol levels a G endotherm appears. The onset temperature is slightly raised at 24% water and remains constant at 17% water with increasing glycerol content. The effect on the ΔT is very proclaimed. The ΔT drops for the starch mixtures with increasing glycerol content. As a result there is a change of shape of the endotherm going from a double endotherm to a single gelatinization endotherm. The excess glycerol endotherm [with more then 66% glycerol (w/w)] has a similar shape as found in the excess water systems, although the

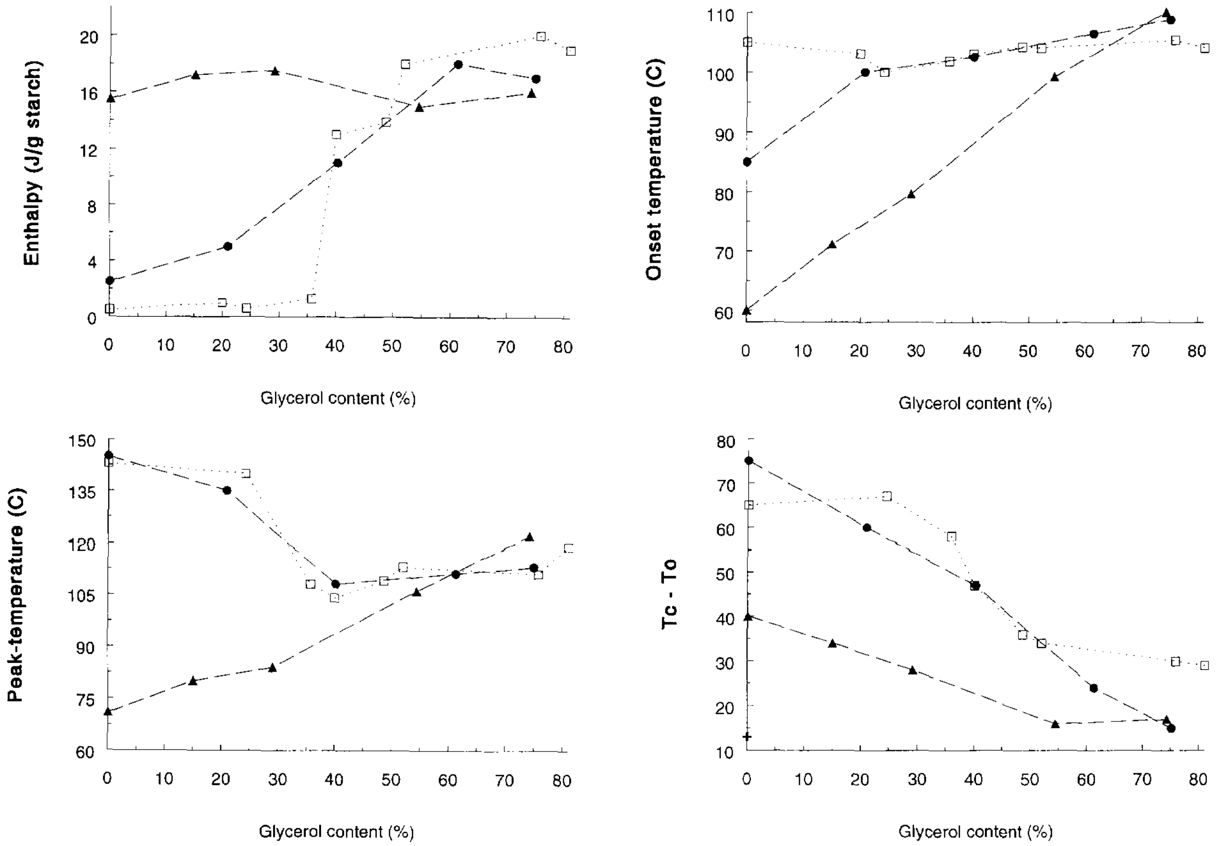


Fig. 4. Enthalpy (a), onset temperature (b), peak temperature (c) and ΔT (d) as a function of water and glycerol content.

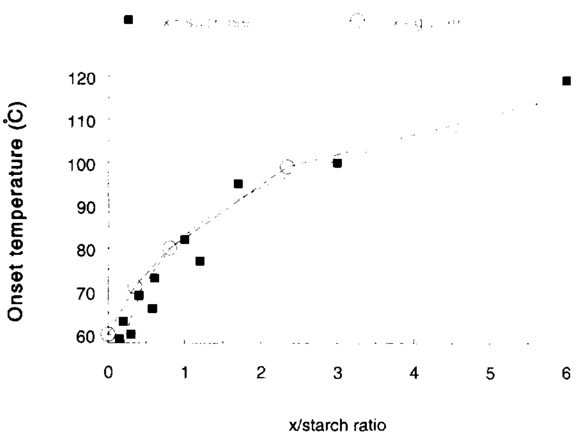


Fig. 5. Onset temperature as a function of sucrose and glycerol content. The starch–water ratio is 1 to 1.

endotherm is shifted to a higher temperature. The onset temperature is 59°C for the water–starch mixture in comparison with approximately 110°C for the glycerol–starch system. At low water content (17% and 24%) the ΔH increases with increasing glycerol content. For these low water contents (17% and 24%) the enthalpy drops when the total amount of plasticizer (glycerol and water) becomes less than approximately 60% (total mass).

(2) Medium water [i.e. $\approx$50% (w/w)]. The effects of glycerol and sucrose on the melting of granular potato starch at a water–starch ratio of 1 : 1 are shown in Figs. 4 and 5, respectively. The effects of the plasticizers glycerol or sucrose are different compared to the excess water situation. When increasing the levels of glycerol or sucrose at a water–starch ratio of approximately 1 : 1, the total enthalpy, ΔH, remains unchanged. The ΔH of the sucrose–starch–water system is approximately 15 ± 2 J/g and the ΔH of the glycerol–starch–water mixture is approximately 17 ± 2 J/g. In the mixtures with less than 66% total plasticizer (i.e. water and glycerol) a double endotherm is obtained. With increasing plasticizer content, glycerol or sucrose, the ΔT decreases to a value obtained for an excess water system. The onset temperature is raised in a similar way as found for the excess water system, going from approximately 57°C to 110°C for glycerol as well as for sucrose. The results for sucrose are in accordance with results previously reported (Eliasson, 1992; Kohyama and Nishinari, 1991).

(3) Excess of water [i.e. >66% (w/w)]. The effects of glycerol on the gelatinization of potato starch at high water levels are shown in Fig. 4. In systems with an excess of water the enthalpy, ΔT and the shape of the observed endotherm remains almost identical with increasing glycerol content (Evans and Haisman, 1982; Gerlsma, 1970; Oosten, 1984). A rise in the onset temperature has been observed from approximately 60°C up to 110°C with increasing glycerol and sucrose contents. The total enthalpy of the transition remains constant.

The effects of water, glycerol and sucrose on the gelatinization and melting parameters are summarized in the Tables 1, 2 and 3, respectively. By a comparison of previously reported results for the gelatinization of potato starch in the presence of water and glycerol at high water–starch ratios (Eliasson, 1992; Evans and Haisman, 1982; Kim and Walker, 1992; Kohyama and Nishinari, 1991) with the results presented in this report, at high, intermediate and low water contents, a more complete picture is obtained of the influence of glycerol on the gelatinization of potato starch over a wide range of water contents. The influence of water and glycerol or sucrose on the gelatinization onset temperature is clearly visible. The effects on the onset temperature can be subdivided in to four regions. At high water contents (i.e. high water–starch ratios) the onset temperature is low and the gelatinization is controlled by water. At low total plasticizer contents the gelatinization temperature is shifted to high values. At low glycerol or sucrose concentrations the onset gelatinization temperature is dropped (below 66%) quite rapidly to 57°C. But at low water contents the onset temperature is only lowered to about 110°C by the addition of a plasticizer, like glycerol or sucrose.

3.3. The melting of dry granular potato starch

Dry starch has been melted with an excess of ethylene glycol and glycerol. The thermograms are shown in Fig. 6. Exothermic transitions are observed with an onset temperature of 75°C and 100°C, respectively for ethylene glycol and glycerol.

Table 2
Effect of glycerol content on the gelatinization and melting parameters of potato starch at different water–starch ratios

Starch–water ratio	Water[a] (%)	Starch[a] (%)	Glycerol[a] (%)	ΔH (J/g starch)	T_o (°C)	T_p (°C)	T_c (°C)	ΔT ($T_c - T_o$)
5–1	17	83	0	0.5	105	148	170	65
	13	67	20	1	103	145	170	67
	13	63	24	0.6	100	140	170	70
	11	51	36	1.3	102	108	160	58
	10	50	40	13	103	108	150	47
	9	42	49	14	104	109	140	36
	8	40	52	15	104	110	138	34
	4	20	76	20	105	111	135	30
	3	16	81	19	104	110	133	29
3–1	24	76	0	2.5	85	145	160	75
	19	60	21	5	100	135	160	60
	14	46	40	11	103	108	150	47
	9	30	61	18	106	111	130	24
	6	19	75	17	109	113	124	15
1–1	49	51	0	16	60	71	104	40
	42	43	15	17	71	80	105	34
	35	36	29	18	80	84	108	28
	23	23	54	15	99	106	115	16
	13	13	74	16	117	122	134	17

[a] On the basis of total mass.

Table 3
Effect of sucrose content on the gelatinization and melting parameters of potato starch at a water–starch ratio of approximately 1 to 1

Water[a] (%)	Starch[a] (%)	Sucrose[a] (%)	ΔH (J/g starch)	T_o (°C)	T_p (°C)	T_c (°C)	ΔT ($T_c - T_o$)
50	50	0	16	57	63	85	28
46	48	7	13	59	61	90	31
45	45	9	15	63	68	89	25
41	46	14	14	60	64	92	32
42	42	17	16	69	75	90	21
41	38	22	15	66	72	84	18
38	38	23	13	73	81	92	19
33	33	33	15	82	95	102	20
35	30	36	16	77	84	99	22
27	27	46	15	95	102	119	24
20	20	60	16	100	104	118	18

[a] On the basis of total mass.

3.4. Melting of recrystallized waxy corn starch and potato starch

The melting and gelatinization profiles of the recrystallized starches are shown in Fig. 7. The observed gelatinization endotherm is ascribed to the melting of the recrystallized B-type amylopectin (as determined with X-ray diffraction) because of the similarity to crystallized waxy corn starch. The slight differences in gelatinization onset temperature and shape are ascribed to the differences in the outer chain length of the amylopectin of potato starch and waxy corn starch. The longer chain length of the potato starch amylopectin results in more stable B-type crystals which melt at relatively high temperatures.

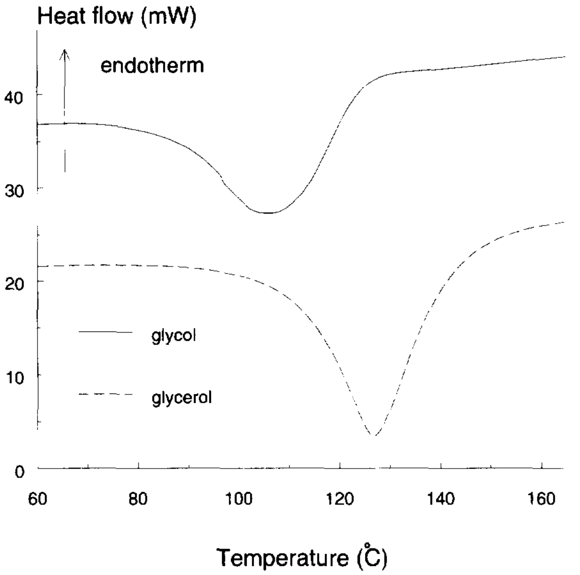
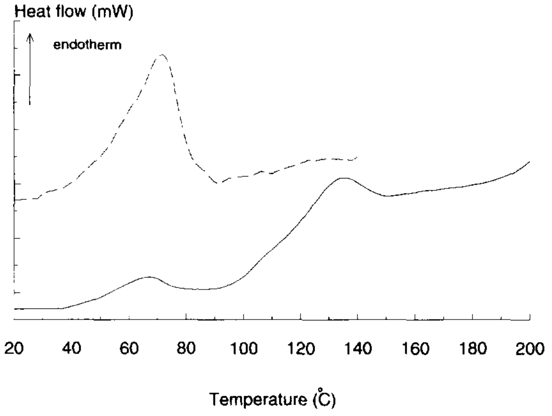


Fig. 6. The thermograms of the heating of dry potato starch with ethylene glycol (top) and glycerol (bottom).



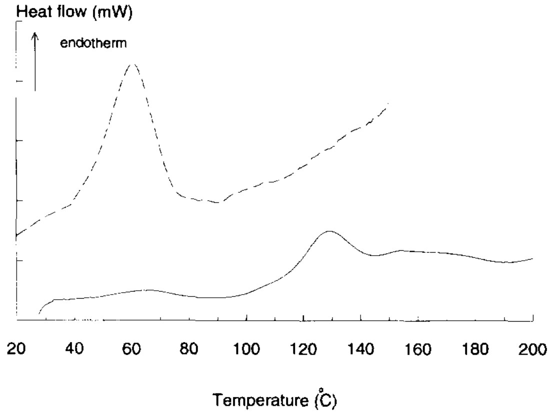


Fig. 7. The thermograms of the gelatinization (80% water, ——) and melting (with 13% water, - - -) of recrystallized waxy corn (a) and potato starch (b).

4. Discussion en conclusions

The influence of glycerol on the gelatinization and melting of granular potato starch is dependent on the water content. The effects for medium water levels (starch–water ratio 1 : 1) are similar to the effects observed for sucrose. Three melting parameters are influenced by composition of the solutes: The onset temperature, the shape as expressed by the melting trajectory (ΔT) and the enthalpy change, ΔH. The effects will be interpreted in terms of these measured thermodynamical parameters and the change in entropy, ΔS.

For granular starch two processes are occurring during gelatinization and melting. The disruption of the macroscopic, spherical ordering of the amylopectin and amylose inside the granule observed as birefringence and the actual melting of the crystalline and helical ordering of the starch molecules, leads to an enthalpic change. The magnitude is mainly regulated by starch–starch interactions. The enthalpy of the melting process of starch crystallites is therefore only the result of breaking interaction forces within the crystals, which correspond to more or less independently ordered starch chain segments. This is in agreement with the relatively low differences in enthalpy for various amylose polymorphs (Biliaderis, 1992). Thus, the enthalpy is not very sensitive for changes in diluent content and differences in ΔS are mainly responsible for shifts in melting onset temperature.

The increase in T_0 is mainly due to a depression of the glass transition temperature, T_g, of the amorphous phase. Low-molecular-mass compounds when present in a glassy or semicrystalline polymer act as a plasticizer in the amorphous phase. The magnitude of this depression depends on the amount of diluent and its compatibility with the polymer (Maurice et al., 1985; Sears and Darby, 1982; Slade and Levine, 1988). In addition to the T_g depression, the equilibrium melting point of a polymer (T_m) is lowered.

The latter effect is of thermodynamic origin and is related to the interaction forces between polymer and diluent (Van den Berg, 1981; Flory, 1953; Williams et al., 1955). In the case of starch the effect of glycerol on the melting onset temperature is much larger than is expected on the basis of the less plasticizing (anti-plasticizer) effect of glycerol compared to that of water. In addition to the anti-plasticizing effect of glycerol, there is an increased interaction of glycerol with the starch polymers as seen by the exothermic transition at very low water contents of the melting of granular starch as well as recrystallized starch. Glycerol decreases the retrogradation rate of waxy corn starch (Van Soest et al., 1994) and exhibits a resonance peak in the solid-state NMR spectra of TPS materials (unpublished results) due to the high interaction forces between glycerol and starch. The granules are more stabilized by the crosslinking effect of glycerol inside the granules. The high interaction of starch with glycerol results in a rise of the activation energy for the melting of the crystallites, which is related directly to the onset temperature of melting. The hydration of the amorphous phase in the granule (mainly amylose) affects the activation energy barrier by destabilization of the crystallites with increasing temperature. This effect has been described as a the opening of a zipper when enough water or plasticizer is present, requiring a cooperativity during melting (Shiotsubo and Takahashi, 1986). The destabilizing effect of water is larger than that of glycerol due to a difference in entropy.

The melting of starch is also influenced by the changes in entropy during the transition. The mobility of water and other molecules in a starch–water system depends highly on the water content, and is lower in samples of high starch content (Biliaderis and Vaughan, 1987; Jaska, 1971; Johnson et al., 1990; Nolan et al., 1986). Water content also affects the conformational freedom of starch as is shown by infrared spectroscopy (Van Soest et al., 1995). The viscosity of starch-diluent systems is decreasing with increasing diluent concentration (Cheer and Lelievre, 1983; Ghiasi et al., 1983). At high plasticizer content, the entropic changes are almost unaffected by a change in plasticizer type, because the entropy of both the excess of water as well as the excess of glycerol or glycol is of the same order of magnitude. TPS obtained after gelatinization has a glass transition temperature far below room temperature and the mobility of the polymer chains is high and the viscosity is low. At low water and glycerol content the entropic contribution to the melting behaviour of starch is an important factor affecting the shape of the endothermic transition, which is broadened at low plasticizer content. The differences in starch chain mobility, and thus the entropy, is regulated by the glass transition temperature which is related to plasticizer content, by the interaction of glycerol with starch and by the macroscopic as well as microscopic viscosity.

The changes in onset melting temperature and melting trajectory at low water contents is of great importance for the melting of starch during the preparation of food products and the processing of granular starch into TPS. In cake systems the control of starch gelatinization, including the influence of sucrose, is of great importance in obtaining a non-collapsing, porous cake structure (Bean and Yamazaki, 1973; Glover et al., 1986). During the processing of native starch into TPS, the water content is relatively low (Stepto et al., 1989). The addition of glycerol has a negative effect on the gelatinization or melting of granular starch. During processing of granular starch into TPS, the addition of glycerol is not favourable and the melting temperatures are above 100°C. Despite this, the addition of glycerol can have a positive effect on the preparation of starch bioplastic materials from TPS because of the improved final properties of the glycerol containing TPS materials, such as: mechanical properties (stress, strain), decreased retrogradation, loss of water and total plasticizer. The high interaction forces between glycerol and starch, compared to water, are possibly favourable for obtaining stronger rubbery materials which are used above their glass transitions temperature or lead to an improvement of the impact strength of the glassy materials. Better stability of TPS to retrogradation and loss of water, results in an improvement of the flow properties and processing.

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