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Valorization of hazelnut cake in compound chocolate: The effect of formulation on rheological and physical properties

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ABSTRACT

The aim of this study was to valorize hazelnut (*Corylus avellana* L) cake (HC), which is a by-product of hazelnut oil industry, in compound chocolate (HCC) as a partial replacer of sugar and milk originated powders (MOP: skimmed milk and whey powder in equal amounts). D-optimal mixture design was used to optimize HCC formulation. The optimum sugar, MOP, and HC amount were selected as 25.0–40.0, 6.0–21.0, and 0.0–15.0 g/100 g, respectively. The Casson model with high R^2 values (0.9882–0.9948) was used to determine yield stress and plastic viscosity values of samples which were varied between 1.47 and 2.35 Pa, and 1.17–1.42 Pa s, respectively. Furthermore, particle sizes and water activity were determined between 25.67 and 78.20 μm and 0.31–0.38, respectively. Total phenolic content in HCC samples, their digestibility, and bioaccessibility ranged from 1389 to 3367; 2601–3955 mg GAE/kg, and 112–187% respectively. Also, hardness and brittleness were ranged between 7.85 and 11.55 N and 0.52–1.02 mm, respectively. The sensorial characteristics of the samples along with flow behavior and physico-chemical properties indicated that HC may be used as a healthy and low-cost ingredient in HCC formulation to partially substitute sugar and MOP.

1. Introduction

Chocolate producers search for alternative and natural ingredients for the production of low calorie, less costly, and healthier chocolate and its derivatives such as compound chocolate which is produced by using vegetable oils instead of cocoa butter (Toker et al., 2016). Nuts, fruits, and vegetables are good sources of polyphenol compounds (Miller et al., 2006). The use of these products or their waste in new formulation is very important for waste management, cost reduction, and enrichment of products with bioactive compounds (Beres et al., 2019). Among nuts, hazelnut cake is an important food by-product from hazelnut oil production with high phenolic content and generally used as animal feed. Accordingly, valorization of this by-product in the production of chocolate will have positive results for both human health and the economy.

Hazelnut, which is a member of the *Betulaceae* family, is included in the *Corylus* genus (Doğan & Bircan, 2010). Common hazelnuts, Turkish hazelnuts (Corylus colurna L.) and Lambert hazelnuts are economically cultivated hazelnuts (Ciftci, 2018). 73% of the world hazelnut production in Turkey, Italy 16%, Spain 3%, and 4% of America and other countries constitute 3% (Alasalvar, Pelvan, & Topal, 2010). Only 10% of the hazelnuts are purchased as hulled hazelnuts and 90% of them are used for industrial purposes as shelled hazelnuts (Stévigny, Rolle, Valentini, & Zeppa, 2007). The main components of the remaining cake with the extraction of hazelnut oil are protein (39.4–42.1%), crude oil (1.8–11.2%) crude fiber (9.2–10.1%), and ash (3.7–8.2%) (Doğan & Bircan, 2010). Hazelnut waste and by-products are potential sources of natural antioxidants due to their phenolic compound content (Contini, Bacceloni, Massantini, & Anelli, 2008; Shahidi, Alasalvar, & Liyana-Pathirana, 2007; Yuan, Eskridge, Isom, & Hanna, 2018). Esposito et al. (2020) prepared an extract from hazelnut shells by-products which had antioxidant and chemopreventive effects on the cancer cell. It was stated that their developed spray-dried microsystems, improved particle dimensions, morphology, and water solubility of extract, and the chemopreventive effects remained unchanged compared with the

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unprocessed extract.

Products with a new formulation need to have a similar quality to conventional chocolate. Texture, taste, and flavor are the quality parameters that affect the chocolate quality, consumer choice, and acceptability. Also, the color and brightness of chocolate and its products significantly affect the consumer's purchasing behavior (Afoakwa, Paterson, Fowler, & Vieira, 2008).

Besides, the particle size distribution of chocolate influences flows properties, texture, and sensory perception. When the particles are large, the point of contact with each other is limited. The refining process increases the particle surface area and the contact points of the particles with each other. Thus, the yield stress value required to break the interaction of particles increases. Furthermore, the coarse particles give the sandy structure sensation (Beckett, 2009). Puleo, Miele, Cavella, Masi & Monaco (2020) revealed that the use of hazelnut pastes with higher particle size perceived as gritty feeling in the mouth. Breen, Etter, Ziegler, and Hayes (2019) showed the difference in the particle size of chocolate can be realized by consumers. Miele, Borriello, Fidaleo, Masi, and Cavella (2020) demonstrated that grinding of hazelnut paste with cocoa mass can decrease the particle size of samples. Cavella, Miele, Fidaleo, Borriello, and Masi (2020) showed the effect of ball mill refining on the reduction of particle size of white chocolate contain hazelnut paste.

Additionally, fat and emulsifier in the formulation have an impact on chocolate texture. Chocolate is an oil-based food product and the softening effect of fats and lubricating effect of emulsifier can reduce friction between the particles and causes a decrease in the hardness (Raoufi, Tehrani, Farhoosh, & Golmohammadzadeh, 2012; Acan et al., 2020). Atik, Bölük, Toker, Palabiyik, and Konar (2020) studied the effect of lecithin and polyglycerol polyricinoleate as the emulsifiers on the milk chocolate and they revealed that viscosity of samples significantly affected by emulsifiers ratio and the lowest hardness values were observed at the Lecithin: PGPR ratio of 1.6–3.0.

By-products of agro-food manufacturing plants contain many bioactive components with health beneficial properties such as polyphenols and the use of these functional ingredients in food formulation can produce novel and healthy food. Esposito et al. (2020) used a polyphenol-rich extract from the hazelnut shells to produce a microparticulate powder to overcome practical difficulties in processing and improve technological properties. Acan et al. (2020) studied the polyphenol contents and their digestibility of chocolate spread enriched with grape by-products. However, the bioaccessibility of bioactive components impacted by different factors such as their release from the food matrix, molecular size, degradation, and hydrolysis in the gastrointestinal tract, therefore, generally the pre and post digestion methods are used in the determination of the percentage of bioaccessibility (Cantele et al., 2020).

To the best of our knowledge, the use of hazelnut cake in compound chocolate has not been studied. Currently, consumers are looking for low-cost, functional, low-calorie and low-sugar, and lower fat content food products. Therefore, this study aimed to use hazelnut cake as the replacer for sugar, milk powder, and whey powder in compound chocolate to produce low-cost products enriched by bioactive components. Moreover, some functional, technological, and sensorial properties of products, as well as phenolic content and *in vitro* digestion were evaluated.

2. Materials and methods

2.1. Hazelnut cake

Hazelnut cake (HC) was obtained as a by-product of hazelnut oil after a pressing process in a plant located in Ordu, Turkey. Hazelnut variety of "tombul" (*Corylus avellana* L.) was used which was grown in Giresun Black Sea Region of Turkey. HC was subjected to a 2-stage grinding process (first 500 μm then 200 μm) to (i) attain homogenous particle size distribution of the components used in compound chocolate (CC) samples (ii) do not affect the mouthfeel adversely.

2.2. Experimental design

In this study, the formulation of hazelnut compound chocolate (HCC) samples with HC was determined by using a Design Expert (Stat-Ease Inc version 7.0, Minneapolis) program. A D-optimal mixture design method was used. The minimum and maximum values of sugar (A), milk originated powders (MOP) (B), and hazelnut pomace (C) were determined in preliminary experiments and industrial applications. According to this, usage levels were used as 25.0–40.0, 6.0–21.0, and 0.0–15.0 g/100 g for sugar, MOP, and HC, respectively. 13 different compound chocolate formulations were formulated (Table 1). Component proportions were expressed as fractions of the total amount (A + B + C) of 61 g.

2.3. Preparation of hazelnut compound chocolate (HCC)

HC (0.0–15.0 g/100 g), powder sugar (25.0–40.0 g/100 g) (SMS Kopuz, Istanbul, Turkey), milk originated powders (MOP) as total skimmed milk powder, and whey powder in equal amounts (6.00–21.00 g/100 g) (Enka, Konya, Turkey), palm oil (10.48 g/100 g, Trio30), (20.96 g/100 g, Beska) (AAK, Istanbul, Turkey), cocoa powder (7.00 g/100 g) (Altinmarka, Istanbul, Turkey), Lecithin (0.40 g/100 g) (Brenntag Chemistry, Istanbul, Turkey), sodium chloride (0.03 g/100 g) (Salina, Konya, Turkey), ethyl vanillin (0.03 g/100 g) (Ekin Chemistry, Istanbul, Turkey), and polyglycerol polyriconalate (PGPR) (0.10 g/100 g) (Palsgaard, Zierikzee, Netherlands) were used in this study. The production process of HCC samples was conducted according to the method described by Toker et al. (2017). The ratios specified in Table 1 were used to produce 2 kg HCC samples for each formulation. Briefly, sugar, cocoa, HC, salt, MOP, and ethyl vanillin were mixed by the low-speed mixer according to the formulations. Then, the palm oil and lecithin which melted at a water bath (60 °C, 20 min) were added to the dry material and pre-mixed for 5 min at medium speed. The obtained compound chocolate paste was subjected to refining-conching by a pilot-scale ball-mill (Alpy, Istanbul, Turkey) (2 h, 45 °C, and 60 rpm). The molten chocolate samples were cooled to 35 °C and were filled in pre-heated polycarbonate chocolate molds (35 °C). Afterward, they cooled in cooling chambers (10 °C, 30 min) and were separated from molds, wrapped in aluminum foils, and stored at 15 °C before the analysis.

2.4. Characterization of hazelnut cake

The AOAC (1985, 1995, and 2007) methods were used to specify the dry solids, protein, fat, and ash content in the HC. The sugar content of HC (glucose, fructose, xylose, and sucrose) was determined by using HPLC-RID (Agilent 1100, USA) and Hypersil APS-2 (5 μm, 100 × 3.0 mm) column according to the method used by Di Mattia et al. (2014).

2.5. Particle size measurement

The particle size of HC and HCC samples was determined by a micrometer (Mitutoyo, Japan) (±0.001 mm) (Beckett, 2009).

2.6. Determination of water activity

Water activity (aw) values of HC and HCC samples were determined according to the method described by Konar (2013) by using LabMaster aw analyzer (Novasina, Switzerland).

2.7. Total phenolic content

To determine the total phenolic content (TPC), extraction of HC and HCC was carried out according to the method described by Di Mattia

Table 1
Study design and the results of particle size, water activity, total phenolic content and *in vitro* digestion of samples.

Sample	Real Values (g/100 g)			Particle size (μm)	Water activity	Pre-digestion (mg GAE/kg)	Post-digestion (mg GAE/kg)	Bioaccessibility %
	A	B	C					
Control	40.000	21.000	0.0000	25.67	0.40	906	1955	215
F1	40.000	6.0060	14.994	78.20	0.38	3367	3779	112
F2	38.501	21.000	1.4990	29.00	0.31	1389	2601	187
F3	31.547	21.000	8.4530	40.50	0.33	1992	3192	160
F4	34.758	16.187	10.055	40.60	0.31	2499	3017	120
F5	37.452	13.841	9.7070	52.00	0.32	2539	3293	129
F6	40.000	13.862	7.1380	40.40	0.34	2020	3002	148
F7	25.004	21.000	14.996	61.50	0.31	3127	3751	119
F8	32.114	13.886	15.000	59.00	0.36	3191	3955	123
F9	35.867	19.275	5.8580	39.00	0.31	1885	2784	147
F10	37.353	11.258	12.390	47.29	0.34	2971	3531	118
F11	38.501	21.000	1.4990	29.00	0.31	1389	2601	187
F12	29.611	18.400	12.989	50.50	0.37	3006	3914	130
F13	40.000	6.0060	14.994	76.17	0.35	3367	3779	112

A; Sugar, B; Total skimmed milk powder and whey powder in equal amounts (MOP), C; Hazelnut cake. Results of analysis were given as mean. Experiments were performed in triplicate.

et al. (2014) with some modifications. Briefly, 5 g of ground sample was mixed with 25 mL hexane (1 h, room temperature) and then centrifuged at 9000 rpm for 5 min. The supernatant was separated, and the solid residue was dried in an oven (40 °C, 4 h). Afterward, 2 g of dried sample was mixed with 10 mL of acetone/water/acetic acid (70/29.8/0.2, v/v/v) solution which is homogenized by ultrasonic water bath (40 °C, 1 h). Then they centrifuged at 9000 rpm for 5 min and the supernatant was passed through a 0.22 μm filter with the help of a syringe.

The method described by Singleton VL (1965) was used to determine the TPC of samples. Briefly, 2.5 mL of 0.2 N Folin solution was added to 0.5 mL of sample extract and then 2 mL of 7.5% sodium carbonate solution was added and then left at 20.0 ± 2.00 °C for 30 min at the dark place. A spectrophotometer (UV-1800, Shimadzu, Kyoto, Japan) was used to measure the absorbance of samples at 760 nm and the TPC content of samples was determined by using Equation (1).

$$TPC\ (mg\ GAE\ /\ kg) = \left[\frac{Absornbance - 0.0351}{0.0107}\right] \times Dilution\ Factor \tag{1}$$

2.8. In vitro digestion assay of TPC

The method explained by Lee, Lee, Chung, and Hur (2016) was performed for bioaccessibility analysis of TPC in the HCC sample with some modifications. The digestion solutions and in-vitro digestion steps of HCC samples were shown in Supplementary File 1 and Supplementary File 2, respectively. Bioaccessibility (%) was calculated as the ratio of post-digestion to pre-digestion of polyphenol (Cantele et al., 2020).

2.9. Color and texture analysis

Color values of HCC samples were analyzed by colorimeter (Chroma Meter CR-400, Konica Minolta, Japan) with six replications. The obtained L^* (brightness), a^* (±red-green) and b^* (±yellow-blue) color values were used for calculation of Chroma (C^*) and hue (h°) values of HCC samples using Equation (2), (3), respectively (Periche, Heredia, Escriche, Andres, & Castello, 2015).

$$C^* = \sqrt{a^{*2} + b^{*2}} \tag{2}$$

$$h^\circ = arctan\left(\frac{b^*}{a^*}\right) \tag{3}$$

Also, the textural properties of HCC samples were analyzed using a texture analyzer (TA.HD Plus, Stable Micro Systems, Godalming, UK) equipped with a 5 kg load cell. The required force for breaking HCC samples (80 × 40 × 4 mm) at room temperature was determined using a 3-point bend ring and applied pre-test, test and post-test speeds were 1, 1, and 10 mm/s, respectively. The results were used to determine the hardness (N), and brittleness values (mm).

2.10. Sensory analysis

Sensory analysis of the HCC samples was carried out by 60 panelists (%60 females, %40 males, 23–46 ages) using a 5-point structured hedonic scale (1 = dislike, 3 = neither like nor dislike, 5 = like) for sweetness, foreign taste, mouthfeel sensation, odor, color, melting in mouth, brittleness and overall acceptability.

2.11. Determination of rheological properties

The stress-strain-controlled rheometer (Anton Paar, MCR 302, Graz, Austria) equipped with cylindrical probe (CC27, Anton Paar, Australia) and Peltier heating/cooling system was used to determine the rheological properties of HCC samples according to the method defined by Toker et al. (2017). The results were fitted to the Casson model (Eq. (4)) to determine the Casson yield and plastic viscosity values.

$$\tau^{0.6} = \tau_0^{0.6} + \eta_{pl}\, \gamma^n \tag{4}$$

where τ is shear stress (Pa), τ_0 is yield stress (Pa), η_{pl} is plastic viscosity (Pa.s), and γ represent shear rate (1/s).

2.12. Statistical analysis

Design Expert (Stat-Ease Inc. version 7.0, Minneapolis) program was used for data analysis optimization. ANOVA, analysis of variance was performed to determine if the differences between the corresponding quality parameter of the samples were statistically significant or not ($P < 0.05$). Regression coefficients of linear, quadratic, cubic, and interaction terms were determined and the factors that were not significant for the model were extracted by Backward Elimination Regression (BER) ($P > 0.1$). The results of the analyses were given as mean ± SD.

3. Results and discussion

3.1. Characterization of HC

The obtained solid content, fat, protein, ash, sugar profile, and total phenolic content of HC (particle size, <200 μm) were shown in Supplementary File 3. Due to the low water activity value of HC, pathogen microorganisms cannot develop, and HC can be valorized in food products. Also, HC, which is an important industrial by-product of hazelnut processing and hazelnut oil production facilities, has high

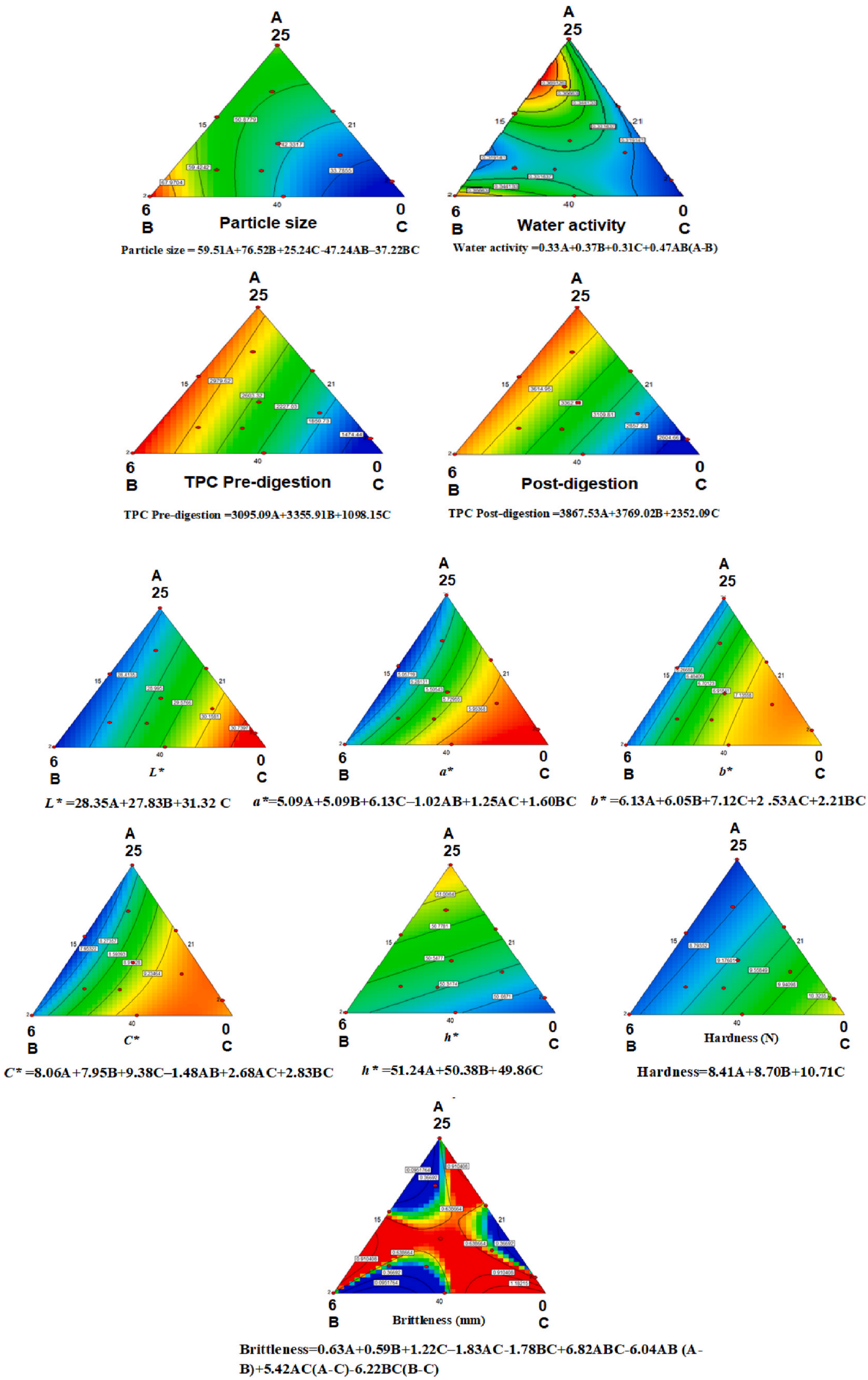

Fig. 1. Effects of formulations on color and textural properties particle size, water activity, and total phenolic content before and after *in vitro* digestion. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

protein content. Our result is in agreement with another study that reported that the by-product of the hazelnut oil industry contains a high level of protein (Sen & Kahveci, 2020). They extracted protein from hazelnut meal and added it in the concentration of 2% and 4% to the functional beverage and they reported that hazelnut cake can be a good protein source for functional beverages. The sugar level of HC was low which may be helpful in the production of chocolate with less sugar content that can help prevent obesity and obesity-related disease. Besides, from a technological aspect of view, sucrose is less hydrophilic than glucose and fructose. Therefore, the lower level of these mono-saccharides in HC can be useful in terms of lower affinity to attract water during processing (such as the conching step) and storage. Also, due to these properties, develop sugar bloom during storage can be decreased (Acan et al., 2020). Furthermore, the TPC of HC was determined as 16.2 g GAE/kg on a dry matter basis. However, TPC of hazelnuts from different regions was determined as 1.343–8.417 mg GAE/g for raw hazelnuts and 1.430–6.817 mg GAE/g for crude pulp (Ceran, 2018) and 59.6 mg GAE/g and 174.5 mg GAE/g for hazelnut shell and hazelnut skin, respectively (Bignami, Bertazza, Cristofori, & Troso, 2005). The difference in the chemical composition and phenolic content of the HC between this study and previous studies may be related to the mineral profile, soil composition, cultivation practices, origin, variety, the way it is processed into oil, the amount of shell, skin, and impurities contained in the hazelnut cake.

3.2. D_{90} value of HCC samples

The particle size (D_{90}) of chocolate has a significant impact on the texture, flow, melting, color, and water activity properties (Konar, 2013). The obtained particle sizes were ranged between 25.67 and 78.20 μm with the highest value at the F1 coded sample and the lowest value at the control sample (Table 1). The effect of formulation on the particle size of HCC samples was modeled by using a quadratic model with the $R^2 = 0.9469$. The model expressing the effect of HC on the particle size of HCC and lack of fit was found to be significant ($P < 0.05$). The interaction between two variables AB on the particle size was shown as significant ($P < 0.05$) while for BC was not significant ($P > 0.05$). Since the effect of AC combination on particle size was not significant ($P > 0.1$), this interaction was excluded from the model by BER. Increase the amount of HP in the formulation caused an increase in particle size of HCC samples (Fig. 1). The particle size values were found to be much higher at the points where amounts of HC were maximum, and MOP was minimum.

The effect of HC usage on particle size may result in changes in other quality parameters. For example, an increase in particle size and particle size distribution may adversely affect sensory properties. Because it causes the development of sandiness. This problem reduces the level of taste for chocolate. Our results are in agreement with the finding of another study, in which 8.00% hazelnuts paste was used in the formulation of cocoa-based creams (Puleo, Miele, Cavella, Masi, & Monaco, 2020). They found that chocolate pastes with particle size higher than 35 μm were perceived as gritty or coarse in the mouth, resulting in lower liking score by consumers. Also, Breen et al. (2019) investigated sensorial characteristics of the dark chocolates produced with particle size (D_{90}) from 19 to 33 μm. Non-expert consumers could realize differences in sensorial properties when particle size of chocolate only changed ~5 μm.

However, this problem can be solved by refining and conching modifications. For example, when HC is used in a universal system like a ball-mill, increasing the processing time and reducing the particle size minimizes the specified risks. Besides, it is possible to use HC first after grinding to a particle size of less than 100 μm in advanced grinders. The effect of grinding on the reduction of particle size of an anhydrous paste based on hazelnut and cocoa was studied by Miele et al. (2020) and the results revealed that an increase of grinding time significantly decreased the particle size (D_{90}) of products. Also, similar results were reported by Cavella et al. (2020) about the effect of ball milling of a white chocolate and hazelnut paste on the reduction of solid particle size and resulted in improvement of stability.

3.3. Water activity

The *aw* values of samples were ranged between 0.31 and 0.38 which was lower than the control sample (0.40) and it was in the desired range to produce chocolate with high quality from the industrial point of view (Table 1). However, a low level of HC improved water activity more than a high level of HC. The low amount of *aw* was considered as a positive factor to attain physical, chemical, and microbiological stability of the product. The effect of the addition of HC on the *aw* of HCC samples was explained by using a cubic model ($R^2 = 0.7257$). The model was found to be significant ($P < 0.05$) while lack of fit was not significant ($P > 0.05$). As is seen in Fig. 1, with an increase in the amount of MOP and HC, the aw of HCC samples increased. Konar (2013) used maltitol and isomalt in the formulation of prebiotic milk chocolate at different conching temperature. They demonstrated that due to the lower hygroscopic power of isomalt compare with maltitol, isomalt caused an increase in the water activity of samples. Also, Konar, Özhan, Artık, Dalabasmaz, and Poyrazoglu (2014) stated that using inulin in the formulation of milk chocolate cause a decrease in the water activity of samples. They concluded that inulin as a hydrophilic component binds to the water molecule and decrease water activity and has a fat-replacement quality. However, in our study, increases in HC caused increases in the water activity which may be related to the fatty nature of HC. More HC means higher fat content and therefore causes higher hydrophobicity behavior of chocolate. As fat cannot bond with water molecules, more water molecules will exist as free water in chocolate and cause an increase in water activity. Also, different parameters might affect aw of chocolate products such as conching temperature, bulking sweeteners (Konar, 2013), chocolate types (Rossini, Norena, & Brandelli, 2011), and process (Carvalho, Romoff, & Lannes, 2018).

3.4. Total phenolic content and in vitro digestion

The values of TPC before and after digestion and % bioaccessibility was demonstrated in Table 1. The TPC obtained after digestion was found to be quite high compared to pre-digestion. The F1, F7, F8, and F13 samples had the highest post-digestion TPC due to their maximum hazelnut cake content. The effect of the addition of HC on TPC was explained by using a linear model (Fig. 1) and the model was found to be significant ($P < 0.05$) with the R^2 values as 0.9809 and 0.9159 for pre-digestion and post-digestion, respectively. The high values of TPC of HCC samples are related to the high TPC amount of HC (Supplementary File 3). Results of this study were in agreement with other studies which demonstrated that adding dried fruit to chocolate can increase the antioxidant capacity of chocolate due to its phenolic content (Komes, Belščak-Cvitanović, Škrabal, Vojvodić, & Bušić, 2013).

It was reported that amine or carboxyl groups of proteins can interact with a benzene ring and hydroxyl groups of polyphenols and produce a network structure that changes the bioavailability of polyphenols (Siebert, 1999). Within the scope of our study, the use of HC with a high protein content of 40.35% on a dry matter basis (Supplementary File 3), presented similar results. The interaction of the protein-phenolic compound before digestion caused the low efficiency of the extraction. While, after *in vitro* digestion of HCC samples, the complex matrix formed by protein-phenolic interaction is degraded, therefore, recovery of phenolic substances is increased and the bioaccessibility of polyphenols was so high. Our results are in agreement with the results of Xiong et al. (2020) which studied the stability of protein-polyphenol aggregate particles, created by complexing polyphenols from blueberry and muscadine grape pomaces. It was stated that the TPC of the protein-polyphenol aggregate particles after digestion was significantly higher than the berry pomace extract. They demonstrated that

Table 2
The color and texture properties, and Casson model parameters of samples.

Sample	Color					Texture		Casson Model Parameters		
	L^*	a^*	b^*	C^*	h^*	Hardness (N)	Brittleness (mm)	τ_0 (Pa)	η_{pl} (Pa.s)	R^2
Control	32.18	6.98	7.98	10.60	48.82	7.85	1.02	2.21	1.37	0.9882
F1	27.79	5.16	6.16	8.03	50.05	8.40	0.56	2.23	1.20	0.9948
F2	30.87	6.16	7.26	9.52	49.71	10.06	0.59	2.03	1.17	0.9916
F3	29.83	5.76	7.06	9.11	50.76	9.89	0.60	1.91	1.24	0.9929
F4	28.80	5.58	6.84	8.79	50.79	8.94	0.66	2.01	1.19	0.9939
F5	29.49	5.67	6.85	8.89	50.39	8.77	0.56	1.80	1.21	0.9930
F6	29.82	5.99	7.18	9.35	50.13	9.32	0.55	2.06	1.19	0.9930
F7	28.40	5.11	6.24	8.07	50.67	8.27	0.63	1.47	1,30	0.9940
F8	27.79	4.79	5.82	7.55	50.52	8.91	0.52	1.91	1,42	0.9938
F9	30.76	6.18	7.56	9.76	50.71	9.16	0.57	2.05	1.17	0.9923
F10	28.08	5.46	6.63	8.59	50.53	10.05	0.58	2.12	1.28	0.9928
F11	30.62	6.09	7.17	9.41	49.68	11.55	0.62	1.78	1.41	0,9912
F12	28.71	5.28	6.66	8.50	51.60	8.52	0.50	2.15	1.29	0,9941
F13	28.11	5.01	6.07	7.86	50.49	8.85	0.62	2.35	1.25	0,9939

Results of analysis were given as mean. Five replicates of the colour and texture experiments were performed. Rheology experiments were performed in triplicate.

complexation of berry polyphenols with edible proteins to form protein-polyphenol aggregate particles, effectively protect polyphenols from degradation. On the contrary, Cantele et al. (2020) was reported that the amount of TPC in the post-digested was significantly lower than pre-digested beverages samples which were enriched by cocoa bean shell. They demonstrated that the solubility in the matrix and degradation by enzymes, salt, and pH causes a decrease in TPC after digestion. This inconsistency with our results may be related to their release from the food matrix, molecular size, and interaction between TPC and food components.

Also, TPC in chocolate and its products can give different results in different studies. Such differences are due to differences in the type and amount of enrichment components in the formulation, the cocoa content and origin, the applied extraction solvents, and the extraction methods. In addition to phenolic compounds, sugar can affect by the lack of selectivity of the Folin-Ciocalteu reagent that reacts with reducing compounds such as vitamin C, amino acids, Cu (I), and carotenoids (Komes et al., 2013).

3.5. Color and textural properties

3.5.1. Color of HCC samples

The color properties of the samples were detailed in Table 2. According to the obtained results, L^*, a^*, b^*, and C^* values of HCC samples were found to be lower than the control sample. The F12 coded sample had the highest h° value with 51.60. The predicted models for color properties of samples were linear (L*, h°) and quadratic (a^*, b^*, and C^*). The models were found to be significant ($P < 0.05$) and lack of fit was not significant ($P > 0.05$). The R^2 values of L^*, a^*, b^*, C^* and h^* were 0.9153, 0.9738, 0.9324, 0.9617, and 0.5180 respectively, which shown that these models successfully can explain the effect of HC-added compound chocolate formulation on the color values. The effect of (AC) and (BC) on a^*, b^*, and C^* values was significant ($P < 0.05$) in the model. Also, the effect of (AB) on a^* value was significant ($P < 0.05$) while effect of (AB) on the b^* was not significant ($P > 0.1$) therefore, it was omitted from the model with BER. The effect of HC on the color properties of HCC samples was shown in Fig. 1 and with increasing of MOP and decreasing of HC the L^*, a^* and b^* values increased. Hazelnut pomace with dark color and sugar and MOP with white color caused changes in product color.

The findings of L* value is consistent with that reported by Acan et al. (2020) which used grape pomace as the replacer for sugar and milk originated powders in the formulation of chocolate. It was stated that as the amount of grape pomace decreased, the L* values increased. However, the L* values in their study (25.30–27.60) were slightly lower than our results (27.79–30.87) which may be related to the difference in the composition of grape pomace and hazelnut cake. Also, the h° values increased with an increase in the amount of HC in chocolate which may be related to an increase in the particle size. Our results are in agreement with those reported in a previous study by Afoakwa, Paterson, Fowler & Vieira (2008) which showed that differences in h° (38.9–43.9) were depended on the particle size and particle size distribution (18–50 µm, D_{90}).

In the chocolate and derivative products, product brightness and color are important parameters affecting the consumer's purchasing potential. Particle size and fat content affect visual properties (Afoakwa, Paterson, Fowler, & Vieira, 2008). Particle size variation over a wide range or the presence of large particles can adversely affect smoothness. In this case, the brightness level may be affected. Also, this may change the microstructure of the samples to promote fat-bloom formation. Also, fat or oil type and used bulking agents such as carob powder, may cause differences in color parameters (Shiehzadeh, 2019). Fats containing triglycerides with low melting temperatures may shorten the shelf life by causing oil migration to the surface. The bulking agents to be used can affect the hygroscopicity properties of the final product, which is an important process and quality parameter for chocolate. Therefore, the raw materials used and the processes applied should be carefully selected.

3.5.2. Texture of HCC samples

The textural properties of HCC samples were detailed in Table 2. Hardness and brittleness were ranged between 7.85 and 11.55 N and 0.52–1.02 mm, respectively. Minimum hardness and maximum brittleness belonged to the control sample. The effect of addition HC on hardness and brittleness of samples was explained by linear and cubic models with the R^2 values of 0.5854 and 0.8772, respectively. The model explaining the effect of HC on the hardness of samples was found to be significant ($P < 0.05$) and lack of fit was not significant ($P > 0.05$), while for brittleness, the model and lack of fit were not significant ($P > 0.05$). The effect of (AC), (BC) and (ABC) on brittleness of products were significant ($P < 0.05$) in the model, however, the effect of (AB) was not significant ($P > 0.05$). Therefore, it was removed from the model with BER. The effect of HC on the texture of HCC samples was shown in Fig. 1 and with an increase in HC amount, the hardness value decreased. The higher value of brittleness was observed in the samples with higher HC-lower MOP, higher sugar-lower HC, and higher MOP-lower sugar content. Also, the interaction term of ABC had a positive correlation with brittleness value.

There is an agreement between our results and the results described reported by Nattress, Ziegler, Hollender, and Peterson (2003). In their study, hazelnut paste (5%, 10%) was added to the dark chocolate formulation and the hardness value decreased as the amount of hazelnut paste increased in the formulation. Hazelnut paste's major component is oil. The increase in the amount of oil causes a decrease in the hardness of

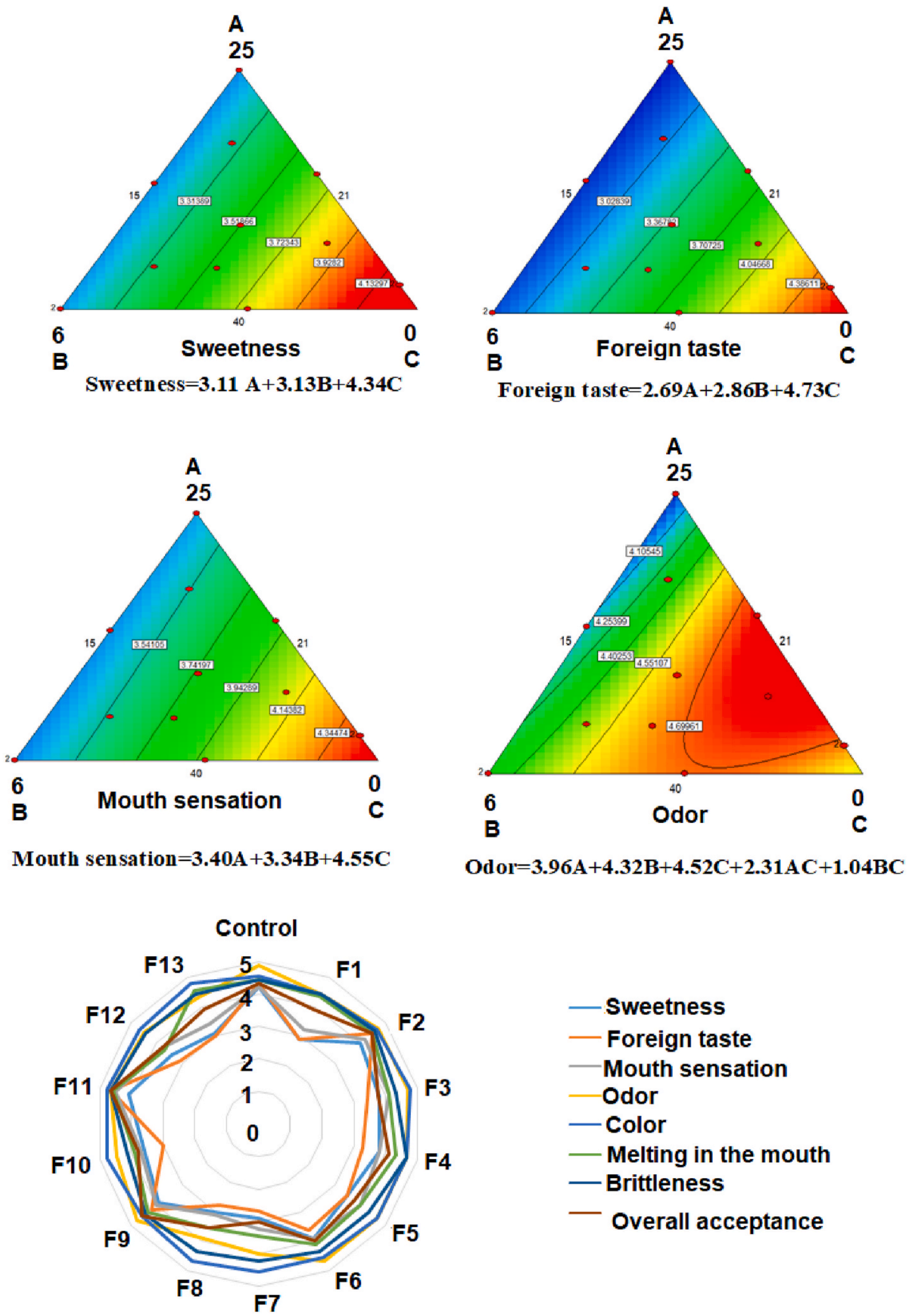

Fig. 2. Sensory properties of hazelnut compound chocolate samples.

the chocolate. However, chocolate should have a hardness above a significant level (Konar, 2013). Besides, the increase in the amount of oil significantly affects product flow properties. The coexistence of oils with different triglyceride structures also increases the risk of fat-bloom (Beckett, 2009).

Furthermore, our outcomes are in agreement with the result reported by Afoakwa, Paterson, Fowler, & Vieira, (2008) which demonstrated that as the particle size of chocolate increased from 18 to 50 μm, hardness values significantly decreased. In our research, as the amount of HC in the formulation increases, particle size increased, and therefore, hardness decreased.

Carvalho, Romoff, & Lannes, (2018) were added freeze-dried kale and grape to the milk chocolate. They demonstrated that the effect of lyophilized grapes on the hardness value of milk chocolate was significant, while it was not significant for lyophilized kale. These results on the hardness value may be due to the difference in particle size. The sample with the highest particle size was milk chocolate containing lyophilized grapes.

3.6. Evaluation of sensory analysis

The sensory analysis helps to identify the degree of liking of the final product by consumers, which can help to select the most suitable formulation. Fig. 2 showed the results of the sensory assessment scores of the HCC samples according to the control sample. In sensory analysis sweetness, foreign taste, mouth sensation, odor, color, melting in the mouth, brittleness, and overall acceptance were evaluated and the results found in the range of 2.8–4.1, 2.6–4.6, 3.1–4.5, 3.9–4.7, 4.4–4.7, 3.4–4.5, 4.1–4.6, and 3.0–4.6, respectively. The control sample scored the highest in sweetness and odor parameters compared to HCC samples.

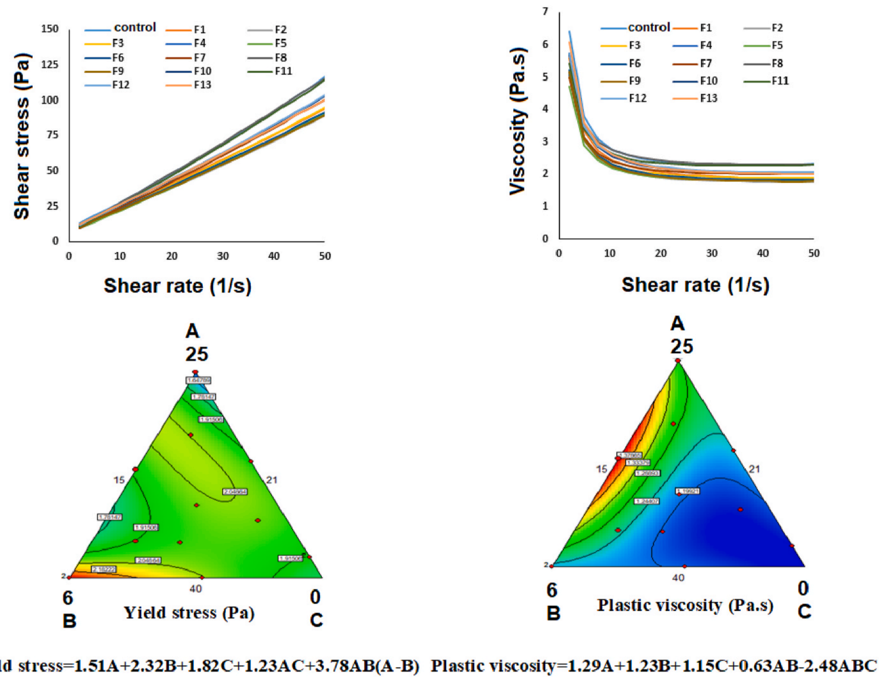

Fig. 3. Effect of formulations on flow behavior of samples.

The effect of HCC samples on the sweetness (R^2 = 0.829), foreign taste (R^2 = 0.951), mouth sensation (R^2 = 0.831), color (R^2 = 0.037), melting in the mouth (R^2 = 0.691), and overall acceptance (R^2 = 0.793) were explained by linear models, while the effect on the odor (R^2 = 0.884) and the brittleness (R^2 = 0.952) was explained with quadratic and cubic models. The model explaining the effect of HCC on the sweetness, foreign taste, mouth sensation, melting in the mouth, odor, brittleness, and overall acceptance was found to be significant ($P < 0.05$) and lack of fit was not significant ($P > 0.05$), while for color both model and lack of fit was not significant ($P > 0.05$).

The effect of HC on some sensorial properties of HCC samples was shown in Fig. 2. As the amount of HC increased, panelist's scores on sweetness, foreign taste, mouth sensation, and odor criteria decreased. The bitterness of HC suppressed the sweetness sense of samples and increased the perception of foreign taste especially when used at a high substitution amount. Our results are consistent with those of Acan et al. (2020) study which reported that as the amount of grape pomace in the formulation of chocolate increased, the scores on sweetness and foreign taste decreased that may be related to the bitterness of phenolic compounds of grape pomace. As mentioned before, the increase in the amount of HC increased the particle size which may produce a sandy structure which produces the problem in the mouth sensation. Therefore, with reducing the particle sizes of the HC by pre-treatment operations such as refining of the CC paste in ball mills for a longer time, the mouth-sensing criteria of HCC samples can be achieved to the consumer desirability level (Konar, 2013; Acan et al., 2020). Nattres, Ziegler, Hollender & Peterson (2003) investigated the effect of use hazelnut puree in the dark chocolate formulation and determined that the increased amounts of hazelnut puree resulted in decrease in chocolate aroma. Chocolate aroma and burnt flavor values were significantly affected by the addition of hazelnut puree to the formulation.

3.7. Flow behavior

Fig. 3 shows the graph of shear stress and viscosity against the shear rate at 40 °C of the HCC samples. The increase in the shear stress to a shear rate of molten samples continues to decrease and the apparent viscosity decreased with increasing shear rate which demonstrated that the HCC samples showed shear-thinning behavior which was in agreement with the previous study (Toker et al., 2016). The Casson model was used to specify yield stress and plastic viscosity (Table 2) which showed high R^2 values (0.9882–0.9948). The yield stress and plastic viscosity values were varied between 1.47 and 2.35 Pa, and 1.17–1.42 Pa s, respectively. Many factors may affect the flow behavior of chocolate products such as the amount and distribution of fat contained in the formulation, the number of solid particles, the size, and shape of the particles, and the type of emulsifier (Glicerina, Balestra, Rosa, & Romani, 2013).

The effect of HCC samples on the yield stress (R^2 = 0.779) and plastic viscosity (R^2 = 0.952) was explained by using cubic and special cubic models, respectively. The model explaining the effect of HCC on the yield stress and plastic viscosity was found to be significant ($P < 0.05$) and lack of fit was not significant ($P > 0.05$). The effect of (AB) and (ABC) on yield stress was not significant ($P > 0.05$), therefore, they were removed from the model with BER. The effect of (AB) and (ABC) on plastic viscosity was found to be significant ($P < 0.05$) in the model. Also, the effect of (AC) on plastic viscosity was not significant ($P > 0.05$) and it was removed from the model by BER. Fig. 3 shows the effect of HP on yield stress and plastic viscosity of HCC samples. As the amount of HC increased, plastic viscosity value increased. When HC and sugar increased and MOP decreased in the formulation, yield stress increased. The rheological character of CC samples was influenced by the particle size of the HC. An increase in the amount of HC caused difficulty in flowing coarse particles over each other which led to an increase in the plastic viscosity value.

Table 3
The results of two step optimization.

	1st Optimization	2nd Optimization
Sugar (g/100 g)	40.000	38.501
MOP (g/100 g)	6.006	21.000
HC (g/100 g)	14.994	1.499
Post-digested TPC (mg GAE/kg)	3768.45	–
Overall acceptability	3.814	4.563
Desirability	0.649	0.919

HC: Hazelnut cake, MOP: Milk originated powders, TPC: Total phenolic content.

Normally, it is expected that chocolate with larger particle size has higher plastic viscosity and yield stress values which can be seen in Fig. 3 as well. Furthermore, the rheological properties of chocolate are affected by two factors: 1) formulation (particle size distribution, type and amount of fat, the concentration of emulsifiers) and 2) process (such as refining, conching, and tempering) (Toker et al., 2016). Accordingly, the combination of formulation and process should be adjusted to the obtained product with good quality. Also, differences between the rheological properties of CC products mainly resulted from the formulation and type of ingredients (especially fatty materials). However, our results differ from some published studies (Cavella, Miele, Fidaleo, Borriello & Masi, 2020; Miele, Borriello, Fidaleo, Masi & Cavella, 2020) which used mill ball refining and grinding to decrease the particle size of chocolate content hazelnut paste. They reported that the reduction of particle size increased the viscosity of products. This inconsistency may be due to the formation of particles which tend to agglomerate during the refining process in products such as chocolate. The particle surface area and its surface properties are extremely important in the Casson plastic yield and Casson plastic viscosity is affected by particle packed volume (Beckett, 2009). At the same time, the increased surface area due to the reduction in particle sizes resulted in increased inter-particle interaction points, a decrease of the packing volume fraction of solids, resulting in a tighter structure product and higher yield stress and plastic viscosity (Cavella, Miele, Fidaleo, Borriello & Masi, 2020; Glicerina, Balestra, Rosa & Romani, 2013).

3.8. Optimization of HCC formulation

Two different optimization targets were selected using the models obtained within the scope of the study. In the first optimization, the TPC and overall acceptability values were targeted as maximum, and in the second optimization, the amount of sugar was selected as the minimum and the general acceptability value was maximum. The HCC samples obtained as a result of optimization formulations were given in Table 3. Desirability values obtained under the first and second optimization conditions were 0.649 and 0.919, respectively. In both optimization conditions, the overall acceptability was selected as maximum. The reason for this was to produce a healthy and functional CC formulation as acceptable by the consumers. The formulations for producing the most preferred (overall acceptability 4.563) HCC samples were shown in Table 3.

4. Conclusion

HC is a by-product of hazelnut oil factories with high phenolic content and generally is used as animal feed. Therefore, the valorization of HC in the production of chocolate will have an important advantage for both human health and the economy. HC was used as a replacer for sugar and milk & whey powder in CC formulation and 13 different experimental points were determined by mixture design. The effect of HC on some physicochemical, rheological, sensorial, and bio-accessibility of phenolic compounds of cocolin samples was investigated. With the optimization study, the product with the highest bioactive and overall acceptability scores was targeted. The results revealed that hazelnut pomace may be used in CC to partially substitute sugar, milk powder, and whey powder. It may increase the functional properties of CC and reduce product costs. Also, this study may be the driving force for the studies aimed at diversifying the valorization of food by-products.

CRediT authorship contribution statement

Kubra Bursa: Methodology, Formal analysis. **Omer Said Toker:** Conceptualization, Writing - original draft. **Ibrahim Palabiyik:** Conceptualization, Writing - original draft. **Mustafa Yaman:** Methodology, Formal analysis. **Nasim Kian-Pour:** Methodology, Formal analysis. **Nevzat Konar:** Conceptualization, Writing - original draft. **Mahmut Kilicli:** Methodology, Formal analysis.

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Appendix A. Supplementary data

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