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Thermogravimetry- and differential scanning calorimetry-based studies of the solid state reactions of starch polysaccharides with proteogenic amino acids

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Abstract

Waxy maize starch (NWS), pasted waxy maize starch (PNWS), amylopectin (AP), and amylose (A) produced dextrins when reacted thermally with proteogenic amino acids. The course of reactions depended on amino acid used. Analysis of diagrams of differential scanning calorimetry (DSC) and thermogravimetry (TG) suggests that all amino acids but ARG and SER reacted with polysaccharides in the point of glassy transition of polysaccharide. Both ARG and SER first decomposed and their decomposition products reacted with polysaccharide, also in the point of polysaccharide glassy transition. Products of reaction of amylose with amino acids are more thermally stable than products from reaction of these acids with amylopectin. Free radicals produced from all amino acids but these from ARG and TRP were C and O free radicals. ARG and TRP produced N free radicals. However, in combination with polysaccharides both these acids, similarly as all other amino acids, produced exclusively C and O free radicals.

Keywords: Amino acids; Amylopectin; Amylose; Dextrins; Polysaccharide free radicals

1. Introduction

Dextrins are products of scission of glycosidic bonds in starch polysaccharides, e.g. in amylose and amylopectin. Scission of these bonds involves either chemicals, chiefly sources of proton [1], enzymes [2] or physical action, for instance, thermolysis [3], and other methods, such as ultraviolet, visible, infrared, and microwave radiation, elevated pressure, sonication, and others [4]. For centuries, dextrins are widely used as binders and/or thickeners in food industry as well as in several non-nutritive applications.

Recently, reports appeared in the literature [5–7] on successful applications of special dextrins as selective depressants for flotation of metal ores. They provide almost complete separation of chalcosite from galena. Such dextrins were prepared on roasting of dry starch with solid proteogenic amino acids [5,8,9]. Thorough adjustment of temperature was a crucial parameter in order to control degree of dextrinisation and avoid carbonisation. Depending on admixed amino acid specific temperature was required for dextrinisation. The temperature adjustment was made based on differential scanning calorimetric (DSC) studies of starch — amino acid blends. Jointly with thermogravimetric

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(TG) studies analysis of DSC-grams provided some details of the reactions between components of the blends [8].

Success in application of such dextrins in depression of complex metal ores prompted us to prepare further series of dextrins potentially useful for the same purpose. Two factors were taken under account in selection of materials:

1. Reactions of starch depend on its contact with reagents. Since starch commonly used for reactions consists of granules shells hinder interior of granules from contact with reagents. Therefore, more severe conditions have to be applied to achieve attempted reactions.
2. Depressing activity of dextrins in metal ore flotation depends on their sorption on particles of minerals. Therefore, structure of dextrins, mainly degree of branching of the polysaccharide chains, might be particularly essential for anticipated effect.

For this sake, studies presented in this report focused on preparation of dextrins from pregelatinised starch, e.g. starch deprived of granular structure as well as from linear amylose, and branched amylopectin. Both the latter starch polysaccharides are not granular and, to a significant extent, amorphous [10]. Joint studies carried out with involvement of DSC and TG techniques provided selection of the thermolysis conditions under which these polysaccharides with one of 17 amino acids could react without any carbonisation. Moreover, pattern of DSC- and TG-grams provided insight in details of these solid state reactions.

These results are supplemented by the studies of the properties of polysaccharide free radicals [11] thermally generated in such reactions. Our former studies [11,12], revealed that unpaired spins were localised on the carbon and oxygen atoms of glucose units of polysaccharides. Steric hindrances of as well as delocalisation of unpaired spin were responsible for unusual stability of those free radicals. Reactions presented in this study involve amino acids, among them also these with sulphur atoms. Potentially, they might form free radicals with free electrons localised on the nitrogen and sulphur atoms. Nothing is known on the stability of such polysacharide radicals.

In this study, the following amino acids were taken for reaction with waxy maize starch, amylose, and amylopectin: alanine (ALA), arginine (ARG), aspartic acid (ASP), cysteine (CYS), glutamic acid (GLU), glycine (GLY), histidine (HIS), isoleucine (ILE), leucine (LEU), lysine (LYS), methionine (MET), phenylalanine (PHE), proline (PRO), serine (SER), threo-nine (THR), tryptophane (TRP), tyrosine (TYR), and valine (VAL).

2. Experimental

2.1. Materials

Corn amylopectin (7.3% w/w of water content), and potato amylose were purchased from Fluka. Native waxy maize starch (9%, w/w water content) was kindly provided by Central Laboratory of the Polish Potato Industry in Poznan.

Ethanol, 96%, analytical grade was purchased from POCH Gliwice, Poland. L-Amino acids were purchased from Sigma. Distilled water was used.

2.2. Methods

2.2.1. DSC–TG measurements

Blends of polysaccharide sample (2 g) with amino acid (0.2 g) were prepared by 2 min. grinding in agate mortar. Thermal DSC–TG analysis was carried out with the NETZSCH STA-409 simultaneous thermal analyser calibrated with standard indium, tin, zinc and aluminium of known purity (99.99%) of known temperature and enthalpy of melting. Samples (approximately 0.020 g) were heated in corrundum crucibles with non-hermetic lids. Corrundum was the standard. The heating was performed under static conditions in the air in the range of 20–450°C with the temperature rate increase of 5 K min^{-1}. Recorded thermograms were analysed with the NETZSCH-TA-ANALYSIS programme. Measurements were duplicated. They provided the ±0.5°C precision in reading of temperature.

2.2.2. Pasting of waxy maize starch

Pasting was performed on 7%w/w of aqueous starch suspensions. Heating at 70°C was continued for 1 h on continuous agitation. Starch was precipitated from the

paste by addition of 96% ethanol. The air-dried material contained 12.7% w/w of water.

2.2.3. Thermolysis to generate free radicals

Sample of polysaccharide (0.1 g) were thermolysed in porcelain crucibles using an ELF 11/6 Eurotherm Carbolite oven with analogous digital temperature stabiliser providing the ±0.5°C heating precision. The samples were heated in the air to 260°C and maintained at this temperature for 1 h. After cooling to room temperature samples were EPR-analysed.

2.2.4. EPR spectra

The spectra were recorded for powdered samples in the X-band region (9.5 GHz, $l = 3.2$ cm) at room temperature. $CuSO_4$ was taken as the standard for the spin abundance (2.4×10^{21} spins g^{-1}) and DPPH was the standard for the *g*-factor. The apparatus was manufactured by Politechnika Wroclawska (Poland). The spectral curves were processed using the 2.8 b MicroCal Origin program.

3. Results and discussion

In the temperature range of 20–450°C, native waxy maize starch (NWS) decomposed similarly as potato starch (PS). Two initial steps were endothermic and two further steps proceeded exothermally. Onset (T_o) and peak (T_p) temperatures for the first peak, which reflected the moisture loss, were lower for PS (35.1°C) than for NWS (52°C). Therefore, one might say that the latter held water more strongly than PS. On the other hand, PS held more humidity (16%) than NWS (9%). It could be accounted for lipids always present in starch of this botanical origin. Desorption of moisture from PS, which started from 35°C, suggested that PS sorbed water more weakly than NWS, possibly on its surface. This point of view found its support by the temperature of the moisture loss by commercial amylopectin (AP) (41°C) and NWS (37°C) precipitated from its paste (PNWS). Isolation procedure of AP and PNWS provided higher surface area and less compact structure of these products in comparison to non-processed, native materials. The second endothermic peak around 260°C was ascribed to the polysaccharide glassy transition accompanied by decomposition, mainly loss of constitutional water [3,8]. Both, T_o and T_p for this effect in polysaccharides (Table 1) decreased in the order of AP > PS > PNWS > NWS. AP as a pure species had the highest T_o and T_p. High position of PS might be interpreted as the result of stabilisation by intra- and inter-molecular hydrogen bonds in naturally formed macrostructure of granules. PNWS could be, in fact, a combination of separated AP and A [13]. The lowest T_o and T_p for NWS could be rationalised in terms of admixture of lipids naturally present in maize starches. NWS, AP, and PS lost in this step totally from 56 to 61.5% of their weight and, because of original macrostructure ruined by pasting, PNWS lost even over 80% of its original weight.

Subsequent exothermic transformations of polysaccharides were assisted by decomposition to low molecular weight, volatile compounds such as carbon mono- and di-oxide, low-molecular hydrocarbons, alcohols, aldehydes, ketones and carboxylic acids [3].

Hardly 10% w/w admixture of amino acids to thermolysed polysaccharides had a clear effect on the process but the role of amino acids could be observed indirectly. Neither exothermic reaction of amino acids with polysaccharides nor their endothermic [14,15] thermal decomposition was manifested by separated peaks in DSC-grams and distinct regions of weight loss in TG diagrams. Such effects could be observed solely in form of their contribution to the thermal effects, chiefly to enthalpies of the processes and accompanying weight loss.

All DSC-grams in Table 2 show the endothermic effect with related T_o and T_p temperatures of ~35 to 48 and ~78 to 85°C, respectively. This effect with enthalpy changes between 287 and 379 J g^{-1} was due to humidity loss. Blends under study might be distinguished into two groups based on the criterion of the character second thermal effect. Blends with ALA, ARG, ASPA, CYS, GLC, GLUA, ILE, LEU, SER, and VAL decomposed endothermally in the second stage whereas blends with HIS, MET, PHE, PRO, THR, TRP, and TYR decomposed exothermically at this stage. Insight in associated enthalpy changes and weight loss might inform whether effect of glassy transition and/or decomposition or other chemical reactions dominate at this stage. Glassy transition and decompositions are presumably endothermic processes whereas such reactions as formation of diketopiperazines from amino acids, esterification of polysaccharides with amino acids (proved in our

Table 1
Parameters of diagrams from the DSC and TG studies of polysaccharides

Polysaccharide	Thermal effect	T_o (°C)[a]	T_p (°C)[a]	DH (J g^{-1})[b]	TG weight loss (%)[c]
Native waxy starch (NWS)	Endo	52.0	86.0	386.8	9.0
	Endo	239.1	254.8	43.0	45.6 (60.4)[d]
	Exo	265.9	316.0	−91.5	
	Exo	329.0	374.2	−551.1	21.7 (81.7)
Amylopectin (AP)	Endo	41.4	84.7	395.2	7.3
	Endo	258.8	273.1	20.0	52.5 (61.5)
	Exo	276.0	286.8	−37.6	20.9 (82.3)[c]
	Exo	296.5	306.5	−2.5	
	Exo	308.8	351.0	−852.6	
Pasted native waxy starch (PNWS)	Endo	37.4	73.8	340.1	12.7
	Endo	247.2	263.8	15.3	62.0 (82.6)[d]
	Exo	281.3	347.1	−1136.3	
Potato starch (PS)[e]	Endo	35	75.6	16.0	
	Endo	256	265	69.1	40.0 (56.0)[f]
	Exo	272	292	−226.1	
	Exo	303	328	−1310.3	

[a] The estimation error is ±0.5°C.
[b] The estimation error is ±3% of reported value.
[c] Figures in parentheses are the total weight losses from the origin to the given point.
[d] This value is common for this and the next DSC effect.
[e] Taken from paper [8].
[f] This value is common for this and two subsequent DSC effects.

recent paper [8]) and formation of polyglucosylamino acids are presumably exothermic.

Thus, based on the pattern of DSC-grams and TG diagrams for NWS-amino acid blends (Table 2) one might accept that all amino acids but ARG and SER reacted with polysaccharide at the point between 185 and 235°C (T_o). If the enthalpy of the reaction of polysaccharide with amino acid was slightly negative the overall enthalpy of this step could remain positive. If highly negative enthalpy of the reaction of amino acid with polysaccharide dominated over positive enthalpy of the polysaccharide transformation (i. e. glassy transition and decomposition) the overall effect turned into exothermic as, for instance, in the case of the thermolysed HIS — NWS blend. ARG and SER had to decompose prior to reaction with polysaccharide because they decomposed [16] below temperature of the second endothermic peak (Table 2). This step of transformation of ARG was observed as a peak with T_o at 206°C, but decomposition of SER could be recognised solely as contribution to the decrease in the weight loss.

The third, exothermic effect occurs at temperature specific for the glassy transition and decomposition of polysaccharide with no admixture (Table 2).

This and subsequent steps corresponded to complex, thermally induced reactions of dextrins formed in the former stages together with thermal changes typical for pure polysaccharides. It was not surprising because these polysaccharides resided in original blends in highly excessive amount.

There were rather quantitative than qualitative differences between the reactivity of NWS and AP (Table 3). Except the blend of AP with ALA, blends behaved qualitatively similarly as these with NWS. However, usually, endothermic reactions of AP began at lower temperature than corresponding reactions of NWS. It could be interpreted in terms of less compact macrostructure of AP than NWS. Four exclusive reactions with GLUA, ILE, TYR and VAL could be caused by either steric obstruction in interactions of AP with these amino acids and/or strong non-favourable sorption of these acids on the surface of AP. The

Table 2
DSC and TG analysis of the reaction of NWS blended amino acids

Amino acid and its m.p.[a]	Thermal effect	Analysis[b]			
		DSC			TG weight loss (%)[e]
		T_o (°C)	T_p (°C)[c]	ΔH (J g^{-1})[d]	
ALA 295 dec	Endo	43.0	81.7	301.4	9.8
	Endo	212.8	237.8	75.8	6.4 (7.1)
	Exo	258.6	280.0s	–	43.7 (60.9)
ARG 207	Endo	41.9	77.7	333.0	8.5
	Endo	206.1	223.0	22.8	2.2 (11.4)
	Exo	259.9	331.5	–	69.6 (80.6)
ASPA 270-1	Endo	43.6	83.7	378.2	8.7
	Endo	206.5	225.6	18.9	39.9 (51.8)
	Endo	235.8	244.5	16.8	
	Exo	272.2	287.0s	–	29.8 (80.6)
CYS dec 258	Endo	45.2	80.9	304.0	7.3
	Endo	197.0	223.1	37.8	8.5 (18.7)
	Exo	274.1	331.3	–	59.7 (80.1)
GLC 262 dec	Endo	34.9	84.4	295.0	9.9
	Endo	199.3	223.1	37.8	5.8 (17.6)
	Exo	255.9	310.4	–	66.1 (86.5)
GLUA 224-5 dec, 247-9 dec	Endo	41.8	84.5	333.0	8.9
	Endo	185.0	200.0	41.9	3.0 (15.8)
	Exo	239.7	276.4s	–	33.8 (61.5)
HIS 277 dec	Endo	48.1	84.7	334.0	8.9
	Exo	228.0	256.5	–	41.3 (52.6)
	Exo	258.8	295.6	–	25.2 (77.8)
ILE 283-4[f]	Endo	47.9	83.4	378.6	9.3
	Endo	198.6	241.6	57.7	8.5 (20.7)
	Exo	257.5	280.5s	–	36.6 (58.1)
LEU 294 dec[f]	Endo	42.9	85.1	309.4	9.5
	Endo	219.3	247.0	35.2	8.1 (19.2)
	Exo	268.4	286.8s	–	39.5 (61.0)
LYS	No reaction observed				
MET 283 dec	Endo	45.0	84.8	312.8	7.6
	Exo	229.9	241.9	−18.6	6.4 (14.6)
	Exo	262.7	321.1	–	61.8 (77.6)
PHE 283 dec	Endo	45.8	84.6	352.8	8.6
	Exo	190.3	212.6	−21.2	5.1 (14.6)
	Endo	246.1	261.5	9.8	41.1 (58.8)
PRO 220-2 dec	Endo	42.8	84.7	303.1	8.3
	Exo	204.7	224.0	–	6.2 (16.5)
	Exo	258.2	287.5s	–	44.7 (61.2)
SER 228 dec	Endo	44.3	83.6	361.4	8.3
	Endo	250.0	255.7	27.9	40.7 (51.0)
	Exo	285.3	320.2	–	25.1 (76.1)

Table 2 (*Continued*)

Amino acid and its m.p.[a]	Thermal effect	Analysis[b]			
		DSC			TG weight loss (%)[e]
		T_o (°C)	T_p (°C)[c]	ΔH (J g^{-1})[d]	
THR 235, 253 dec	Endo	44.9	84.8	321.6	7.9
	Exo	219.1	236.1	−22.7	6.3 (14.4)
	Exo	257.8	280.5s	–	41.0 (55.4)
TRP 289 dec	Endo	45.2	87.9	331.7	7.5
	Exo	215.7	239.3	−150.5	3.8 (12.7)
	Exo	258.0	317.7	–	64.0 (76.8)
TYR 290-5	Endo	42.9	81.2	304.4	9.9
	Exo	235.6	256.7	−65.2	4.3 (16.0)
	Exo	269.1	318.2	–	64.3 (80.3)
VAL 298	Endo	43.9	84.5	287.4	10.2
	Endo	213.3	243.4	33.9	8.3 (19.7)
	Exo	256.1	294.0s	–	37.9 (57.6)

[a] Melting points cited after [6].
[b] Precision in estimation of temperatures is within ±0.5°C, and error in estimations of enthalpy does not exceed ±3% of reported value.
[c] Shoulders are denoted by "s".
[d] When a value is not given a base line for the estimation could not be established.
[e] Total weight loss to a given point are given in parentheses. Ranges of the TG weight loss are linked to the corresponding DSC effects.
[f] In sealed capillary.

patterns of the weight loss in TG analyses were similar for both polysaccharides.

In order to facilitate these solid state reactions, pasted NWS (PNWS) was blended with solid amino acids. Results of this study are presented in Table 4. Reactions with PNWS required essentially higher temperature (T_o) with T_p of that effect almost unchanged.

In our former papers [11,12] thermal stability of starches was presented in terms of their affinity to the decomposition into free radicals. Differential thermal analysis (DTA) together with thermal gravimetry showed that free radicals were thermally generated at temperatures within the range of 260–280°C.

Under applied conditions ASP, ILE, PHE, and VAL did not generate free radicals under conditions applied. TRP, GLY, and SER had distinctly lower thermal stability, which decreased in above order. The population of free radicals from TRP exceeded 20.8×10^{15} g^{-1} and from GLY and SER it reached almost 8.5×10^{15} and 7×10^{15} g^{-1}, respectively. The population of free radicals from other amino acids was between 5×10^{15} and 0.23×10^{15} g^{-1}. All amino acids but TRP produced one epr signal with v between 9.5001 and 9.5138. g-Factor in all relevant spectra was 1.9861 and 2.0220. These values were typical for C- and O-radicals. Only for the radical produced from ARG $g = 2.1920$ suggesting that this could be a N-radical. Spectrum of the radical from TRP was split into two signals both of $v = 9.5108$, and $g = 2.1790$ and 2.000. It might be assumed that also TRP formed N-radical.

Thermolysis of NWS produced a fairly negligible, 0.25×10^{15} g^{-1}, population of free radicals. Admixture of amino acids significantly increased the concentration of free radicals (Table 5).

It declined from 70% in the case of admixture of ILE to 1.5 for admixture of PHE in the order of ILE ⩾ GLU > VAL > HIS > GLY > ARG > MET = ALA > SER > LYS > PRO > TYR > TRP > THR > CYS > LEU = ASP > PHE.

Blends of amino acids with commercial AP appeared to be more stable to free radical decomposition (Table 5). The free radical concentration ranged from 4.64×10^{15} to 0.24×10^{15} g^{-1} and the order of the effect of particular amino acids was entirely different from the order for admixtures with NWS showing different thermal stability of resulting dextrins to such

Table 3
Parameters of the DSC and TG analyses of AP blends with amino acids

Amino acid	Thermal effect	Analysis[a]			
		DSC			TG weight loss (%)[d]
		T_o (°C)	T_p (°C)[b]	ΔH (J g^{-1})[c]	
ALA	Endo	37.0	84.6	391.5	9.2
	Exo	229.5	253.9s	–	6.9 (18.6)
	Exo	258.6	287.4s	–	42.0 (60.5)
ARG	Endo	40.3	82.3	381.8	9.8
	Endo	207.6	224.8	12.2	2.5 (12.8)
	Exo	241.9	289.5s	–	44.3 (59.1)
ASPA	Endo	39.2	78.5	348.3	8.8
	Endo	206.0	225.6	39.4	3.8 (17.5)
	Endo	235.2	243.8	30.9	39.9 (54.0)
	Exo	264.1	281.4s	–	23.1 (77.1)[e]
CYS	Endo	38.9	78.8	328.7	8.3
	Endo	184.3	211.8	46.9	6.9 (17.9)
	Exo	266.5	277.6	–	41.2 (59.9)
GLUA	Endo	35.3	82.9	277.3	7.8
	Endo	181.4	199.3	64.3	2.1 (11.0)
	Exo	245.1	285.8s	–	38.4 (50.3)
GLY	Endo	43.4	85.5	370.2	8.9
	Endo	209.8	224.4	19.1	6.1 (17.0)
	Exo	231.0	303.7	–	38.1 (57.0)
HIS	Endo	38.7	79.6	414.3	7.8
	Exo	227.8	257.9s	–	42.2 (50.3)
	Exo	261.5	293.0	–	23.4 (73.7)[e]
ILE	Endo	42.0	84.7	354.7	7.9
	Endo	210.7	238.4	41.9	7.6 (16.0)
	Exo	260.4	325.5	–	63.2 (81.5)
LEU	Endo	39.3	86.6	375.2	7.7
	Endo	216.6	243.5	40.1	6.5 (17.2)
	Exo	261.5	326.4	–	64.3 (83.0)
LYS	No reaction observed				
MET	Endo	40.1	86.6	349.8	8.9
	Exo	222.2	239.2	−19.7	5.9 (16.5)
	Exo	264.8	323.1	–	63.5 (22.0)
PHE	Endo	41.6	82.8	349.8	9.1
	Exo	190.7	210.0	−18.0	4.4 (13.8)
	Endo	263.3	269.6	2.5	43.6 (59.6)
	Exo	272.3	279.7	–	24.8 (84.1)
PRO	Endo	41.0	83.7	338.6	6.8
	Exo	198.7	221.3s	–	43.3 (57.3)
	Exo	256.3	315.1	–	26.8 (84.1)
SER	Endo	41.0	83.9	405.3	7.5
	Endo	209.9	219.6	2.4	2.1 (11.2)
	Exo	256.9	323.0	–	68.9 (81.6)

Table 3 (*Continued*)

Amino acid	Thermal effect	Analysis[a]			
		DSC			TG weight loss (%)[d]
		T_o (°C)	T_p (°C)[b]	ΔH (J g^{-1})[c]	
THR	Endo	38.5	78.1	357.8	8.1
	Exo	216.0	235.9	−17.6	8.1 (19.0)
	Exo	257.5	303.7	–	39.6 (60.1)
TRP	Endo	40.5	78.2	375.6	7.3
	Exo	210.8	238.4	−139.6	3.4 (11.2)
	Exo	258.9	305.9	–	39.5 (50.7)
TYR	Endo	40.4	75.5	417.1	8.6
	Exo	242.1	256.2	−51.3	4.8 (15.6)
	Exo	267.4	323.0	–	66.5 (82.0)
VAL	Endo	41.4	82.2	362.3	7.3
	Endo	212.6	243.4	52.1	8.3 (15.3)
	Exo	260.4	293.9s	–	39.1 (56.0)

[a] The maximum error in reading temperatures is ±0.5°C. Error in estimations of enthalpy does not exceed ±3% of reported value.
[b] Shoulders are denoted by "s".
[c] When the base line could not be drawn the value was not estimated.
[d] Total weight loss up to the indicated temperature is given in parentheses.
[e] The value is common for this and the subsequent DSC effect.

Table 4
Parameters from the DSC and TG measurements of PNWS – amino acid blends

Amino acid	Thermal effect	Analysis[a]			
		DSC			TG weight loss (%)[d]
		T_o (°C)	T_p (°C)[b]	ΔH (J g^{-1})[c]	
ARG	Endo	52.8	76.2	333.2	9.5
	Endo	206.0	213.0	9.5	3.9 (15.7)
	Endo	216.7	222.4	39.5	39.5 (55.2)[e]
	Exo	242.0	277.8	–	
HIS	Endo	39.1	73.0	334.5	9.8
	Exo	241.0	256.7	−34.0	41.7 (56.3)
	Exo	266.6	333.1	–	23.6 (80.0)
LYS	Endo	40.4	73.6	260.9	11.1
	Exo	?	280.5	–	43.1 (57.3)
	Exo	284.8	329.0	–	23.5 (80.7)
PHE	Endo	45.8	75.0	261.7	8.2
	Exo	200.2	223.2	−31.6	6.0 (18.1)
	Exo	269.7	282.4s	–	37.5 (57.3)[e]
TRP	Endo	49.6	73.7	219.4	5.0
	Exo	218.5	239.3	−94.9	4.3 (12.1)
	Exo	262.1	340.6	–	49.0 (81.1)

[a] The precision in reading of all temperatures does not exceed ±0.5°C. The error in estimations of enthalpy does not exceed ±3% of reported values.
[b] Shoulders are denoted by "s".
[c] If base line could not be drawn estimations were impossible.
[d] Total weight loss up to the given point is given in parentheses.
[e] The value is common for this and the subsequent DSC effect.

Table 5
Characteristics of free radicals generated from NWS-, AP-, and A-amino acid blends

Amino acid		Conc. $n \times 10^{15}$ (g)	v_1	g_1	v_2	g_2
None	NWS	0.25 ± 24.74%	9.5139	1.9976 ± 0.0037		
	AP	No free radicals detected				
	A	1.45 ± 2.86%	9.5145	1.9950 ± 0.0013		
ALA	NWS	17.23 ± 0.63%	9.5084	1.9842 ± 0.0024	9.5084	1.9948 ± 0.0036
	AP	15.40 ± 0.23%	9.5101	1.9946 ± 0.0017	9.5101	1.9901 ± 0.0023
ARG	NWS	22.61 ± 0.24%	9.5054	2.0023 ± 0.0004		
	AP	3.92 ± 0.00%	9.5129	1.9866 ± 0.0009	9.5129	1.9994 ± 0.0046
	A	1.31 ± 1.59%	9.5112	1.9960 ± 0.0013		
ASPA	NWS	2.25 ± 0.92%	9.5142	1.9897 ± 0.0006		
	AP	33.26 ± 0.41%	9.5106	1.9947 ± 0.0017	9.5106	1.9910 ± 0.0019
	A	0.68 ± 5.26%	9.5157	1.9922 ± 0.0016		
CYS	NWS	2.63 ± 0.00%	9.5061	1.9899 ± 0.0016		
	AP	1.33 ± 0.00%	9.5111	1.9876 ± 0.0020		
GLC	NWS	26.02 ± 0.70%	9.5145	1.9896 ± 0.0009		
	AP	7.65 ± 3.60%	9.5197	1.9930 ± 0.0016		
	A	0.24 ± 8.66%	9.5142	1.9966 ± 0.0013		
GLUA	NWS	59.70 ± 0.30%	9.5116	1.9898 ± 0.0037		
	AP	54.97 ± 0.66%	9.5117	1.9908 ± 0.0044		
	A	2.82 ± 0.74%	9.5125	1.9944 ± 0.0023		
HIS	NWS	28.68 ± 1.28%	9.5137	1.9867 ± 0.0008	9.5137	1.9907 ± 0.0020
	AP	9.32 ± 0.77%	9.5117	1.9957 ± 0.0026	9.5117	1.9907 ± 0.0019
	A	3.01 ± 3.01	9.5115	1.9912 ± 0.0015		
ILE	NWS	70.43 ± 0.45%	9.5187	1.9870 ± 0.0020		
	AP	38.79 ± 0.23%	9.5092	1.9944 ± 0.0022	9.5092	1.9847 ± 0.0014
LEU	NWS	2.27 ± 1.59%	9.5159	1.9920 ± 0.0009		
	AP	45.40 ± 0.80%	9.5075	19941 ± 0.0022		
LYS	NWS	12.47 ± 0.17%	9.5117	1.9841 ± 0.0020	9.5117	1.9911 ± 0.0014
	AP	40.78 ± 0.73%	9.5020	1.9935 ± 0.0024		
	A	0.94 ± 0.00%	9.5130	1.9918 ± 0.0001		
MET	NWS	17.49 ± 0.43%	9.5067	1.9836 ± 0.0023	9.5067	1.9901 ± 0.0028
	AP	6.61 ± 2.27%	9.5126	1.9870 ± 0.0003	9.5126	1.9998 ± 0.0023
	A	1.27 ± 1.63%	9.5126	1.9898 ± 0.0018		
PHE	NWS	1.52 ± 3.61%	9.5078	1.9951 ± 0.0022		
	AP	1.26 ± 2.86%	9.5083	1.9936 ± 0.0009		
	A	2.00 ± 1.04%	9.5114	1.9934 ± 0.0009		
PRO	NWS	8.72 ± 1.33%	9.5109	1.9906 ± 0.0026	9.5109	1.9989 ± 0.0031
	AP	14.38 ± 1.01%	9.5109	1.9936 ± 0.0001	9.5109	1.9882 ± 0.0029
SER	NWS	16.50 ± 0.55%	9.5124	1.9845 ± 0.0021	9.5124	1.9964 ± 0.0030
	AP	8.95 ± 0.23%	9.5101	1.9946 ± 0.0017	9.5101	1.9901 ± 0.0023
	A	3.59 ± 3.23%	9.5106	1.9948 ± 0.0011		
THR	NWS	6.73 ± 1.41%	9.5114	1.9888 ± 0.0018	9.5114	1.9960 ± 0.0033
	AP	30.21 ± 0.54%	9.5020	1.9878 ± 0.0014	9.5020	1.9932 ± 0.0022
TRP	NWS	6.93 ± 0.60%	9.5110	1.9885 ± 0.0012		
	AP	23.96 ± 0.30%	9.5070	1.9942 ± 0.0023		
	A	4.64 ± 0.78%	9.5104	1.9905 ± 0.0020		

Table 5 (*Continued*)

Amino acid		Conc. $n \times 10^{15}$ (g)	v_1	g_1	v_2	g_2
TYR	NWS	7.57 ± 0.55%	9.5073	1.9889 ± 0.0016		
	AP	22.66 ± 0.42%	9.5126	1.9916 ± 0.0025		
VAL	NWS	30.83 ± 0.51%	9.5075	1.9856 ± 0.0019	9.5075	1.9947 ± 0.0036
	AP	10.06 ± 0.90%	9.5109	1.9870 ± 0.0003	9.5108	1.9866 ± 0.0025

kind decomposition. The population of free radicals generated from amino acid blends with A ranged hardly from 3.6 to 0.24 (Table 5). Thus, products of the reaction of A with amino acids were much more thermally stable than corresponding reaction products of AP. Although *g*-factor for radicals generated from ARG and TRP might suggest that they were N-radicals both amino acids in blends with polysaccharides produced only C and/or O free radicals. Several free radicals produced from amino acid blended NWS and AP, but not A, showed splitting of their signals. The *g*-factors split reached no more than 0.013 unit. Simultaneously, such splitting in free radical from the thermolysis of TRP reached value of 0.179. TRP was the sole amino acid which thermolysed in the plain state producing free radicals with splitting signal. Coupling of unpaired spin with the hydrogen atom of magnetic momentum of (1/2) could be responsible for the splitting. If the C–H bond of the carbon atom carrying unpaired spin and the p-orbital with unpaired spin occupied the same plane coupling constant would be close to zero, in order to reach maximum when the bond and that orbital were perpendicular to one another. High coupling constant observed in N-radical from TRP suggested a shift of the spin density from the carbon atoms towards the nitrogen atom.

4. Conclusions

1. Proteogenic amino acids react with polysaccharides providing novel dextrins.
2. The course of reactions depended on amino acid used. All amino acids but ARG and serine reacted with polysaccharides in the point of polysaccharide glassy transition. ARG and serine first decomposed and their decomposition products reacted with polysaccharide, also in the point of its glassy transition.
3. Dextrins resulting from reaction of amylose with amino acids are more thermally stable than dextrins from reaction of these acids with amylopectin.
4. Free radicals produced from all amino acids but these from ARG and TRP were C and O free radicals. ARG and TRP produced N free radicals.
5. In combination with polysaccharides arginie and TRP, similarly as all other amino acids, produced exclusively C and O free radicals.

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