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Improvement of Antioxidant Activity and Physical Stability of Chocolate Beverage Using Colloidal Cinnamon Nanoparticles

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Abstract
In this study, the functionality of colloidal cinnamon nanoparticles in improving the antioxidant activity and suspension stability of a chocolate beverage formulated with two types of cocoa powder (natural and alkalised) was investigated. Cinnamon-loaded nanoparticles based on shellac and xanthan gum prepared using anti-solvent precipitation were incorporated in the chocolate beverage in multilevel proportions. The results showed that the addition of the nanoparticles improved the total phenolic content up to 40% and antioxidant activity up to 60% depending on the level of the nanoparticles added. Improvement of the physical stability of the chocolate beverage was observed regardless of the cocoa powder type. As the sedimentation index of the beverages made with alkalised and natural cocoa powders after 96 h was 5.7 and 85.7, respectively, the stabilisation effect of the nanoparticles seemed to be significantly influenced by the characteristics of the beverage raw material. The prevention of cocoa particle sedimentation was attributed to the colloidal network that originated from xanthan gum as shown by Cryo-SEM imaging or the increased viscosity of the mixture (i.e. from 2.4 to 27.7 mPa s at a shear rate of 50 s^{-1}). Incorporation of the colloidal cinnamon nanoparticles had no significant effect on pH and a slight effect on the colour of the chocolate beverages. The formulated nanoparticles could be a promising complement to "ready-to-drink" products to enrich the bioactive content and prolong suspension stability.

Keywords Chocolate beverage · Cinnamon · Antioxidant · Hydrocolloids · Nanoparticles

Introduction

Cocoa (*Theobroma cacao* L.), the main ingredient of chocolate, is naturally rich in bioactive compounds, such as polyphenols and methylxanthines (Carrillo et al. 2014). It is native to Central America and was the main ingredient of a spiced beverage by the Aztecs and the Mayas. After being introduced in Europe by the Spanish, chocolate drinks formulated with sugar and spices were widely consumed from England to Italy by the mid-eighteenth century (Cidell and Alberts 2006). Until to date, chocolate beverages are still very popular. They have even been developed and marketed as easy-to-consume products, such as "instant hot chocolate" and "ready-to-drink chocolate", and have been a subject in many advanced studies (Peters et al. 2011; Dogan et al. 2011; Rivas et al. 2018; Benković et al. 2013). In the development of chocolate beverage products, sedimentation of cocoa particles is a technological challenge to resolve. Sedimentation significantly affects the appearance of the products and subsequently influences the product acceptability and consumer liking. Some efforts have been carried out by food technologists to overcome this issue, such as by incorporating hydrocolloids as stabilising agents (Dogan et al. 2013).

Aside from that, bioactive compounds' degradation during cocoa processing is an essential issue. It is notable that

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fermentation, drying, roasting and alkalisation play significant roles in the degradation of polyphenols (Oracz et al. 2015; Wollgast and Anklam 2000; Żyżelewicz et al. 2016). Some of the bioactive compounds, such as catechin, epicatechin, procyanidin B1 and procyanidin B2, have been reported to be present in cocoa powder at low levels in the range of 0.01–0.12% (*w*/*w*) (Schinella et al. 2010). To overcome this issue, food technologists have made efforts to increase the content of bioactive compounds in cocoa-derived products. Two different approaches can be applied, namely (a) modifying the process to prevent polyphenol degradation and (b) enriching the final product with polyphenols derived from plant substances (Di Mattia et al. 2017; Muhammad et al. 2018). The latter has been proven in a number of studies using various polyphenol-rich plant materials, such as raspberry leaves, nettle leaves, mangosteen pericarp, blackberry, goji berry, black mulberry, peanut skins, ginger and cinnamon, either as dry powdered material, extract or encapsulated form (Belščak-Cvitanović et al. 2012; Albak and Tekin 2014; Belščak-Cvitanović et al. 2015; Sim et al. 2016; Dean et al. 2016; Morais Ferreira et al. 2016; Gültekin-Özgüven et al. 2016; Muhammad et al. 2017; Lončarević et al. 2018). Encapsulation of the polyphenols before adding them into food can mask their bitterness and enhance their oxidation stability (Joye and McClements 2014). Jaeger et al. (2009) suggested that exposing the beneficial health effects of foods, such as polyphenol-rich beverages, to consumers may enhance their appeal to consumers.

In our previous work, nanoparticles made of a combination of shellac, xanthan gum and cinnamon extract have been successfully fabricated (Muhammad et al. 2018). Shellac as a biopolymer is a mixture of polar and non-polar compounds primarily containing polyhydroxy polycarboxylic esters, anhydrides and lactones (Sedaghat Doost et al. 2019). Shellac can be utilised for the encapsulation of bioactive compounds owing to its unique properties, including hydrophobic nature, sustainable origin, good film-forming properties, excellent gloss, low gas permeability and recognition as food additive (E904) (Byun et al. 2012; Farag and Leopold 2011; Stummer et al. 2010). It has been previously shown that quercetin flavanol was successfully incorporated within core–shell nanoparticles of shellac with a high encapsulation efficiency (Sedaghat Doost et al. 2018). Xanthan gum, used in the formulation of the nanoparticles as a stabilising agent, is a natural polysaccharide that has been widely used in many food products (Habibi and Khosravi-Darani 2017). Cinnamon (genus *Cinnamomum*) has gained considerable attention in the food industry as it is rich in bioactive compounds, such as polyphenols. Cinnamon and its derivatives are also of medical interest due to their antioxidant, anti-inflammatory, antitumor, anticancer, antidiabetic and anti-hypertriglyceridemia potencies (Muhammad and Dewettinck 2017; Ribeiro-Santos et al. 2017).

In our previous study, the incorporation of nanoparticles, which were in the lyophilised form, significantly improved the phenolic content and antioxidant activity of milk and white chocolates (Muhammad et al. 2018). In addition, we found that the odour alteration of chocolate with non-encapsulated cinnamon extract was more pronounced than that of chocolate with the cinnamon nanoparticles indicating that the encapsulation of cinnamon using a shellac–xanthan gum complex has a positive impact in preventing odour alteration of the cinnamon-enriched chocolates. Nevertheless, it was shown in the released study that a high amount of phenolic compounds (around 70%) was still entrapped in the chocolate matrix. This is caused by the fact that the cinnamon extract is hardly released from the solid matrix of the chocolate bar. In that condition, it can be expected that cinnamon has a low bioavailability during the digestion process resulting in a low antioxidant activity. Based on that result, a less complex matrix, such as a beverage, may be better as food carrier for the delivery of nanoparticles containing bioactive compounds to the gastrointestinal tract. In addition, the involvement of lyophilisation in the nanoparticle fabrication applied in our previous work may lead to a harder particle structure resulting in a more difficult release of the polyphenols from the nanoparticles. Therefore, a modification of the nanoparticle production process is required. By eliminating the lyophilisation step, a colloidal form can be achieved, and, thus, it can be further applied in a chocolate beverage.

The use of the colloidal cinnamon nanoparticles in the chocolate beverage is hypothesised to be able not only to enhance the antioxidant properties but also to prevent chocolate particle sedimentation due to the presence of xanthan gum in the nanoparticles. It was shown in the earlier studies that the incorporation of this hydrocolloid in chocolate beverages influences the suspension stability, albeit, it also affects the rheological behaviour and appearance (Toker et al. 2012; Toker et al. 2013; Dogan et al. 2016). Thus, this study was carried out to investigate the functionality of the colloidal cinnamon nanoparticles in improving antioxidant and physical properties of chocolate beverages.

Materials and Methods

Materials

Cinnamon powder (*Cinnamomum burmanii* Blume), originating from Kerinci (Indonesia), was obtained from CV. Orizho (Indonesia). Shellac fine powder SSB 55 Astra FP (SSB Stroever GmbH & Co. KG, Bremen, Germany) and xanthan gum (Satiaxane CX 931, Cargill France SAS) were used to fabricate colloidal nanoparticles. Natural and alkalised cocoa powders were obtained as gift samples from Cocoa Processing

Co. Ltd. (Ghana) and Barry Callebaut Belgium NV (Belgium), respectively.

Preparation of Colloidal Cinnamon Nanoparticles

The cinnamon solution was prepared by stirring 10 g of cinnamon powder in 100 ml (i.e. 79 g) ethanol for 48 h at 20 °C, followed by removing the residue using a vacuum filter. An anti-solvent precipitation method was used to fabricate colloidal cinnamon nanoparticles in a shellac–xanthan gum system according to the protocol of Muhammad et al. (2018). Shellac (2.0 g) was dissolved in ethanol (49.0 g) and, then, mixed with the cinnamon solution (49.0 g). Separately, xanthan gum (0.6 g) was prepared in distilled water (299.4 g). The shellac–cinnamon extract solution was injected using a syringe into the xanthan gum solution, and, then, the solvent was evaporated in a vacuum rotary evaporator (Laborota 4000 Heidolph, Germany) at 50 °C to form colloidal cinnamon nanoparticles.

Preparation of Chocolate Beverage

A simple chocolate beverage model system containing sucrose and cocoa powder was prepared according to the formulation of Dogan et al. (2013). Briefly, 12 g sucrose and 6 g cocoa powder were added into 120 ml distilled water (80 °C) and then stirred under closed conditions using a magnetic stirrer for 15 min to let the mixture reach ambient temperature. Separately, distilled water was mixed with the colloidal cinnamon nanoparticles in multilevel ratio (4:0, 3:1, 1:1, 1:3 and 0:4). Finally, this mixture (60 ml) was added to the sucrose–cocoa powder dispersion at ambient temperature. Beverage samples formulated without cocoa powder incorporated with colloidal cinnamon nanoparticles were prepared to better investigate the functionality of colloidal nanoparticles in chocolate beverages. Chocolate beverage samples made of alkalised cocoa powder containing the individual materials used for the nanoparticle fabrication (i.e. shellac, xanthan gum and cinnamon) were also prepared as control samples to get a better understanding of the effect of those materials on the antioxidant properties and physical stability of the beverages.

Physical Analysis of Cocoa Powder

The wettability and solubility of the cocoa powder were determined according to the method of Dogan et al. (2016). In the wettability test, 4 g of the cocoa powder was poured into a cylindrical container containing 40 ml of water at 80 °C, and, then, the time required for all particles to disappear was recorded by visual assessment. The result was expressed as wetting time (s). In the solubility test, 4 g of the cocoa powder in 40 ml of water at 80 °C was continuously stirred for 30 min and, then, centrifuged at 13,102 g. Finally, 15 g of supernatant was dried in an oven at 120 °C to a stable weight.

The particle size of the cocoa powder was measured as a suspension in water using a Malvern Mastersizer 3000 (Malvern Instrument Ltd, UK), while the colour of the cocoa powder was determined using a colourimeter (Minolta Model CM-2500D Spectrophotometer, Konica Minolta Sensing, Tokyo, Japan). The results were expressed in terms of the CIELAB system where L* is the lightness component, a* is the green to red component and b* is the blue to yellow component. Chroma (C*) and °Hue were calculated using Eq. (1) and Eq. (2), respectively.

$$C^* = \sqrt{a^{*2} + b^{*2}} \quad (1)$$

$$^{\circ}\mathrm{Hue} = \tan\left(b^*/a^*\right) \quad (2)$$

Fat Content Analysis of Cocoa Powder

Approximately 4 g of cocoa powder was mixed with 45 ml of distilled water and 55 ml of HCl (25%) and then boiled for 15 min. The sample solution was filtered using a filter paper. After the filter paper containing the sample was dried, it was then extracted with petroleum ether (200 ml) for 4 h in a Soxhlet apparatus. The solvent was, then, evaporated using a rotary evaporator at 50 °C to obtain the fat.

Particle Size Measurement of the Colloidal Cinnamon Nanoparticles

The *z*-average particle size of the colloidal cinnamon nanoparticles was measured using Photon Correlation Spectroscopy (PCS100M, Malvern Instrument Ltd., UK) at 25 °C. A few drops of the colloidal dispersion was appropriately diluted in distilled water. The *z*-average particle diameter was obtained by cumulant analysis of the autocorrelation function obtained from the light scattered at a scattering angle of 150°.

Total Phenolic Content and Antioxidant Analysis

Folin–Ciocalteu Method

The Folin–Ciocalteu method, following the procedure described by Udayaprakash et al. (2015), was used to estimate the total phenolic content of the cocoa powder, the colloidal cinnamon nanoparticles and the chocolate beverage. The sample (200 µl) was well-mixed with distilled water (1 ml) and Folin–Ciocalteu reagent (200 µl). After incubation for 6 min, 7% Na_2CO_3 solution (2.5 ml) and distilled water (2.1 ml) were added to the mixture. UV–visible spectrophotometry (Varian Cary 50 Bio, Agilent Technology) was used to measure the absorbance at 760 nm after 90 min incubation at ambient temperature. The total phenolic content was expressed by means of the epicatechin equivalent.

Ferric-Reducing Antioxidant Power Assay

Briefly, 2.5 ml of phosphate buffer (0.2 M, pH 7) and 2.5 ml of 1% potassium ferricyanide were added into 1 ml of the sample. The mixture was incubated at 50 °C for 30 min in a water bath. After adding 2.5 ml of 10% trichloroacetic acid, the solution was centrifuged for 10 min to separate larger aggregates. The supernatant (2 ml) was mixed with distilled water (2 ml) and 0.1% $FeCl_3$ (0.4 ml), and, then, the absorbance was measured at 700 nm. A standard plot of ascorbic acid was used to calculate the ferric-reducing antioxidant power (FRAP) activity (Udayaprakash et al. 2015).

Phosphomolybdenum Method

The phosphomolybdenum method according to Udayaprakash et al. (2015) was also carried out to confirm the antioxidant activity of the samples. The sample (0.5 ml) was added into 4.5 ml of the reagent solution consisting of 0.6 M sulphuric acid, 28 mM sodium phosphate and 4 mM ammonium molybdate at the ratio of 1:1:1. The mixture was maintained in a water bath at 95 °C for 90 min. Afterwards, the sample was cooled down to room temperature, and, then, the absorbance was measured at 695 nm. The total antioxidant content was calculated by means of a standard plot of tannic acid.

2,2-Diphenyl-1-Picrylhydrazyl Assay

The protocol by Muhammad et al. (2018) with a slight modification was followed to conduct 2,2-diphenyl-1-picrylhydrazyl (DPPH) radical-scavenging activity analysis of the colloidal cinnamon nanoparticles and the chocolate beverage. The sample was diluted with distilled water (50 times), and, then, 100 μl of the diluted sample was added into 4 ml DPPH (0.1 mM). The absorbance was measured at 517 nm after incubation under dark conditions for 30 min. The inhibition of the radical reaction of the samples was calculated using Eq. (3).

$$\text{inhibiton} = \left(1 - \frac{\text{Abs sample}}{\text{Abs control}}\right) \times 100\% \qquad (3)$$

Brix°, pH Value and Colour of the Chocolate Beverage

Brix° (total soluble solids) of the samples was estimated using a density meter (Anton-Paar, DMA 5000), and the pH value was measured using a pH meter (Schott Instruments, LAB 850), respectively. The measurements were done at 20 °C in triplicate for each sample. A colourimeter was used to determine the colour (L*, a* and b* values) of the chocolate beverages. In addition to C* and °Hue, the colour difference (ΔE*) between the chocolate beverages containing the colloidal cinnamon nanoparticles (1) and control (2) was calculated using Eq. (4).

$$\Delta E = \sqrt{\left(L_1^* - L_2^*\right)^2 + \left(a_1^* - a_2^*\right)^2 + \left(b_1^* - b_2^*\right)^2} \qquad (4)$$

Rheological Measurement of the Chocolate Beverage

Apparent viscosity measurements were conducted using an AR2000-ex rheometer (TA Instruments) equipped with concentric DIN cylinder (cylinder 42.00 mm; rotor outer radius 14.00 mm; stator inner radius 15.00 mm). The geometry gap was set at 5920 mm. Shortly, 20 g of chocolate beverage was analysed at 20 °C and subjected to a shear rate range of 10 to 50 s^{-1}.

Stability Test of the Chocolate Beverage

The physical stability of the chocolate beverages was observed by visual assessment, and, then, the sedimentation index (SI) was calculated after 24 and 96 h using a formula described in the study of Rivas et al. (2018) as shown in Eq. (5) where V is the initial sample volume and V_S is sediment volumes.

$$SI = (V_S/V) \times 100 \qquad (5)$$

Microstructural Observation

Firstly, the sample was lyophilised to remove water. Afterwards, a few grams of the lyophilised sample was diluted in a few drops of water. The samples were placed on the cryo-specimen holder and, then, cryo-fixed in slush nitrogen (− 210 °C) and transferred to the cryo-unit in the frozen state. Consecutive steps of fracturing, sublimation (20 min, − 70 °C), sputter-coating with platinum for 4 min and transferring into the microscope were conducted before the sample was observed at − 140 °C. A JEOL JSM 7100F SEM equipped with a PP3010T Cryo-SEM Preparation System (Oxford Instruments) was used to observe the microstructural properties of the colloidal cinnamon nanoparticles and the chocolate beverages.

Statistical Analysis

Data analysis was performed by SPSS 23.0 Software (SPSS Inc., Chicago, IL). Duncan's multiple-range test (DMRT) was used to compare the means in one-way ANOVA. The differences were considered significant at 0.95 confidence level. Pearson's test was carried out to determine the correlation coefficient between the proportion of the colloidal cinnamon nanoparticles and the physicochemical characteristics of the chocolate beverages.

Results and Discussion

Characteristic of the Cocoa Powder

The physical properties of the cocoa powder samples are summarised in Table 1. It was shown that the average particle size of natural and alkalised cocoa powder was about 28.5 and 18.5 μm, respectively. The alkalised cocoa powder has a longer wetting time and a higher level of soluble solids than the natural one. Soluble solid is an important parameter determining the quality of cocoa powder in the making of chocolate beverage as it influences the sensory properties, particularly taste perception (Benković et al. 2013). In the colour parameter, a darker colour was observed in the alkalised cocoa powder. These results are reasonable since the alkalisation of cocoa powder is mainly performed to modify the physical properties of cocoa powder and to improve the dispersibility of the cocoa powder in water. During the alkalisation, polymerisation of pigments occurs resulting in a darker colour (Andres-Lacueva et al. 2008; Oracz et al. 2015).

It was found that the alkalised cocoa powder used in this study contained a higher total phenol and antioxidant activity than the natural one. Theoretically, alkalization leads to a significant reduction of phenolic content (around 60–80% depending on the type of the compounds and the degree of alkalisation) due to oxidation of polyphenols at alkaline pH. In addition to the degradation of polyphenols, epimerisation may happen during the alkalisation which negatively affects the antioxidant activity (Andres-Lacueva et al. 2008; Payne et al. 2010; Mazor Jolić et al. 2011). However, in this study, the phenolic content and the antioxidant activity of both samples are not comparable since the cocoa powders were obtained from different sources. The polyphenol content of cocoa depends on the variety, the growing region and the processing conditions (Oracz et al. 2015).

Characteristics of the Colloidal Cinnamon Nanoparticles

It was found that the nanoparticles have a spherical shape with a smooth surface (Fig. 1). The *z*-average size of the colloidal nanoparticles was 162 nm as observed by photon correlation spectroscopy. The colour properties of the colloidal dispersions of cinnamon nanoparticles were as follows: $L^* = 40.35 \pm 0.2$; $a^* = 10.15 \pm 0.1$; $b^* = 9.52 \pm 0.1$; $C^* = 14.0 \pm 0.1$; °Hue = 46.6 ± 0.1. In the antioxidant activity analyses using the Folin–Ciocalteu method, FRAP (ferric-reducing antioxidant power) assay and phospomolybdenum method, the colloidal cinnamon nanoparticles were identified to have a total phenolic content of 171.2 ± 2.7 μg epicatechin equivalent/ml with (FRAP) activity of 1.25 ± 0.1 mmol l^{-1} ascorbic acid equivalent/ml and an antioxidant activity of 404.5 ± 35.1 μg tannic acid equivalent/ml.

Total Phenolic Content and Antioxidant Properties of the Chocolate Beverages

Figure 2 shows that the beverages formulated without cocoa powder incorporated with colloidal cinnamon nanoparticles demonstrated antioxidant activity whereby the activity was in line with the proportion of the nanoparticles. At similar water-to-colloid ratio, the antioxidant activity of the beverages

Table 1 Physicochemical properties and antioxidant activity of cocoa powder

Parameter	Natural cocoa powder	Alkalised cocoa powder
Fat content (%)	12.5 ± 1.7	10.2 ± 1.4
Particle size, D(4,3) (μm)	28.5 ± 0.7	18.5 ± 0.2
Wetting time (s)	44 ± 8	122 ± 22
Soluble solid (%)	19.2 ± 0.6	26.8 ± 0.3
Colour, SCE mode		
L*	47.3 ± 0.5	33.7 ± 0.7
a*	12.6 ± 0.2	18.8 ± 0.9
b*	28.3 ± 0.7	53.1 ± 0.4
Chroma (C*)	31.0 ± 0.7	56.7 ± 0.7
Hue	24.1 ± 0.3	20.5 ± 0.7
Total phenolic content (mg EE/g cocoa powder)	41.1 ± 0.4	45.2 ± 0.8
Antioxidant activity (mg TAE/g cocoa powder)	59.5 ± 4.6	82.8 ± 11.7

SCE, specular component excluded; EE, epicatechin equivalent; TAE, tannic acid equivalent

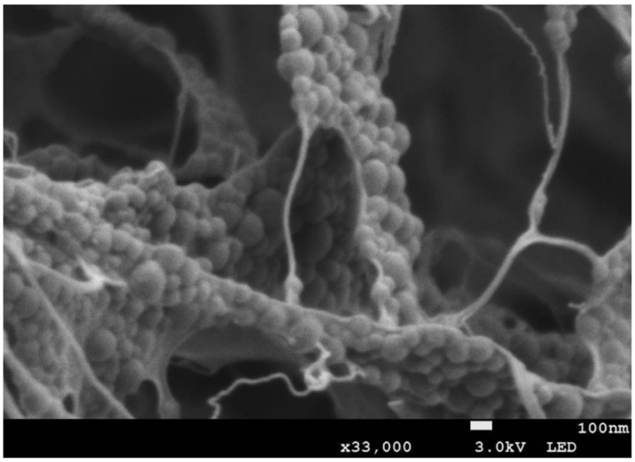

Fig. 1 SEM image of the colloidal cinnamon nanoparticles

was lower than that of the chocolate beverage incorporated with nanoparticles indicating that the cocoa powder also significantly contributed to the antioxidant activity of the chocolate beverages.

The enhancement of total phenolic content and antioxidant activity of the chocolate beverages of both cocoa powder types by the addition of the colloidal cinnamon nanoparticles was observed. The significant correlation between nanoparticle proportion and antioxidant properties of the chocolate beverages was confirmed by Pearson's correlation analysis (Table 2). Furthermore, highly significant correlations between the results of all employed antioxidant assays were verified. The results are in excellent agreement with our earlier study using chocolate matrices (Muhammad et al. 2018). The improved antioxidant activity of the chocolate beverage incorporated with the colloidal nanoparticles was mainly due to the presence of cinnamon extract (Fig. 3). As shown, the presence of either shellac or xanthan gum was not able to improve the phenolic content and antioxidant activity of the chocolate beverage. As 8 mg of concentrated cinnamon extract was present per millilitre of colloidal nanoparticle dispersion, the chocolate beverages formulated with the colloidal nanoparticles at a ratio of water to colloidal dispersion of 4:0, 3:1, 1:1, 1:3 and 0:4 contained 0, 67, 133, 200 and 267 mg cinnamon extract per 100 ml beverage, respectively (considering the 1/3 dilution during beverage production). Thus, the presence of cinnamon extract at a concentration of 267 mg per 100 ml chocolate beverage improved the total phenolic content up to 40% and antioxidant activity up to 60% depending on the antioxidant assay used.

It was shown that the chocolate beverages formulated using alkalised cocoa powder had a higher total phenolic content and antioxidant activity when assayed using FRAP and phosphomolybdenum method. This is because the alkalised

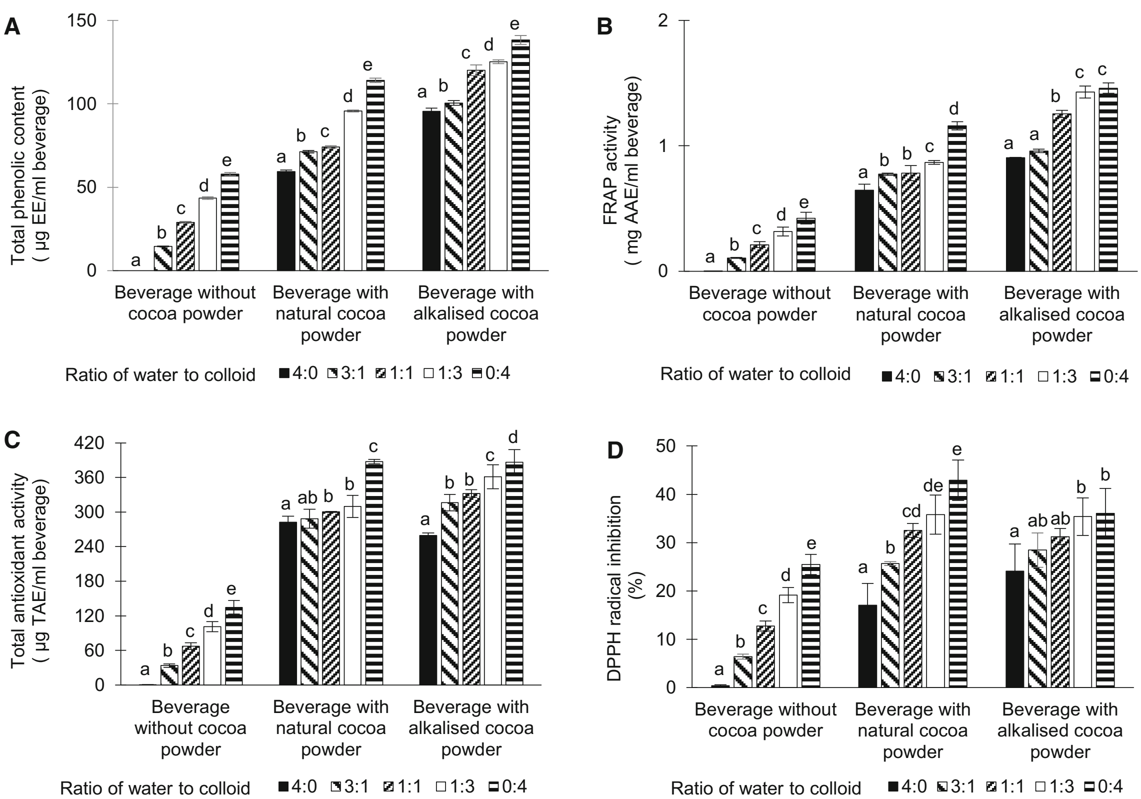

Fig. 2 (**a**) Total phenolic content, (**b**) ferric-reducing antioxidant power (FRAP) activity, (**c**) total antioxidant activity and (**d**) DPPH-radical scavenging activity of beverage. The statistical analysis was performed separately for each type of beverage. Mean values within each type of beverage with different lowercase letters differ significantly ($p < 0.05$)

Table 2 Correlation coefficients among antioxidant properties of chocolate beverages enriched with colloidal cinnamon nanoparticles

Parameter	Chocolate beverage with natural cocoa powder					Chocolate beverage with alkalised cocoa powder				
	Nanoparticles proportion	Phenolic content	FRAP activity	Antioxidant activity	DPPH	Nanoparticles proportion	Phenolic content	FRAP activity	Antioxidant activity	DPPH
Nanoparticle proportion	1.000					1.000				
Phenolic content	0.969**	1.000				0.974**	1.000			
FRAP activity	0.898**	0.931**	1.000			0.956**	0.955**	1.000		
Antioxidant activity	0.837**	0.899**	0.934**	1.000		0.712**	0.699**	0.830**	1.000	
DPPH	0.926**	0.885**	0.818**	0.748**	1.000	0.909**	0.898**	0.708**	0.622**	1.000

**Significant at $p < 0.01$

cocoa powder contained a higher total amount of phenols and a higher antioxidant activity than the natural one (Table 1). It points out that the antioxidant activity of chocolate beverages is strongly affected by that of the raw materials. In some cases, the antioxidant activity of enriched chocolate beverage was below the expectation since the addition of a higher proportion of the colloidal cinnamon nanoparticles resulted in no significant difference (e.g. FRAP activity of chocolate beverages made from natural cocoa powder formulated with the colloidal nanoparticles at the ratio of water-to-colloid 3:1 and 1:1). This may be because of an antagonistic effect between the antioxidants from the cinnamon and the cocoa. Our previous study showed that antioxidant interaction between cinnamon and cocoa, either synergetic or antagonistic, depends on the type of cocoa powder, antioxidant compounds in cocoa powder, ratio between cinnamon and cocoa and the type of the antioxidant assessment (Muhammad et al. 2017).

The improvement of the phenolic content and antioxidant activity in the enriched chocolate beverages indicates that the polyphenols of the colloidal cinnamon nanoparticles were protected against degradation during the chocolate beverage production applied in this study. A study by Budryn et al. (2016) showed that thermal treatment during food manufacture leads to a significant degradation of the phenolic content in nanoparticles when evaluated in several food models (bread, cookies, meat stuffing, mushroom stuffing, nutty filling and caramel cottage) suggesting that the nanoparticles containing polyphenols may be more suitable to be incorporated in food that does not require a high temperature during the manufacture. Also, a study by Sedaghat Doost et al. (2018) demonstrated that heat exposure could cause a significant increase in the particle size of colloidal nanoparticles and subsequently may induce a structure change. Therefore, in this study, incorporation of colloidal cinnamon nanoparticles in the chocolate beverages was conducted after the initial mixture (sucrose–cocoa powder dispersion) was cooled down to room temperature.

The increase of phenolic content and antioxidant activity in the chocolate beverages through addition of colloidal cinnamon nanoparticles indicates that the nanoparticles may be a prospective complement to the formulation of a functional chocolate beverage having beneficial effects on health. Moreover, the

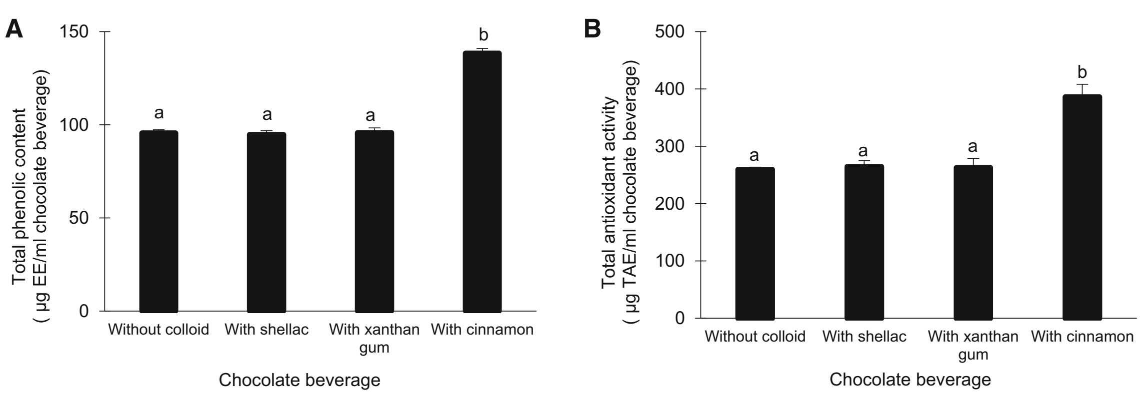

Fig. 3 (**a**) Total phenolic content and (**b**) total antioxidant activity of chocolate beverages incorporated with colloids made from each material used for nanoparticle fabrication (shellac, xanthan gum and cinnamon extract). Mean values with different lowercase letters differ significantly ($p < 0.05$)

outstanding performance of the nanoparticles and the chocolate beverages in different antioxidant activity test systems means that the nanoparticles have a wide range of mode of action for inhibiting oxidation. The antioxidant mechanism of the FRAP method is based on the ability of the antioxidant for the reduction of Fe^{3+} to Fe^{2+}, while the DPPH assay is based on the reduction of radicals by hydrogen atom transfer from H^{-} donors. The use of a high-antioxidant cinnamon extract is preferable in the manufacturing of polyphenol- and antioxidant-rich cinnamon beverage compared to that of a large amount of single antioxidant as it may have an adverse effect on health (Shahidi and Ambigaipalan 2015). Furthermore, a considerable number of studies have revealed the potential health benefits of cinnamon and its derivatives, particularly as an anti-inflammatory, antitumor, anticancer, antidiabetic and anti-hypertriglyceridemia agents (Muhammad and Dewettinck 2017). The phytochemicals in cinnamon, such as phenolic and volatile compounds, play a significant role in bringing about those beneficial effects (Ribeiro-Santos et al. 2017). Thereby, the incorporation of the colloidal cinnamon nanoparticles in the chocolate beverage can be hypothesised not only to improve the phenolic content and antioxidant activity but also to introduce other health-promoting properties of the chocolate beverage. However, to challenge this hypothesis, further studies on the beneficial effect of chocolate beverage enriched with the colloidal cinnamon nanoparticles are still required.

Brix°, pH Value and Colour of the Chocolate Beverages

The Brix° value indicates the total soluble solid content of the chocolate beverages. Generally, all Brix° values of the samples were in a very narrow range within a range from 8.3 to 8.6 and 8.5 to 8.8 for the chocolate beverages with natural and alkalised cocoa powder, respectively. A slight variation of total soluble solids in the chocolate beverages with the colloidal cinnamon nanoparticles arose from the soluble matter of cinnamon and xanthan gum as the main components of the nanoparticles. Typically, alkalised cocoa powder has a higher level of soluble solids than the natural one; thereby, it resulted in higher Brix° values. The range of Brix° values obtained in this study was comparable to that reported by Dogan et al. (2011). Similarly, there was only a very slight variation in the pH values of the chocolate beverages attributable to the enrichment with the colloidal cinnamon nanoparticles. The pH level of the chocolate beverages with natural and alkalised cocoa powder was in the range of 5.4–5.5 and 6.6–6.7, respectively. As expected, the chocolate beverages formulated using alkalised cocoa powder have a higher pH value than those using natural cocoa powder due to the involvement of alkaline during alkalisation process. Based on those results, it can be concluded that, in general, the incorporation of the colloidal cinnamon nanoparticles has a limited effect on the Brix° and pH value of the chocolate beverages.

Colour is an important parameter directly influencing product acceptability (Popov-Raljić and Laličić-Petronijević 2009). In this study, the specular component excluded (SCE) mode was used to observe the colour value, since the SCE value has a high association with the human eye reflection (Saputro et al. 2016). In general, it was observed that the incorporation of the colloidal cinnamon nanoparticles increased the L* value and decreased both the a* and b* values. This resulted in an increase in °Hue and a decrease in C* value indicating that colour appearance and brown intensity of the chocolate beverages changed (Fig. 4). For some samples, the degree of the colour difference (ΔE) of the enriched chocolate beverages and the control was lower than 3 meaning that the colour difference was not recognisable for the human eye; however, most of the samples had ΔE larger than 3 meaning that the difference was obvious (Żyżelewicz et al. 2014). However, the colour alteration was still considered in the acceptable range as shown in Fig. 6.

The colour properties of the beverages made from natural and alkalised cocoa powders were different to some extent. The alkalised cocoa powder resulted in a darker colour with less lightness compared to the natural powder. It is obvious since the colour properties of the raw materials were also different (Table 1). It is widely known that during the alkalisation, the alkaline pH allows the occurrence of polymerisation of pigments responsible for the brown colour of cocoa beans (Oracz et al. 2015; Andres-Lacueva et al. 2008). The result obtained in this study implies that the colour of the final product is highly influenced by the colour properties of its raw materials.

Rheological Behaviour of the Chocolate Beverages

Knowledge on the rheological behaviour of chocolate-derived products is substantial, not only from the stabilisation effect viewpoint but also from the organoleptic perspective since the rheological behaviour can represent the product's mouthfeel (Dogan et al. 2011; Saputro et al. 2017; Zyzelewicz et al. 2010). Figure 5 shows that the incorporation of colloidal cinnamon nanoparticles increased the apparent viscosity of the chocolate beverages regardless of the type of cocoa powder and the increase was confirmed at all tested shear rate levels (from 10/s to 50/s). The result obtained in this study is reasonable since xanthan gum, an important part of the colloidal cinnamon nanoparticles, exhibits thickening properties with pseudoplastic behaviour within a wide range of temperature and pH (Casas et al. 2000). The Pearson's test verified the high correlation between xanthan gum proportion and apparent viscosity. For instance, when analysed at the representative shear rate in the mouth (50/s), it was found that the correlation coefficient of the chocolate beverage made from natural cocoa

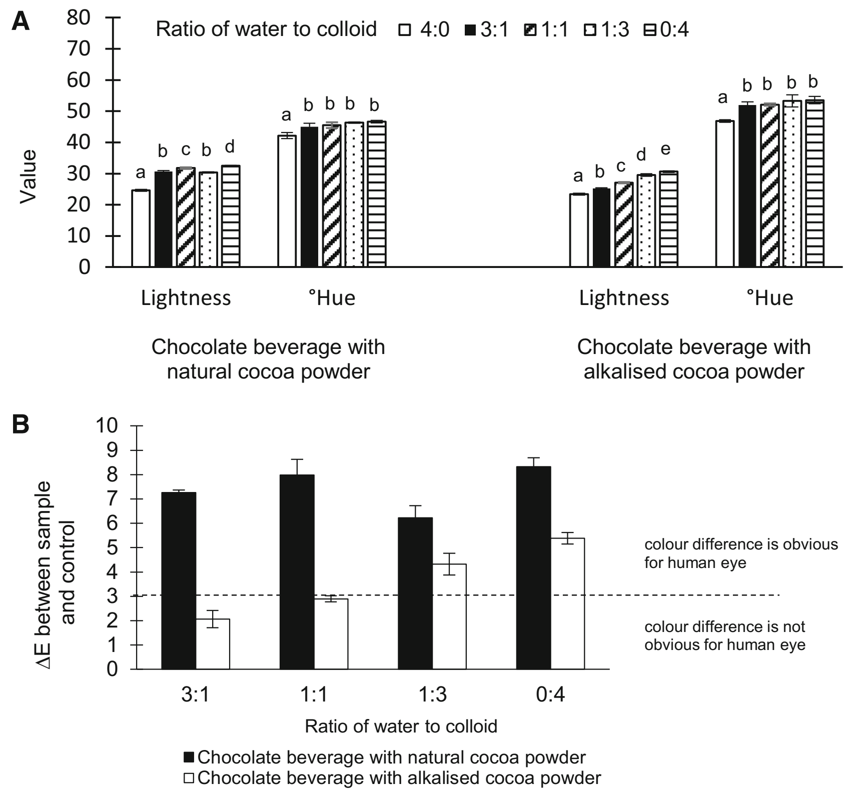

Fig. 4 Effect of the colloidal cinnamon nanoparticles incorporation on the colour of the chocolate beverages (**a**) and the difference in colour between the enriched chocolate beverages and the control (**b**). Mean values within each colour parameter with the same lowercase letter do not differ significantly ($p > 0.05$)

powder and alkalised cocoa powder was 0.998 and 0.994, respectively; both of them were significant at the 0.01 level. This result is in accordance with the previous study by Dogan et al. (2013) mentioning the significant effect of gum concentration on the rheological behaviour of prebiotic hot chocolate beverage.

It was notable that the apparent viscosity of chocolate beverages with alkalised cocoa powder was higher than that of the beverages with natural cocoa powder at all tested ratios and shear rate levels. For instance, the apparent viscosity of the chocolate beverages with alkalised cocoa powder at a shear rate of 50/s was 2.4 and 27.6 × 10 mPa s for the samples with a ratio of water to colloids of 4:0 and 0:4, respectively, whereas values of 1.7 and 24.6 mPa s were recorded for the chocolate beverages formulated with natural cocoa powder. Several factors influence the rheological behaviour of suspensions, including the particle volume fraction, particle shape, interactions between particles and particle size distribution (Jeffrey and Acrivos 1976). As shown, the particle size of the alkalised cocoa powder is smaller than the natural one (Table 1). The viscosity of a suspension with smaller particles (the chocolate beverages formulated with alkalised cocoa powder) can reasonably be higher owing to the greater number of particle–particle contacts per unit volume (Mueller et al. 2010).

In addition to providing an evidence on the rise of the viscosity, Fig. 5 also noticeably indicates that the chocolate beverages enriched with the colloidal cinnamon nanoparticles had a shear thinning behaviour as the apparent viscosity of the beverages decreased with an increase in shear rate. A similar phenomenon was also previously reported by Dogan et al. (2011). The shear thinning behaviour happened possibly because, during the shearing, hydrodynamic forces disrupt the xanthan gum entanglements and, subsequently, break the network structure (Dogan et al. 2015). Due to the absence of xanthan gum in the chocolate beverage without the colloidal cinnamon nanoparticles, the shear thinning behaviour was not found in those particular samples.

Physical Stability of Chocolate Beverages

Chocolate beverages are prone to sedimentation because of the insolubility of the cocoa particles whereas the appearance of a product is decisive for the consumer's preference. This study shows the functionality of the colloidal cinnamon nanoparticles in enhancing the suspension stability of the chocolate beverages. As shown in Fig. 6, after a storage of 24 and 96 h, the appearance of the chocolate beverages with the colloidal cinnamon nanoparticles was better than those without. The results of the sedimentation index determination show that this parameter was reduced along with a higher proportion of the colloidal cinnamon nanoparticles incorporated in the chocolate beverages. The anti-settling effect of the colloidal nanoparticles was clearly because of the presence of xanthan gum

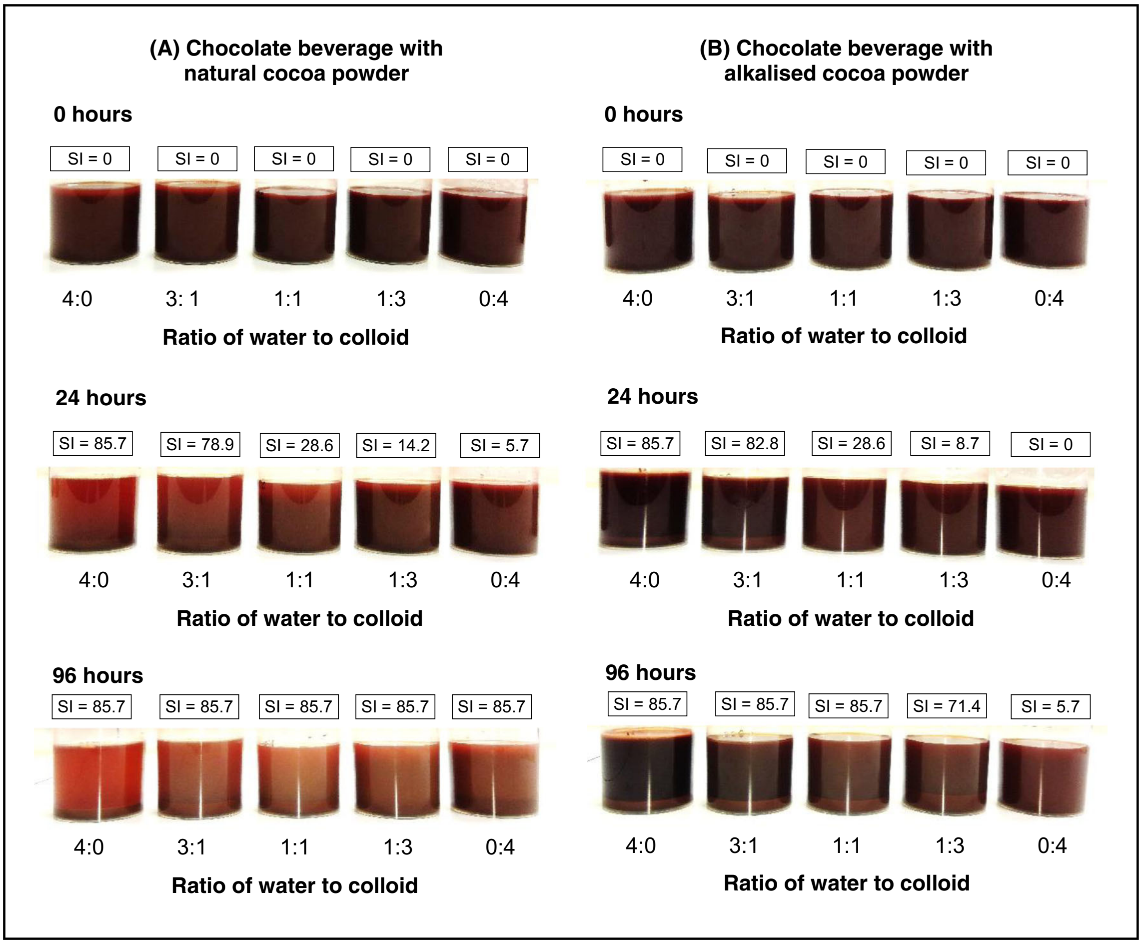

Fig. 6 Appearance and sedimentation index (SI) of the chocolate beverage with natural cocoa powder (**a**) and alkalised cocoa powder (**b**) as a function of composition and storage time

(Fig. 7). Sedimentation was not detected until the end of the assessment (sedimentation index = 0). The presence of either shellac or cinnamon had no significant effect on the improvement of the suspension stability of the chocolate beverage. It was observed that the particles of the chocolate beverages formulated without xanthan gum had fully settled within 24 h after preparation (sedimentation index = 85.7). According to Yaginuma and Kijima (2006), a stable suspension system in the chocolate beverage can be achieved through interaction between the cocoa particles and its stabiliser. Some studies have shown that xanthan gum exhibits hydrogen bonding when combined with other materials (Patel et al. 2013; Outuki et al. 2016).

The sedimentation velocity of a solid particle in a Newtonian liquid follows from the Stokes equation (Eq. (6)), where g represents gravitational acceleration, r is the radius of the particle, ρ_p is the density of the particles, ρ_l is the density of the liquid and η is the viscosity. According to Eq. (6), viscosity has a significant role in the sedimentation velocity: the higher the viscosity, the slower the sedimentation velocity. As previously shown (Fig. 5), the incorporation of the colloidal cinnamon nanoparticles significantly improved the apparent viscosity of the chocolate beverages especially at low shear rate, which is typical for gravitational sedimentation. Thus,

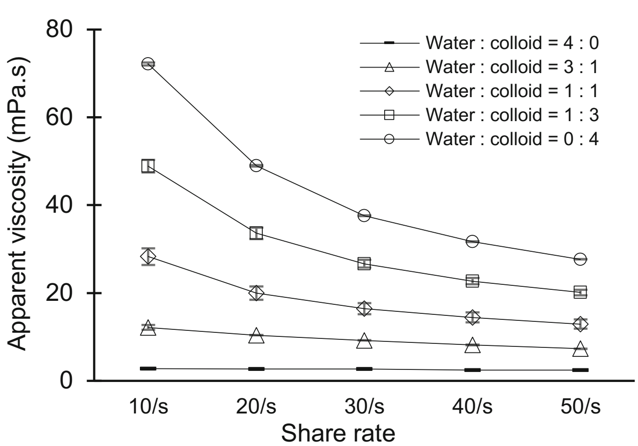

Fig. 5 Effect of the colloidal cinnamon nanoparticles incorporation on the apparent viscosity of chocolate beverages

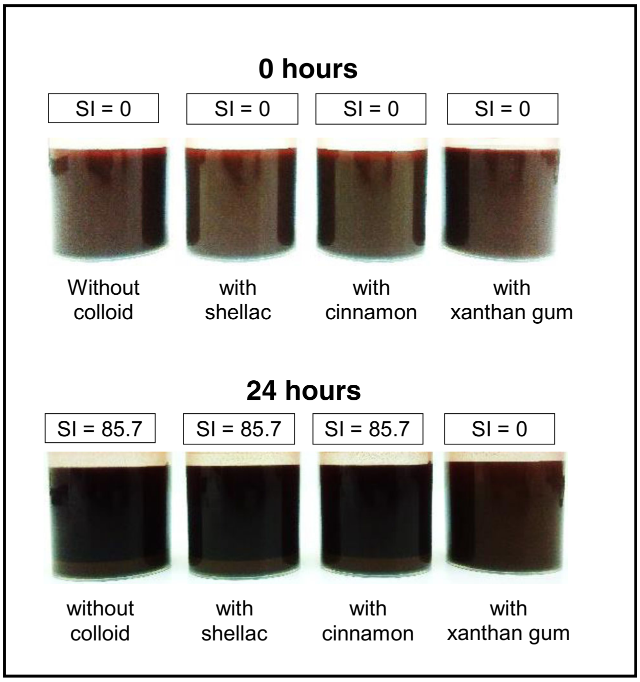

Fig. 7 Appearance and sedimentation index (SI) of the chocolate beverages incorporated with colloids made from each material used for nanoparticle fabrication (shellac, xanthan gum and cinnamon extract) as a function of storage time

the stabilisation of the chocolate beverage containing the colloidal cinnamon nanoparticles by the mechanism of viscosity enhancement has been confirmed.

$$v_{\mathrm{sedimentation}} = \frac{2}{9} g \frac{.r^2.(\rho_p - \rho_l)}{\eta} \quad (6)$$

The stabilisation effect was more pronounced in chocolate beverages made of alkalised cocoa powder than in those made of natural cocoa powder. As shown in Table 1, the natural cocoa powder had a bigger particle size than the alkalised powder. Based on Eq. (6), it is clear that the bigger particle size leads to a higher sedimentation velocity. The soluble solid content of the alkalised cocoa powder was higher than the natural one meaning that the insoluble part of the natural was higher than that of the alkalised cocoa powder. As insolubility of the cocoa particles is the main factor of the sedimentation, a higher proportion of insoluble matter in the cocoa powder leads to a faster sedimentation process of the chocolate beverage. In addition, Dogan et al. (2016) stated that fat content of the cocoa powders can also contribute to the settling speed of the cocoa particles. The outcomes of this particular analysis denote that the stabilisation effect of the colloidal cinnamon nanoparticles is significantly influenced by the initial conditions of the cocoa powder as the raw material of the chocolate beverage.

Microstructural Properties of Chocolate Beverages

To get a better insight about the stabilisation effect of the colloidal cinnamon nanoparticles, the microstructural properties of the chocolate samples were observed. As the gravitational force still acts during storage, sedimentation may occur. Arranging a strong physical network in the system to resist the gravitational force during storage is an effective way to prevent particles from sinking. Figure 8 shows that in the chocolate beverage incorporated with the colloidal cinnamon nanoparticles, a network structure existed, while it did not appear in

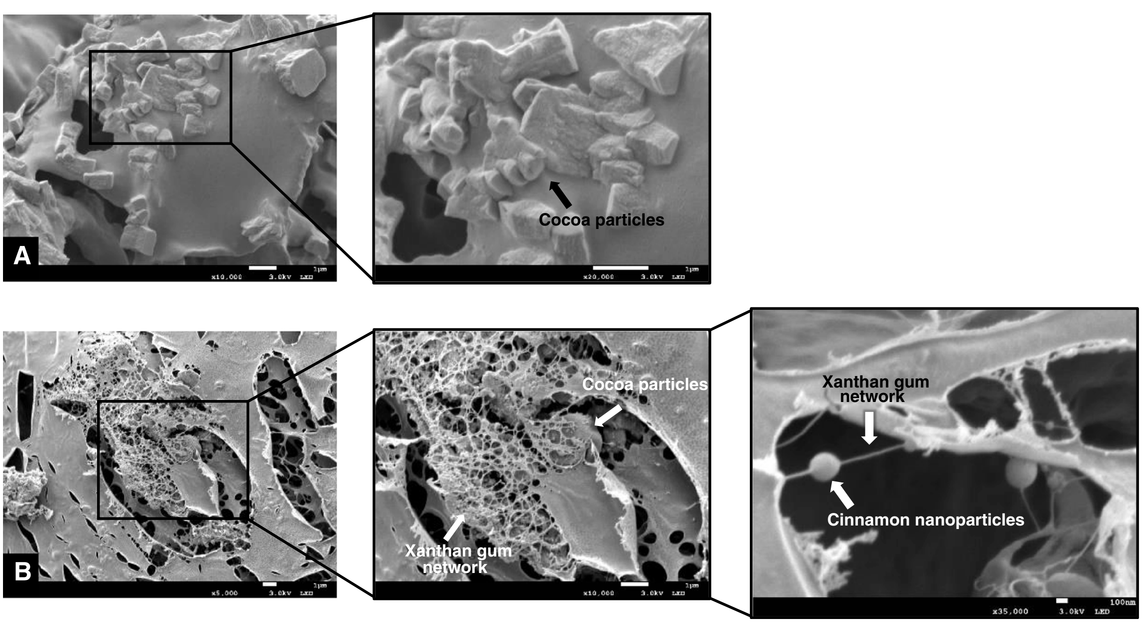

Fig. 8 Microstructural properties of chocolate beverage without colloidal cinnamon nanoparticles (**a**) and with colloidal cinnamon nanoparticles (**b**)

the sample without the nanoparticles. The network structure originated from xanthan gum as an important part of the colloidal cinnamon nanoparticles suspension which can physically entrap the particles. In an earlier study, Katzbauer (1998) has stated that the three-dimensional network formed by the associated xanthan gum chains can prevent separation of insoluble solid particles when applied in salad dressing. The network structure is also the main reason of the viscosity improvement.

Conclusion

This study clearly demonstrated that colloidal cinnamon nanoparticles improved the total phenolic content and antioxidant activities of chocolate beverages suggesting that the nanoparticles may be a prospective complement to the formulation of a functional chocolate beverage. The role of antioxidants in preventing destructive chain reactions in the living system by scavenging the free radicals has been widely published in many papers advising that it can be useful for a preliminary prediction of the potential health benefits. However, the data on total phenolic content and antioxidant activity are not sufficient to define the overall health effects of food. Consequently, advanced studies on the health effects of the chocolate beverages are still needed. The incorporation of the nanoparticles substantially enhanced the suspension stability of the chocolate beverages with a limited effect on the Brix° and pH values. The presence of xanthan gum played a significant role in the prevention of sedimentation due to its ability to create a network structure and to rise the viscosity resulting in the reduced sedimentation velocity of cocoa particles in the chocolate beverage. The findings in this study suggest that the use of the colloidal cinnamon nanoparticles in enriching chocolate beverages to improve their physicochemical and antioxidant properties is technically feasible. As a previous study has shown the potential use of the shellac–xanthan complex for the masking of undesirable aroma of cinnamon, further studies investigating the aroma profile of cinnamon-enriched chocolate beverage involving encapsulated and non-cinnamon extract as well as evaluating the consumer acceptance of the products may be interesting.

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Compliance with Ethical Standards

Conflict of Interest The authors declare that they have no conflict of interest.

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