

Study of L-glutamic Acid Influence on the Thermal Behaviour of Native Wheat Starch

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By processing the mixtures of native wheat starch and L-glutamic acid, in dry roasting conditions, esterified dextrins are formed, which can be used as ingredients in functional foods, having the role of dietary fibers. This work presents the influence of L-glutamic acid additions in different proportions, on the thermal stability and on the oxidative decomposition of native wheat starch, using TG/DTG and DTA analysis. Samples of native wheat starch, L-glutamic acid and a series of five mixtures of these two have been taken under work. The thermal studies were conducted in dry roasting conditions, in dynamic regime, in the range of 35-500°C, in an open system, in air atmosphere, at a $\beta = 10^\circ\text{C}/\text{min}$ heating rate. Changes in the chemical structure of the samples, after heat treatment up to 225°C, were highlighted by FTIR analysis in the 600-4000 cm^{-1} domain. The results of the study show that, under dry roasting conditions, in the presence of L-glutamic acid, the thermal stability of the wheat starch decreases due to changes in the architecture of the granules. These changes were assigned to the action of the water formed during the L-glutamic acid transformation into pyroglutamic acid, respectively from the esterification of the latter with the dextrin formed from the starch. The data of this study has applications in practice for establishing some processing parameters of wheat starch and L-glutamic acid mixtures, to obtain dextrins with functional properties characteristic to dietary fibers.

Keywords: glutamic acid, native wheat starch, esterified dextrins, TG/DTG, DTA, FTIR

Due to their global availability and their affordable price, starches from different vegetal sources (wheat, corn, rice, potatoes, cassava, sago, etc.) are very attractive raw materials [1] both for food and non-food products. Starches are biopolymers, essentially consisting from α -D-glucopyranose cycles, linked by α -(1,6) and/or α -(1,4) glucoside bonds forming amylose chains (essentially linear polymer) and amylopectin (branched polymer) [2, 3] in different proportions. In their native state, starches are organized into granules with a complex semicrystalline structure, provided with an outer membrane [4, 5]. The range of uses of native starches expanded spectacularly by the application of physical, chemical and/or enzymatic treatments [6], which act more or less on the architecture of the granules [3] and lead to the obtaining of the ingredients called modified starches [7, 8]. Due to their improved functional properties [9,10], modified starches may be used as ingredients in refrigerated, frozen, instant or functional foods [11]. They are also used as emulsion stabilizers, as fat substitutes or for flavor encapsulation [12]. Dextrinization (pyroconversion) is one of the frequently used in practice ways of modifying starches, and the products thus obtained are called dextrins, pyrodextrins, British gums, etc. [10]. The dextrinization occurs by simply heating the native starch powders, in the absence or presence of small amounts of acid (which act as a catalyst) [13-15]. This method of thermal processing, whose major feature is that it runs without the addition of water, is known in practice as dry roasting [12]. Several authors have reported that rice starch [16], potato starch [17-19], or tapioca starch [20, 21], by undertaking hydrothermal treatment, are combined (esterified) with α -L-amino acids. It has been reported relatively recent that under dry

roasting conditions, dextrins obtained from corn starch [22] or potato starch [22-26], are esterified with amino acids, thus obtaining double modified starches (dextrinised and esterified). It was also highlighted that potato dextrins esterified with glutamic acid, and phenylalanine respectively, can be used as ingredients in functional foods with the role of dietary fibers.

Taking into account the complexity of the processes that occur during the heat treatment of native starches [27-29], and especially of modified starches [22-24], it is important to know their thermal behaviour, in order to avoid incorrect processing. The TG/DTG and DTA thermal analysis, carried out in open system, allows the simulation of thermal processing and provides useful data about the thermo-oxidative degradation of starches [27]. Complementary information with regard to the changes in the chemical structure of the product obtained after the application of the different treatments can be obtained by the spectrometric analysis in the IR range [30-33].

In general, the studies on the thermal behaviour of mixtures of starches with amino acids were held using starches which have been previously subject to hydrothermal treatment, i.e. have been gelatinized [17-21]. Data regarding the thermal decomposition of native wheat starch, in the presence of glutamic acid under conditions that simulate processing by dry roasting (without added water, open system, dynamic regime, air atmosphere) have not been found in the literature.

Considering these aspects, the aim of this work was to study the thermal behaviour of native wheat starch (WS) in the presence of L-glutamic acid (GA) under dry roasting conditions, respectively the acquisition of data regarding

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the influence of the composition of WS:GA mixture on this behaviour.

Experimental part

Materials and methods

L-glutamic acid (GA) $C_5H_9NO_4$ and native wheat starch (WS) with 10% humidity were supplied by Sigma-Aldrich and were used without further purification. Five WS:GA mixtures were prepared, in different molar proportions, relative to the dry mass: D102 (1.0:0.2), D104 (1.0:0.4), D106 (1.0:0.6), D108 (1.0:0.8) and D110 (1.0:1.0). In case of WS, the molar mass of the glucopyranose unit was taken into account. The preparation of the mixtures has been done according to *Kapusniak* method [34], by mixing both components followed by 3 min. grinding in an agate mortar.

TG/DTG and DTA Analyses

Samples of ~ 10 mg of WS, GA and WS:GA mixtures were simultaneously subject to the TG/DTG and DTA analysis, in uncovered platinum crucibles, using a STA 409 Luxx thermal analyzer produced by Netzsch-Germany. The measurements were carried out in non-isothermal conditions, in the 30-500°C range, in dynamic air atmosphere (100 mL/min), at a $\beta = 10^\circ\text{C}/\text{min}$ heating rate. An empty crucible was used as reference. The experimental data were processed using the Netzsch Proteus software. The thermogravimetric parameters were evaluated from the data provided by the TG and DTG curves and the thermal parameters have been identified from the DTA curves. All determinations have been repeated three times and the average values were used.

FTIR Analysis

A series of samples of WS, GA and WS:GA mixtures were treated in the thermal analyzer, under the same conditions, in the range of 30-225°C. Using a Bruker Vertex 70 spectrophotometer equipped with ATR cell (Attenuated Total Reflection) the FTIR spectra of the samples thus decomposed were collected, in the wave length range of 600-4000 cm^{-1} .

Results and discussions

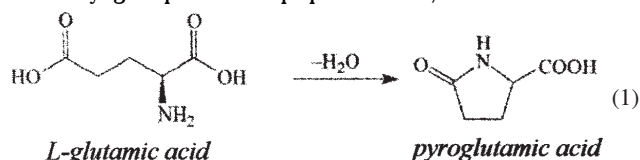
GA samples

The TG, DTG and DTA thermoanalytical curves, recorded for GA, are shown in figure 1, and the thermogravimetric

and thermal parameters evaluated from these curves are presented in table 1.

From the DTA curve it can be seen that over the temperature of 130°C an endothermic process begins, which up to 206°C is not accompanied by mass loss and which may be assigned to the melting of the sample. This assignment is in accordance with the data from the literature, where different values for the GA melting point falling within in the range of 199-225°C are reported [22, 35, 36]. The TG and DTG curves show that, in the range of 35-500°C, the studied sample has two well separated stages of decomposition, which occur after the melting stage.

The first stage of mass loss ($T_p = 213^\circ\text{C}$) is accompanied by an endothermic effect recorded on the DTA curve, with maximum intensity at 215°C. The recorded value of mass loss ($\Delta m_{\text{exp}} = 12.9\%$ - table 1), is very close to the one calculated for the elimination of one water molecule (12.25%). Therefore, this stage may be assigned to the intramolecular condensation process of the amino group and terminal carboxyl group of the GA, according to the equation (1). The elimination of one water molecule occurs and the pyroglutamic acid (PGA) [37-41], which has one carboxyl group and one peptide bond, is formed.



In the second stage of decomposition, which reaches the maximum speed at 307°C (table 1.), about 50% of the initial mass of the sample is lost. The data reported in the literature regarding to this stage, are generally obtained in inert atmosphere and indicate the occurrence of complex processes. Thus, in GA pyrolysis under isothermal conditions at 300°C, dehydration, deamination and decarboxylation processes were highlighted. At this temperature, unreacted GA (5%), PGA, pyrrolidinone, pyrrolidone, glutarimide and diketopiperazine as well as volatile compounds: water, ammonia, HCN and oxides of carbon were identified [42, 43]. Therefore, the endothermic effect ($T_p = 303^\circ\text{C}$) recorded on the DTA curve of the studied

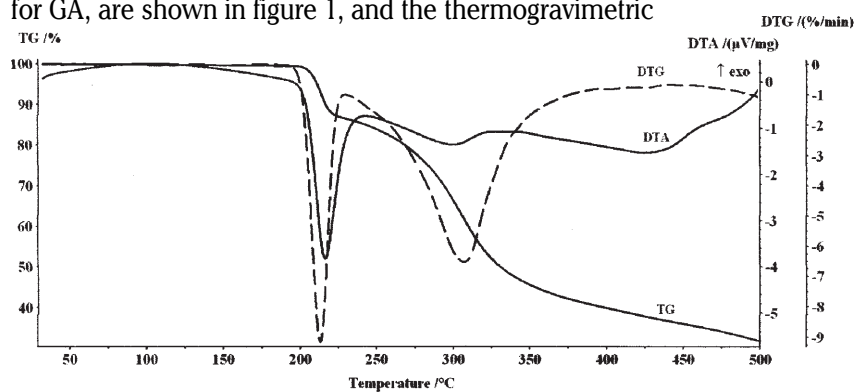


Fig. 1. Thermoanalytical curves of GA

Decomp. stage	TG/DTG results				DTA results	
	T_o^a (°C)	T_p^b (°C)	T_f^c (°C)	Δm_{exp}^d (%)	T_p^e (°C)	
I	206	213	230	12.9	215	endo
II	230	307	409	47.2 (60.1) ^f	303	endo, 328 exo
III	409	-	500	8.3 (68.4)		exo
				R = 31.6		

Table 1
THERMAL DECOMPOSITION
PARAMETERS OF GA OBTAINED
FROM THE TG/DTG, DTA DATA*

* The values represent the mean of three determinations; Decomp. = Decomposition; a - DTG onset temperature; b - DTG peak temperature; c - DTG final temperature; d - Experimental mass loss; e - DTA peak temperature; f - The date in parentheses report the total experimental mass loss measured from the beginning of the decomposition to the given point; R = Residual mass at the 500°C; endo = endothermic effect; exo = exothermic effect

sample may be assigned to the decomposition process of the PGA formed in the previous stage. The exothermic process ($T_p = 328^\circ\text{C}$) can be assigned to the thermal oxidation of the decomposition products of the PGA.

Above 409°C , the decomposition continues more slowly, without separation on the DTG curve and the residual mass recorded at the completion of the analysis represents 31.6% of the initial mass. The exothermic process that occurs over 440°C is not completed up to 500°C .

WS samples

Table 2 shows the thermogravimetric and thermal parameters of the WS sample evaluated from the TG, DTG and DTA thermoanalytical curves presented in figure 2 and figure 3.

The WS sample was subject to analysis without the addition of water, in solid state, and as a result, the heat treatment conditions correspond to dry roasting processing. The thermogravimetric data show that on the range of $35\text{--}500^\circ\text{C}$, WS presents three stages of decomposition separated on the DTG curve. The first stage of mass loss, accompanied by an endothermic process ($T_p = 98^\circ\text{C}$), is a physical dehydration of the WS [26].

After a thermal stability plateau, in the range of $268\text{--}339^\circ\text{C}$, a very fast stage appears, wherein the sample loses about half of the initial mass, followed by a much slower stage which is poorly separable on the DTG curve ($T_p = 362^\circ\text{C}$). At temperatures higher than 385°C , the decomposition of the sample continues slowly, without separation on DTG curve, so that the residual mass recorded at the end of the analysis, represents 23.5% of the initial mass. Reports in the literature show that in dry roasting conditions, the dextrinization of the starch occurs by depolymerization processes, i.e. the cleavage of the polymer chains (endothermic effect) and repolymerization processes, in which new connections between carbon atoms of glucopyranose cycles (exothermic effect) are formed. These links are different than those present in native starch [13, 44, 45]. Therefore, the endothermic effect, recorded from 150°C on the DTA curve of the studied sample, and which up to 268°C is not accompanied by

mass loss, can be assigned to the overlapping of the depolymerization and repolymerization processes that take place during the dextrinization of the WS. Above 268°C , the shape of the DTA curve of the studied sample is asymmetric and presents a series of endothermic processes, with peaks at 288°C , 299°C and 314°C , respectively an exothermic process with the maximum at 374°C . According to the data from the literature, the endothermic processes can be assigned to the chemical dehydration and to the thermal decomposition [27], with the thermal condensation of the hydroxyl groups of the starch chains, having as a result the formation of ether segments, water and other small molecules (CO , CH_4 , C_2H_2 , $\text{C}_2\text{H}_4\text{O}_2$) [46]. Also, dehydration processes of the neighboring hydroxyl groups from the glucopyranose cycles, which lead to the formation of $\text{C}=\text{C}$ bonds or to the cleavage of the cycles, have been highlighted. With the increase in temperature, benzene and furan rings are formed, linked together by $-\text{CH}_2-$ or $-\text{CH}_2-\text{O}-\text{CH}_2-$ residues, which results in the formation of a cross-linked system [27]. The exothermic process recorded on the DTA curve can be assigned to the thermal oxidation of the decomposition products of the sample. The asymmetrical shape of the curve suggests that the thermal oxidation processes begin before the end of the endothermic processes which means the exothermic processes partially overlap the endothermic ones [47]. These data show that the thermal decomposition of the WS takes place through very complex processes.

It can be seen that both WS and GA present one major decomposition stage with temperatures T_p at close values (312°C , 307°C respectively).

WS:GA mixtures samples

Thermoanalytical curves obtained for the WS:GA studied mixtures are shown in figure 2 and figure 3 and the parameters of the highlighted decomposition stages are presented in table 3. The assignment of stages has been done based on data obtained from the thermal analysis of the mixtures constituents, i.e. pure WS, respectively pure GA. The data contained in table 4, obtained from mass loss balance, provide more

Decomp. stage	TG/DTG results				DTA results	
	T_o^a ($^\circ\text{C}$)	T_p^b ($^\circ\text{C}$)	T_f^c ($^\circ\text{C}$)	Δm_{exp}^d (%)	T_p^e ($^\circ\text{C}$)	
I	48	88	150	9.5	98 endo	
II	268	312	339	45.9 (55.4) ^f	288, 299, 314 endo	
III	339	362	385	7.9 (63.3)	374 exo	
IV	385	-	500	13.2 (76.5)	exo	
						R = 23.5

* The values represent the mean of three determinations; Abbreviations and notations - see Tab. 1.

Table 2
THERMAL DECOMPOSITION PARAMETERS OF WS OBTAINED FROM THE TG/DTG, DTA DATA*

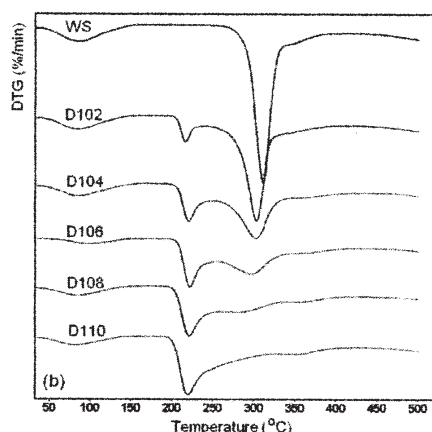
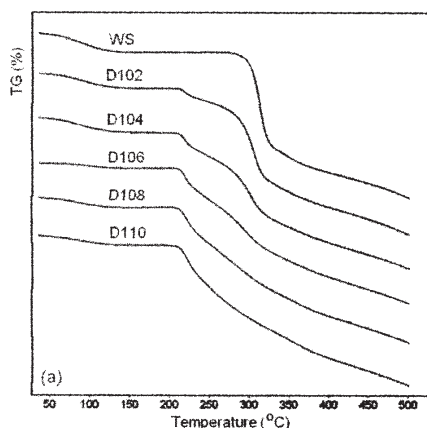


Fig. 2. Thermogravimetric curves of WS and WS:GA mixtures.

a) - TG curves; b) - DTG curves

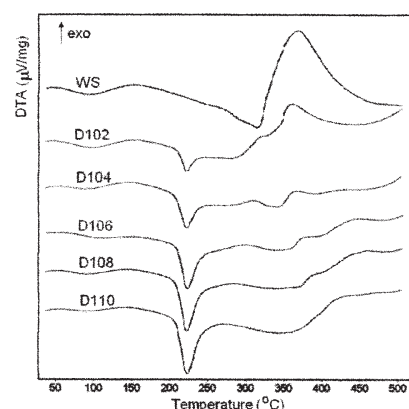


Fig. 3. DTA curves of WS and WS:GA mixtures

Samples	Decomp. stage	TG/DTG rezults				DTA rezults
		T _o ^a (°C)	T _p ^b (°C)	T _f ^c (°C)	Δm _{exp} ^d (%)	T _p ^e (°C)
D102	I	48	87	152	7.5	95 endo
	II	211	218	243	5.6 (13.1) ^f	220 endo
	III	243	303	330	38.5 (51.6)	316 exo
	IV	330	-	500	23.2 (74.8)	358 exo
R = 25.2						
D104	I	47	83	154	6.5	90 endo
	II	210	218	239	11.3 (17.8)	219 endo
	III	239	299	335	31.7 (49.5)	309 exo
	IV	335	-	500	20.2 (69.7)	364, 427 exo
R = 30.3						
D106	I	51	84	150	5.6	91 endo
	II	211	218	242	15.2 (20.8)	220 endo
	III	242	293	335	26.5 (47.3)	299 exo
	IV	331	-	500	17.1 (64.4)	372, 446 exo
R = 35.6						
D108	I	49	82	152	4.9	89 endo
	II	211	218	249	18.1 (23.0)	219 endo
	III	249	279	333	22.0 (45.0)	277 exo
	IV	333	-	500	22.5 (67.5)	382, 458 exo
R = 32.5						
D110	I	48	81	151	4.4	87 endo
	II	210	220	243	25.6 (30.0)	220 endo
	III	243	-	327	21.6 (51.6)	263 exo
	IV	327	-	500	18.6 (70.2)	429, 471 exo
R = 29.8						

* The values represent the mean of three determinations; Abbreviations and notations - see Tab.1.

Samples	A			B		C	
	Δm_{calc} (%)	$\Delta m_{\text{exp}} - \Delta m_{\text{calc}}$ (%)	Δm_{calc} (%)	$\Delta m_{\text{exp}} - \Delta m_{\text{calc}}$ (%)	R_{calc} (%)	$R_{\text{exp}} - R_{\text{calc}}$ (%)	
WS:GA	1	2	3	4	5	6	
0	1	2	3	4	5	6	
D102	7.9	- 0.4	2.0	3.6	24.8	0.4	
D104	6.8	- 0.3	3.5	7.8	25.8	4.5	
D106	5.9	- 0.3	4.6	10.6	26.5	9.1	
D108	5.3	- 0.4	5.4	12.7	27.1	5.4	
D110	4.7	- 0.3	6.1	19.5	27.5	2.3	

* The values are the mean of three determinations; A - calculated based on experimental data obtained in the first stage of decomposition of WS, and on the composition of the mixtures; B - calculated on the basis of equation (1) and the mixtures' composition; C - calculated based on experimentally obtained residue at 500°C, in WS respectively GA and on mixtures' composition; Δm_{calc} - calculated mass loss; Δm_{exp} - mass loss obtained experimentally; R - residue

information regarding the assignment of these stages.

The WS:AG mixtures subject to analysis present three decomposition stages, separated on the DTG curves. Based on data obtained from the thermal analysis of pure WS (table 2), it can be said that the first stage of decomposition of the mixtures (Note I - table 3) and the accompanying endothermic process are due to the elimination of WS moisture contained in the samples. From the balance-sheet data presented in table 4, col.1 and col.2, it can be seen that the weight loss values (Δm_{calc}), calculated for this stage, based on the mass decrease recorded for pure WS (9.5%) and the composition of the mixtures, are close to the ones obtained experimentally (Δm_{exp} - table 3). These results indicate that the first decomposition stage of the WS:GA mixtures, can be assigned exclusively to the dehydration of the starch. The endothermic process recorded on the DTA curves of the mixtures, which up to approx. 210°C is not accompanied by mass loss, can be assigned to the melting of the GA, respectively to the dextrinization of the WS from the samples.

For the second stage that occurs with mass loss, both temperatures T_o and T_p evaluated from the TG/DTG curves, as well as temperatures T_p evaluated from the DTA curves

of the mixtures, have values close to those recorded in the first decomposition stage of pure GA (table 1). Based on these parameters, this stage can be assigned to the transformation of the GA contained in the mixtures, in PGA, according to eq. (1) as shown in the analysis of pure GA. But comparing the values of the mass loss (Δm_{exp}) obtained experimentally for this stage, with the ones computed based on equation (1) and on the composition of the WS:GA mixtures (Δm_{calc}) (fig.4, col.3 and col.4) differences are found, that increase significantly with the increase of GA content in the samples.

In the third stage of decomposition, the WS:GA mixtures undergo the most significant mass loss. Both the mass loss values and the corresponding T_p temperature values (evaluated from the TG/DTG curves) are lower than those recorded in the major decomposition stage of pure WS and of pure GA samples and they decrease significantly (from 38.5 to 21.6%, respectively from 303 to 279°C) with the increasing of GA content in the samples. For the sample with the highest content in GA (D110) this stage of mass loss, is not separated on the DTG curve. Also, from the analysis of the DTA curves, it can be seen that with the increasing of GA content in the samples, the temperature T_p values, corresponding to the exothermic process that

Table 3
THERMAL DECOMPOSITION
PARAMETERS OF WS:GA MIXTURES
FROM TG/DTG AND DTA DATA*

Table 4
BALANCE OF MASS LOSS
RECORDED IN THE THERMAL
DECOMPOSITION OF INVESTIGATED
WS:GA MIXTURES*

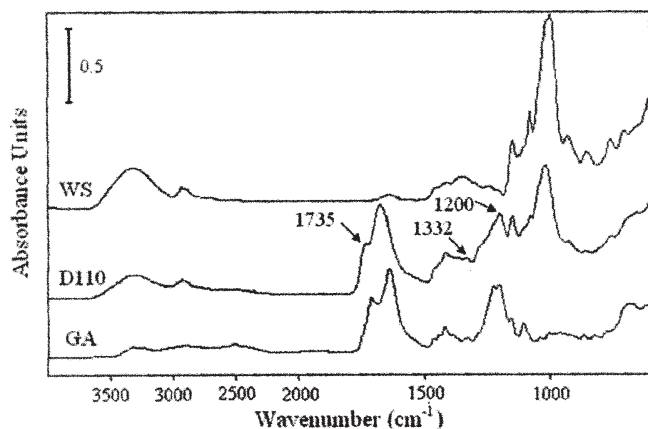


Fig.4. FTIR spectra of WS, GA and D110 thermally decomposed up to 225°C

WAVENUMBER (cm ⁻¹)			ASSIGNMENT [32, 33, 48, 49]
WS	GA	D110	
3317	3317	3313	OH, NH
2927	2899	2923	OH, CH
-	1710	-	C=O (carboxil)
-	-	1735	C=O (ester)
-	1638	1674	C=O (I peptide)
-	1463	-	N-H (II peptide)
-	1440	-	OH (carboxil)
-	1418	1416	N-H (peptide)
-	1328	-	C-O (carboxil)
-	-	1332	C(O)-O (ester)
-	1223, 1204	-	C-O (carboxil)
-	1154, 1105	-	C-O (carboxil)
-	-	1200	C(O)-O-C (ester)
1149-928	-	1149-927	Starch finger print

Table 5
ASSIGNMENT OF CHARACTERISTIC BANDS
FROM FTIR SPECTRA OF THERMALLY
DECOMPOSED SAMPLES UP TO 225°C

accompanies the third stage of decomposition of the studied mixtures, decrease from 316 to 263°C. These data suggest that with the increasing of the GA content in the samples, a more advanced overlap of II and III decomposition stages of the WS:GA mixtures occurs. Since a single stage is separated on the DTG curve of sample D110 (equimolar WS:GA mixture) in the range of 210-327°C, it can be concluded that the overlap of these stages became practically total.

It can be noted that the endothermic processes, with peaks in the range of 288-314°C, highlighted in the case of pure WS decomposing, are not separated on the DTA curves of the mixtures.

These differences in the thermal behaviour of the mixtures, compared to that of pure WS, lead to the hypothesis that, under the action of temperature, an interaction between the dextrin obtained from WS and the PGA formed from GA takes place. Taking into consideration the fact that the PGA has one carboxyl group and the dextrin has hydroxyl groups, under the given conditions, the esterification between these groups is possible [17, 24] i.e. the formation of an esterified dextrin. In order to verify this hypothesis, pure WS, pure GA respectively the WS:GA mixtures samples were thermally decomposed up to 225°C, temperature at which the dextrin and the PGA formation already occurred. The FTIR spectra of the decomposed samples were recorded. Figure 4 presents the spectrum recorded for sample D110 (WS:GA equimolar mixture) together with those of the pure WS and pure GA. The assignment of the characteristic bands extracted from these spectra is found in table 5.

In the FTIR spectrum of the GA sample, thermally decomposed up to 225°C, both bands formed due to the carboxyl group located at 1710, 1440, 1328-1105 cm⁻¹, and

those formed due to the peptide group (formed according to eq. (1) by intramolecular cyclization of the GA), located at 1638, 1463 and 1418 cm⁻¹ were identified. The presence of these bands in the spectrum of the sample confirms the transformation of the GA in PGA, a fact which is also marked out from the thermal analysis data. From the FTIR spectrum of the thermally decomposed D110 sample (under similar conditions), it can be seen that in addition to the characteristic bands of the peptide bond (1674 and 1416 cm⁻¹), specific bands from the ester group bonds, located at 1735, 1332 and 1200 cm⁻¹ appear. The starch fingerprint can also be found, situated in the range of 1149-927 cm⁻¹. These results confirm the hypothesis according to which, in the case of WS:GA mixtures, under the action of temperature, the hydroxyl groups of the dextrinised WS esterify the carboxyl group of the PGA formed from GA, and form an esterified dextrin.

In conclusion, in the case of WS:GA mixtures, in the range of 210-330°C, two chemical reactions take place that run with the removal of water as follows: the transformation of the melted GA in PGA and the esterification between the PGA and the dextrin formed by the WS, at an earlier stage. The quantity of water formed in those reactions increases equivalently to the content of GA in the mixture. By its strong plasticising action, the formed water contributes to the destruction of the architecture of the starch granules [50], which results in the decreasing of the thermal stability of the WS. This explains the fact that with the increasing in GA content in the investigated mixtures, the temperature at which the WS from these mixtures decomposes decreases, and a more advanced overlapping of stages II and III takes place. This overlap is responsible for the discrepancy between the calculated value (Δm_{calc}) and the recorded (Δm_{exp}) value of the mass loss in stage II, assigned to the

transformation of the GA in PGA (table 4, col. 3 and col. 4).

In the last stage, the decomposition of the studied mixtures is slower, without separation on the DTG curve and is accompanied by an extended exothermic effect. The mass loss recorded on the TG curves in this stage (stage IV - table 3) has values close to those obtained in the range of 339 - 500°C in the case of pure WS (stage III + stage IV - table 2). The shape of the recorded DTA curves suggests that, in the temperature range of 330-500°C, complex thermo-oxidative processes occur. For all WS:GA mixtures, the residue values (R - table 3) recorded on the TG curves are higher than for pure WS (R - table 2). As shown in the table 4, col. 5 and col. 6., the experimental values of the residue (R_{exp}) are also higher than those calculated (R_{calc}) based on the composition of the mixtures respectively, on the basis of the experimentally obtained residue in the case of pure samples. Though the WS decomposition in the presence of GA begins at lower temperatures, it progresses more slowly than in the case of pure WS, which suggests the changing of the decomposition mechanism.

Regarding the processing parameters of the WS:GA mixtures to obtain dextrins with functional properties characteristic to dietary fibers, the following specifications can be made. In practice, in order to obtain dietary fibers, the thermal processing must be conducted in such manner so the advanced thermal degradation of dextrin is avoided. The temperature at which this degradation begins is dictated by the GA contained in the processed mixture, by its effect of decreasing the thermal stability of dextrin. As a result, the maximum processing temperature is inversely proportional to the GA content in the mixture. In order to achieve the degree of esterification of the dextrin which provides the desired functional properties of the end product, the lower processing temperature can be compensated by a longer processing period.

Conclusions

The thermal analysis data indicates that the decomposition of the WS in the presence of GA, under conditions that simulate dry roasting processing (no added water, open system, dynamic regime, air atmosphere) takes place by a mechanism different from that of pure WS.

During the heat treatment of the WS:GA mixtures in various molar ratios, the following processes have been shown to happen: the elimination of moisture, the dextrinization of the WS, the melting of the GA followed by its transformation into PGA, the esterification of the PGA with the dextrin formed from the WS and an advanced stage of decomposition accompanied by the thermal oxidation of the decomposition products.

The data from the FTIR analysis confirmed the fact that during thermal processing by dry roasting, esterified dextrin is formed in the WS:GA mixtures and also the fact that, under the same conditions the GA transformed in PGA.

GA decreases the thermal stability of the WS: GA mixtures. GAs effect of decreasing the thermal stability of the mixtures was assigned to the water formed by the transformation of the GA in PGA, respectively by the esterification of the latter with the dextrin formed from the WS. Therefore, the significant difference between the thermal behaviour of pure WS and WS mixed with GA consists in the fact that the temperature values in stage III of major decomposition of the mixtures are lower than in the case of pure WS, i.e. the thermal stability of the latter is higher.

Also, the results of this study indicate the fact that the

amount of GA contained in the WS:GA mixtures controls the maximum temperature for the processing in order to obtain esterified dextrins with functional properties characteristic to dietary fibers.

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