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Optimization of resistant starch formation from high amylose corn starch by microwave irradiation treatments and characterization of starch preparations

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ABSTRACT

The effects of microwave irradiation on resistant starch (RS) formation and functional properties in high-amylose corn starch, Hylon VII, by applying microwave-storing cycles and drying processes were investigated. The Response Surface Methodology (RSM) was used to optimize the reaction conditions, microwave time (2–4 min) and power (20–100%), for RS formation. The starch:water (1:10) mixtures were cooked and autoclaved and then different microwave-storing cycles and drying (oven or freeze drying) processes were applied. The RS contents of the samples increased with increasing microwave-storing cycle. The highest RS (43.4%) was obtained by oven drying after 3 cycles of microwave treatment at 20% power for 2 min. The F, p (<0.05) and R^2 values indicated that the selected models were consistent. Linear equations were obtained for oven-dried samples applied by 1 and 3 cycles of microwave with regression coefficients of 0.65 and 0.62, respectively. Quadratic equation was obtained for freeze-dried samples applied by 3 cycles of microwave with a regression coefficient of 0.83. The solubility, water binding capacity (WBC) and RVA viscosity values of the microwave applied samples were higher than those of native Hylon VII. The WBC and viscosity values of the freeze-dried samples were higher than those of the oven-dried ones.

1. Introduction

Starch is the second most abundant carbohydrate in nature beside cellulose and is potentially digestible by the amylolytic enzymes secreted by the human digestive tract [1]. Starch has distinctive properties varying in molecular structure, organization of granule, morphological properties, crystallinity, gelatinization and pasting, and enzyme digestibility [2]. Since the starch residue is not determined in the excrements of humans, starch is considered to be absorbed completely by body [3]. However, there is a starch portion, called as resistant starch (RS), that cannot be digested in the small intestine, but fermented in the large intestine and produces short-chain fatty acids [4,5]. In last decades, RS has gained a great deal of interest because of its numerous health effects and functional benefits in foods [6]. The general behavior of RS is physiologically similar to that of soluble and fermentable dietary fibers [7]. It has been reported by many researches that the RS had positive health effects such as increasing laxation, reducing digestive tract cancers [8], lowering postprandial glucose response [9], preventing gall stone formation [10], lowering blood lipid levels [11], and increasing minerals absorption [5].

The RS has been classified into five general subtypes as RS_1–RS_5. The RS_1 includes physically inaccessible starch that is locked within cell walls and food matrixes. The RS_2 is composed of native starch granules that contain uncooked starch [12–15]. The RS_3 includes retrograded or crystalline starches formed after cooking [14–17]. The RS_4 includes chemically modified or repolymerized starches [13–15,18]. The RS_5 is an amylose-lipid complex starch [18,19]. The retrograded RS (RS_3) has high thermal stability that makes it to be stable in cooking conditions, so to be used as functional ingredient in foods [20].

Starch properties can be changed by heat and moisture applications that produce physical modifications within the granules [21]. The amount of RS formed during processing depends on the severity of the conditions such as moisture, temperature, number of heating/cooling cycles, autoclaving, storing, and drying. The

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producing of RS from different sources of native starch by using autoclaving-cooling-storing system is common [22–26].

There is an increasing trend to the use of microwave applications in food processing. The microwave energy is more efficient than the conventional heating and ensures homogenous operation in complete material and greater penetrating depth [27]. There are some studies related to the interaction of microwave energy with starch following the investigations undertaken by Muzimbaranda and Tomasik [28] and Lewandowicz et al. [29]. Some of these studies confirmed that the microwave cooking enhanced the digestibility of corn starch [30,31] while others showed that the microwave heating followed by cooling increased the gelatinization temperature [6,32] or induced the RS_3 formation [33].

Besides numerous findings, there is still no comprehensive study on effects of microwave energy on physicochemical, functional, and structural properties of various starches and resistant starch formation. Therefore, in this study, the effects of microwave irradiation on RS formation and functional properties in high amylose corn starch, Hylon VII (%70 amylose), by applying different microwave-storing cycles and drying (oven or freeze drying) methods were investigated. The Response Surface Methodology (RSM) was used to optimize the reaction conditions (microwave power and time) for the preparation of the RS samples.

2. Experimental

2.1. Materials

High amylose corn starch sample Hylon VII (about 70% of amylose) was supplied from Ingredion Incorporated (Westchester, IL, USA). The chemicals used in the study were of analytical grade.

2.2. Experimental design for the resistant starch (RS) formation

The influence of microwave power and irradiation time on the RS formation efficiency was measured by using a Response Surface Methodology (RSM). The RS content was selected as the dependent variable, where microwave power and irradiation time were chosen as the independent variables while generating the experimental design by Design Expert (Stat-Ease, Minneapolis, MN, USA).

Preliminary experiments were conducted to select the approximate range for each independent variable. The microwave powers from the highest as 800 W (100%) to the lowest as 160 W (20%) and the irradiation times up to 8 min were tested. As irradiation time, 4 min was found to be the upper limit for the highest power (100%) without ebullition of the samples. Therefore, the 9 conditions were generated in the main experimental design as the microwave power varied from 20 to 100% and the irradiation time varied from 2 to 4 min. The temperatures of the samples after microwave treatment changed between 66.0–99.6 °C for the lowest and the highest microwave power-time combinations, respectively.

2.3. Resistant starch (RS) formation

Native Hylon VII sample was suspended in distilled water (630 g: 6300 mL) and cooked for 45 min by stirring in a pan on an electric element to disperse the starch sample. The mixture was divided to 21 jars as equal amounts and autoclaved for 30 min at 121 °C. After autoclaving, the samples were cooled to 60 °C and then microwave irradiation (Fakir MW80200, Turkey) was applied at the conditions of designed experiment times and powers. Then the samples were stored in oven at 95 °C for 24 h. The microwave-storing cycle was repeated for three times. The samples were also collected at certain points; after cooking, autoclaving and 1st cycle of microwave-storing treatment. The samples were oven-dried at 50 °C or freeze-dried. The dried samples were ground to pass a 212 μm sieve and stored at room temperature until further analyses.

2.4. Resistant starch (RS) content determination

The RS contents of the samples were measured by using the Megazyme Resistant Starch Kit (Megazyme Int. Ireland Ltd. Co., Wicklow, Ireland) according to the Approved Method 32–40 [34]. In brief, the samples were incubated with α-amylase and amyloglucosidase (AMG) for 16 h at 37 °C to hydrolyze non-resistant starch to glucose. The RS was recovered by centrifugation and then dissolved in KOH and hydrolyzed to glucose with AMG. Glucose was measured with glucose oxidase/peroxidase reagent by spectrophotometer (Shimadzu UV Mini 1240). The results were reported as means of duplicate analyses.

2.5. Birefringence of starch samples

The birefringence of the starch samples were observed by polarized light microscope Olympus (BX53-P, Tokyo, Japan). Powder starch sample and distilled water were placed on the microscope slide with a glass coverslip. The field was then viewed under polarized light microscope.

2.6. Solubility and water binding capacity of starch samples

Solubility and water binding capacity (WBC) values of the starch samples were determined by using a method based on Singh and Singh [35] as modified by Ozturk et al. [23]. For each sample, 0.5 g was added to 5 mL distilled water and vortexed for 15 s every 5 min. After 40 min, it was centrifuged (Heraus Labofuge, Germany) at 2100*g* for 10 min. Supernatant and precipitate were dried at 100 °C separately. Solubility (%) and WBC (%) values were calculated as in Eqs. (1) and (2). The results were reported as means of duplicate analyses.

$$Solubility\,(\%) = \frac{weight\ of\ dry\ supernatant}{sample\ weight} * 100 \quad (1)$$

$$WBC\,(\%) = \frac{weight\ of\ wet\ precipitate - weight\ of\ dry\ precipitate}{sample\ weight} * 100 \quad (2)$$

2.7. Pasting properties of starch samples

Pasting properties of the starch samples were tested by using a Rapid ViscoAnalyzer (RVA 4, Newport Scientific, Australia). In this assay, 4 g (14% moisture basis) starch sample and 25 g distilled water (adjusted to correct for sample moisture) were placed in an aluminum canister. The RVA pasting curve was obtained by using a profile created for high amylose corn starches [23] by slight modification as the initial equilibrium at 30 °C for 6 s, heating to 95 °C over 5 min, holding at 95 °C for 10 min, cooling to 40 °C over 5 min and holding at 40 °C for 2 min. Cold viscosity, peak/maximum viscosity, breakdown and final viscosity values were evaluated with the data analysis software (Thermocline for Windows, Newport Scientific, Australia). The results were reported as means of duplicate analyses.

2.8. Statistical analysis

Data were analyzed by using one-way analysis of variance (ANOVA). When significant ($p < 0.05$) differences were found, Duncan's test was used to determine the differences among means.

Table 1
RS contents of treated Hylon VII samples for 1 and 3 cycles of microwave-storing and different drying.

Sample	Reaction conditions		RS content (%)			
	MP (%)	Time (min)	1 cycle		3 cycles	
			Oven-dried	Freeze-dried	Oven-dried	Freeze-dried
Cooked	–	–	32.1 f	30.5 bc	32.1 d	30.5 c
Autoclaved	–	–	33.3 e	28.8 c	33.3 d	28.8 d
5	20 (−1)	2.0 (−1)	38.4 a	30.4 b	43.4 a	34.6 a
7	100 (+1)	2.0 (−1)	37.3 bc	32.1 a	39.2 c	33.5 ab
3	40 (−0.5)	2.5 (−0.5)	35.9 de	32.1 a	43.3 a	33.5 ab
4	80 (+0.5)	2.5 (−0.5)	38.0 ab	31.1 bc	42.4 ab	32.8 b
1	60 (0)	3.0 (0)	36.7 cd	31.3 bc	39.3 c	33.5 ab
8	40 (−0.5)	3.5 (+0.5)	36.3 de	30.8 bc	39.8 c	33.3 ab
6	80 (+0.5)	3.5 (+0.5)	34.1 ge	31.8 bc	39.9 c	32.6 b
2	20 (−1)	4.0 (+1)	35.5 ef	31.6 bc	40.3 bc	34.5 a
9	100 (+1)	4.0 (+1)	34.9 fg	31.1 bc	38.3 c	33.5 ab

For each sample, means with different letters within each column are significantly different ($p < 0.05$).
Coded values are shown in pharentheses; RS, resistant starch; MP, microwave power.

Paired *t*-tests were carried out to compare the RS contents and other properties of oven-dried and freeze-dried samples, and also the samples treated for 1 and 3 cycles of microwave applications.

To describe the relationship between the RS (dependent variable) and microwave power and irradiation time (independent variables), the response values (RS content) were fitted by regression models using Design Expert (Stat-Ease, Minneapolis, MN, USA). Three-dimensional response surface plots were also developed.

3. Results and discussions

3.1. Resistant starch (RS) content

The experimental points generated by Design Expert Software, their coded values, and the observed responses (RS%) are shown in Table 1. The RS content of native Hylon VII sample was found as 42.7%. Native Hylon VII starch sample was in granular form and expected to include only RS_2, which could be degraded with sufficient heat treatment (around 150 °C) [23]. Total RS contents of the samples cooked for 45 min and autoclaved for 30 min at 121 °C prior to oven-drying were found as 32.1% and 33.3%, respectively. The samples which were freeze-dried after cooking and autoclaving had lower RS contents (30.5% and 28.8%, respectively) than oven-dried samples. Therefore, it was consistent that the cooking and autoclaving processes lowered the amount of natural RS_2 found in native Hylon VII while transforming RS_2 to thermostable RS_3 during drying periods by retrogradation. RS_3 formation showed increasing values with microwave-storing cycles after autoclaving by oven drying. Paired *t*-test revealed that the increasing the microwave-storing cycle (from 1 to 3 cycles) increased the RS contents regardless of drying conditions ($p < 0.05$). This increase showed that the microwave irradiation cycle was effective on RS_3 formation. Storing time (95 °C for 24 h) between microwave cycles resulted in longer incubation periods which improved the possibility of reaction among amylose chains, so that double helixes were formed to increase the RS [36,37]. The highest total RS values (43.4 and 43.3%) were obtained by oven drying after 3 cycles of microwave treatment at 20% (160 W) power for 2 min and 40% (320 W) power for 2.5 min, respectively.

The RS contents of oven-dried samples were higher than those of freeze-dried samples as revealed by paired *t*-test ($p < 0.05$). The higher RS contents of oven-dried samples were due to suitable conditions for retrogradation. During drying period at 50 °C in oven, the starch molecules can re-associate and form tightly packed structures stabilized by hydrogen bonding. These compact structures limit the accessibility of the digestive enzymes [7]. During freeze-drying, the starch chains have limited mobility and cannot freely interact to retrograde. Hence, the molecular structure is not as packed in as the structure formed during oven-drying and the former limits the accessibility of digestive enzymes to a minor extent. Similar results were also found in previous studies [23,38].

In order to describe the relationship between the dependent variable (RS) and the independent variables (microwave power and irradiation time), the empirical regression equations were developed by Design Expert Software. The response values (RS content) were fitted by first order polynomial (linear) regression models for both 1 and 3 cycles of microwave-storing treated and oven-dried samples. Whereas second order polynomial (quadratic) regression model was suitable for the freeze-dried samples which were subjected to 3 cycles of microwave-storing treatment. However, the RS data obtained for the samples produced by 1 cycle of microwave-storing and freeze-drying were not fitted by a regression model. ANOVA analyses for the models (of the RS contents of the samples) are presented in Table 2. As the RS data of the samples that were subjected to 1 cycle of microwave-storing and freeze-drying were not fitted by a regression model, ANOVA analysis could not be performed. The *F*, *p* (<0.05) and R^2 values of the models indicated that the selected models were reliable. The microwave power (MP as *A*) had significant effect on the RS content of the samples that were freeze-dried after 3 cycles of microwave-storing treatment ($p = 0.0208$), while did not significantly affect the RS contents of the samples that were oven-dried after both 1 and 3 cycles of microwave-storing treatments ($p > 0.05$). In case of the oven-dried samples, microwave irradiation time (t as *B*) had significant effect on the RS contents ($p = 0.0165$ for 1 cycle and $p = 0.0414$ for 3 cycles). However, microwave irradiation time did not significantly affect the RS contents of the freeze-dried samples treated with 3 cycles of microwave-storing ($p > 0.05$).

The final estimative response model equations for the RS contents of the samples, in terms of coded factors, generated by Design Expert Software are given in Eqs. (3)–(5). In the equations, Y_1, Y_2 and Y_3 are the RS contents (%) of the samples treated with 1 cycle of microwave-storing prior to oven-drying, 3 cycles of microwave-storing prior to oven-drying and 3 cycles of microwave-storing prior to freezer-drying, respectively. The *A* and *B* are the coded values of independent variables (microwave power and irradiation time, respectively).

$$Y_1 = 36.34 - 0.35A - 1.41B \quad (3)$$

$$Y_2 = 40.66 - 1.32A - 1.40B \quad (4)$$

$$Y_3 = 32.97 - 0.56A\text{-}0.060B + 0.024AB + 1.01A^2 \quad (5)$$

Eqs. (3)–(5) were plotted in Fig. 1a, b and c, respectively as 3D response surface plots. In general, it is expected in response

Table 2
Significance of the regression models (F values) and the effects of variables on RS contents of the samples treated for 1 and 3 cycles of microwave-storing prior to drying.

Source of variance	1 cycle			3 cycles					
	Oven-dried			Oven-dried			Freeze-dried		
	df	*F*	*p*	df	*F*	*p*	df	*F*	*p*
Linear									
A (MP)	1	0.67	0.4445	1	5.23	0.0622	1	13.72	0.0208*
B (t)	1	10.87	0.0165*	1	5.89	0.0414*	1	0.16	0.7117
Interaction									
AB	–	–	–	–	–	–	1	0.021	0.8928
Quadratic									
A^2	–	–	–	–	–	–	1	13.08	0.0224*
Residual	6			6			4		
Model	2	5.77	0.0401*	2	5.56	0.0431*	4	6.74	0.0457*
R^2	0.6528			0.6183			0.8250		

RS, resistant starch; MP, microwave power; t, irradiation time; df, degrees of freedom.
* Significant factors ($p < 0.05$).

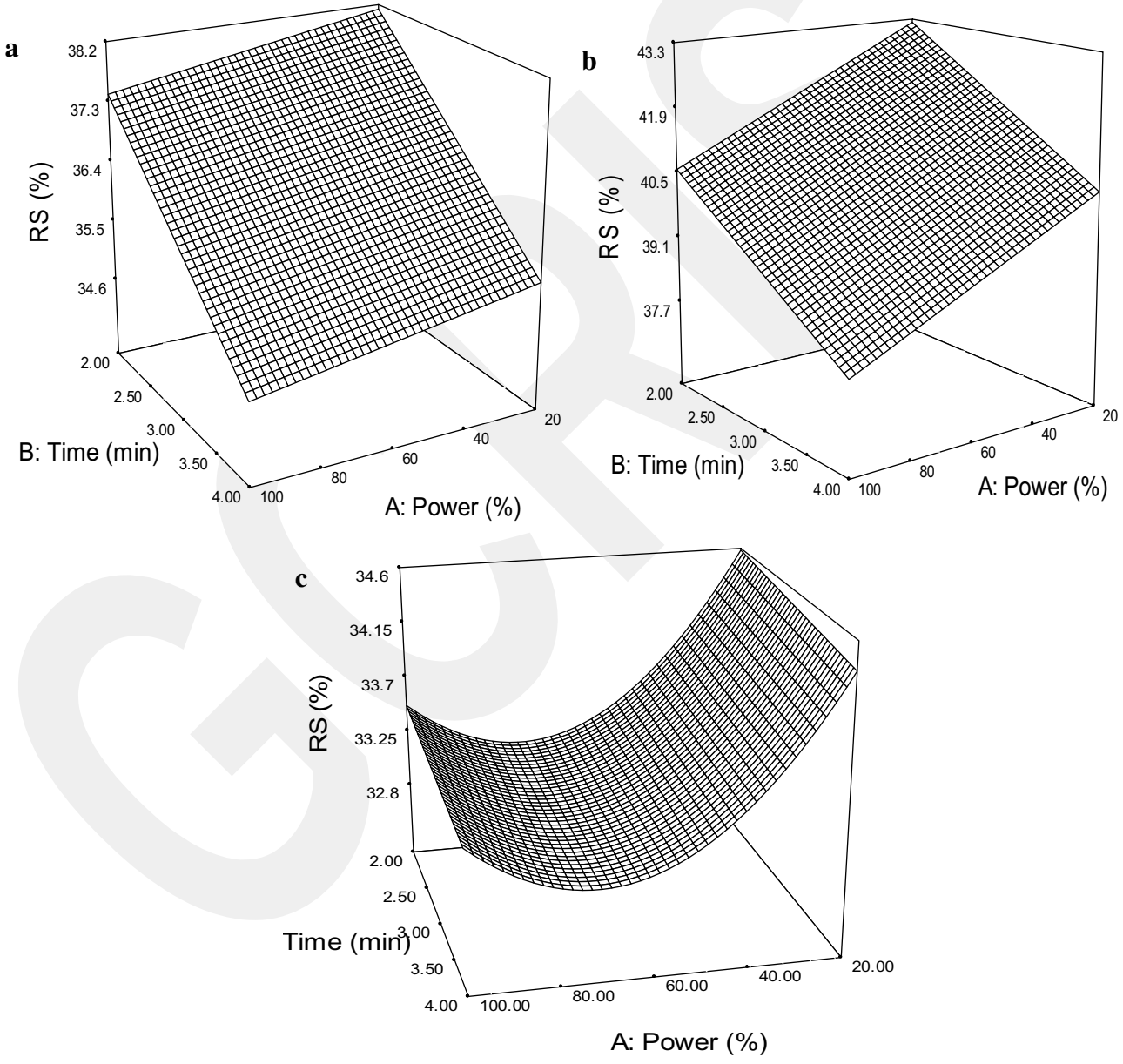

Fig. 1. 3D response surface plots of resistant starch (RS) content of the samples treated with 1 cycle of microwave-storing and oven drying (a), 3 cycles of microwave-storing and oven drying (b) and 3 cycles of microwave-storing and freeze drying (c) as a function of microwave power (%; A) and irradiation time (min; B).

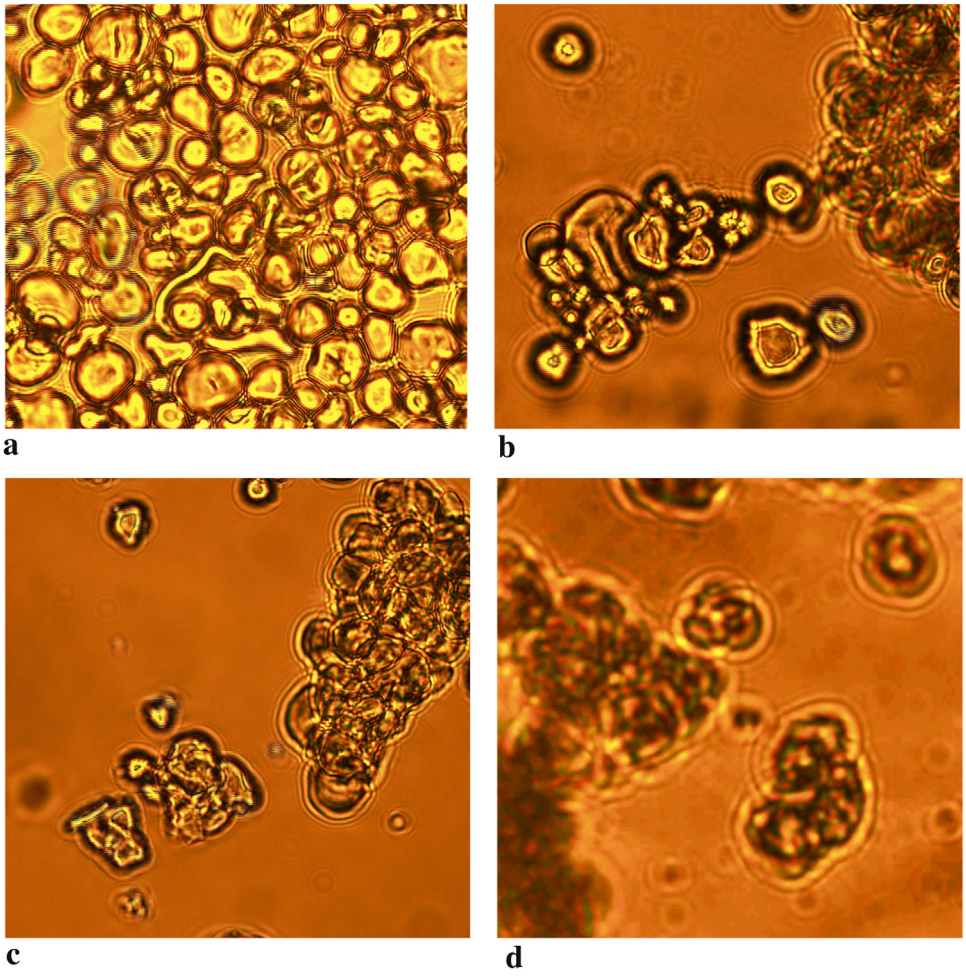

Fig. 2. Polarized light microscope images of the native Hylon VII (a) and heat treated starch samples (b: cooked, c: autoclaved, d: 3 cycles of microwave at 100% power for 4 min).

surface methodology that by changing the independent variables, the dependent variables reach to a maximum or minimum value (optimum value) and then start to decrease or increase. However, in some practical experiments, independent variables can be limited so the optimum point could not be defined within the designed surface method values [39]. It was observed in Fig. 1a and b that the RS contents changed by changing the irradiation time and power variables, however could not reach to an optimum point since the optimum point was probably out of the experimental designed values.

It is well known that the RS determination methodology [34] used in this study can not differ RS_2 from RS_3 and estimates only overall RS content, thus the RS_3 content could not be determined certainly. Degradation of RS_2, and therefore the formation of RS_3, increased with microwave treatment in low intensity conditions. However, it was thought that the high amount of RS_2 in granule (native Hylon VII) which could not transform to RS_3 under designed microwave irradiation conditions made the overall RS values to be high. This is also revealed by the birefirengence results. The polarized light microscope images of the selected starch samples are shown in Fig. 2. Even though, the samples were cooked for 45 min by stirring in a pan, autoclaved for 30 min at 121 °C, and microwave treated; the results showed that there were still granular starches or Maltese crosses in all heat treated samples. On the other hand, high degradation of RS_2 at higher power and longer time treatments might be the reason of reduced calculated values of the overall RS even the formation of RS_3 were increased at the same conditions. Therefore, the reason of not reaching a maximum RS value was predicted to because of the total RS content did not show apparent increase or decrease.

It was observed in Fig. 1c that the RS contents of the freeze-dried samples which were treated with 3 cycles of microwave-storing decreased to a minimum point and then increased. The higher RS values were determined for high microwave power-long time and low microwave power-short time treatments, while lower RS contents were found at average power-time conditions. It was thought that the high amounts of RS_2 in native Hylon VII starch was the reason of the high RS content at low intensity treatment conditions. Higher gelatinization temperatures (around 150 °C) of high amylose corn starches than those of regular starches was considered to be the reason of incomplete degredation of RS_2 at 121 °C in autoclave [7,23]. The increase in transformation of RS_2 to RS_3 with high intensity treatment conditions was probably the cause of increasing of RS after the minimum point.

3.2. Solubility and water binding capacity values of starch samples

The effects of microwave-storing treatments and different drying conditions on solubility and water binding capacity (WBC) values of Hylon VII sample for 1 and 3 cycles of applications are shown in Table 3. The solubility and WBC values of cooked, autoclaved and microwave-storing applied samples were higher than those of native Hylon VII ($p < 0.05$). The starch granules were

Table 3
Functional properties of the native and treated Hylon VII samples for 1 and 3 cycles of microwave-storing and different drying.

Sample	Reaction conditions		Solubility (%)				Water binding capacity (%)			
	MP	Time	1 cycle		3 cycles		1 cycle		3 cycles	
	(%)	(min)	Oven-dried	Freeze-dried	Oven-dried	Freeze-dried	Oven-dried	Freeze-dried	Oven-dried	Freeze-dried
Native	–	–	0.83 d	0.83 c	0.83 c	0.83 c	139.0 b	139.0 e	139.0 d	139.0 f
Cooked	–	–	1.46 bcd	1.60 bc	1.46 bc	1.60 bc	264.3 a	395.0 bc	264.3 bc	395.0 bc
Autoclaved	–	–	1.80 bc	0.87 c	1.80 ab	0.87 c	259.8 a	426.0 ab	259.8 bc	426.0 ab
5	20 (−1)	2.0 (−1)	2.55 a	2.50 ab	1.76 ab	2.09 ab	256.3 a	413.3 ab	256.0 bc	398.9 bc
7	100 (+1)	2.0 (−1)	2.15 ab	1.93 ab	2.24 a	2.15 ab	252.5 a	378.7 cd	244.6 c	435.7 a
3	40 (−0.5)	2.5 (−0.5)	1.72 bc	2.56 ab	1.66 ab	2.68 a	260.4 a	402.3 abc	254.8 bc	409.2 abc
4	80 (+0.5)	2.5 (−0.5)	1.80 bc	2.84 a	1.47 b	2.32 ab	270.0 a	402.0 abc	269.1 a	381.3 cd
1	60 (0)	3.0 (0)	1.47 bcd	2.59 ab	1.86 ab	2.34 ab	268.5 a	399.4 bc	260.4 bc	343.3 e
8	40 (−0.5)	3.5 (+0.5)	1.26 cd	2.92 a	1.89 ab	2.76 a	273.9 a	400.1 bc	247.0 bc	353.9 de
6	80 (+0.5)	3.5 (+0.5)	1.53 bcd	2.71 a	1.33 bc	2.93 a	272.4 a	361.0 d	248.7 bc	332.4 e
2	20 (−1)	4.0 (+1)	1.16 cd	2.15 ab	1.46 bc	2.38 ab	264.7 a	409.7 abc	249.3 bc	355.2 de
9	100 (+1)	4.0 (+1)	1.32 cd	2.85 a	1.82 ab	2.85 a	260.0 a	435.5 a	243.2 c	394.7 bc

For each sample, means with different letters within each column are significantly different ($p < 0.05$).
Coded values are shown in pharentheses; MP, microwave power.

Table 4
Pasting properties of the native and treated Hylon VII samples for 1 cycle of microwave-storing and different drying.

Sample	Reaction conditions		Oven-dried					Freeze-dried				
	MP (%)	Time (min)	CV (cP)	PV (cP)	B (cP)	FV (cP)	PT (°C)	CV (cP)	PV (cP)	B (cP)	FV (cP)	PT (°C)
Native	–	–	6 b	22 g	−22 i	62 e	95 a	6 e	22 f	−22 g	62 i	95 a
Cooked	–	–	17 a	194 bc	120 b	105 d	86 bcd	34 d	100 e	24 f	198 g	87 b
Autoclaved	–	–	16 ab	239 a	130 a	130 bcd	92 a	45 cd	522 a	107 a	1008 a	95 a
5	20 (−1)	2.0 (−1)	24 a	198 b	92 d	195 a	86 bcd	43 cd	149 d	35 e	322 d	87 b
7	100 (+1)	2.0 (−1)	22 a	153 f	70 gh	122 cd	88 bc	43 cd	167 cd	43 d	314 de	65 ef
3	40 (−0.5)	2.5 (−0.5)	20 a	153 f	67 h	144 bc	87 bc	51 bc	173 cd	43 d	360 c	71 cd
4	80 (+0.5)	2.5 (−0.5)	19 a	181 cd	82 e	166 ab	86 bcd	59 ab	180 c	61 c	312 de	69 cd
1	60 (0)	3.0 (0)	21 a	164 def	74 fgh	153 bc	86 bcd	40 cd	178 cd	44 d	293 e	68 de
8	40 (−0.5)	3.5 (+0.5)	19 a	171 de	70 gh	198 a	83 d	37 d	166 cd	44 d	326 d	65 ef
6	80 (+0.5)	3.5 (+0.5)	18 a	161 ef	78 ef	126 cd	84 bcd	37 d	153 cd	43 d	247 f	71 cd
2	20 (−1)	4.0 (+1)	19 a	174 de	76 efg	149 bc	83 d	37 d	166 cd	36 e	336 cd	70 cd
9	100 (+1)	4.0 (+1)	16 ab	192 bc	103 c	126 cd	86 bcd	62 a	211 b	72 b	417 b	72 c

For each sample, means with different letters within each column are significantly different ($p < 0.05$).
Coded values are shown in pharentheses; MP, microwave power; CV, cold viscosity; PV, peak viscosity; B, breakdown; FV, final viscosity; PT, pasting temperature.

Table 5
Pasting properties of the native and treated Hylon VII samples for 3 cycles of microwave-storing and different drying.

Sample	Reaction conditions		Oven-dried					Freeze-dried				
	MP (%)	Time (min)	CV (cP)	PV (cP)	B (cP)	FV (cP)	PT (°C)	CV (cP)	PV (cP)	B (cP)	FV (cP)	PT (°C)
Native	–	–	6 b	22 g	−22 g	62 e	95 a	6 d	22 e	−22 g	62 h	95 a
Cooked	–	–	17 ab	194 b	120 b	105 b	86 d	34 abc	100 c	24 c	198 c	87 b
Autoclaved	–	–	16 ab	239 a	130 a	130 a	92 abc	45 a	522 a	107 a	1008 a	65 f
5	20 (−1)	2.0 (−1)	21 a	99 d	32 de	129 a	87 d	36 ab	79 d	11 e	160 de	69 e
7	100 (+1)	2.0 (−1)	19 a	94 d	36 d	85 cd	92 abc	19 cd	67 d	9 e	118 g	75 cd
3	40 (−0.5)	2.5 (−0.5)	20 a	89 de	29 ef	110 b	90 bcd	30 bc	72 d	3 f	168 d	72 cde
4	80 (+0.5)	2.5 (−0.5)	19 a	90 de	32 de	95 bc	91 abc	29 bc	95 c	15 d	197 c	71 de
1	60 (0)	3.0 (0)	19 a	91 d	23 f	133 a	89 cd	28 bc	72 d	6 ef	128 fg	75 cd
8	40 (−0.5)	3.5 (+0.5)	16 ab	89 de	31 de	105 b	92 abc	21 bc	69 d	6 ef	136 fg	76 c
6	80 (+0.5)	3.5 (+0.5)	17 ab	76 ef	30 de	63 e	94 ab	25 bc	77 d	7 ef	141 ef	75 cd
2	20 (−1)	4.0 (+1)	16 ab	69 f	27 ef	72 de	93 abc	25 bc	68 d	7 ef	130 fg	73 cde
9	100 (+1)	4.0 (+1)	14 ab	117 c	55 c	88 c	93 abc	30 bc	156 b	48 b	278 b	72 cde

For each sample, means with different letters within each column are significantly different ($p < 0.05$).
Coded values are shown in pharentheses; MP, microwave power; CV, cold viscosity; PV, peak viscosity; B, breakdown; FV, final viscosity; PT, pasting temperature.

degraded by heat treatments and so free amylose chains dissolved easily and bound more water. The solubility values of microwave treated and freeze-dried samples were higher than those of their respective cooked and autoclaved samples. The WBC values of microwave treated samples did not change significantly ($p > 0.05$) as compared with those of cooked and autoclaved samples. The solubility values decreased with increasing of irradiation time in oven-dried samples for 1 cycle treatment while they were similar within the different time-power applications for 3 cycles of treatment. According to paired *t*-test, the solubility values did not change ($p > 0.05$) while the WBC values reduced ($p < 0.05$) by increasing the microwave-storing cycle. Decreasing of WBC could be caused by increasing of double helix formation among the amylose chains during longer storing period in 3 cycles treatment. There were significant ($p < 0.05$) differences between the drying methods in terms of solubility and WBC values which were determined by

paired *t*-test. This could be caused by different mechanisms of oven and freeze drying [37,40].

3.3. Pasting properties of starch samples

The effects of microwave-storing treatments and different drying conditions on pasting properties of Hylon VII sample for 1 and 3 cycles of microwave-storing applications are shown in Tables 4 and 5, respectively. All viscosity values of cooked, autoclaved and microwave applied samples were higher than those of the native Hylon VII ($p < 0.05$). This was in agreement with some of the previous studies [23,40] and was probably due to the excessive degradation of the starch granules and increase in solubility by heating. However, microwave application reduced the viscosity values as compared to the autoclaved samples ($p < 0.05$). It was reported that vibrations during microwave irradition caused to degrade glycosidic bonds [41], which could be the reason of viscosity reduction. There were significant ($p < 0.05$) differences between the drying methods and microwave-storing cycles in terms of viscosity values seen by paired *t*-test results. The cold viscosity values of oven-dried samples were lower than those of freeze-dried ones. The low cold viscosity was thought to be due to loose rearrangement of the starch chains with hydrogen bonds. The loose rearrangement of starch chains with a higher number of hydrogen bonds in oven-dried samples limited water absorption in early stage of the RVA test and resulted in lower cold viscosity [23]. This was parallel with the data of WBC. Similarly, the final viscosities of freeze-dried samples were significantly ($p < 0.05$) higher than those of oven-dried ones that confirmed the freeze-dried samples might form better and more stable gels.

The pasting temperature values of the treated starches were generally lower than that of the native Hylon VII sample. The reduction of the pasting temperature was caused by the degradation of the starch granules by heating. The diversity of decrease among pasting temperatures for the 1 cycle treatment were more considerable than for the 3 cycles treatment as compared to the native Hylon VII. According to these data, it was thought that the microwave irradiation served an effective function on degrading of starch granules and forming of new inter- and intra-molecular hydrogen bonds between amylose chains [20].

4. Conclusions

The digestibility of native Hylon VII starch decreased with the increasing number of microwave-storing cycles. The RS formation in studied conditions was found sufficient to design a model with response surface method. The RSM results showed that the microwave power affected the RS contents of the samples which were treated by 3 cycles of microwave-storing prior to freeze-drying significantly. Besides, the microwave irradiation time affected the RS contents of the samples which were oven-dried after the treatment of 1 and 3 cycles of microwave-storing significantly.

The solubility and WBC values of microwave treated samples were higher than native Hylon VII. The differences in the solubility and WBC values of the samples were found between the drying methods. Throughout drying, starch molecules formed tightly packed structures (RS_3 regions) highly stabilized by hydrogen bonding. The tightly packed structures limited the accessibility of water in oven-dried starches. During freeze drying, by instant vacuum of the ice molecules made the structure to become more porous in freeze-dried samples. These porous structures could increase the solubility and WBC of freeze-dried starches. The RVA viscosity values of the treated samples increased while pasting temperatures decreased as compared to native Hylon VII. The results showed that the microwave irradiation treatments increased the RS contents and also improved the functional properties of high amylose corn starch.

Conflicts of interest

The authors have declared no conflicts of interest.

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