

Thermal reactions of starch with proteogenic amino acids

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Abstract

Thermolysis of 1:1 (mole/mole) blends of potato starch (PS) with 1 of 13 proteogenic amino acids (AA) was carried out. Thermolysis was monitored thermogravimetrically (TGA) with involvement of differential thermogravimetry (DTGA) and calorimetrically (differential scanning calorimetry, DSC). Resulting dextrans were characterised with pH of their aqueous solutions, IR spectra and nitrogen content.

In the blends of alanine (Ala), aspartic acid (Asp), glutamic acid (Glu), glycine (Gly), isoleucine (Ile), threonine (Thr), and valine (Val) with starch (PS) esterification predominated. Arginine (Arg), histidine (His), and phenylalanine (Phe) reacted with PS preferably with involvement of their amino groups. In the blends with proline (Pro) and leucine (Leu), PS reacted with decomposition products of these acids.

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1. Introduction

It is known [1] that yellow dextrans, so-called British gums, are major products of thermolysis of starch. Water and small quantity of low molecular compounds such as carbon dioxide, methane, and ethene are the products of dextrinisation. It is also known that reaction of starch with carboxylic acids results in their esterification with starch [2]. However, proteogenic amino acids (AA) thermal reaction of which with starch has paid our attention, also undergo transformations under conditions applicable for thermolysis of starch. Diketopiperazines, α,β -unsaturated carboxylic acids, and amines are common products of their thermolysis. Formerly [3],

solid state thermal reactions of proteogenic AA with starch polysaccharides leading to novel dextrans [4] for selective depression in flotation of complex metal ores [5] were described. In those studies, investigated polysaccharide-to-AA proportion in the reaction mixtures was kept on the 10:1 (w/w) level. Low concentration of AA provided only limited insight in details of the reactions between starch and AA. Our former interpretation of results was based on studies on thermal decomposition of AA carried out by Rodante and Macosu [6] Rodante et al. [7] who ignored, to a certain extent, state of knowledge of the subject (see, for instance, original papers [8–11]). After elegant studies of thermolysis of proteogenic AA published recently [12–18], the thermal reaction of starch with AA can be re-examined. Thus, the title reaction on 1:1 (mole AA/mole of glucose unit) reaction mixtures of granular potato starch (PS) and AA was studied in this project.

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2. Experimental

PS Superior (16.0% of water content) was a commercial product isolated in Namysłów Potato Enterprise (Poland).

α -L-AA: alanine (Ala), arginine (Arg), histidine (His), isoleucine (Ile), aspartic acid (Asp), glutamic acid (Glu), leucine (Leu), phenylalanine (Phe) proline (Pro), threonine (Thr), tryptophane (Trp), and valine (Val) as well as achiral glycine (Gly) of >98% purity were purchased from Sigma, Lublin, Poland.

Homogenous blends of PS with AA were prepared by thorough shaking of equimolar ratio of both components followed by 30 min grounding in a mortar. In case of PS, the molar mass of a D-glucose unit was taken into account.

Dextrins were prepared by 1 h heating of blends prepared as above in porcelain crucibles at temperatures below these under which a deep thermal decomposition of blends took place. These temperatures were found from differential scanning calorimetric (DSC)/thermogravimetric (TGA) measurements described above. These temperatures ($^{\circ}\text{C}$) were as follows: PS + Ala–233; PS + Arg–210; PS + Asp–218; PS + Glu–193; PS + Gly–217; PS + His–254; PS + Ile–236; PS + Leu– 231; PS + Phe–195; PS + Pro–195; PS + Thr–217; PS + Trp–221; PS + Val–231. Thermolyses were performed in the ELF 11/6 EUROTHERM CARBOLITE oven (Hope, England) equipped with a digital temperature stabiliser providing stabilisation with the $\pm 0.5^{\circ}\text{C}$ precision. Elemental analysis for nitrogen was taken with a semi-micro-scale instrument of own construction operating according to the Dumas method [19].

TGA, differential thermogravimetric (DTGA), and DSC analyses were performed with simultaneous thermal analyser STA 409C of NETZSCH (Selb, Germany). Samples (approximately 20 mg) were placed in corundum crucibles non-hermetically closed with lids and heated in the air from 20 to 500°C at the $5^{\circ}\text{C}/\text{min}$ rate of the temperature increase. The thermograms recorded with a precision of $\pm 0.5^{\circ}\text{C}$ were analysed with a NETZSCH-TA-ANALYSIS software.

IR-spectra were recorded with 2.000 resolution in KBr discs with FTIR NEXUS NICOLET spectrophotometer (Madison, WI, USA) in the region of $4000\text{--}400\text{ cm}^{-1}$.

3. Results and discussion

Table 1 presents results of the thermogravimetric analysis of PS and its 1:1 (mole/mole) blends. TGA-gram of PS consisted of three effects and corresponding DTGA-gram showed two peaks.

The first effect in both diagrams certainly could be related to the loss of surface sorbed, capillary and included water [20]. Admixture of any AA with few exceptions (blends with Asp, Glu, and Pro) resulted in one additional distinguishable step of decomposition. One could assume that this additional step might originate from the thermal decomposition of admixed AA. Pattern of the blend with Asp did not seem to be any particular case because Asp itself decomposed in two steps. Using this argument, blends with Phe and Trp behaved exceptionally because pure acids decomposed in two steps, whereas when admixed to PS, they contributed to thermograms of PS with a single decomposition step. Comparison of data in Tables 1 and 2 revealed that initial decomposition of pure and admixed Arg did not change.

The decomposition point of Ala, Gly, Pro, Thr, and Trp in the blend with PS declined in respect to that of pure acid. Depression in either melting or decomposition point is a common symptom of contamination of one compound with another and it results from the formation of eutectics. It should be underlined that in PS blends with Asp, Glu, Ile, Leu, Phe, and Val decomposition of these AA begun at higher temperatures than in case of pure AA. This finding could speak in favour of stabilisation of AA due to formation of complexes with PS. Such interaction could involve hydrogen bonding between the hydroxyl groups of PS and negatively charged, dissociated carboxylic groups of AA. Also an interaction between positively charged ammonium groups of AA and lone electron pair orbitals of the oxygen atoms of the hydroxyl groups of PS could be taken into account. The second step could belong to the decomposition of the product of reaction of PS with AA. It is known that heating of carboxylic acids with starch resulted in esterification of these acids [2]. Except both acidic AAs, Asp and Glu, esterification of AA seemed to be unlikely because negatively charged deactivated carboxylate groups to esterification.

Behaviour of blends of PS with Asp and Glu could be tentatively accounted for esterification. The his-

Table 1
 Thermogravimetric characteristics (TGA and DTGA) of PS and its 1:1 (mole/mole) blends with AA

Amino acid	Decomposition step	TGA T_i^a (°C)	Δm^b (%)	DTGA T_p^c (°C)
None (PS)	I	35.3	16.0	72.3
	II	246.1	40.3 (54.3)	284.5
	III	302.8	30.6 (86.8)	
Ala	I	48.8	8.5	83.3
	II	233.3	31.5 (41.3)	
	III	268.5	26.4 (67.7)	258.0
	IV	316.2	19.1 (86.8)	291.9
Arg	I	47.4	5.3	76.6
	II	209.6	13.2 (19.7)	231.1
	III	250.0	30.4 (50.1)	288.8
	IV	340.8	23.7 (73.8)	490.5
Asp	I	45.7	5.2	87.3
	II	218.4	4.6 (11.0)	233.2
	III	238.0	8.2 (19.2)	252.6
	IV	259.4	24.5 (43.3)	285.1
	V	311.9	25.3 (69.0)	398.8
	VI	433.2	8.4 (77.4)	
Gly	I	42.7	8.3	84.9
	II	219.0	22.5 (33.7)	
	III	255.3	23.9 (57.6)	244.4
	IV	312.5	26.8 (84.4)	296.8
Glu	I	48.8	3.6	89.8
	II	193.0	73.2 (76.4)	208.1
Ile	I	54.9	7.0	81.2
	II	235.9	41.1 (50.1)	260.2
	III	266.7	24.2 (74.3)	293.7
	IV	303.2	20.4 (94.7)	
Leu	I	44.3	7.8	82.0
	II	230.7	44.8 (53.5)	263.2
	III	270.5	21.1 (75.5)	293.8
	IV	301.5	20.3 (95.8)	
Phe	I	52.2	4.4	87.6
	II	194.6	31.8 (37.5)	218.7
	III	232.7	31.2 (68.6)	289.4
	IV	311.3	17.4 (86.1)	
Pro	I	46.6	6.0	87.3
	II	195.1	56.0 (63.0)	231.1
	III	302.5	28.3 (91.3)	277.4
Trp	I	45.6	5.8	77.5
	II	221.3	14.1 (20.7)	242.3
	III	258.3	25.3 (46.1)	298.4
	IV	328.9	16.2 (62.4)	
Thr	I	47.7	3.2	91.4
	II	217.3	38.1 (33.5)	241.5
	III	254.2	26.7 (70.2)	294.0
	IV	326.6	18.1 (88.3)	
Val	I	40.2	8.0	78.7
	II	234.7	41.6 (54.2)	262.0
	III	280.2	24.3 (76.2)	294.5
	IV	306.2	19.4 (95.5)	

^a The initial temperature in °C.

^b The weight loss in the given decomposition step. Figures in parentheses report a total weight loss from the origin to the given point.

^c The peak temperature.

Table 2
DSC of PS and its 1:1 (mole/mole) blends with AA

Amino acid	T_0 (°C)	T_P (°C)	ΔH (J/g)
None (PS)	42.7	75.6	572.4
	256.4	270.4	69.1
	272.0	291.8	-226.1
	302.8	328.3	-1310.3
Ala	48.2	86.4	280.2
	243.9	259.0	106.3
	272.7	307.6	-607.3
	314.0	367.3	-943.7
Arg	52.1	81.6	267.0
	231.9	228.0	98.5
	271.4	318.6	-453.1
	350.1	394.4	227.3
	437.3	484.3	-174.1
Asp	43.9	88.0	262.6
	217.1	233.2	195.3
	241.7	252.6	237.9
	268.1	292.7	-285.4
	303.5	346.5	-901.2
Gly	57.4	85.6	304.6
	149.6	173.8	12.4
	195.7	247.2	155.1
	261.8	307.1	-575.7
	367.7	462.1	-958.1
Glu	48.1	90.2	192.7
	182.4	204.8	281.8
His	48.8	91.5	95.3
	231.8	257.0	-67.9
	269.1	308.2	-241.3
	330.8	446.2	-702.7
Ile	56.6	84.6	246.5
	242.9	260.2	193.1
	273.4	320.4	-562.7
Leu	57.9	83.4	269.7
	228.7	263.5	194.4
	276.8	321.2	-489.9
Phe	48.7	89.6	232.6
	186.6	208.2	-29.2
	215.8	222.6	29.7
	232.0	241.4	-50.2
	257.7	266.8	46.2
	283.1	300.5	-133.2
Pro	317.2	337.6	-113.6
	50.0	91.1	263.7
	172.7	210.0	32.1
	228.7	258.3	-444.2
	317.3	383.3	-442.1
409.2	421.7	-86.4	

Table 2 (Continued)

Amino acid	T_0 (°C)	T_P (°C)	ΔH (J/g)
Thr	69.0	92.7	131.9
	209.4	232.4	-28.5
	232.4	245.4	99.7
	258.9	263.9 (s) ^a	-
	275.5	303.9	-165.6
	329.2	442.1	-878.1
Trp	43.7	78.2	266.4
	201.6	241.3	-312.2
	271.0	291.3	-32.7
	294.9	308.6	-55.0
Val	315.7	323.8	-26.1
	47.9	80.4	266.3
	197.8	262.0	270.6
	273.5	280.2	-933.3
	280.2	321.6	-908.7

^a A shoulder.

tory of further decomposition of particular blends together with corresponding DTGA-grams might suggest that AA reacted with PS giving products which, frequently, were more thermally stable as indicated by initial temperatures, T_i , and weight loss, Δm , specified in Table 1. These values were frequently higher than relevant values for original PS and AA. Only for PS blends with Ala, Glu, Gly, and Pro heating resulted in a decrease in minimum temperature of DTGA peak and an increase in the weight loss. This might suggest that these acids did not react with PS but products of their decomposition could react either with PS or with resulting dextrans.

Fig. 1 presents DSC-grams for PS, given AA, and their 1:1 (mole/mole) blends. Inspection of these diagrams delivered essential arguments helpful in discussion of the reactions between these components.

Thus, in Fig. 1a DSC-grams for PS, Ala and their blend are compared. Decomposition of Ala and PS took place practically at the same range of temperature. Maximum in the DSC-gram of the blend appeared also in the same region but its pattern resembled neither Ala nor PS. DSC-gram of Ala consisted of two overlapped endothermic peaks. The maximum of the evidently complex peak in the DSC-gram of the blend fitted the shoulder of the decomposition peak of Ala. Because in this peak the pattern of the DSC-gram of PS could not be distinguished one could suppose that products of decomposition of Ala might

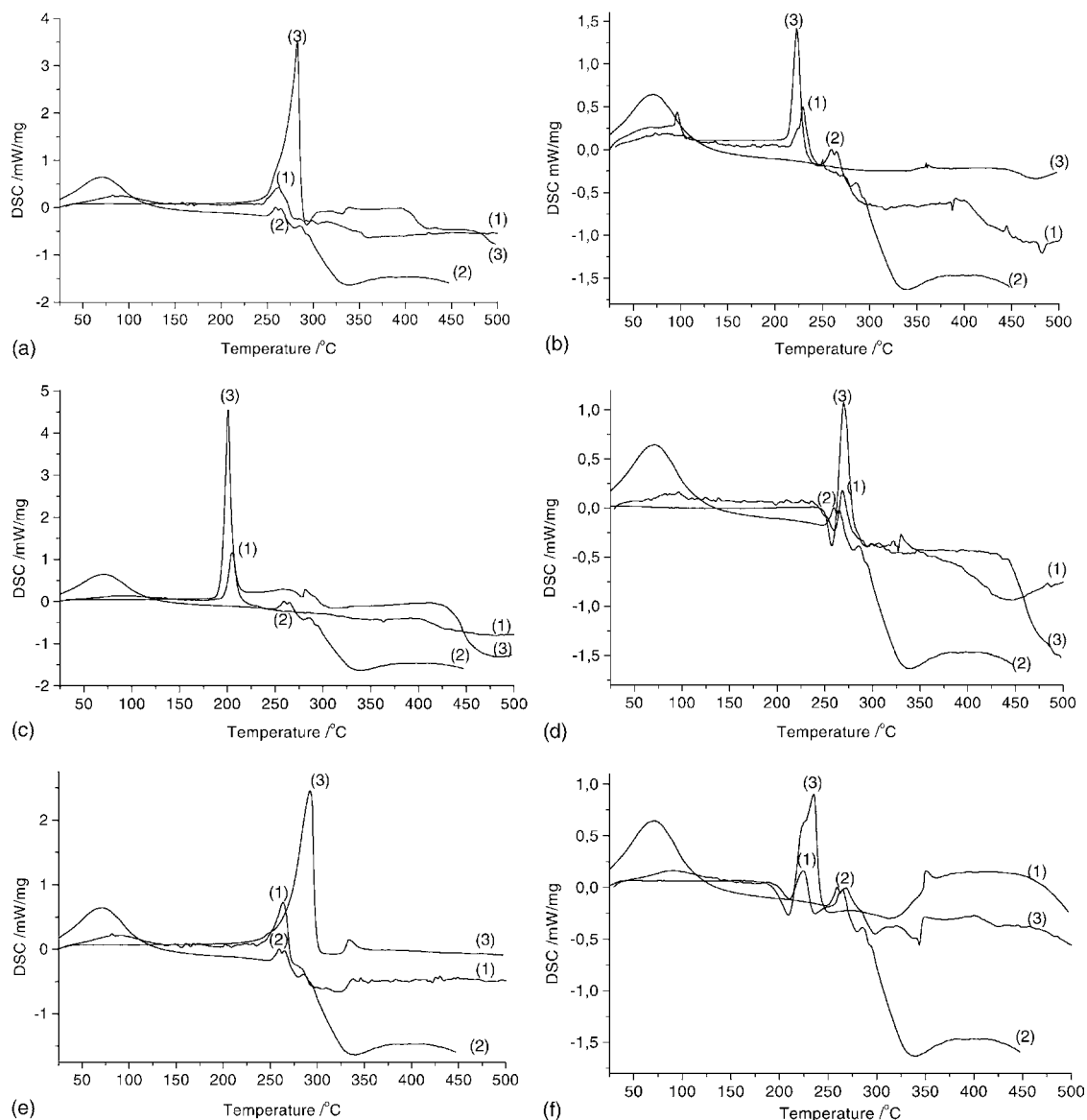


Fig. 1. DSC-grams of blends of PS with Ala (a), Arg (b), Glu (c), His (d), Ile (e), and Phe (f). In every diagram curve for the blend is denoted by 1. Curves denoted by 2 and 3 for PS and given AA, respectively, are also added for comparison.

react with PS. Comparison of relevant enthalpies of transitions for PS, Ala and Ala + PS, all being endothermic transitions, led to a striking facts. The value for Ala + PS was by over one order lower than that for Ala and approximately only by 70% higher than that for PS. It strongly suggested that decompositions of Ala and PS were assisted by exothermic reaction

of non-decomposed Ala with PS or by exothermic reactions between products of their decomposition.

Thermolysis of the PS–Arg blend gave a product decomposing endothermically after Arg and prior to PS. Apart from the main peak, the DSC-gram of that product had a shoulder on the low-temperature side of the main peak, which could suggest that a part of

non-decomposed Arg contaminated this product. The DSC-gram showed no fragments suggesting presence of unchanged PS (Fig. 1b). Also in this case, balance of enthalpies of transitions suggested intervention of exothermic processes.

The profiles of the DSC-grams of Asp and Asp–PS blend were almost identical. A low intensive DSC-gram of PS seemed to be hidden under intensive peaks of Asp. Enthalpy changes for the first endothermic transition for Asp and for Asp–PS blend were only slightly lower from value for the Asp–PS blend calculated as a sum of half of enthalpy found for PS and half of enthalpy measured for Asp. Thus, a slow reaction between Asp and PS could be postulated.

A similar diagnosis was valid for the behaviour of Glu and PS in their blend. The DSC-gram of the Glu–PS blend did not contain any fragment suggesting that unchanged PS survived heating with Glu. The first endothermic peak, the sole peak in the DSC-gram, was only slightly shifted to a higher temperature in respect to decomposition of pure Glu. The DSC-gram of the Gly–PS blend (Fig. 1c) suggested a slow reaction of Gly with PS. Small decrease in enthalpy of transition in respect to that calculated as above for the blend supported this point of view.

There was no evidence for a reaction of His with PS. First step in the DSC-gram of His was exothermic and such was the first step in the DSC-gram of its blend with PS. Points of transitions of His and PS were in the same region of temperature. Thus, endothermic stage of decomposition of PS could reduce the exothermic effect of transition of His (Fig. 1d). The pattern of PS in the DSC-gram of the blend might be hardly distinguished.

The main endothermic peak of decomposition of Ile had a low-temperature tail. The DSC-gram of Ile with PS (Fig. 1e) and Leu with PS consisted of main endothermic peaks with their maximum at temperature, which might correspond to the peak hidden under main peak of Ile and Leu, respectively. Peaks of PS could be hidden under these peaks because decomposition of PS and as well Leu occurred at the same temperature regions. The low-temperature patterns of these DSC-grams contained shoulders, which could belong to transition in PS.

Essential changes could be observed between DSC-grams of PS, Phe and their blend (Fig. 1f). Thermal transitions up to 300 °C in Phe were manifested

subsequently by an exothermic, two double endothermic, and exothermic peaks, respectively. In the DSC-gram of the Phe–PS blend the first peak of exothermic transition retained, following it a double endothermic peak turned into a single, symmetric peak, and the third endothermic, double peak took a more complex pattern. No peaks originating from PS could be distinguished.

DSC-grams of PS–Pro blends could not be accounted for superposition of DSC-grams of PS and Pro. Thus, a conclusion could be drawn that PS reacted with products of the Pro decomposition.

Similar analysis of DSC-grams of Thr, PS, and their blend allowed conclusion that PS could react with decomposing Thr. The pattern of DSC-grams of Trp, PS, and their blend suggested that both components could decompose independently. Analysis of DSC-grams for Val, PS, and their blend might indicate that Val reacted with decomposing PS, that is, with dextrin. Table 2 collects characteristics of DSC-grams discussed above.

Supplementary information on thermal reaction of PS with AA came from the balance of the weight loss during processes under study (Table 3).

Experimental weight losses from thermolyses of PS and AA provided calculation of theoretical weight losses for resulting dextrins. In some cases (blends of PS with Ala, Ile, Leu, Thr, and Val), the weight losses were lower than these calculated whereas in the others (blends of PS with Arg, Asp, Gly, Glu, Phe, Pro, and Trp) they were higher than these calculated. In the first case, one might assume that blending stabilised components thermally. In the second group of blends, destabilising interactions between PS and AA might be assumed. However, one should take into account that AA and PS did not react in the solid state. Water included in PS (16%) as well as water evolved on decomposition of PS and on reaction of PS with AA, for instance, esterification and on condensation of two molecules of AA into linear and/or cyclic dipeptides (diketopiperazines) could stimulate reactions. Thus, the course of decomposition of AA, that is condensation, decarboxylation and/or deamination could be essential for the result of the balance of the weight loss. Extent to which eutectic could be formed could also be an essential factor.

It has been shown [21] that several hours lasting heating of PS–AA blends to 200–220 °C generated

Table 3

Balance of the weight loss in the thermolysis of PS, AA and their 1:1 blends, nitrogen content and pH of their aqueous solutions

Weight loss in 1:1 (mole/mole) PS:AA blends (%)				Nitrogen content (%)		pH ^c
AA	Calculated ^a a	Found b	Δ a–b	Calculated ^b	Found	
Ala	68.1	57.9	10.2	5.5	4.6	7.20
Arg	35.9	43.6	–7.7	16.7	15.4	10.00
Asp	37.2	37.3	–0.1	4.7	5.6	3.64
Gly	45.8	46.4	–0.6	5.9	6.7	5.98
Glu	29.7	39.1	–9.6	4.5	7.4	3.43
His				13.2	15.8	7.91
Ile	75.3	62.6	12.7	4.8	3.5	6.58
Leu	74.8	65.9	8.9	4.8	5.7	6.96
Phe	56.0	62.9	–6.9	4.3	3.0	7.99
Pro	40.5	56.0	–15.5	5.1	5.7	9.51
Thr	68.4	64.8	3.6	5.0	5.7	7.43
Trp	35.9	39.4	–3.6	7.7	8.4	6.88
Val	68.4	66.0	2.4	5.0	4.9	6.56

^a Calculated as the sum of 0.55 part of the weight loss for PS in the steps I and II of its decomposition (Table 1) and 0.55 part of the weight loss of given AA (Table 2).

^b Nitrogen content in the original PS–AA blends.

^c Average of five runs.

so-called secondary food aromas. They were constituted of azaheteroaromatic compounds, derivatives of pyrazine, pyrrole, and pyridine [22]. Production of dextrans in this project took place at the same temperature region. It implied that analysis of the nitrogen content in these dextrans could be beneficial for interpretation of the processes under study. Results of elemental analysis for nitrogen in blends prior and after the thermolysis (Table 3) shed a light on the path of decomposition of AA and potential reaction of AA with PS.

One might see that dextrans obtained from blends of PS with Ala, Arg, Phe, and Val contained less nitrogen than original blend. Such result could be afforded solely when reactions proceeded with evolution of volatile low molecular nitrogen containing products such as ammonia, amines, cyanic acid and/or azaheterocyclic aromas. All these products but aromas were identified in course of studies of thermolysis of AA [8–18]. Dextrans obtained from the blends of PS with Asp, Gly, Glu, His, Ile, Leu, Pro, Thr, Trp, and Val contained more nitrogen than original blends. Such results could be afforded when transformation of AA involved either their condensation with evolution of water or decarboxylation, PS decomposed

faster than AA and their reaction products, and when reaction products of PS with AA decomposed without evolution of volatile nitrogen containing products. DSC-gram of Ala, PS and their Ala–PS blend showed that both components decomposed almost simultaneously and their blend, that is, eventual reaction products of PS with AA decomposed also in the same region. Arg decomposed prior to the product of its reaction with PS and PS decomposed after that product. Thus, one might suppose that the nitrogen loss could take place already on decomposition of Arg. However, decomposition of the reaction product of Arg with PS could also be taken into account. Phe transformed in the first endothermic step in order to decompose in the second step. Its third endothermic transformation took place at the same temperature region as the region of decomposition of PS. The DSC-gram of the Phe–PS blend strongly suggested reaction of Phe with PS and decomposition of that product. The elemental analysis documented that low-molecular nitrogen-containing products were formed on that decomposition. In the blend of PS with Val decomposition products of PS (dextrans) could react with Val and resulting modified dextrans lost low-molecular nitrogen-containing compounds.

The higher than calculated nitrogen content in dextrans from reactions of PS with Asp and Glu could result from decarboxylation of these AA as well as esterification of these acids with PS. The sequence of the transformations and related temperatures suggested that products of decomposition of these AA might react with PS. The same considerations applied to the blends of PS with His, Ile, and Leu led to the conclusion that dextrinised PS could react with AA and resulting products decomposed further without evolution of low-molecular nitrogen compounds. In blends of PS with Pro, Thr, and Trp these AA first transformed and the products of these transformations could optionally react with PS. The resulting dextrans held nitrogen and their decomposition produced nitrogen-free low-molecular products.

It was likely that acidic AA (Asp and Glu) could cause hydrolytic scission of PS into dextrans but deficiency of water may line out importance of these reactions. Moreover, they could also be esterified by PS. Aqueous solutions of dextrans from PS thermolysed with Asp and Glu were acidic (Table 3). Thus, one could assume that esterification and decarboxylation of these AA were not completed. Basic AA (Arg and His) could preferentially attack PS with involvement of their basic centres. Resulting glucosylamino acids could be precursors of azaheterocyclic rings. All remaining neutral AA could react either as acidic or basic AA.

A variety of possibilities of reactions could result from transformations without involvement of the carboxylic groups of these acids but reactions in which these acids were not fully consumed would lead to the same result. The $\text{pH} > 7$ measured for aqueous solutions of dextrans produced with Arg and His could be rationalised similarly. The $\text{pH} > 7$ noted in the aqueous solutions dextrans produced with Ala, Pro, Thr, and Phe suggested that the carboxylic groups were removed by decarboxylation or, eventually, they disappeared being involved in condensations or esterification. Amide moieties in diketopiperazines could be a site of a weak basicity.

Insight in the IR spectra of components and resulting dextrans was helpful in verification of these considerations. The spectra were taken for as-produced dextrans. They could be mixtures of non-reacted components, products of transformation of AA without

participation of PS, reaction products of AA with PS and their decomposition products. Therefore, the spectra provided only limited information.

IR spectra of dextrinised PS did not differ from the spectrum of original PS [1,23,24]. The sole essential changes were observed in the region of $980\text{--}1200\text{ cm}^{-1}$. Usually, the most intensive peak at 984 cm^{-1} in the spectrum of native PS after heating starch moved to 1020 cm^{-1} . This shift could be caused by a change in the status of the hydroxyl groups involved in interaction with sorbed and included water [25–29]. Thus, the following facts could be of particular interest in differential spectra of dextrans: (i) resemblance of the spectra of dextrans and substrates. The resemblance would inform that either substrates did not react or the reaction was incomplete. Lack of resemblance could inform that reagents completely transformed on thermolysis; (ii) presence of the pattern of starch in the differential spectra of (PS + AA) – PS with modifications of the peaks in the regions of $1020\text{--}1200$ and $1350\text{--}1450\text{ cm}^{-1}$. Such bands would inform that PS could be modified in reaction either with AA or products of their decomposition; (iii) appearance of the spectra in the region of $1600\text{--}1750\text{ cm}^{-1}$. The spectrum of PS contained one peak at 1650 cm^{-1} . In the same region, but always below 1700 cm^{-1} peaks of stretching vibrations of the carboxylate group could be seen. In a consequence of thermolysis of the PS–AA blends, one could anticipate that new bands in this region could appear. Appearance of the bands above 1700 cm^{-1} could be considered as an argument for the esterification of AA with PS because the vibrations of the carbonyl group in ester used to reside in this region. New bands generated in the region $1600\text{--}1700\text{ cm}^{-1}$ could be associated with the formation of the amide bands but amides could be formed without participation of PS, for instance formation of diketopiperazines; (iv) changes in the pattern of stretching vibrations of the amino groups. Vanishing of corresponding peaks in the spectra of basic AA would point to the involvement of the amino groups in reactions. In the contrary generation of such bands in the differential spectra of dextrans generated in the presence of neutral AA could speak in favour of the esterification of PS with these AA in consequence of which the NH_3^+ group was deprotonated.

In differential spectra of PS reacted with Asp, Glu, Ile, Thr, and Val bands at 1718.5, 1740, 1720, 1745, and 1716.5 cm^{-1} appeared. These bands were absent in spectra of corresponding AA and, of course, PS. This band could be assigned for stretching vibrations of the carbonyl group in esters. In the differential spectrum of the product from thermolysis of blend of PS with Ala, the band at 1621 cm^{-1} received a shoulder on the higher weight number side suggesting an overlapped band with its maximum slightly above 1700 cm^{-1} . Simultaneously, there were no bands in this spectrum, which could be assigned to stretching vibrations of the primary amino group. In the spectrum of Ala it was found at 3443 and 3543 cm^{-1} . Thus, Ala could be assumed to react with involvement of both its functional groups. Similar behaviour could be deduced in case of Gly. On thermolysis of PS with that AA, a band at 1670 cm^{-1} was generated and it covered a band at higher wave number located above 1700 cm^{-1} . Remaining AA definitely were not esterified by PS. It was likely that His and Phe reacted with PS with involvement of their amino groups. Their differential spectra did not show stretching vibrations of the amino groups which resided in the spectra of original acids in the region of 3530–3400 cm^{-1} . Because differential spectra were entirely different from the spectra of original AA and PS one could assume that after reaction moieties of these AA underwent further deep changes. Similarly, deep changes could be noted in the differential spectra of products from thermolysis of blends of PS with Pro and Leu. Definitely, no esters were formed but there was also no clear evidence that these AA reacted with PS with involvement of their amino groups. It could be likely that products of their thermal decomposition could react with PS. Because differential spectra of products of thermolysis of Trp with PS were very similar to the spectra of original Trp and PS one could assume that under reaction conditions Trp reacted with PS very slowly and concentration of the reaction products in the investigated sample was low. It should be underlined that in all differential (PS + AA) – PS peaks resembling spectrum of PS could readily be distinguished. However, because the pattern of these spectra, particularly in the regions of 1020–1200 and 1350–1450 cm^{-1} , significantly changed as compared to spectra of PS reaction of AA or products of their decomposition with PS or dextrins should be accepted in every case.

4. Conclusions

Esterification of Asp, Glu, Ile, Thr, and Val with PS was a predominating reaction and esterification of Ala and Gly with PS did not predominate over other reactions. Arg, His, and Phe reacted with PS preferably with involvement of their amino groups. Under reaction conditions applied Trp reacted with PS similarly as Ala, Gly, Arg, His, and Phe but very slowly. In the blends with Pro and Leu, PS reacted possibly with products of decomposition of these acids.

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