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Production of buckwheat starch-myristic acid complexes and effect of reaction conditions on the physicochemical properties, X-ray pattern and FT-IR spectra

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ABSTRACT

In this study, the effect of reaction parameters on complex index (CI%) value of complexes formed between buckwheat starch (BS) and myristic acid (MA) was investigated. The temperature (60–90 °C) and MA to BS ratio (0.1–0.8 mmoL/g) were determined as the most effective parameters and their effect on CI% was evaluated using response surface methodology. The MA to BS ratio, temperature, and interaction between them had an influence on CI%. The CI% of BS-MA complexes increased with increasing MA ratio until a certain level of MA. Principal component analysis (PCA) was used for correlation analysis between parameters. Swelling power and paste clarity of BS decreased with complex formation while syneresis increased. Peak and final viscosity values of the BS-MA complexes were significantly lower than those of BS. FT-IR revealed the complex formation led to change in starch structure. The XRD confirmed the BS-MA complex formation but the BS-MA produced using 0.1 mmoL/g at 60 °C was not detected by XRD due to having low crystallinity, and expectedly, the lowest relative crystallinity value was achieved with this sample among complex samples. All results showed that the buckwheat might be an alternative starch source for starch-lipid complex formation.

1. Introduction

Starch, one of the main components of cereal-based foods, has a significant effect on the quality properties of processed foods [1]. Moreover, it is widely used as a functional ingredient in non-food industrial products such as pharmaceuticals, cosmetics, papers, and textiles [2]. Its properties of biodegradability, food grade, availability, low toxicity, gelling, binding, stabilizing agent, film forming ability etc. make starch a promising material [3,4]. Alternative starch sources are searched around the world due to the widespread utilization of starch in the food and non-food industry and the increasing demand for starch [5]. Common buckwheat (*Fagopyrumesculentum Moench*) can play a role as an alternative to conventional cereal with approximately 70% starch content [6]. Common buckwheat has been widely cultivated and consumed around the world [6,7]. Buckwheat starch (BS) was also a potential source for innovative food and non-food applications [8]. Among starches, BS has A-type crystallinity pattern, and its degree of polymerization of amylose is 1020–1380 [9]. In addition to this, retrogradation rate of BS is lower than that of corn and wheat starch due to the fact that it has lower degree of polymerization and moleculer weight [9]. Amylose content of BS ranged from 15% to 25% [10]. This ratio is generally higher than some starch types such as rice (8.6–24.8%) [11]. Although BS has these advantages, it has not been extensively studied as a modified starch.

The native starch has some drawbacks such as insolubility in cold water, lower gelatinization temperature and retrogradation which restrict it to utilize in food applications. Therefore, native starch is modified chemically (acid hydrolysis, oxidation, amylose-lipid complex formation, and cross-linking) and physically (pre-gelatinization, heat-moisture treatment, and annealing) to overcome these drawbacks [6,8]. These modifications might also cause changes in pasting, retrogradation, crystalline, physicochemical, functional and digestibility of starch. In addition to this, consumer concerns about the environment increase the production of chemically modified-starches with “clean label” [12]. Lipids are commonly used as food and environmental friendly chemicals in starch modifications [13]. The presence of

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endogenous lipid or the addition of lipid to starch causes amylose-lipid complex formation during food processing and storage [14,15]. It is well known that the hydrocarbon chains (apolar part) of lipid molecules can interact the hydrophobic cavity of amylose with hydrophobic interactions, thus amylose which is a linear glucan polymer can form a single helical inclusion complex (amylose-lipid complex) [1,16,17]. As a result, the inside of the helical cavity is hydrophobic while the outside of the amylose helix is hydrophilic [1]. Previous studies showed that amylopectin, which is branched polymer of starch, can also participate in starch-lipid complex formation [7,18–22]. However, the complex forming ability of amylopectin is considered to be much weaker than that of amylose [7,20]. Since amylopectin has many numerous and short branches, the necessary helical conformation of the backbone is hindered [7,20]. According to Hasjim et al. [18], the complex formation between amylopectin and lipid is prevented due to steric hindrance created by the highly branched structure of amylopectin molecules. In addition, they reported that amylopectin can have long chains using the debranching reaction, thus it can form complexes more effectively [18]. In previous studies, waxy corn starch [19] and waxy rice starch [20] were used to form complexes with lipids using debranching pretreatment. On the other hand, except for debranching treatment, a long branch chain of amylopectin can also form a helical complex with lipids. In literature, with the utilization of native waxy starch, amylopectin-lipid complex formations were observed [7,21–25]. In addition to this, Wang et al. [7] stated that amylopectin can form complexes with lipid, and carbon chain length of fatty acids was not determinative for the complexation of amylopectin. However, they reported that the interaction mechanism between amylopectin and lipid still remains unclear [7]. Limited experimental evidence showed that the major factor affecting the complex formation of amylopectin with lipid was the structural arrangement of amylopectin [24].

In recent years, researches related to starch-lipid complex formation are increased. The change in functionality resulting from the formation of the amylose-lipid complex has attracted the attention of the food industry, human nutrition and other disciplines [26]. Starch-lipid complexes were defined as a new fraction of dietary fibers by Codex Alimentarius in 2008 [27], therefore were of interest to nutrition science [1,28]. Due to their dietary fiber property, starch-lipid complexes led to a decrease in postprandial glycemic response and it can prevent metabolic syndromes such as type-2 diabetes, obesity, hypertension and heart disease [28,29]. Starch-lipid complexes were also used as fat replacer [30,31]. However, in recent years, the starch-lipid complexes are also used in other fields of science. Amylose-lipid complexes were used as carriers of bioactive molecules including essential fatty acids, lipophilic vitamins, unsaturated fatty acids, etc. [32]. They were used as a delivery system to protect compounds that are sensitive to oxidation and heat, such as unsaturated fatty acids [33–36]. In recent years, starch-lipid complexes are also used to produce biodegradable edible packaging films [32,37]. It is stated that, starch-lipid complexes improve the hygroscopic properties and mechanical strength of the biofilms which seems another advantage beside its advantage to overcome the environmental hazard posed by synthetic and non-biodegradable packaging [32]. Therefore, understanding the physicochemical and functional change occurred in starch as a result of starch-lipid complex formation has a great importance for the future studies, especially in the food, science, human nutrition, and other related sciences.

Previous studies showed that the physicochemical, functional, morphological, structure, thermal and digestibility properties of starch significantly changed with amylose-lipid complex formation [1,3,5,6,21,38–42]. Yassaroh et al. [41] reported that the starch-fatty acid complex showed higher pasting temperature, lower pasting viscosity and less swelling power. Wang et al. [7] stated that complex formation led to decrease in swelling power and viscosity behavior. In addition, many studies showed that the formation of amylose-lipid complex and their characteristics are influenced by reaction pH, time and temperature, type, chain length, saturation degree and concentration of fatty acid, and starch source [1,2,19,20,28,38,41,43,44]. These factors can be analyzed using optimization methods. There are some studies investigating the effect of different fatty acids (capric, lauric, myristic, palmitic, stearic, oleic) on the formation of starch-lipid complex using various starch sources [1,44,45]. According to these studies, myristic acid had the highest ability to form amylose-lipid complex [1,44,45]. Even though, there are several studies investigating the effect of the factors on amylose-lipid complex formation between various starches and lipids/fatty acids, to the best of author's knowledge there is no study on the amylose-lipid complex formation between buckwheat starch (BS) and fatty acids. Therefore, this study would be worthwhile to determine optimum reaction conditions to obtain desirable BS-fatty acid complexes for next studies.

Hence, in this study, BS was modified using MA to form BS-MA complexes. BS was isolated from buckwheat flour (BF) with high purity and reacted with MA under various reaction conditions (temperature, pH, MA to BS ratio and time). The optimum reaction condition (temperature and MA to BS ratio) to achieve the highest complex formation was investigated using response surface methodology (RSM). BS-MA complexes were characterized in terms of swelling power (SP), syneresis, paste clarity and pasting properties. X-ray diffraction and FT-IR analysis were also conducted to investigate the effect of modification on the chemical structure of the samples. In addition, the main effects of different variables on CI and the relationship among analyzed parameters was determined using PCA.

2. Materials and methods

2.1. Materials

Buckwheat flour (BF) was supplied from Helaliye Ltd. (Karaman, Turkey) and stored at 23 °C until analysis. Myristic acid (C14:0) was obtained from Sigma Aldrich (Germany). Other chemicals were of analytical grade unless stated otherwise.

2.2. Starch isolation

Buckwheat starch (BS) was isolated according to the method of Gao et al. [46] with some modification (Fig. S1).

2.3. Chemical composition of buckwheat flour and starch

Moisture, ash, total lipid and protein (N, 6.25) content of BF and BS were determined using AACCI methods of 44-15A, 08-01, 30-25.01 and 46-11A, respectively AACCI [47]. The starch content of the BF and BS were analyzed using Total Starch Kit (Megazyme, Ireland) according to the AOAC Method 996.11 [48]. Amylose-amylopectin ratio of BS was measured using Amylose/Amylopectin Assay Kit (Megazyme, Ireland).

2.4. Preparation of buckwheat starch-myristic acid (BS-MA) complexes

BS-MA complexes were produced according to Reddy et al. [3] with some modifications (Fig. S2).

2.4.1. Preliminary study: Selection of the most effective parameters in complex formation

Two-level factorial design (Design Expert, Stat-Ease, Minneapolis, MN, USA) was used to evaluate the significant conditions effecting starch-lipid complex formation between BS and MA. Based on the studies in the literature, the independent variables (low and high levels) were chosen as follows; temperature (T): 40–90 °C, pH: 5–8, incubation time (t): 0.5–24 h, and MA to BS ratio: 0.5–2 mmoL/g (Table 1). Complex index value (CI%) was chosen as the dependent variable to estimate starch-lipid complex formation efficiency. Experimental data were analyzed and the effects of independent variables (pH, T, t, MA to BS

Table 1
Experimental points and the response (CI (%) of the preliminary study.

Run	Reaction conditions				CI (%)
	pH	t (h)	MA to BS ratio (mmoL/g)	T (°C)	
1	8 (+1)	0.5 (−1)	2.0 (+1)	40 (−1)	53.37^{b}
2	5 (−1)	0.5 (−1)	0.5 (−1)	40 (−1)	36.93^{b}
3	5 (−1)	24 (+1)	2.0 (+1)	40 (−1)	47.92^{b}
4	8 (+1)	24 (+1)	0.5 (−1)	40 (−1)	42.04^{b}
5	5 (−1)	0.5 (−1)	2.0 (+1)	90 (+1)	94.97^{a}
6	5 (−1)	24 (+1)	0.5 (−1)	90 (+1)	92.35^{a}
7	8 (+1)	0.5 (−1)	0.5 (−1)	90 (+1)	83.46^{a}
8	8 (+1)	24 (+1)	2.0 (+1)	90 (+1)	79.29^{a}

Coded values are shown in parentheses.
a-b: For each sample, means with different letters within each column are significantly different ($p < 0.05$).
t: Incubation time; MA: Myristic acid; BS: Buckwheat starch; T: Reaction temperature; CI: Complex index.

ratio) on the CI% were determined.

2.4.2. Experimental design for the production of BS-MA complexes

Response surface methodology (RSM) was used to optimize the starch-lipid complex formation conditions between BS and MA to obtain maximum CI%. Based on the results of preliminary study, reaction temperature (T) and MA to BS ratio was selected as the most effective parameters for the formation of BS-MA complexes. Therefore, temperature (T) and MA to BS ratio were chosen as two independent variables while CI% was selected as dependent variable. Fifteen experimental combinations were created with three points in the center. The reaction was carried out at constant pH (pH 5) for a constant time (0.5 h). Temperature and MA to BS ratio varied from 60 to 90 °C and from 0.1 to 0.8 mmoL/g, respectively (Table 2).

2.5. Determination of complex index (CI%)

The degree of starch-lipid complex formation was determined using CI%. The CI% of the BS-MA complexes was determined according to the method of Tang and Copeland [16] with some modifications (Fig. S3). This method was based on the measurement of amount of iodine complexed with free amylose component of the BS-MA complexes relative to the native starch [42,49].

2.6. X-ray diffraction analysis

The crystalline structure of the native BS and BS-MA complexes were investigated using X-Ray diffractometer (Empyrean, PANalytical, Netherlands), operating at a current of 40 mA and voltage of 45 kV. Samples were exposed to CuKa radiation (wavelength; 0.15405 nm) and scanned between 2Θ ranges of 5–40°. Data were analyzed using software. The BS and BS-MA complexes were in powder form and were not pre-treated prior to analysis. The relative crystallinity (RC%) of samples was calculated using Origin Pro 2019 software (Origin Lab Corporation, USA) described method by Chao et al. [43].

2.7. Fourier transformed infrared spectroscopy (FT-IR) analysis

The FT-IR spectra of native BS and BS-MA complexes were obtained using Fourier Transformed Infrared Spectrometer (Thermo Nicolet Avatar 370). The spectra were obtained in the range of 4000–400 cm^{-1} at total scan numbers of 32 times.

2.8. Determination of pasting properties

Pasting properties of native BS and BS-MA complexes were measured using Rapid Visco Analyser (RVA 4500, Perten, Sweden) according to the AACC 76-21.01 method [47]. In brief, 3.0 g of starch sample (14% moisture basis) and 25 mL of water were placed in RVA canister. Heating-cooling process was applied using Std 1 profile (Fig.S3). Peak viscosity, peak time, final viscosity, and pasting temperature were obtained from curves.

2.9. Determination of swelling power

Swelling power (SP) of native BS and BS-MA complexes was determined by Reddy et al. [50] with slight modifications (Fig. S4).

2.10. Determination of syneresis

The syneresis of native BS and BS-MA complexes were determined according to method described by Singh et al. [51] with slight modifications (Fig. S5).

Table 2
Experimental points and the response (CI%) of RSM design.

Sample ID	Reaction conditions				CI (%)	SP (g/g)	Syneresis (g/g)			Paste clarity (T %)			
	pH	t (h)	MA to BS ratio (mmoL/g)	T (°C)			24 h	48 h	120 h	0 h	24 h	48 h	72 h
Native BS						20.70^{a}	0.50^{i3}	0.52^{h2}	0.61^{e1}	5.50^{a1}	4.79^{a2}	4.36^{a3}	4.19^{a3}
BS-MA-0.1-60	5	0.5	0.1	60	40.1^{e}	7.34^{de}	0.65^{cd3}	0.66^{d2}	0.71^{c1}	2.60^{b1}	2.02^{b2}	2.01^{b2}	1.96^{b2}
BS-MA-0.45–60	5	0.5	0.45	60	94.5^{a}	6.27^{fghi}	0.63^{de2}	0.64^{def2}	0.74^{bc1}	1.28^{g1}	1.18^{e23}	1.19^{f2}	1.16^{fg3}
BS-MA-0.8-60	5	0.5	0.8	60	95.0^{a}	6.26^{fghi}	0.63^{de3}	0.68^{cd2}	0.74^{bc1}	1.62^{e1}	1.46^{d2}	1.46^{e2}	1.49^{d2}
BS-MA-0.275–67.5	5	0.5	0.275	67.5	78.5^{c}	6.37^{fghi}	0.62^{def2}	0.61^{efg2}	0.73^{bc1}	1.52^{f1}	1.38^{d1}	1.41^{e1}	1.39^{e1}
BS-MA-0.625–67.5	5	0.5	0.625	67.5	94.5^{a}	5.62^{i}	0.56^{h2}	0.61^{efg2}	0.74^{bc1}	1.05^{h1}	1.03^{fg1}	1.04^{gh1}	1.06^{gh1}
BS-MA-0.1-75	5	0.5	0.1	75	46.3^{d}	6.90^{defg}	0.67^{bc12}	0.66^{de2}	0.72^{bc1}	2.15^{c1}	1.82^{c2}	1.75^{c2}	1.81^{c2}
BS-MA-0.45-75	5	0.5	0.45	75	94.7^{a}	5.98^{hi}	0.58^{gh2}	0.57^{g2}	0.67^{d1}	1.11^{h1}	1.01^{fg2}	1.01^{h2}	1.01^{h2}
BS-MA-0.45-75	5	0.5	0.45	75	94.6^{a}	6.05^{ghi}	0.57^{gh2}	0.57^{g2}	0.67^{d1}	1.09^{h1}	1.02^{fg1}	1.00^{h1}	1.00^{h1}
BS-MA-0.45-75	5	0.5	0.45	75	94.5^{a}	5.92^{i}	0.58^{gh2}	0.58^{g2}	0.66^{d1}	1.11^{h1}	1.02^{fg2}	1.00^{h2}	1.02^{h2}
BS-MA-0.8-75	5	0.5	0.8	75	93.9^{a}	6.82^{efgh}	0.58^{fgh2}	0.59^{fg2}	0.65^{d1}	1.34^{g1}	1.19^{e2}	1.18^{f2}	1.18^{f2}
BS-MA-0.275-82.5	5	0.5	0.275	82.5	86.5^{b}	7.70^{d}	0.61^{efg2}	0.63^{def2}	0.72^{bc1}	1.11^{h1}	1.00^{g2}	1.00^{h2}	0.98^{h2}
BS-MA-0.625-82.5	5	0.5	0.625	82.5	95.0^{a}	7.06^{def}	0.63^{de3}	0.65^{de2}	0.74^{bc1}	0.96^{i1}	0.89^{h2}	0.88^{i2}	0.87^{i2}
BS-MA-0.1-90	5	0.5	0.1	90	86.1^{b}	10.12^{b}	0.70^{ab1}	0.71^{bc1}	0.73^{bc1}	1.96^{d1}	1.79^{c2}	1.62^{d3}	1.72^{c23}
BS-MA-0.45-90	5	0.5	0.45	90	95.0^{a}	8.59^{c}	0.72^{a1}	0.73^{ab1}	0.75^{b1}	1.15^{h1}	1.11^{ef1}	1.09^{g1}	1.12^{fg1}
BS-MA-0.8-90	5	0.5	0.8	90	94.6^{a}	8.52^{c}	0.69^{ab3}	0.76^{a2}	0.82^{a1}	0.78^{j1}	0.75^{i1}	0.77^{j1}	0.75^{j1}

a-j: For each analysis, means with different letters within each column are significantly different ($p < 0.05$).
1-3: For each analysis, means with different numbers within each row are significantly different ($p < 0.05$).
BS: Buckwheat starch; MA: Myristic acid (0.1, 0.275, 0.45, 0.625, 0.8 mmol/g); t: Incubation time; T: Reaction temperature (60, 67.5, 75, 82.5, 90 °C); CI: Complex index; SP: Swelling power; T%: Transmittance.

2.11. Determination of paste clarity

Paste clarity of BS and BS-MA complexes pastes were measured using the method described by Nemţanu et al. [52] with slight modifications (Fig. S6).

2.12. Statistical analysis

The data were analyzed by one-way analysis of variance (ANOVA) followed by Duncan's multiple-range tests with significance level of 5% ($p < 0.05$), using the IBM SPSS Statistics version 24.0 (SPSS Inc., Chicago, IL). Paired *t-test* was performed to compare the properties of samples produced by two-level factorial design.

In the preliminary experiment part, a two-level factorial design with 2^3 experimental trials was carried out for the evaluation of relationship between the CI% (dependent variable) and independent variables (pH, temperature, time, and MA to BS ratio). The response values (CI%) were processed using Design Expert (Stat-Ease, Minneapolis, MN, USA). According to results of two-level factorial design, RSM was used to optimize the reaction conditions. The effect of independent variables (T and MA to BS ratio) on the CI% of the samples was determined by regression equations created by Design Expert program. In addition, Pearson correlation analysis and principal components analysis (PCA) were performed to investigate the correlation of analyzed parameters and variables among each other using XLSTAT (Version 2014.5.03, Addinsoft, NY, USA).

3. Results and discussion

3.1. Composition of BF and BS

Total ash, protein, fat and starch content of BF were 1.95%, 11.65%, 3.52% and 70.91%, respectively. Similar results were stated in the literature. Bahmanyar et al. [53] reported the ash, fat and protein content of buckwheat flour as 1.40%, 3.44% and 9.39%, respectively. Based on the study of Wang et al. [54], starch content of buckwheat flour sample was 67.41%. Isolation of starch from buckwheat flour caused significant decreases in ash, protein and fat contents, as expected. Ash, protein, fat, and starch content of BS were 0.09%, 0.34%, 0.47% and 92.80%. These results agree with the study of Liu et al. [6]. Amylose content of BS was 18.4%. Slightly higher amylose content values were found in the literature [6,8,55]. This may be due to varietal difference.

3.2. The most effective parameters in complex formation

The experimental points produced using two-level factorial design for the selection of the most effective parameters in complex formation, their coded values, and the observed responses (CI%) are presented in Table 1. The difference between CI% of samples produced at the same reaction temperature and different pH values (pH 5 and 8) was not significant ($p > 0.05$), according to the paired *t*-test. For example, the CI % of BS-MA complexes produced at 40 °C and pH 5 were 36.93% and 47.92%. On the other hand, the BS-MA complexes produced at the same temperature and pH 8 had 53.37% and 42.04% CI% values (Table 1). Similarly, Yotsawimonwat et al. [20] investigated the pH effect on complex formation between debranched waxy rice starch and decanoic acid. In addition to this, they reported that the extent of complex formation remained constant between pH from 5 to 7.

Similar to utilization of different pH values, different incubation times (0.5 and 24 h) at the same temperature for the complex formation did not significantly affect the CI% value of samples (Table 1). The samples produced at 90 °C for 0.5 h had 94.97% and 83.46% and the other samples (90 °C, 24 h) had 92.35% and 79.29% CI% values. Reddy et al. [3] also observed that the complex formation between native high amylose corn starch and stearic acid was not significantly affected by changing incubation time from 6 to 12 and 24 h. There are many studies in the literature that observed complex formation for different times such as 2 min [38], 8 min [28], 30 min [42,56] or 48 h [2]. However, in our study, the complex formation for 30 min reached a plateau and above 30 min incubation time did not affect the CI%.

At the same reaction temperature (40 and 90 °C), the CI% of the samples produced using different MA to BS ratio were not significant ($p > 0.05$). Kawai et al. [38] investigated that the effect of fatty acid concentration on CI% of starch-fatty acid mixture and reported the CI% increased as the amount of fatty acid increased until optimum fatty acid concentration. Similar result was reported by Chao et al. [43] in maize starch-lauric acid complex. In our study, it seems that MA to BS ratio (0.5 mmoL/g) might be higher than the optimum lipid concentration for BS-MA complex formation. In other words, MA to BS ratio (0.5 mmoL/g) might be higher than the fatty acid level at which BS-MA reaches its maximum complex index value.

On the other hand, the CI% of the samples produced at 40 °C had significantly ($p < 0.05$) lower than those produced at 90 °C, as revealed by paired *t*-test ($p < 0.05$). It was indicated that the increase in heating temperature enhanced the starch-lipid complex formation. According to Seo et al. [2], the increase in reaction temperature led to rise in starch mobility, and expectedly, physical contact between starch and lipid facilitated. Similar trend was also observed in amylomaize-fatty acid complexes produced at 30, 50 and 70 °C by Marinopoulou et al. [44]. Some reports showed that the amylose-lipid complex formation was occurred at low temperature as low as 30 °C [28,42,44,57]. On the other hand, gelatinized starch was extensively used in amylose-lipid complex formation [21,23,28,56]. According to Chang et al. [23], utilization of gelatinized starch in amylose-lipid complex formation provided more leaching amylose for complex helix formation.

A two-level factorial design with four factors (T, t, pH and MA to BS ratio) was carried out using 2^3 factorial designs in order to investigate the effective factors on CI% value of BS-MA complexes. ANOVA for the two-level factorial design is presented in Table S1. The F, p (<0.05) and R^2 value of the model indicated that the model was significant. The temperature (T) was the only significant factor effecting the CI% ($p = 0.006$). Among the insignificant factors, MA to BS ratio ($p = 0.464$) had the highest influence on CI%. These results were in accordance with the result of paired *t*-test.

3.3. Effect of MA to BS ratio and temperature (T) on complex formation

CI% values of BS-MA complexes produced using various MA to BS ratio and temperature (T) are shown in Table 2. BS-MA complexes produced at same reaction temperature generally had higher CI% as the MA to BS ratio increased. This increase was found to be significant in some BS-MA complexes ($p < 0.05$). The significant increases were observed in the CI% of the BS-MA complexes produced at 60, 75 and 90 °C as the MA to BS ratio increased from 0.1 mmoL/g to 0.45 mmoL/g ($p < 0.05$). At 67.5 °C and 82.5 °C, increasing the MA to BS ratio from 0.275 to 0.675 mmoL/g resulted in a significant increase in the CI% of BS-MA complexes (from 78.5% to 94.5% and from 86.5% to 95%, respectively) ($p < 0.05$). However, the difference between CI% of the BS-MA complexes produced using 0.45 and 0.8 mmoL/g MA to BS ratio at 60, 75 and 90 °C were not significant ($p > 0.05$). The CI% of the BS-MA complexes produced at 60 °C were 40.1%, 94.5% and 95.0% when the MA to BS ratio were 0.1, 0.45 and 0.8 mmoL/g, respectively. The CI % of BS-MA complexes produced at 75 °C ranged from 46.3% to 94.7%, whereas the CI% of the BS-MA complexes prepared at 90 °C were higher (86.1–95.0%). These results of this study agreed with previous works. Similar to our study, some studies showed that the complex formation increased with increase in the fatty acid amount until reaching a plateau at specific fatty acid amount and then, the complex formation remained constant [5,38,43,49,58].

The BS-MA complexes produced using 0.1 mmoL MA/g BS at 60 °C and 75 °C had the lowest CI% values (40.1% and 46.3%) ($p < 0.05$) among the samples, and the rise in reaction temperature to 90 °C led to a

significant ($p < 0.05$) increase in CI% (Table 2). In addition to this, the increase in temperature from 67.5 to 82.5 °C had a significant ($p < 0.05$) effect CI% value of the BS-MA complexes produced using 0.275 mmoL MA/g BS, (78.5% and 86.5%, respectively). It might be due to the fact that the starch hardly interacted with fatty acid when the lower amount of fatty acid was found in the starch-fatty acid system. The increase in reaction temperature lead an increase in the starch mobility [2], thus, the interaction between starch and fatty acid facilitated. On the other hand, for the BS-MA complexes produced using an MA to BS ratio of 0.45, 0.625, and 0.8 mmoL/g, the increase in reaction temperature had no significant effect on the CI% values. It was clear that the increase in reaction temperature did not affect the CI% of samples when the MA to BS ratio was higher than certain ratio (>0.275 mmoL MA/g BS) in the system. Seo et al. [40] observed that the complex formation was not affected by the difference in temperature between 70 and 90 °C. This situation was attributed that the mild heating might provide adequate mobility for the interaction of starch with fatty acid and thus, the increase in temperature affected slightly complex formation [40].

To describe the effect of reaction temperature (T) and MA to BS ratio on the CI% of samples, the CI% results were fitted by the second-order polynomial (quadratic) regression model. ANOVA analysis for the model is presented in Table S2. The F value (18.98), the *p*-value

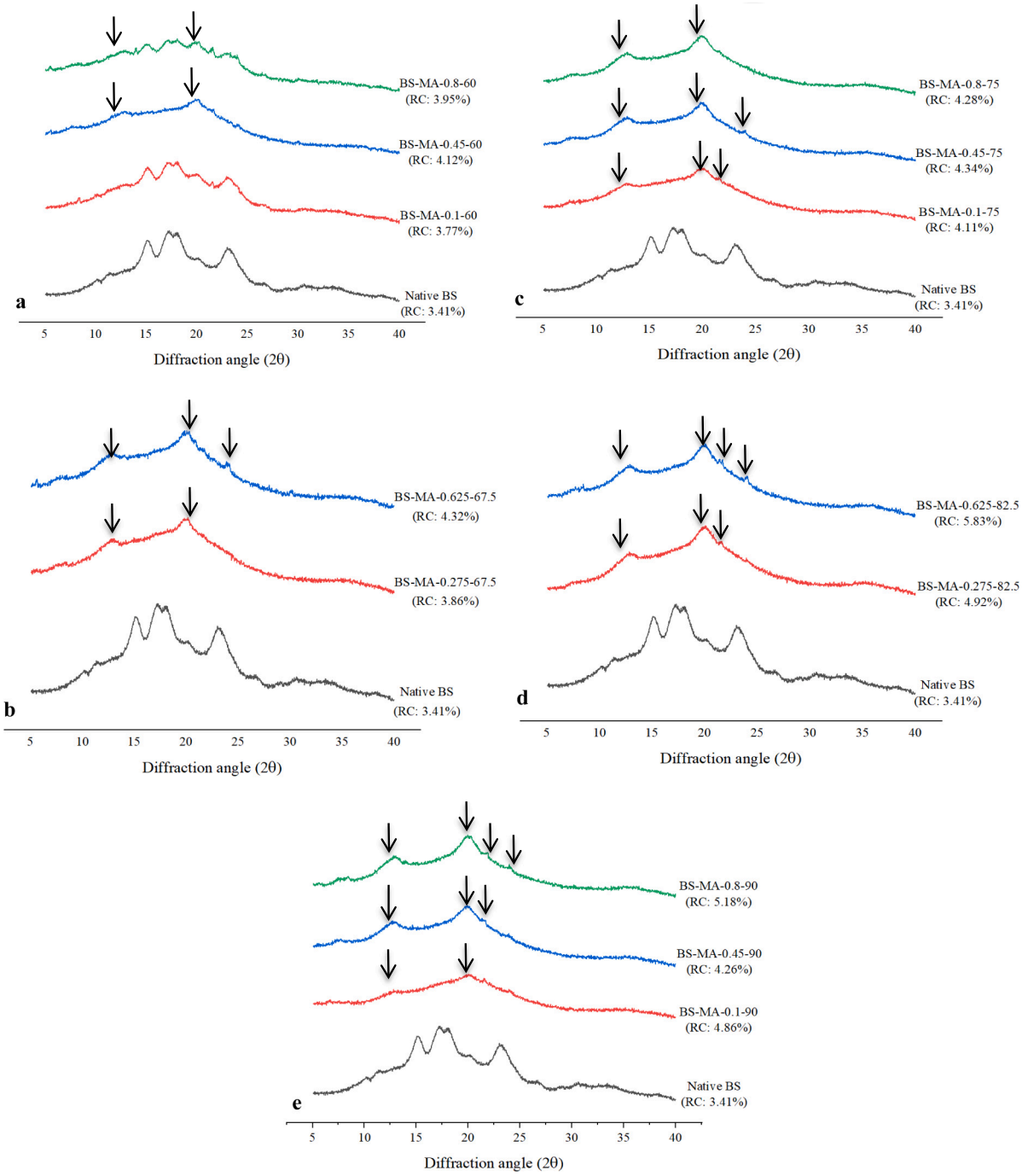

Fig. 1. X-ray diffraction (XRD) patterns and relative crystallinity (RC) of BS and BS-MA samples. BS: Buckwheat starch; MA: Myristic acid; BS-MA: Buckwheat starch myristic acid complex; 0.1, 0.275, 0.45, 0.625, 0.8: MA concentration; 60, 67.5, 75, 82.5, 90: Reaction temperature (°C); a) BS-MA complexes produced at 60 °C; b) BS-MA complexes produced at 67.5 °C; c) BS-MA complexes produced at 75 °C; d) BS-MA complexes produced at 82.5 °C; e) BS-MA complexes produced at 90 °C.

(0.0003), and R^2 (0.9223) of the model indicated that the model was reliable. Significance analysis of the coefficients of each factor showed that the MA to BS ratio (coded as A), the temperature (coded as B) and second-order (A^2) coefficient of MA to BS ratio had an influence on the CI% of the BS-MA complexes ($p \leq 0.0001$, $p = 0.0186$ and $p = 0.0018$, respectively). The coefficient of the interaction term between the linear effects of reaction temperature and MA to BS ratio (coded as AB) was also significant ($p = 0.0066$). On the other hand, the second-order (B^2) coefficient of temperature was non-significant ($p > 0.05$) on the CI% of the BS-MA complexes. Final estimative response model equation for the CI% of BS-MA complexes, in terms of the coded factors, was generated by Design Expert Software and given as follows (Eq. (1)):

$$\text{CI}\ (\%) = 93.07 + 17.60\text{A} + 7.19\text{B} - 11.39\text{AB} - 19.10\text{A}^2 + 5.50\text{B}^2 \quad (1)$$

in which A and B are the coded values of independent factors (MA to BS ratio and reaction temperature, respectively).

Fig. S7 represents the effects of MA to BS ratio and reaction temperature on the CI (%) value of BS-MA complexes. As can be observed from Fig. S7 increasing the reaction temperature and MA to BS ratio caused an increase in the CI (%) value of the BS-MA complexes.

3.4. X-ray diffraction (XRD)

The X-ray diffractograms of native BS and BS-MA complexes are illustrated in Fig. 1. The native BS displayed the typical A-type patterns with peaks at 15.2°, 17.3°, 18.09° and 23.15° (2Θ) diffraction angle [59]. All BS-MA complexes (except BS-MA-0.1-60) exhibited the peaks at 2Θ of 13.0° and 20.0° which are attributed to the V-type structure of the formed complexes [44]. The absence of V-type peaks in BS-MA-0.1-60 might be due to the fact that the inclusion complexes did not have sufficient crystallinity to be obtained as a peak in X-ray diffraction, as shown in Fig. 1a [19]. Similar results were observed in BS-MA complexes produced according to two-level factorial design (Figures are not shown). The samples produced at 40 °C had similar peaks with the native BS at the specific A type crystalline diffraction angle, whereas the samples produced at 90 °C had a V-type structure having a peak at 2Θ of 20.0°. It seems that complex formation at 40 °C did not directly affect the XRD pattern of BS-MA complexes. Moreover, the intensity of V-type crystalline peaks increased with increase in MA to BS ratio from 0.1 to 0.45 and 0.8 and from 0.275 to 0.625 mmoL MA/g at same temperature (production temperature at 60, 67.5, 75 and 82.5 °C). The peaks observed at 2Θ of 21.3° and 23.9° were identified as the crystalline pattern of free FA (fatty acid) aggregates [7,16].

RC% was calculated as the ratio of area of V-crystal peaks (13.0° and 20.0°) to the total area under the X-ray diffractograms [43]. The native BS showed the lowest relative crystallinity (RC%) (3.41%) and the starch-lipid complex formation led to increase in RC, as expected. The RC of the complexes ranged from 3.77% to 5.83%. Lowest value was observed for BS-MA produced using 0.1 mmoL MA/g at 60 °C while the highest value was observed for BS-MA produced using 0.625 mmoL MA/g at 82.5 °C. The increase in reaction temperature generally caused increases in RC of BS-MA complexes. For example, in case of the samples produced using 0.275 and 0.625 mmoL MA/g; the samples produced at 67.5 °C had RC of 3.86 and 4.32%, whereas the samples produced at 82.5 °C had higher RC. Similar increases were observed in the literature [41,44]. It was might be due to the fact that higher kinetic energy allows to helices more moving. Thus, helices having higher energy form interact with each other easier to form more nuclei and they transform themselves into crystals [44]. According to Mapengo et al. [12], hydrothermal treatment of maize starch with stearic acid led to increase in RC. This situation might not only be a result of amylose-lipid complexes formation, but also the increase in hydrogen bonding of the amylopectin chains among each other with the effect of hydrothermal treatment [12]. At the same reaction temperature (60 °C, 67.5 °C, 75 °C and 82.5 °C), the increase in the MA to BS ratio (from 0.1 to 0.45 mmoL MA/g and from 0.275 to 0.625 mmoL MA/g) led to increase in the RC value. For example, the BS-MA complexes produced using 0.275 mmoL MA/g at 82.5 °C had a RC of 4.92%, the ones produced 0.625 mmoL MA/g had higher RC value (5.83%). This situation might be related to the increase in complex formation, as seen in Table 2. Similar result was reported by Li et al. [15], who observed that the increase in fatty acid concentration from 0.5 to 2% caused a significant increase in RC and CI of starch-palmitic acid complex. However, there was no correlation between CI and RC (Table S3). Similar findings were stated in the literature. For example, Li et al. [15] observed that when the palmitic acid concentration increased from 2 to 5%, the CI % decreased while the RC increased. Sun et al. [1] also showed that the RC of samples having different fatty acids of was not directly changed with change in CI value, indicating many factors affecting the crystallinity. On the other hand, at reaction temperature of 60 and 75 °C, the increase in MA to BS ratio (from 0.45 to 0.8 mmoL MA/g) decreased the RC of samples. The decrease indicated that the crystal structure was destroyed with complex formation in high concentration of myristic acid at 60 and 75 °C. Yan et al. [58] also reported that the crystallinity of the amylose-fatty acid complex nanoparticles decreased from 54.22% to 36.38% with the palmitic acid addition changed from 0 to 20%. In addition to this, Yan et al. [58] observed that CI of samples increased with increase in palmitic acid concentration. These findings implied that there are many factors that affect the RC, as also stated above. For BS-MA complexes produced at 90 °C, the highest RC value (5.14%) was achieved with sample having 0.8 mmoL MA/g, while the lowest RC value (4.24%) belonged to sample produced using 0.45 mmoL MA/g. The increase with increase in MA to BS ratio (from 0.1 and 0.45 to 0.8 mmoL/g) at 90 °C might be due to un-complexed fatty acids. Many factors contribute the crystalline structure of starch-fatty acid complexes such as the formation of double helix amylopectin, single helix amylose-fatty acid complex, free fatty acids [60,61]. Although this study indicated that the washing with diethyl ether was enough to remove free myristic acid, the trapped fatty acids might not all be removed due to different interaction of the trapped fatty acid at the different reaction temperature, as stated by Lu et al. [60]. In addition to this, Lu et al. [60] reported that these crystalline fatty acids might result from the physically trapped fatty acid crystals in other regions of the complexes rather than within the helices.

3.5. Fourier transform infrared spectroscopy (FT-IR)

The FT-IR spectra of native BS and BS-MA complexes are shown in Fig. 2. Native BS and BS-MA complexes had peaks at 3300 and 1640 cm^{-1}, which were attributed to water [27]. The absorption band at 2900 indicated the stretching vibration of C—H bond [62]. The peaks at 2100 cm^{-1} was associated with free water [27]. The peaks between 1340 and 1400 cm^{-1} related to stretching OH groups of water [63]. The spectra region between 800 and 1200 cm^{-1} is associated with the intermolecular hydrogen bonds of double helices of amylose and amylopectin or amylose-amylopectin complexes [27,64]. In comparison with native BS, the bands at 2846 cm^{-1} was observed in the spectra of all BS-MA complexes (except BS-MA-0.1-60) (Fig. 2), which was attributed to asymmetric stretching vibration of CH_3 and CH_2 of fatty acids [1,7]. The absence of this peak in BS-MA-0.1-60, indicates that the complex formation was too little (CI value; 40.1%) to be detected by FT-IR. This observation also agreed with XRD results. Similar relation between complex formation and FT-IR value was also reported by Wang et al. [7]. In addition, the intensity of the peak at 2846 cm^{-1} increased as MA to BS ratio increased (from 0.1 to 0.45 and 0.8 mmoL/g and 0.275 to 0.625 mmoL/g). The results indicate that increase in MA to BS ratio enhanced complex formation, which was also in agreement with XRD and CI% results.

3.6. Swelling power (SP)

Swelling power of native BS and BS-MA complexes are shown in

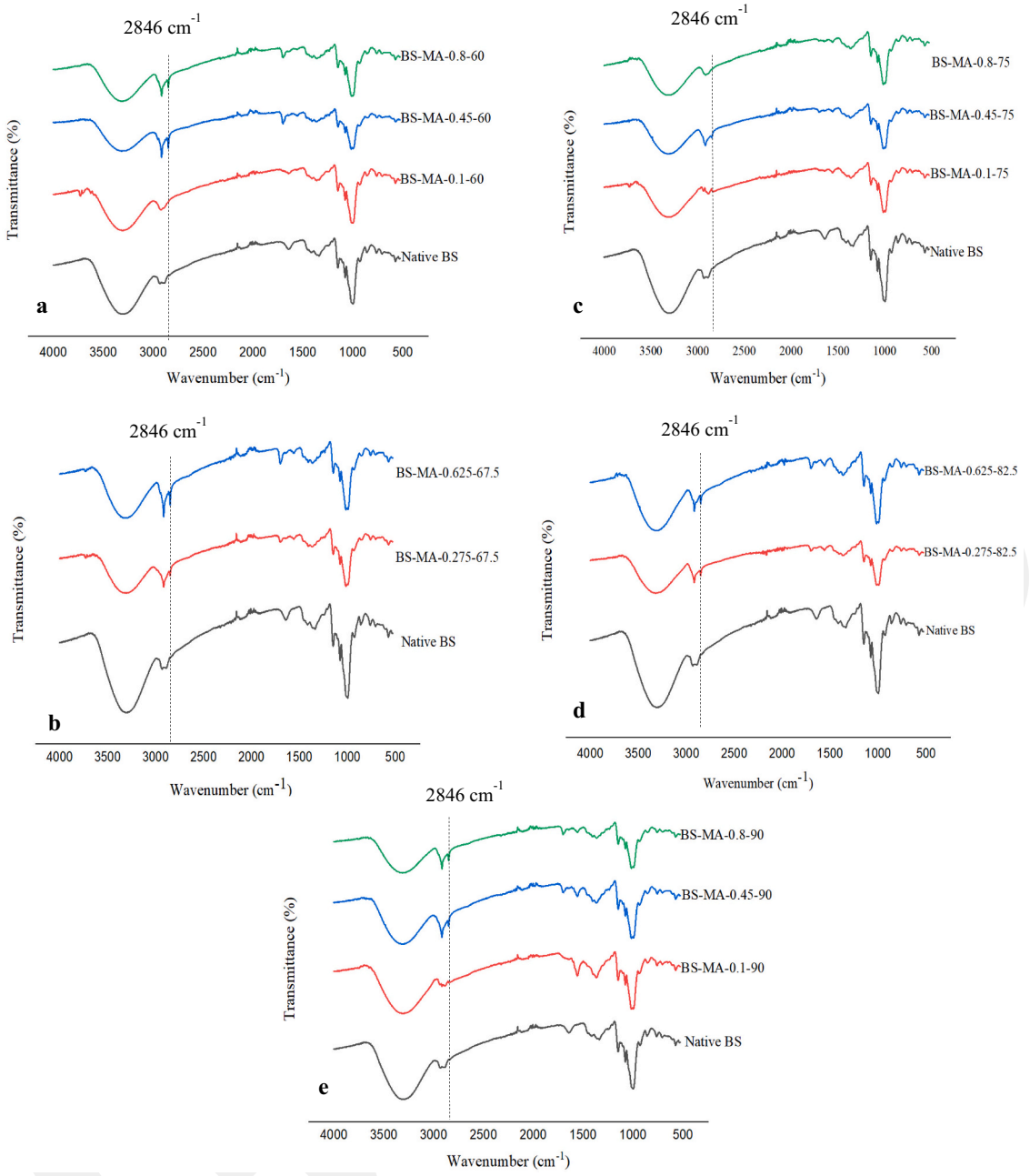

Fig. 2. FT-IR spectra of native BS and BS-MA samples. BS: Buckwheat starch; MA: Myristic acid; BS-MA: Buckwheat starch myristic acid complex; 0.1, 0.275, 0.45, 0.625, 0.8: MA concentration; 60, 67.5, 75, 82.5, 90: Reaction temperature (°C); a) BS-MA complexes produced at 60 °C; b) BS-MA complexes produced at 67.5 °C; c) BS-MA complexes produced at 75 °C; d) BS-MA complexes produced at 82.5 °C; e) BS-MA complexes produced at 90 °C.

Table 2. Native BS had the highest SP (20.70 g/g). SP values of the BS-MA complexes were significantly lower than that of the native BS. Similar results were also reported in the literature. Wang et al. [7] observed that amylose-lipid complex of wheat starch with different fatty acids had lower SP than native starch. The decrease may be due to fact that the amylose-lipid complex may be found as an insoluble film on the starch granule surface, inhibiting the transportation of water into granules [7]. At the same reaction temperature, the increase in the MA to BS ratio (from 0.1 to 0.45 and 0.8) caused significant ($p < 0.05$) decreases in the SP. For example, in case of the samples produced at 60 °C; the one produced using 0.1 mmoL/g MA had a swelling power of 7.34 g/g, whereas the sample produced using 0.45 and 0.8 mmoL/g had significantly lower swelling power (6.27 g/g and 6.26 g/g, respectively). The results agree with CI%, XRD and FT-IR results. On the other hand, at the same MA to BS ratio, the increase in the reaction temperature from 60 to 90 °C (from 75 °C to 90 °C) significantly increased the SP ($p < 0.05$). This situation may be related to the change in amylopectin ratio during production of amylose-lipid complex. According to Tester and Morrison [65] amylopectin had primary role in swelling of granule. At 90 °C reaction temperature, the high temperature increased the leaching of un-complexed amylose and amylopectin from granule [66].

3.7. Pasting viscosity properties

The pasting viscograms of the native BS and BS-MA complexes are shown in Fig. 3. Native BS starch sample had a regular pasting curve, whereas amylose-lipid complex formation changed the pasting behavior significantly. The peak viscosity of BS was 3392 cP. Amylose-lipid

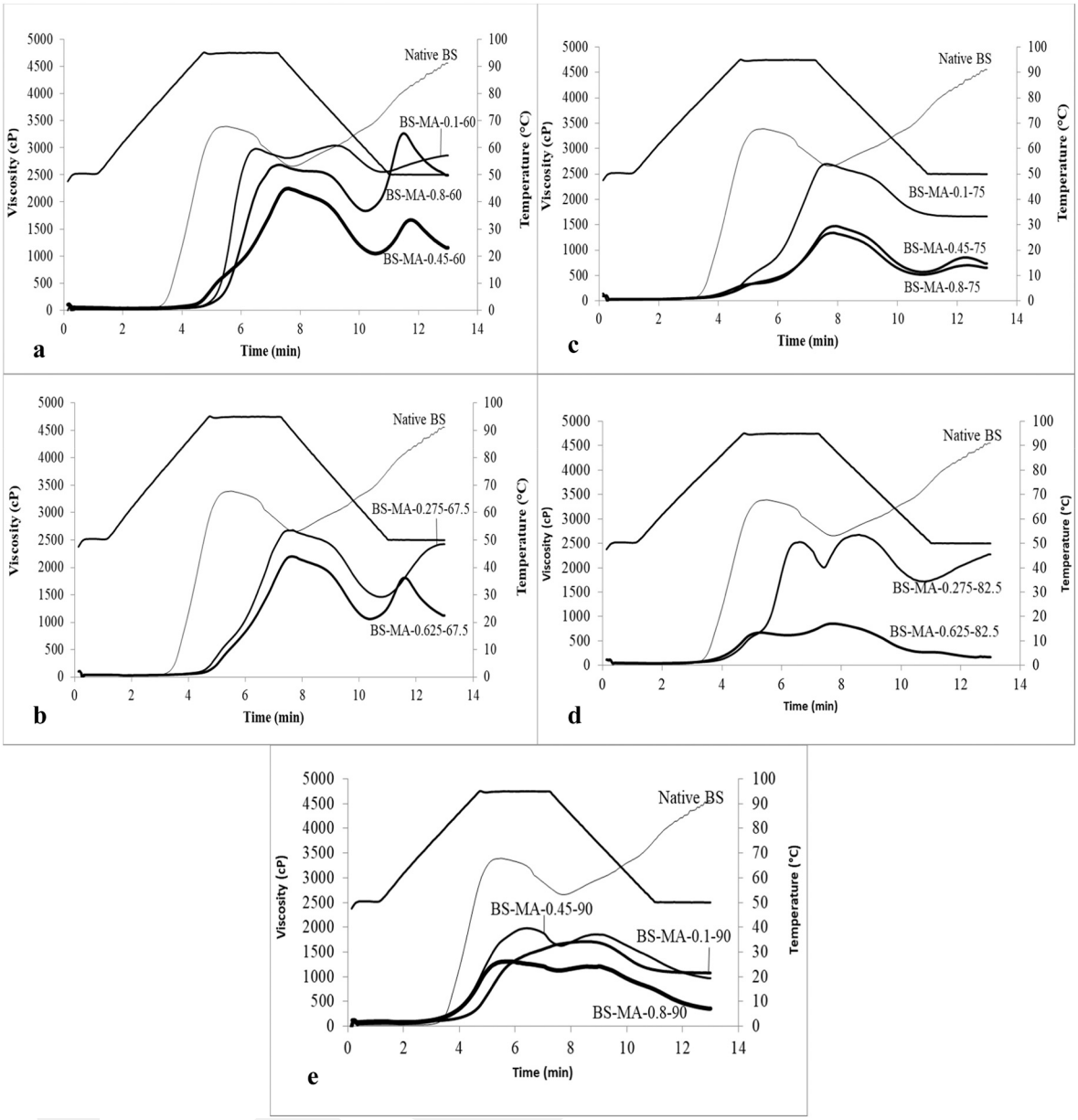

Fig. 3. Pasting viscosity graphs of native BS and BS-MA starch samples. BS: Buckwheat starch; MA: Myristic acid; BS-MA: Buckwheat starch myristic acid complex; 0.1, 0.275, 0.45, 0.625, 0.8: MA concentration; 60, 67.5, 75, 82.5, 90: Reaction temperature (°C); a) BS-MA complexes produced at 60 °C; b) BS-MA complexes produced at 67.5 °C; c) BS-MA complexes produced at 75 °C; d) BS-MA complexes produced at 82.5 °C; e) BS-MA complexes produced at 90 °C.

complex formation decreased the peak viscosity of BS. These values of BS-MA complexes ranged from 704 to 2977 cP. The decrease in peak viscosity of BS was similar to the findings of Sun et al. [1] with complex formation that the maize starch-myristic acid complex had a lower peak viscosity than native maize starch. This situation was related to the reduction in intermolecular interaction between starch chains with amylose-lipid complex formation [1]. For the peak viscosity of BS-MA complexes produced at same temperature (Fig. 3a-d), it was clearly shown that the peak viscosity of BS-MA complex with lower MA to BS ratio (0.1 and 0.275 mmoL/g) was generally higher. The results suggested that the increase in MA to BS ratio improved the complex formation, which was consistent with the results of CI%, XRD, FT-IR and SP. The BS-MA complexes that were slightly affected from the increase in the MA to BS ratio were the ones produced at 90 °C (Fig. 3e). It may be due to the presence of the amylose content released from the granules in the starch fatty acid system. The amylose content is one of the important factors affecting the peak viscosity [67]. The heating process and the difference in temperature during complex production released the amylose from the starch granule. When the BS-MA complexes produced at 90 °C, the amount of non-complexed amylose may be higher in the slurry. Thus, the effect of the increase in MA to BS ratio on peak viscosity of BS-MA complexes produced at 90 °C may not be observed clearly.

The peak time was 5.47 min for BS, however the complex formation led higher peak time values (5.73–7.00 min). In other words, the time taken to reach peak viscosity of BS was delayed with complex formation. Similar trends were also observed in the literature [16,42,68]. It might be due to the fact that the fatty acid increased the hydrophobicity of the granule, as a result the samples had greater resistance to hydrothermal disruption during pasting [42,68]. Similar to peak time results, the pasting temperature of BS (76.7 °C) increased with complex formation. These values ranged from 80.75 to 94.65 °C. The increase was attributed to inhibition of starch granule swelling by complex formation with lipid, thus the pasting delayed and pasting temperature raised, as also observed in peak time [69].

The complex formation of BS with MA decreased the final viscosity of BS from 4555 cP to 357–2855 cP. Sun et al. [1] investigated the effect of using seven different fatty acids on pasting properties of amylose-lipid complexes. Similar to our results, they reported that the final viscosity of all amylose-fatty acid complexes were lower than that of native starch. According to Mapengo et al. [12], the amylose-lipid complex formation obstructed the hydrogen bonds between starch chains during pasting resulting a decrease in the viscosity. BS-MA complexes produced using 0.1 and 0.275 mmoL/g at the same temperature had higher final viscosity than the others. In addition to these, the final viscosity of BS-MA complexes produced using same MA to BS ratio at 60 °C slightly changed with increase in temperature to 75 °C. On the other hand, final viscosity values of BS-MA complexes produced using the same MA to BS ratio at 60 and 67.5 °C declined with an increase in temperature to 90 and 82.5 °C, respectively. This situation may be due to the fact that the increase in production temperature led to a higher degree of bonding among polymer chains [12,41]. According to Mapengo et al. [12], the changes in the pasting properties were related to the increase in molecular entanglements (amylose and linear amylopectin), i.e., bonding between starch chains. Hoover and Manuel [70] reported that cross-linking interaction occurred both starch chains within amorphous and crystalline region of granule by intermolecular hydrogen bonding due to association of starch chains. However, they also stated that this interaction was greater in amorphous region of granule. Similarly, Yassaroh et al. [41] presented lower final viscosity of amylose-lipid complex produced using heat-moisture treatment at 145 °C than that of samples produced at 125 °C. In addition to these, complex production temperature affected the complex stability and crystal structure of starch-fatty acid complexes [16], therefore pasting properties was influenced.

Besides, some BS-MA complexes had new viscosity peaks during cooling and holding stage, as can be seen in Fig. 3. Previous studies also showed similar peak formation [1,7,39,71]. Sun et al. [1] reported that the amylose lipid complex could show this type of behavior in order to increase in final viscosity to a certain level. The observation of second peak viscosity was attributed to the presence of enough fatty acid in the system to form a complex with non-complexed amylose [71].

3.8. Syneresis

The syneresis values of native BS and BS-MA complexes are shown in Table 2. Native BS had the lowest syneresis values after 24 h, 48 h and 120 h storage (0.50, 0.52 and 0.61 g/g, respectively). Amylose-lipid complex formation significantly increased the syneresis value of BS-MA ($p < 0.05$), ranged from 0.56 to 0.72 after 24 h storage. Generally, the increase in storage time resulted in significant increases in the syneresis of the BS-MA complexes ($p < 0.05$). After storage for 48 and 120 h, the syneresis values of BS-MA complexes varied from 0.57 to 0.76 g/g and from 0.65 to 0.82 g/g, respectively. These results indicated that the starch-lipid complex formation decreased the starch gel stability against retrogradation at low temperature, i.e. 4 °C [72] and more water was separated from the starch pastes than from native BS. The increase in syneresis with complex formation may be expected, since this complex formation prevented amylose interaction and junction zone between each other [12], and thus, gel structure was not formed completely and water released easier from gel than native starch gel. Handarini et al. [72] reported that starch-lipid complex formation led to increase in syneresis degree of native starch. However, during storage, syneresis value of BS and BS-MA complexes increased due to the fact that the interaction between amylose and amylopectin chains led to development of junction zones and release of water from gel [73].

For the BS-MA complexes produced at 60 °C, the change in MA to BS ratio did not significantly affect the syneresis value for 24, 48 and 120 h storage time (Table 2). At the reaction temperature of 67.5 °C, the syneresis value of BS-MA complex produced using 0.675 mmoL/g MA was significantly lower than that of using 0.275 mmoL/g MA for 24 h storage time. This situation may be related to amylose aggregation and decrease in the apparent amylose content. According to Wani et al. [73], during storage, amylose aggregation and crystallization was completed within the initial of storage while amylopectin aggregation and crystallization occurs over a longer period. Similar result was also observed in BS-MA complexes produced at 75 °C. The utilization of higher MA to BS ratio (0.45 and 0.8 mmoL/g) caused a lower syneresis value in comparison with BS-MA complexes produced using 0.1 mmoL/g MA after storage for all time. The BS-MA-0.1-75 had the lowest CI value as compared to samples produced at same temperature, as seen in Table 2. On the other hand, at the reaction temperature above the pasting temperature of BS (82.5 and 90 °C), the difference of syneresis value of BS-MA complexes for different MA to BS ratio was not significant ($p > 0.05$), except for BS-MA-0.1-90 and BS-MA-0.8-90 after 48 and 120 h storage. After 24 and 48 h storage, the highest syneresis value of BS-MA complexes belonged to BS-MA produced at 90 °C. The highest syneresis value for 120 h storage was recorded with BS-0.8-90 (0.82 g/g). This observation for samples produced at 90 °C may be related to two situations. In the first situation, the amylose-lipid complex formation at 90 °C may prevent the hydrogen bonding between starch chains [12] and production at higher temperature may affect the starch structure, thus a weak gel was formed and water released from gel was facilitated. In addition to this, higher production temperature may lead to hydrogen bonding interaction among polymer chains [12], this structure also affected the gel strength and its ability of water release. The final viscosity value of BS-MA produced at 90 °C supported this situation. Wani et al. [73] reported that structural differences including degree of polymerization of amylose, amylopectin chain length, proportion of short chains influenced the syneresis tendency of starch. In the second situation, when the complex production temperature was above the gelatinization temperature, the leaching of amylose and amylopectin content from starch granule may be higher. Non-complexed amylose and amylopectin in starch-fatty acid system may result in higher syneresis. Jayanthi et al. [74] reported that the leaching of amylose and amylopectin led to increase in amylose content, which caused an increase in syneresis. BS-MA-0.8-90 had the highest syneresis value due to higher content of leaching of amylose-amylopectin and using MA above the plateau level during complex formation. When lipid is used above a certain concentration, lipids have a tendency to self-associate rather than forming complex with amylose [16]. In BS-MA-0.8-90, non-complexed lipids can be self-associated, so this structure may inhibit the interaction of amylose and gel structure weaken.

The syneresis value of samples produced using same MA to BS ratio at 60 °C was generally higher than that of produced at 75 °C. It was associated with change in starch structure, as stated above. On the other hand, the reaction temperature at 90 °C, the syneresis value increased compared to BS-MA complexes produced at 75 °C. According to Hasjim et al. [18], the complex production temperature affected crystalline structure and stability of amylose-lipid complex. The increase may be related to change in leaching amylose content, stability and structure of BS-MA.

3.9. Paste clarity

Paste clarity values of native BS and BS-MA complexes are presented in Table 2. The native starch had the highest paste clarity values among the samples stored for the same storage time. The initial paste clarity value of the BS was 5.50%, whereas the initial paste clarity values of BS-MA complexes significantly ($p < 0.05$) decreased to 0.78–2.60%. Similar trend was observed in the samples subjected to the same storage period. For example, after 48 h storage, the BS had a paste clarity of 4.36%, while the BS-MA complexes had significantly ($p < 0.05$) lower paste clarity values (0.77%–2.01%). The decrease in paste clarity after BS-MA complex formation may be due to the fact that amylose-lipid complexes prevented the re-alignment of amylose as also stated by D'Silva et al. [42]. The BS-MA complexes produced using 0.1 and 0.275 mmoL/g MA had higher paste clarity values compared to BS-MA complexes produced

at same temperature ($p < 0.05$). For example, in case of the samples produced at 67.5 °C; after all storage periods, the one produced using 0.275 mmoL had a paste clarity of 1.52, 1.38, 1.41, and 1.39%, whereas the sample produced using 0.625 mmoL MA /g had significantly lower paste clarity values (1.05, 1.03, 1.04, and 1.06%, respectively). In addition, for all storage periods at the same reaction temperature (60, 75 and 90 °C), the paste clarity of samples produced 0.1 mmoL MA /g were considerably higher than the samples produced 0.45 and 0.8 mmoL MA /g. This situation was related to lower amylose-lipid complex content, in line with CI results.

At the reaction temperature of 60 and 75 °C, the BS-MA complexes produced using 0.8 mmoL/g MA had significantly higher paste clarity than that of using 0.45 mmoL/g ($p < 0.05$). When amylose-lipid complex formation was produced at a temperature lower than 90 °C, the amylose-lipid complexes were less crystalline and more unstable (chemically and physically) [18,38]. In addition, the interaction between amylose-fatty acid may be weak when the MA concentration was higher than critical level. Therefore, the complex stability of BS-MA-0.8-60 and BS-MA-0.8-75 were lower than that of samples produced using 0.45 mmoL/g MA at 60 and 75 °C. Thusly, paste clarity was not affected as much as the samples produced using 0.45 mmol/g MA at the same temperature. This trend was similar to the SP results.

Similar result was also observed in yam starch-palmitic acid complex by Li et al. [15], who presented that the paste clarity diminished with increase in CI% and FA concentration (from 0% to 1%). However, they showed that the increase in FA concentration (from 2% to 3%) did not change the CI%, and raised the paste clarity of samples. In addition, Li et al. [15] have found that the paste clarity was decreased from 1.60% to 0.56% with no change in CI% when the addition of FA increased from 4% to 5%. These results indicate that many factors influence the paste clarity including FA concentration, amylose aggregates, amylose-amylopectin content and its chain lengths, intra or intermolecular bonding, granule swelling, granule remnant, starch paste degree, interfering substance, granule size [15,75–77].

The paste clarity of samples was generally decreased with increase in production temperature. This situation may be related to rise in apparent amylose content with increase in production temperature, as observed in syneresis results. According to Tessema and Admassu [75], the decrease in amylose content diminished compactness of the amorphous region of starch, thus light transmittance of starch paste was facilitated. In addition, at reaction temperature of 90 °C, the uncomplexed amylose chains may be bonded among each other, as stated above. This occurred structure may obstruct the transmission of light. Similar to syneresis result, the BS-MA-0.8-90 had the lowest paste clarity value due to the fact that self-associated between un-complexed lipids at 90 °C prevented light transmittance.

The storage of the paste caused a decrease in the transmittance of samples and the decrease was significant in some samples. For example, the initial paste clarity of BS (5.50%) decreased significantly ($p < 0.05$) with increase in storage time. After 24, 48 and 72 h, these values were 4.79%, 4.36%, and 4.19%, respectively. In case of the sample produced using 0.8 mmoL/g MA at 75 °C had 1.34% initial paste clarity, whereas the sample had significantly lower paste clarity value after 24 h storage (1.19%). In addition to, this value slightly decreased after 48 and 72 h storage (1.18% and 1.18%, respectively). The decrease might be related to re-association of amylose chains during storage [78].

3.10. Principal component analysis

Principal components analysis (PCA) was performed to investigate the relationships among analyzed parameters including CI, RC, peak viscosity, peak time, pasting temperature, final viscosity, SP, syneresis (24, 48, and 120 h), and paste clarity (0, 24, 48, and 72 h). After application of PCA to 14 analyzed parameters, the variances were accounted for by PC1 and PC2. The score plots of PC1 and PC2 explained 73.22% of the total variances in the whole data set. The score plots of PC1 and PC2 are shown Fig.S8. It illustrated the correlations between the variables. In addition, Table S3 shows the Pearson correlation matrices of the variables. The CI and pasting viscosity values (peak and final viscosity) were strongly connected due to the angle between them was near to 180° as an indication of negative correlations (Fig. S8a). The correlation between perceived CI and pasting viscosity values (peak and final viscosity) were − 0.566 and − 0.580, respectively ($p < 0.05$) (Table S3). CI also negatively correlated with paste clarity. In addition to this, the angle between the paste clarity of 0-72 h (0, 24, 48 and 72 h) was about 0° and resulted in the correlation among them, indicating a unity. Final viscosity and paste clarity were correlated parameters that could be seen from plot of the component loading vectors (Fig. S8a) and Pearson correlation coefficients (Table S3). By the way, peak viscosity was well correlated with final viscosity due to their closer correlation coefficents to 1 (0.937, $p < 0.05$), as seen in Fig. S8a. Similarly, peak time and pasting temperature were well correlated between each other (0.651, $p < 0.05$), and expectedly, pasting temperature was negatively correlated with SP (−0.575, $p < 0.05$). RC was negatively correlated with peak and final viscosity (−0.604 and − 0.645, $p < 0.05$, respectively).

Plot of principal components core vectors illustrated in Fig.S8b. The samples produced using 0.1 mmoL/g MA to BS ratio are on the right side of the plot. This location was related with the paste clarity and pasting viscosity properties. In addition to this, the increase in reaction temperature led to significant increase in CI of samples produced with 0.1 mmoL/g MA to BS ratio as state above, and expectedly CI was accounted for PC1. On the other hand, the syneresis (48 h) and SP was considered as two of the main effects in PC2, and the samples produced 0.45 mmoL/g MA to BS ratio are located on the left side of the plot. As seen in the Fig. 8b, the samples produced at 82.5 °C are also on the left side of plot.

4. Conclusion

In this work, BS was modified using MA for the production of starch-lipid complex. The most effective parameters (reaction temperature, time, MA to BS ratio and pH) on production of BS-MA complex were determined using two-level factorial design. To obtain maximum CI%, RSM was employed to optimize the reaction temperature and MA to BS ratio. Second-order polynomial (quadratic) regression models were fitted to describe the relationship between the response (CI%) and the independent variables (Temperature and MA to BS ratio). The results indicated that the temperature, MA to BS ratio and interaction between them had a significant effect on CI% of BS-MA complexes. However, the CI% of BS-MA complexes did not change with increase in temperature when the MA to BS ratio was higher than 0.45 mmoL MA/g BS.

In addition, the present study showed that the different temperatures and MA to BS ratios affected the SP, syneresis, pasting properties and paste clarity of BS. Complex formation delayed the pasting. Paste clarity and SP decreased and syneresis increased with complex formation. Besides, XRD results showed that the BS can form V-type complexes when certain temperature and MA to BS ratio, as revealed by FT-IR. Overall, the results indicated that the BS seemed to have amylose-lipid complex formation ability as a new alternative starch. Thus, in our next study, investigating of starch-lipid complex formation of BS with other fatty acids is needed.

CRediT authorship contribution statement

Betül Oskaybaş Emlek: Conceptualization, Software, Validation, Formal analysis, Writing - Original Draft, Writing - Review & Editing, Visualization.

Ayşe Özbey, Conceptualization, Methodology, Validation, Writing - Review & Editing, Supervision, Project administration, Visualization.

Levent Yurdaer Aydemir, Conceptualization, Methodology, Validation, Writing - Review & Editing, Supervision, Project administration, Visualization.

Kevser Kahraman, Conceptualization, Methodology, Validation, Writing - Review & Editing, Supervision, Project administration, Visualization.

Declaration of competing interest

The authors have declared no conflict of interest.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.ijbiomac.2022.03.189.

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