Food Bioprocess Technol (2013) 6:1044–1058
DOI 10.1007/s11947-011-0742-0

ORIGINAL PAPER

Physical Properties of Non-Agglomerated Cocoa Drink Powder Mixtures Containing Various Types of Sugar and Sweetener

Maja Benković · Ana Belščak-Cvitanović · Draženka Komes · Ingrid Bauman

Received: 25 August 2011 / Accepted: 16 November 2011 / Published online: 4 December 2011
© Springer Science+Business Media, LLC 2011

Abstract Characterization of flow properties represents a crucial step in the production of powdered composite mixtures. Mixing of cocoa powders with different sugars is the first step in the production of this type of beverages, which leads to a change in the mixtures flow properties. The objective of this work was firstly to determine the physical properties of non-agglomerated powdered cocoa and sugar mixtures and, after that, to determine which physical properties of cocoa powders are influenced by sugar addition and in what way they are influenced by sugars. Mixtures were formulated by two cocoa powders containing different amounts of fat and 11 different kinds of sugar or sweetener. A significant change was found in the median diameter, poured bulk density, compression and decompression force of the mixtures compared to the sole components' physical properties. All the mixtures display a decreasing compaction coefficient with increase of flow speed, which indicates that these powder mixtures flow more freely at higher transport speeds. An increase of cake height ratio was detected in all the mixtures, indicating that all the mixtures were susceptible to caking and that they formed a strong cake. Insolubility of the mixtures was influenced significantly by the median diameter of the sugar particles added to the mixture. Addition of sugars and sweeteners to the cocoa powder reduced the red and yellow colour components, but the type of sugar or sweetener did not produce a considerable difference in the colour of the cocoa drink mixtures.

M. Benković (✉) · A. Belščak-Cvitanović · D. Komes · I. Bauman
Faculty of Food Technology and Biotechnology,
University of Zagreb,
Pierottijeva 6,
10000 Zagreb, Republic of Croatia
e-mail: mbenkovic@pbf.hr

Keywords Cocoa · Flow properties · Mixture · Sweetener

Introduction

Powdered ingredients are frequently used for the production of different food mixtures. They differ in particle size, shape, bulk density, flow and reconstitutional properties. A crucial step in the production of powdered mixtures is the behaviour determination of powdered material in order to avoid some major problems in industrial environment, such as clumping, poor flow or even the environmental issues of fine powder emissions into the atmosphere. Particle size characterization is of great importance if we take into the consideration that powders with smaller particles exhibit poor flow properties. Smaller particles usually cause handling problems, with powders being more cohesive as the particle size decreases (Fitzpatrick 2005, 2007; Rennie et al. 1999; Teunou et al. 1999). Additionally, compression and decompression phenomena of food powders are a widely studied and a very important segment of food powder research. The newest research related to these phenomena was done on freeze-dried grape fruit powder by Telis and Martinez-Navarrete (2010) who used TA.XT.Texture Analyser for a confined compression test which gave reproducible and significant results in terms of the maximum force attained during compression. Ghosal et al. (2010) used the powder flow analyser to test the compression and flow characteristics of corn starch with the addition of maltodextrin and gum Arabic, while Abu-hardan and Hill (2010) stated that powder flow analyser testing methods (caking strength and cohesion index) were relatively new measures and their precision and relevance are yet to be determined.

One of the most widely used powders consisting of small particles in food industry is cocoa powder. It is produced in

the final stage of cocoa processing by grinding or pulverizing cocoa cake made during the cocoa nibs pressing phase. Grinding is typically carried out with hammer and disk or pin mills. The fineness of the cocoa powder is determined by a combination of factors, such as the fineness of the liquor, type of alkalization and the final grinding step (De Muijnck 2005). Particle size of the cocoa powder is achieved during the liquor grinding process and is almost invariably fixed (Minifie 1989). During the grinding process, it is relevant to ensure that the cocoa butter present in the powder crystallizes and settles in its stable form, which helps prevent discoloration and lump formation.

Besides colour and flavour, a range of other characteristics (pH, fineness, alkalinity, wetability, solubility, density and microbiological quality) define the cocoa powder (De Muijnck 2005). It is known that non-agglomerated cocoa powder has very poor reconstitutional properties (Galet et al. 2004). The alkaline type of cocoa powder (pH between 6.2 and 7.5) is generally used in cocoa beverage powders. It shows improved dispersability compared to the natural cocoa powder (pH between 5.0 and 5.9). The presence of 10–12% cocoa butter compromises reconstitution of the cocoa beverage powders constituted with this ingredient (Vissotto et al. 2010). A lot of research were done on agglomerated and commercially available cocoa drink powders (Vissotto et al. 2010; Yanes et al. 2002; Kowalska and Lenart 2005; Eduardo and Lannes 2007; Gerhards et al. 2004; Vu et al. 2003; Omobuwajo et al. 2000; Shittu and Lawal 2007); however, only few were done using non-agglomerated cocoa powder (Galet et al. 2004). There is practically no information on the physical properties of cocoa drink powder mixtures with emphasis on the addition of different types of sugar and sweetener. The addition of sugar particles to cocoa powder leads to changes in some physical properties due to the particle–particle interactions. Flow properties of such mixtures should be characterized since mixing of particulate solids, in this case, cocoa powder and sugars, represents a starting stage of powdered cocoa beverage production.

The objective of this work was to determine the physical properties of non-agglomerated cocoa powder and sugar mixtures, i.e., to determine which physical properties of cocoa powders containing two different fat contents are influenced by sugar addition and in what way.

Materials and Methods

Cocoa Powders and Sugars

The cocoa powders with two different fat contents (10–12% and 16–18%) used in this study were supplied by local chocolate industry Zvečevo (Požega, Croatia) and sucrose, glucose, maltodextrine and erythritol were obtained from Cargill (Krefeld, Germany). Fructose was obtained from Merck (Darmstadt, Germany), isomaltulose was obtained from Beneo-Palatinit (Manheim, Germany), inuline and oligofructose were obtained from Beneo-Orafti (Tienen, Belgium), aspartame/acesulfam K sweetener blend (50%/50%) was obtained from Brenntag (Vienna, Austria) and Stevia sweetener was purchased from a local pharmacy (produced by Kal, USA).

Formulation of Experimental Sugar and Cocoa Drink Mixtures

The basic cocoa/sugar ratio used for the preparation of mixtures was 70% sugar and 30% cocoa powder since this ratio is commonly used in industrial cocoa beverage preparation (Minifie 1989). The experimental design for the mixture preparation is shown in Table 1. The amount of sugars and sweeteners used was adjusted according to the relative sweetness of selected sugars and sweeteners (Table 1). The

Table 1 The experimental formulations for cocoa powder drink preparation (mass percentage) (According to Belščak-Cvitanović et al. 2010)

	Relative sweetness	A	B	C	D	E	F	G	H	I	J
Cocoa powder	–	30	30	30	30	30	30	30	30	30	30
Sucrose	1	70	60	35	35	30	–	–	–	–	–
Glucose	0.7	–	–	–	35	–	29.5	–	20	–	–
Fructose	1.1	–	–	–	–	–	10	–	–	–	–
Trehalose	0.45	–	10	–	–	–	30	–	9	–	10
Isomaltulose (Palatinose)	0.45	–	–	–	–	20	–	10	–	20	19
Eritrythol	0.7	–	–	35	–	20	–	10	–	9	–
Stevia	300	–	–	–	–	–	0.5	–	1	1	1
Aspartame/acesulfame K	–	–	–	–	–	–	–	0.7	–	–	–
Maltodextrin	–	–	–	–	–	–	–	30	20	20	–
Inuline	–	–	–	–	–	–	–	19.3	20	10	20
Oligofructose	–	–	–	–	–	–	–	–	–	10	20

cocoa powder and sugar fractions were mixed in a T2F Turbula mixer (Willy A. Bachofen Maschienenfabrik, Muttenz, Switzerland) for 10 min to obtain a homogenous blend. Before mixing the sugars with cocoa, the physical properties of the sole sugar mixtures were determined.

Particle Size

Particle size distribution, span and uniformity of the components, as well as of the sugar mixtures and the cocoa drink powder mixtures, were determined using Mastersizer 2000 equipped with the Scirocco 2000 dry dispersion unit (Malvern Instruments, Worcestershire, UK).

Bulk Density

The bulk density (BD) of each sample was determined using the mass/volume relationship (Omobuwajo et al. 2000; Jain and Bal 1997). The powder was poured into a graduated empty plastic container of predetermined tare weight, the mass and the volume of the sample in the container were marked down and the poured bulk density was calculated by dividing the sample mass with the sample volume. The measurements were repeated ten times.

Cohesion, Powder Flow Speed Dependency and Caking

Cohesion properties, powder flow speed dependency and caking properties of the components and the mixtures were tested using a powder rheometer, TA.HDPlus Powder Flow Analyser coupled with the TA. HDPlus Texture Analyser (Stable Micro Systems, Surrey, UK).

A fixed sample volume (160 mL) was poured into a glass container prior to testing. Prior to testing, the instrument performed a 2-cycle sample preparation step. Compaction property was examined when the rotating blade moved downwards and the cohesion property while moving upwards at the tip speed of 50 mm s^{-1} During the downward movement, the maximum force for the compression was determined, while during the upward movement the maximum force for decompression was determined.

Powder flow speed dependency (PFSD) test offers information about the speed flow properties of powders. The test started with two conditioning cycles which were followed by cycles run at a tip speed of 10, 20, 50 and 100 mm s^{-1} and two final cycles at 10 mm s^{-1}. The area under the positive part of the curve, which is the work of compaction, was calculated using Texture Exponent 32 software (Stable Micro Systems, Surrey, UK). Flow stability (FS) was then calculated by dividing the mean compaction coefficient of the first two 10 mm s^{-1} cycles by the compaction coefficient of the last two 10 mm s^{-1} cycles. Flow stability of close to 1 has shown that the powder was unchanged by the PFSD test. Flow stability different to 1 has shown that the powder has changed due to attrition or changes in particle shape.

Caking test began with two conditioning cycles. The blade levelled the top of the powder column and measured the height of the column, after which it moved down through the column at a tip speed of 20 mm s^{-1} and compacted the powder to a pre-defined force (usually 750 g). When the blade reached the required force, it sliced up through the powder at 10 mm s^{-1} and repeated the compaction cycle four more times. At the beginning of every cycle, the blade measured the height of the column and the height of the powder cake was recorded when the target force was reached. The fifth time the target force was reached, the blade cut through the formed powder cake at the bottom of the vessel and measured the force required to perform the task. This force was recorded as the cake strength and represented the work required to cut the cake (g mm), and the mean cake strength was the average force to cut the cake expressed in grams. The column height ratio (current cycle column height divided by initial column height) and the cake height ratio (current cycle cake height divided by initial column height) were recorded to give information about the settlement and compaction of the powder column.

Insolubility

The amount of insoluble compounds in cocoa drink powder mixtures was determined using a method described by Vissotto et al. (2010) with some modifications. A total of 20 g of cocoa drink powder was added to 150 mL distilled water at 25 °C in a 400-mL beaker. The powder was then manually mixed with the liquid. The solution obtained was filtered in a vacuum system consisting of a Buchner funnel and a vacuum conical flask. The mass retained on the filter paper was dried at 60 °C to a constant weight. The dry powder mass was then weighed on an analytical balance. Insolubility was calculated using the following equation:

$$\text{Insolubility}(\%) = \frac{\text{mass of the sample on the paper after filtration and drying}}{\text{initial mass of the sample}} \times 100$$

Colour Measurement

The colour of the samples was measured in a Minolta colorimeter, using cells 6 cm in diameter and 3.8 cm in height and with a 0.5-in. diaphragm. Translucency of samples was previously checked by measuring the diffused reflection of 3.5-cm layer thickness on both black and white (X=78.8, Y=83.32, Z=87.94) backgrounds according to Judd and Wyszecki (1967) and Yanes et al. (2002). Reflection spectra were registered and colour parameters for 10° vision angle and D65 illuminant (L—brightness, a—redness, b—

yellowness, ΔE—total colour difference) were calculated. The total colour difference was obtained by taking into account the L, a, and b parameters of samples and mixtures A (separately for cocoa powders with 10–12% fat and 16–18% fat) as the standard products since these mixtures have the same composition as the usual commercially available cocoa drink mixtures. Measurements were done in triplicate.

Statistical Analysis

The results were analysed statistically using Statistica 7.0 software (StatSoft Inc., Tulsa, USA) to determine the average value and standard error. Variance analysis, with a significance level of α=0.05%, was performed to determine the influence of composition of powdered cocoa drink mixtures on their physical properties regarding the fat content of cocoa powder.

Results and Discussion

Mixing sugar and cocoa powders represents the first step in cocoa drink powder production. The physical properties of such mixtures differ significantly from the properties of sugars and cocoa separately. This change in properties affects the behaviour of the mixture and thus industrial handling operations which follow mixing, such as conveying or agglomeration, have to be adjusted according to the mixtures' properties. This paper presents a characterisation of physical properties of non-agglomerated sugar mixtures and sugar/cocoa mixtures.

Particle Size Distribution

Particle size distribution, span and uniformity of sugars and sugar mixtures used in cocoa drink powder formulations are shown in Table 2, while particle size distribution, span and uniformity of the cocoa drink powder mixtures are shown in Table 3.

In Tables 2 and 3, it can be seen that sugar mixtures exhibit a much higher median diameter d (0.5) than sole cocoa powders. As a result of mixing two types of powders with a big difference in median diameter, the median diameter of the mixtures is lower than the median diameter of the sole sugars, with the exception of sample C. Cocoa powder particles, with a small median diameter d (0.5)=10.27 μm

Table 2 Particle size distribution, span and uniformity of sugars and sugar mixtures used in cocoa drink powder formulations (mean ± SD)

	d (0.1) [μm]	d (0.5) [μm]	d (0.9) [μm]	D [3, 2] [μm]	D [4, 3] [μm]	Span	Uniformity
Sugars							
Sucrose	349.50±2.01	596.02±42.03	991.86±19.91	546.33±20.46	637.94±12.64	1.08±0.02	–
Glucose	57.99±1.00	166.43±1.42	421.58±15.82	111.90±9.21	211.16±9.12	0.69±0.02	–
Fructose	311.39±3.16	477.81±11.32	725.27±5.27	452.20±10.14	501.01±15.22	0.87±0.02	–
Trehalose	137.71±5.06	217.50±5.02	409.71±5.44	312.40±8.46	411.36±12.44	1.25±0.04	–
Isomaltulose	31.04±1.19	109.76±3.20	270.55±3.01	52.22±5.22	138.87±4.37	2.18±0.05	–
Eritrythol	233.8±9.16	417.80±10.34	609.92±9.62	460.12±14.99	522.14±13.45	0.90±0.02	–
Stevia	15.63±1.00	175.22±4.43	312.44±9.63	24.66±1.14	230.42±9.65	1.69±0.03	–
Aspartame/acesulfame K	12.97±0.80	198.39±11.57	580.93±9.38	25.10±1.16	252.07±5.07	2.86±0.06	–
Maltodextrin	22.19±1.14	188.49±1.26	407.86±7.64	50.37±1.92	205.09±5.09	2.05±0.03	–
Inuline	52.62±6.44	113.05±2.05	212.73±5.12	81.30±1.64	128.19±2.86	1.42±0.02	–
Oligofructose	31.04±6.23	109.76±1.30	270.55±6.17	52.22±2.01	138.87±2.93	2.18±0.02	–
Sugar mixtures							
A = sucrose	349.50±23.52	596.02±21.20	991.86±9.13	546.33±14.05	637.94±31.61	1.08±0.05	–
B	204.65±11.01	491.67±15.17	930.90±25.44	307.19±7.68	533.65±16.78	1.48±0.06	0.46±0.02
C	133.97±5.74	445.72±6.94	875.71±16.71	185.19±10.91	481.68±4.90	1.66±0.05	0.50±0.02
D	65.44±1.64	305.32±11.69	966.64±12.62	143.12±2.33	424.06±17.17	2.95±0.07	0.94±0.02
E	168.19±10.91	430.81±3.77	937.33±5.02	309.50±13.16	498.61±9.22	1.79±0.05	0.56±0.02
F	57.77±3.06	239.70±17.03	711.66±28.90	122.12±5.06	320.95±11.50	2.73±0.07	0.85±0.03
G	41.52±1.33	178.46±9.88	458.14±18.19	64.14±3.70	221.82±7.37	2.33±0.07	0.72±0.02
H	45.90±4.78	158.33±4.37	422.85±8.46	70.60±6.98	204.03±10.03	2.38±0.07	0.74±0.03
I	49.42±0.45	193.64±6.50	446.74±20.21	76.21±2.31	229.66±8.38	2.05±0.05	0.64±0.02
J	52.22±4.91	155.18±8.17	377.00±12.62	88.46±4.55	192.88±1.23	2.10±0.05	0.67±0.02

d (0.1), d (0.5), d (0.9), D [3, 2] and D [4, 3], respectively, represent 10%, 50% and 90% of all particles finer than this size, Sauter mean diameter and mean particle diameter

Table 3 Particle size distribution, span and uniformity of the cocoa drink powder mixtures

Sample	*d* (0.1) [μm]	*d* (0.5) [μm]	*d* (0.9) [μm]	*D* [3, 2] [μm]	*D* [4, 3] [μm]	Span	Uniformity
Cocoa powder with 10–12% fat							
CP	9.03±0.06	17.09±0.15	32.27±0.10	15.60±0.11	26.92±0.12	1.65±0.03	0.87±0.01
A	10.94±0.15	527.76±7.27	1,035.07±11.16	44.30±1.26	538.62±2.76	1.94±0.02	0.57±0.01
B	9.91±0.10	471.93±7.96	1,025.03±14.04	38.37±0.93	494.47±4.32	2.15±0.03	0.67±0.01
C	10.90±0.06	523.12±3.52	1,090.56±19.83	43.59±2.09	544.29±3.54	2.06±0.04	0.62±0.01
D	9.74±0.11	220.45±3.08	860.65±10.47	34.43±0.99	344.60±2.18	3.86±0.04	1.25±0.01
E	11.92±0.13	388.84±7.27	877.04±9.67	46.71±2.07	426.81±7.29	2.23±0.02	0.66±0.01
F	9.17±0.20	160.74±5.06	532.98±3.40	30.81±0.63	225.56±4.06	3.26±0.03	1.08±0.02
G	9.18±0.13	112.88±1.26	476.73±5.07	29.49±1.20	202.01±2.83	4.14±0.05	1.44±0.03
H	9.16±0.19	94.48±1.20	355.46±4.22	28.59±0.89	165.51±1.99	3.66±0.02	1.38±0.02
I	9.40±0.18	149.07±1.16	859.45±9.63	31.64±1.30	285.23±1.13	5.70±0.04	1.56±0.02
J	8.99±0.10	103.75±2.19	349.90±3.54	23.46±0.65	163.03±0.96	3.29±0.02	1.22±0.01
Cocoa powder with 16–18% fat							
CP	12.85±0.22	23.33±0.20	46.45±0.19	21.54±0.10	35.43±0.09	1.44±0.03	0.80±0.01
A	13.89±0.19	489.78±3.43	1,011.96±17.29	53.12±1.63	502.98±5.98	2.04±0.05	0.62±0.01
B	13.69±0.13	414.29±2.99	898.22±10.43	50.41±1.21	898.22±14.04	2.14±0.06	0.67±0.02
C	15.34±0.21	521.48±4.12	1,057.97±19.83	60.59±0.98	537.52±4.75	2.00±0.04	0.59±0.01
D	13.14±0.09	203.00±2.04	797.40±7.26	43.91±0.99	317.84±3.84	3.87±0.06	1.24±0.03
E	13.18±0.10	295.58±3.88	766.13±5.13	46.98±0.78	348.86±2.33	2.55±0.03	0.81±0.02
F	13.43±0.12	184.87±1.00	557.03±2.92	43.25±0.92	238.32±1.96	2.94±0.04	0.97±0.02
G	12.14±0.08	108.29±1.33	441.48±4.16	31.09±0.76	191.77±1.92	3.99±0.05	1.40±0.02
H	11.79±0.08	87.10±0.76	299.78±3.40	30.71±0.81	128.50±1.33	3.31±0.03	1.08±0.03
I	12.55±0.13	133.84±0.96	495.59±7.16	38.94±0.72	217.07±1.85	3.61±0.03	1.26±0.01
J	11.82±0.09	95.65±0.88	310.01±2.65	34.47±0.77	131.07±1.06	3.12±0.04	1.00±0.02

d (0.1), *d* (0.5), *d* (0.9), *D* [3, 2] and *D* [4, 3], respectively, represent 10%, 50% and 90% of all particles finer than this size, Sauter mean diameter and mean particle diameter

for cocoa powder with 10–12% fat and *d* (0.5)=23.33 μm for cocoa powder with 16–18% fat, when mixed with sugars, show an increase in *d* (0.5). For that reason, they show better flow properties since powders consisting of bigger particles are not as susceptible to cohesion and caking as powders with smaller particles (Fitzpatrick 2005). The increase in *d* (0.5) with the addition of sugar particles to cocoa powder particles can be predicted by the following equations:

For cocoa powder mixtures with 10–12% fat:

$$d(0.5) = 1.04 \times d(0.5)\ (\text{sugar mixtures}) - 60.76$$

For cocoa powder mixtures with 16–18% fat:

$$d(0.5) = 0.93 \times d(0.5)\ (\text{sugar mixtures}) - 46.71$$

Also, *d* (0.1) of the cocoa drink powder mixtures corresponded to cocoa powder particles, which were the smallest particles present in the mixture. The *d* (0.9) values were significantly higher for the prepared mixtures than the ones exhibited by sole cocoa powder (Table 3). The highest *d* (0.9) values were exhibited by mixtures A, B and C in both cocoa powder with 10–12% fat mixtures and cocoa powder with 16–18% mixtures. Furthermore, as shown in Table 3, the span of the particle size distributions increases with the number of mixture components and the difference of particle sizes of the components added to the mixture. Uniformity of the sugar mixtures exhibited lower values than those determined for cocoa powder mixtures, indicating that the addition of small cocoa powder particles made it more difficult to produce a mixture with the same uniformity as the sugar mixtures. Furthermore, statistical analysis revealed significant positive correlations between all the distribution parameters (*d* (0.1), *d* (0.5), *d* (0.9), *D* [3, 2] and *D* [4, 3]) of the sugar mixtures and cocoa powder drink mixtures. Particle size distribution span and uniformity of the cocoa drink powder mixtures prepared with cocoa powder containing 16–18% fat showed a significant dependence on the span and uniformity of the sugar mixtures (R= 0.85, $p<0.05$). A significant influence of the span and uniformity of the sugar mixtures was found on the span of cocoa powder mixtures prepared with cocoa powder containing 10–12% fat (R=0.62, $p<0.05$).

Bulk Density

Figure 1a and b shows the differences in poured bulk density of sugars (Fig. 1a), sugar mixtures and sugar/cocoa powder mixtures for two different types of cocoa powder used in this study (Fig. 1b).

Sugar mixtures exhibited higher values for bulk density than cocoa powders, while the bulk density of the cocoa/sugar mixtures ranged between the values exhibited by sole cocoa powder and sole sugar mixtures. The highest bulk density values were exhibited by sugar mixtures (BD= 964.97 kg m^{-3} for mixture B constituted from sucrose and glucose) as shown in Fig. 1b. A linear expression can also be used in the prediction of the increase of poured bulk density of cocoa powder when adding sugar:

For cocoa powder mixtures with 10–12% fat:

$$BD_{10-12} = -1,357 + 1.92 \times BD_{\text{sugar mixture}}$$

For cocoa powder mixtures with 16–18% fat:

$$BD_{16-18} = -147.70 + 0.98 \times BD_{\text{sugar mixture}}$$

The addition of sugar mixtures to cocoa powders had a stronger effect on mixtures made with cocoa powder with 16–18% fat (R=0.86, p<0.05) than on the mixtures consisting of cocoa powder with a lower fat content (R=0.68, p<

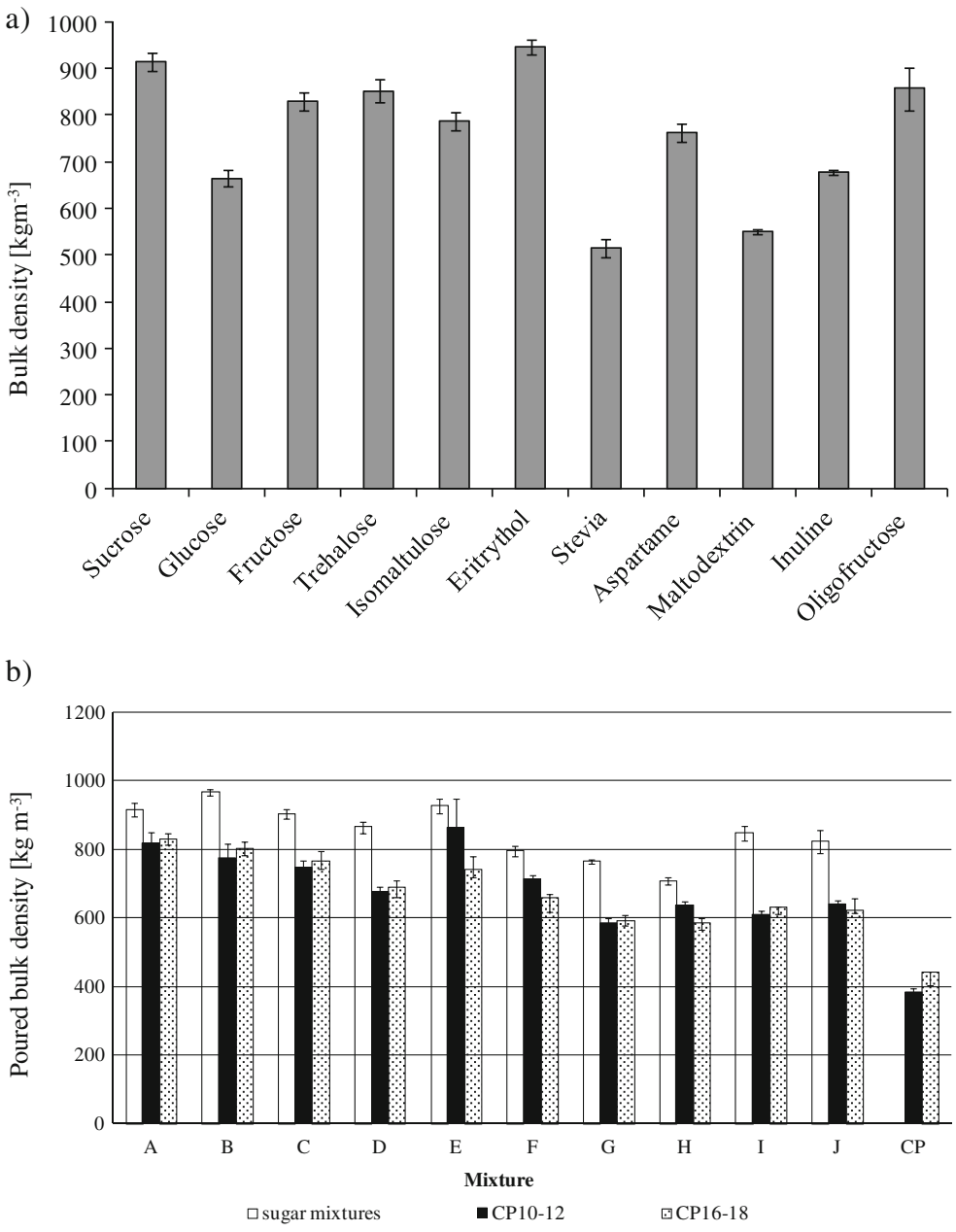

Fig. 1 Bulk density values of sugars (**a**), sugar mixtures (**b**) and cocoa powder drink mixtures (**b**)

0.05). Statistical analysis has also shown that this influence was not considered significant, although the *p*-levels cannot be neglected (p=0.06). The explanation for this result could be the difference in particle size of the two cocoa powders, where cocoa powder containing 10–12% fat was built up of particles with very small diameter, which tend to stick on the sugar crystal surfaces. Based on statistical analysis, it was noticed that sucrose, maltodextrin and inulin had the biggest influence on the changes in poured bulk density. Mixtures containing sucrose (mixtures A–E) showed a higher poured bulk density than mixtures without sucrose, which presents a logical finding since sucrose is a sugar with the second highest bulk density (Fig. 1a). Erythrytol, actually, had the highest bulk density, but because it was used in cocoa drink powder preparation in smaller quantities than sucrose its influence was not as significant.

Cohesion, Powder Flow Speed Dependency and Caking

Cohesion

By employing the compression and decompression test (also known as quick test), maximum compression and decompression forces were recorded and the results are shown in Figs. 2 and 3.

It can be seen from the results shown in Figs. 2 and 3 that the maximum force required for compression is higher for all the samples than the maximum force required for decompression. Similar results were obtained by Ghosal et al. (2010) who also referred to the compression and

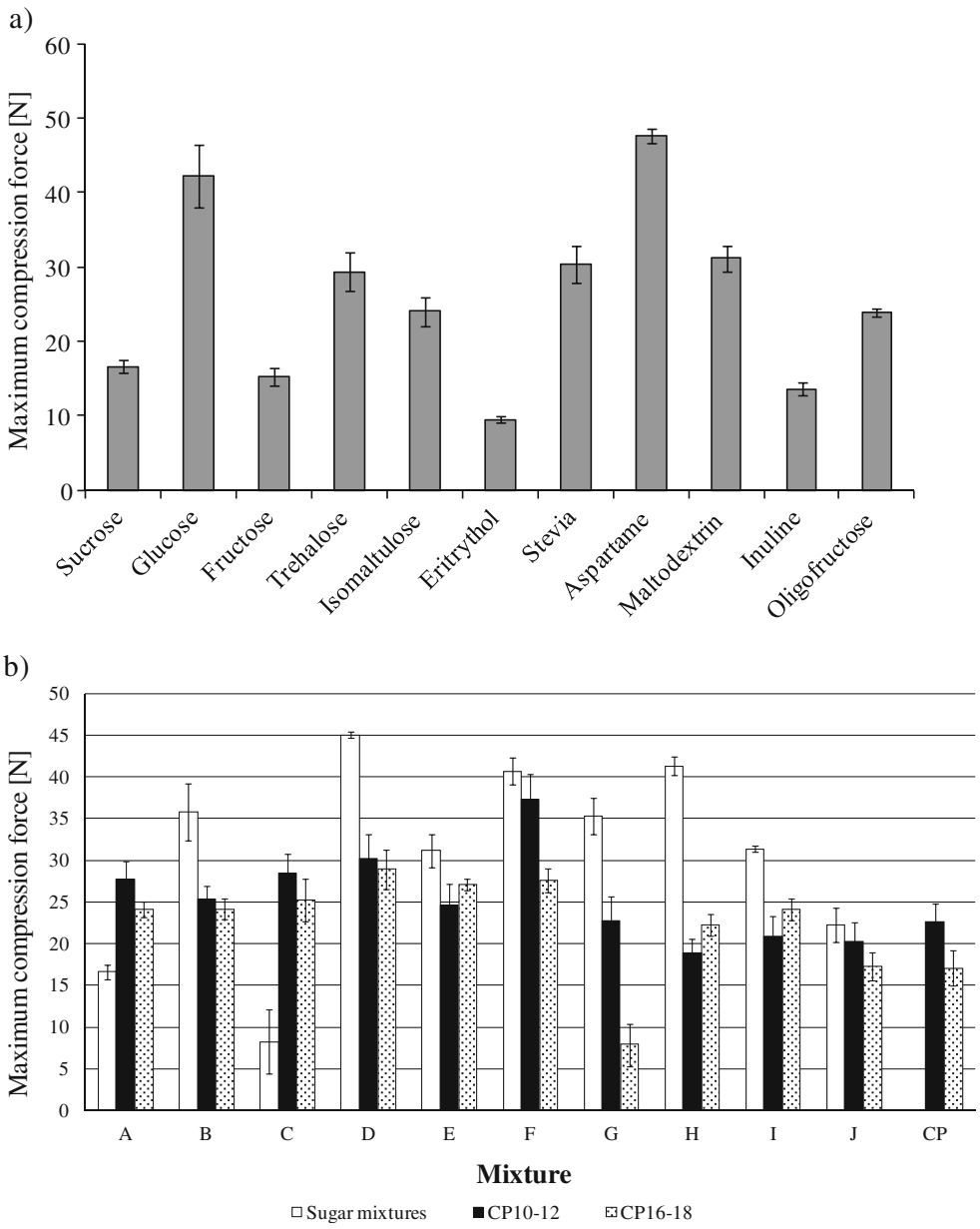

Fig. 2 Maximum compression force: **a** sugars, **b** sugar and cocoa powder mixtures

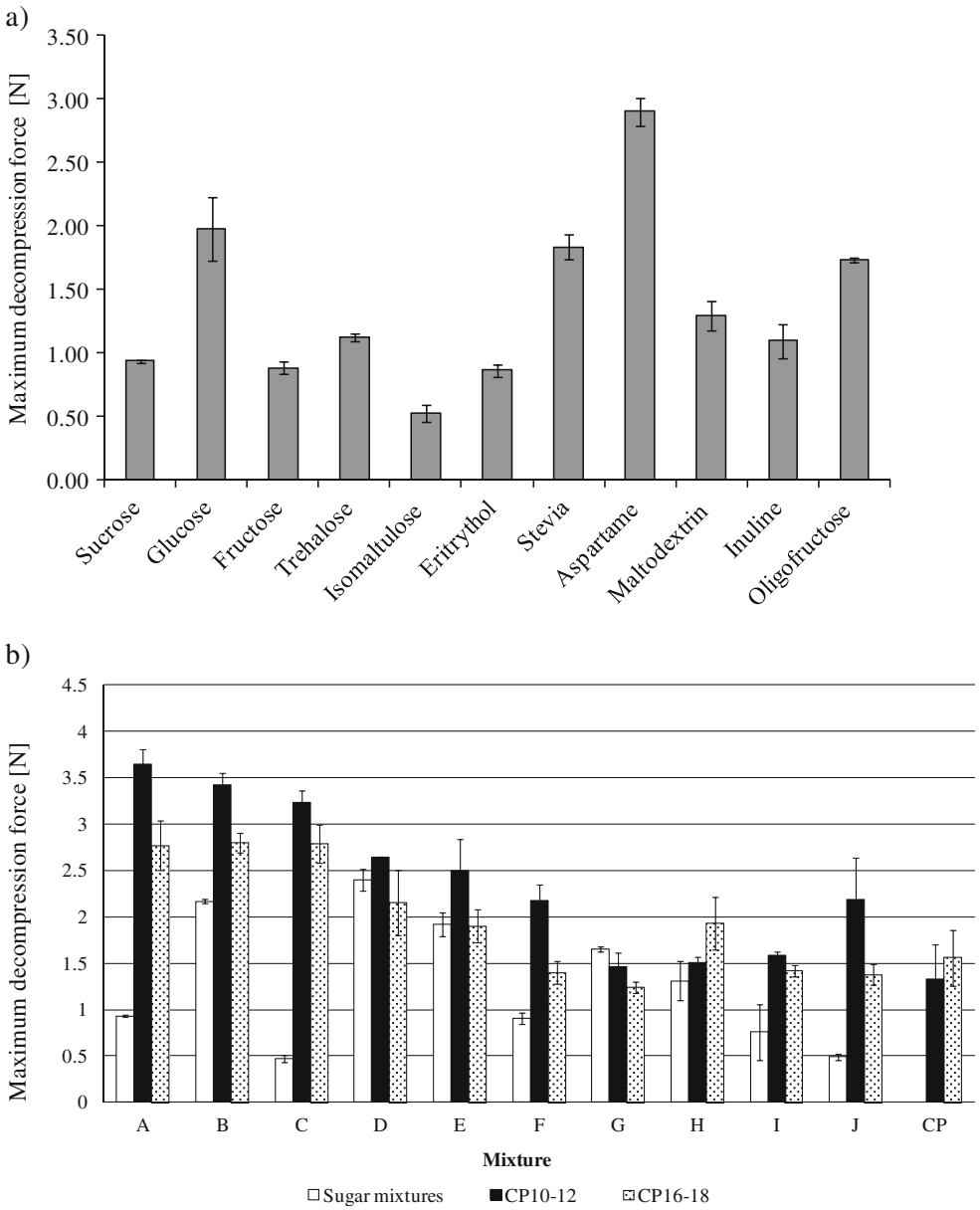

Fig. 3 Maximum decompression force: **a** sugars, **b** sugar and cocoa powder mixtures

decompression energy and concluded that the area of the compression zone is always higher than that for decompression, as demonstrated in the force/time curve obtained during the compression/decompression test.

A significant statistical influence has been found between the maximum compression force and the maximum decompression force ($p=0.020$) of sole sugars used in this study. In the case of sugar addition to cocoa powder, a change in compression and decompression force was visible. All the sugar mixtures, with the exception of mixture C, exhibited higher compression forces which diminished when cocoa particles were added to the mixture. A different behaviour was detected with the maximum decompression force, where all the sugar mixtures, with the exception of mixture G, exhibited lower decompression forces which could be explained when connected to particle size. Cocoa powder showed *d* (0.5) value of 17.09 μm (cocoa powder with 10–12% fat) and 23.33 (cocoa powder with 16–18% fat), which was significantly smaller than particles of mixtures containing sugar. The surface area between smaller particles was much bigger than that of bigger particles; therefore, there was a bigger probability of particle–particle interactions and bondage. A larger force was required to compress sugar mixtures and a lower force was required to decompress them, which was a favourable property for industrial transportation of sugar powders. On the other hand, the presence of smaller cocoa powder particles in cocoa mixtures decreased the *d* (0.5) value of sugar mixtures, introducing smaller particles to the mixtures and therefore making them more susceptible to particle–particle interactions and making them easy to compress and harder

to decompress. One can also notice that the compression force of pure cocoa powder with 10–12% fat is higher, while it is lower for cocoa powder with 16–18% fat. Although cocoa powder with 10–12% fat consisted of smaller particles, it was harder to compress it. These phenomena could be connected to the amount of fat and the surface composition of the powder, as shown by Özkan et al. (2002). On the other hand, a rise in the decompression force of cocoa powder with 10–12% fat could be seen with the addition of sugar particles, which meant that once the cocoa/sugar mixture is compressed, it becomes more difficult to decompress, which was not a favourable property for industrial handling and conveying of these cocoa/sugar mixtures.

Powder Flow Speed Dependency

Powder flow properties may change with increasing or decreasing flow speeds. Dependence of the compaction coefficient of mixtures towards the speed with which they flow is shown in Fig. 4.

As can be seen in Fig. 4, all of the mixtures exhibited a decrease in compaction coefficient values with an increasing flow speed. A decrease in compaction coefficient values indicated that all the powder mixtures became more freely flowing as their flow speed increased. Consequently, the lowest values of compaction coefficients were obtained for the 100 mm s^{-1} cycle for all the samples. These results

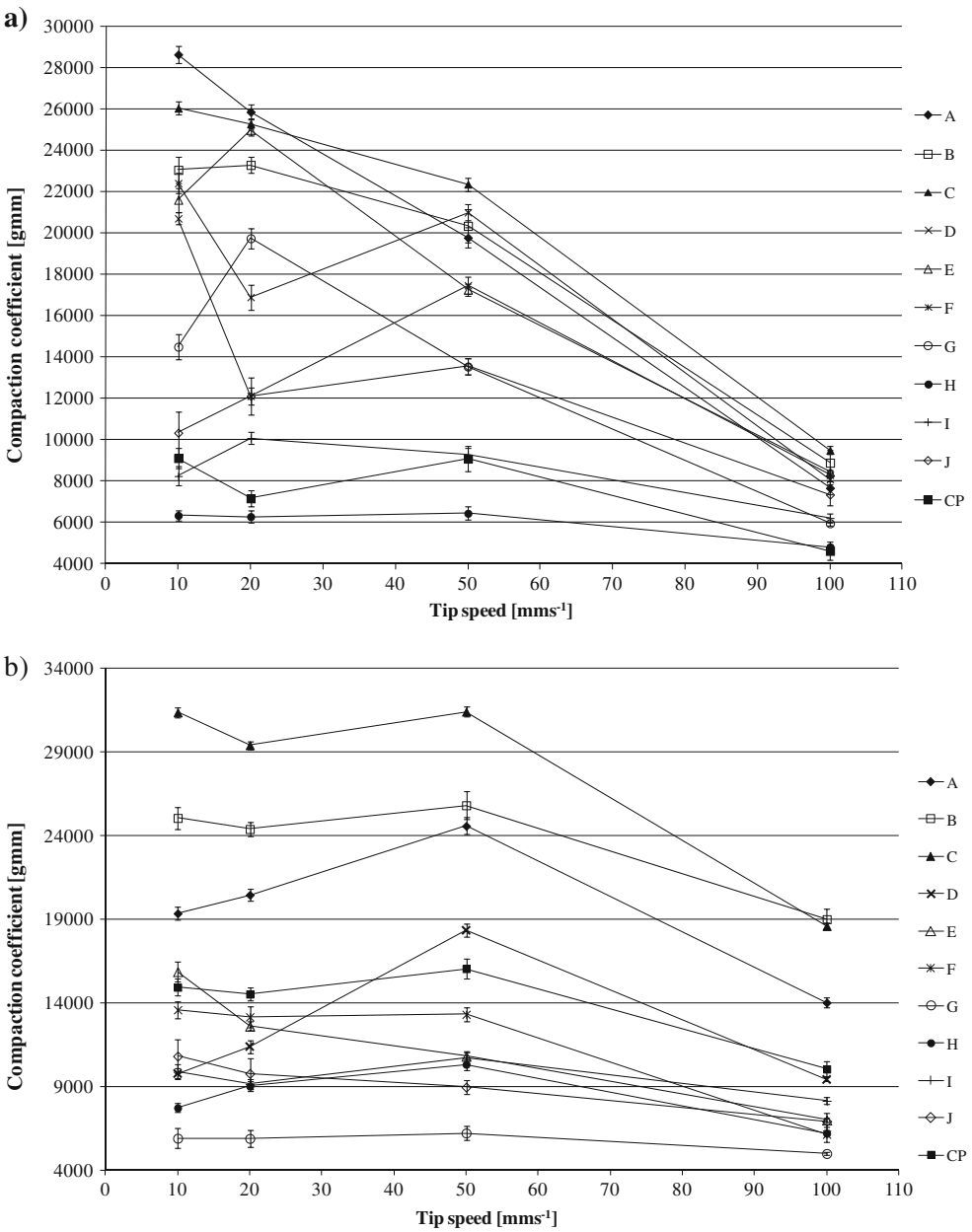

Fig. 4 Compaction coefficient profiles: **a** cocoa powder with 10–12% fat, **b** cocoa powder with 16–18% fat

suggested that cocoa/sugar mixtures should be conveyed through a production facility with higher flow speeds. Also, our future experiments should include testing of flow properties at speeds even higher than 100 mm s^{-1}, which was the highest tip speed at which the PFSD test was performed in this research. Sole cocoa powder containing 10–12% fat had the lowest compaction coefficient values, but it showed the same trend of decreasing compaction coefficients with higher flow speed as all the other cocoa/sugar mixtures made with cocoa powder containing 10–12% fat (Fig. 4a). As for sole cocoa powder with 16–18% fat, its compaction coefficients were in the same range as all the other cocoa/sugar mixtures made with cocoa powder containing 16–18% fat (Fig. 4b). It is important to emphasize that the results for compaction coefficients obtained during the PFSD test should be coupled with the flow stability values shown in Fig. 5. If the powder flow stability value is less than or greater than 1, it means that the powder has undergone changes during the PFSD test. All of the cocoa/sugar mixtures had flow stability values which differ from 1 (Fig. 5), which confirmed the compaction coefficient data obtained during the test. All of the powder samples had undergone changes during the PFSD test, which could be the result of a change in particle friability, and as a consequence of these changes, the mixtures flow more freely at higher conveying speeds. In a future research, it is important to determine the optimal transport speed of these powders since too low speed can result in underfilling and too high speed can result in overfilling in the production environment. Flow stability values are shown in Fig. 5.

Flow stability gives important information about the flow resistance of the powder and it is assessed during the PFSD

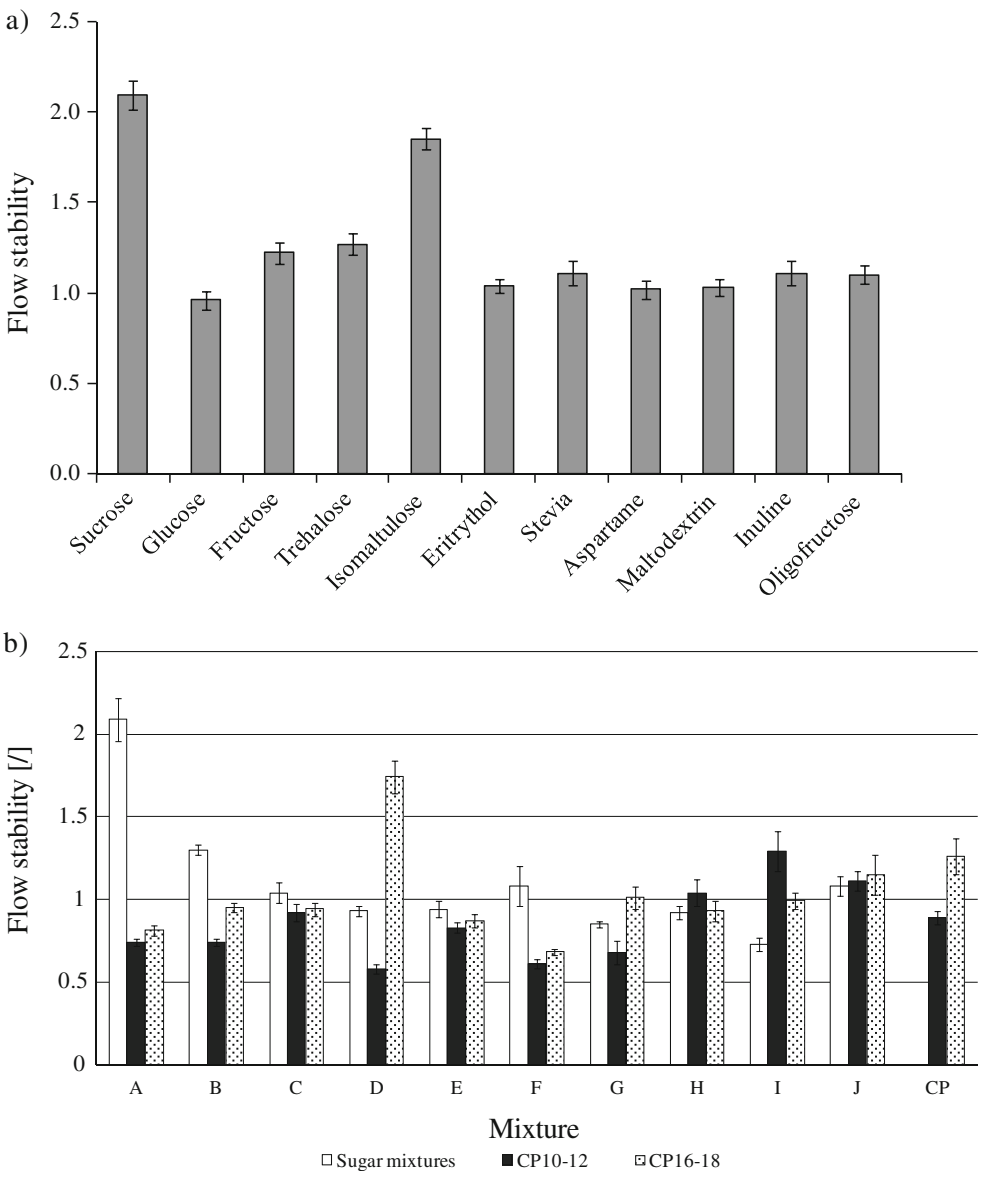

Fig. 5 Flow stability values for sugars (**a**), sugar mixtures (**b**) and cocoa powder drink mixtures (**b**)

test. All of the samples tested in this study showed FS values different to 1, which meant that all of them have undergone changes during the test. The most unstable powder was crystalline sucrose, whose flow stability value differs significantly to optimal value 1 (FS=2.09) (Fig. 5a). It has been observed that a part of the sucrose crystals were shattered during the rotation of the blade in the cylinder, and after the breaking up, segregation was visible in the cylinder among the particles, with the smallest particles travelling through the spaces between the big particles to the bottom of the cylinder, while the bigger crystals settled on the top of the cylinder. If this sugar was to be transported using a worm gear or if it were transported at high flow rates, the crystals would break down and cause a significant change in flow properties. Among the sugar mixtures, mixture D exhibited the best flow stability (FS=1.04) (Fig. 5b). All cocoa/sugar mixtures made with cocoa powder containing 10–12% fat showed flow stability values lower than 1, with an exception of mixtures H, I and J (Fig. 5b). All of the mixtures showed unfavourable properties for the production environment. The same observation was made for cocoa/sugar mixtures made with cocoa powder containing 10–12% fat, with the exception of mixtures D, H and J which had flow stability values higher than 1. These results implied that their flow properties should be modified in the production environment, whether by using flow agents or avoiding mixing sugars with poor flow properties into the mixture. Experiments carried out with ingredients for cocoa–sugar mixtures showed a regular pattern of the change of the flow stability value.

Caking

Caking is the tendency of the powder to form large agglomerates during storage and transportation. Cake height ratio (mm) of five compression cycles during the caking test was recorded and the results are shown in Fig. 6.

All the mixtures showed an increase in cake height ratio, which represented a characteristic behaviour of a powder with a high tendency to cake. These results had to be combined with the values for mean cake strength obtained by the same test. A high mean cake strength and an increase of the cake height ratio means that the powder is very susceptible to caking. All samples showed a similar trend of cake height ratio increase, with several exceptions. It was visible that the cake height ratios of sole cocoa powder containing 10–12% fat were lower than those of the mixtures (Fig. 6a), which suggested that there were significant changes in the caking properties of cocoa powder with 10–12% with the addition of sugar particles. However, the same observation could not be made for cocoa powder with 16–18% fat, whose cake height ratios were in the same range as all the mixtures (Fig. 6b).

Mean cake strength value also gave relevant information about the powders tendency towards caking. Results are shown in Fig. 7.

Sugars used in this study exhibited different mean cake strength values, ranging from 6.01 g (erythrytol) to 255.71 g (sucrose) (Fig. 7a). Cocoa/sugar mixtures showed higher mean cake strength than sugar mixtures, with the exception of sugar mixtures A and B (Fig. 7b). These mixtures exhibited disputable properties while performing the caking test, such as crystal breakage and segregation, which might have influenced the final test results for these two samples (A and B). A method different to helical blade movement through the cylinder should be used for assessing the caking properties of samples comprising large crystals which are easy to break. Cocoa/sugar mixtures made with cocoa powder which consists of 10–12% fat showed the highest mean cake strength values, with the exception of sugar mixtures A (sole sucrose) and B (sucrose and glucose) (Fig. 7b). A significant impact of particle size of all the mixture components on the mixture mean cake strength has been found, with the R values ranging from −0.77 for the impact of sugar mixtures d (0.5) on the cocoa powder with 10–12% fat to −0.74 for the impact of sugar mixtures d (0.5) on the cocoa powder with 16–18% fat mean cake strength. Generally, powders consisting of particles with smaller diameters exhibit higher mean cake strength values. Furthermore, median diameter had a significant influence ($p<0.05$) on sugar cake strength ($p=0.023$), an increase in the median diameter led to an increase of mean cake strength. A significant difference was found between cake strength and flow stability of mixtures made with cocoa powder containing 10–12% fat ($R=-0.361$, $p=0.005$) and between flow stability and cake strength of cocoa powder mixtures with 16–18% fat. It appeared that the cake formed at the end of the 5th caking cycle showed negative correlation with the FS value—samples with lower FS value showed higher cake strength.

This cognition represents important information about the properties of these types of mixtures which must be taken into consideration while handling them in industry. All of the mixtures used in this study were susceptible to caking and formed a strong cake that was very difficult to break. In production environment, these mixtures would show difficulties discharging from storage vessels.

Insolubility

The objective of this method was to determine the amount of insoluble compounds in the cocoa drink powder mixtures. While the determination of insolubility index was of primary importance for the quality of instant powders (Straatsma et al. 1999), it was also important to determine the amount of insoluble compounds in non-agglomerated mixtures, especially of those composed of different sugar

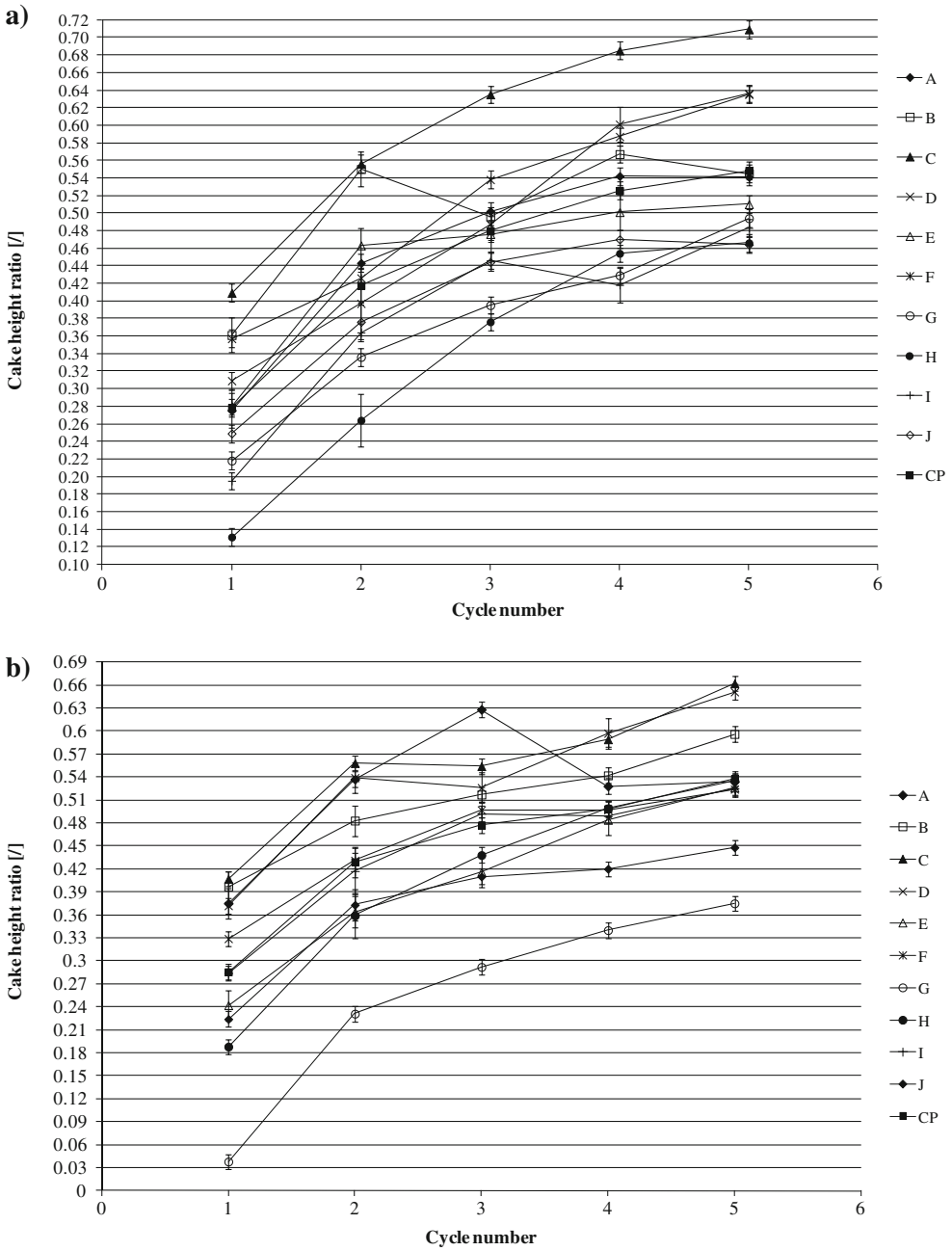

Fig. 6 Cake height ratios of cocoa drink powder mixtures: **a** cocoa powder with 10–12% fat, **b** cocoa powder with 16–18% fat

types with different granulometric structure. For that reason, it was possible to determine the influence of particle size on the insolubility of the mixtures. Since the sugars represent the most soluble compounds of cocoa drink powder mixtures (Shittu and Lawal 2007), their granulometric structure is expected to have a significant influence on the reconstitution properties of the mixtures, which was confirmed with results shown in Table 4.

A significant influence ($p<0.05$) was found between sugar mixture particle sizes d (0.5) and the insolubility of the cocoa/sugar mixtures, with an increase in the mass percentage of insoluble compounds as the d_{50} of the sugars mixtures decreases. Prediction of the percentage of insoluble compounds could be described using following equations:

For cocoa powder mixtures with 10–12% fat:

$$INS_{10-12} = 22.87 - 0.008 * d(0.5) \text{ (sugar mixtures)}$$

For cocoa powder mixtures with 16–18% fat:

$$INS_{16-18} = 22.99 - 0.005 * d\ (0.5) \text{ (sugar mixtures)}$$

These results are opposite to those obtained by Straatsma et al. (1999), who showed that the insolubility index increases with the particle diameter. However, their research

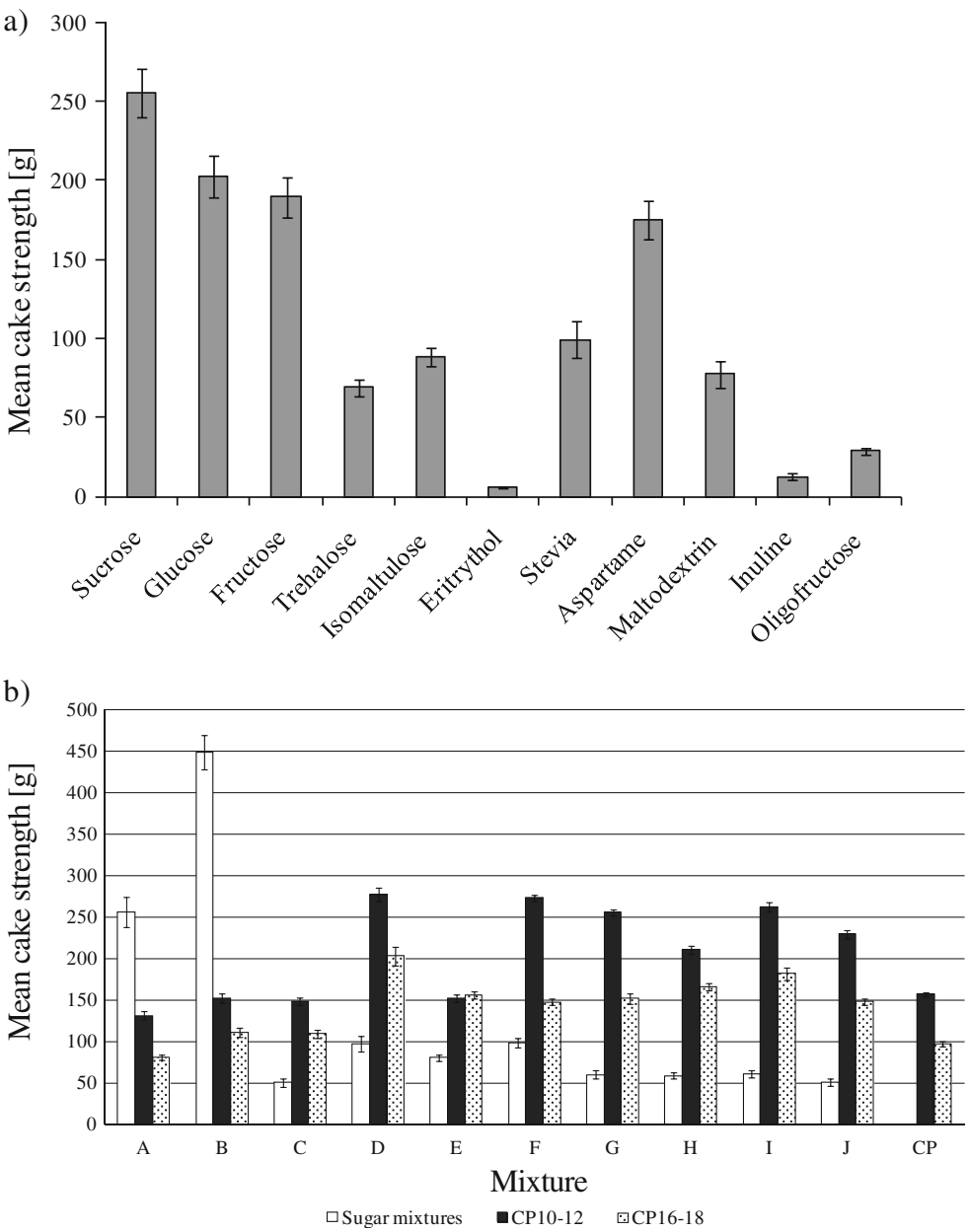

Fig. 7 Mean cake strength of sugars (**a**), sugar mixtures (**b**) and cocoa powder drink mixtures (**b**)

was based on insolubility determination of milk powders after drying, and in our research dry powders were used at the beginning of the mixing process, without any additional drying, agglomeration or instantization. Cocoa powder particles, which have a significantly smaller d_{50} than the sugar particles, when in contact with the sugar crystals, tend to stick to the crystal surface forming a thin layer of particles. Since the cocoa powder contains a certain percentage of fat, the layer formed on the surface of the sugar crystals acts as a boundary layer, which makes the dissolution of the particles more difficult and therefore leaving a greater amount of water-insoluble particles. Sole cocoa powders exhibited greater insolubility values than their mixtures (Table 4).

Colour

The colour measurements of cocoa powders are usually applied for the estimation of cocoa quality (Ilangantileke et al. 1991). The consistency of a product colour is also important to food manufacturers because it reinforces the image of constant product quality. Colour variation between batches may create the impression of inconsistent production and quality control. The colour of a product containing cocoa has always been an indicator of taste due to the relationship between colour, the quantity of cocoa, the degree of alkalization and the consequent flavour modifications. Natural cocoa powders have a characteristic light to

Table 4 Insolubility and colour of cocoa powder drink mixtures

	Insolubility (%)	Colour			
		L	a	b	ΔE
Cocoa powder with 10–12% fat					
CP	71.87±1.12	46.42±0.01	15.83±0.01	28.21±0.01	6.25±0.02
A	19.30±0.66	50.33±0.01	13.08±0.02	24.19±0.01	*
B	18.11±0.52	50.75±0.00	12.72±0.02	23.66±0.01	0.79±0.28
C	21.00±1.01	50.23±0.01	13.19±0.01	24.63±0.01	0.47±0.09
D	20.88±1.23	53.11±0.02	12.38±0.01	23.24±0.02	3.03±0.17
E	14.82±0.78	50.27±0.02	12.85±0.03	24.24±0.01	0.28±0.02
F	20.73±1.22	52.93±0.04	12.49±0.01	23.28±0.05	2.82±0.07
G	22.14±1.34	52.14±0.01	12.78±0.01	23.07±0.01	2.15±0.38
H	22.38±2.06	53.68±0.01	12.29±0.02	22.40±0.02	3.88±0.15
I	20.15±1.00	51.92±0.05	12.62±0.02	23.69±0.01	1.73±0.06
J	22.11±0.99	51.30±0.01	13.16±0.03	24.29±0.01	0.98±0.14
Cocoa powder with 16–18% fat					
CP	76.12±4.67	42.98±0.17	16.76±0.05	27.88±0.13	5.26±0.00
A	18.33±1.02	45.58±0.04	14.28±0.01	24.04±0.06	**
B	21.74±2.12	46.88±0.04	13.70±0.01	23.25±0.01	1.63±0.19
C	21.34±0.78	45.49±0.04	14.74±0.02	25.12±0.04	1.19±0.28
D	21.33±1.39	50.10±0.03	13.01±0.03	22.42±0.06	4.97±0.36
E	22.05±1.76	45.99±0.01	14.17±0.02	24.48±0.01	0.67±0.17
F	21.74±0.89	50.09±0.03	13.09±0.01	20.53±0.01	5.84±0.35
G	22.64±2,22	49.82±0.01	13.22±0.01	21.37±0.03	5.12±0.10
H	22.12±1.54	51.12±0.02	12.95±0.01	20.96±0.01	6.48±0.66
I	22.03±0.85	49.53±0.01	13.17±0.02	22.38±0.01	4.43±0.28
J	21.14±0.77	48.51±0.03	13.76±0.02	22.74±0.01	3.26±0.36

* Standard mixture for mixtures prepared with cocoa powder$_{10\text{-}12\%\ fat}$

** Standard mixture for mixtures prepared with cocoa powder$_{16\text{-}18\%\ fat}$

medium brown colour, while the treatment of cocoa with alkali, also known as dutching, darkens the cocoa ingredients, changes the taste by reducing bitterness and increases the dispersability of cocoa powder. Most cocoa powder manufacturers indicate whether their cocoas have been lightly, medium or heavily alkalized or they describe the colour.

In this study, natural, non-alkalized cocoa powders were used for the preparation of cocoa drink mixtures. As can be seen from the results in Table 4, all cocoa powder mixtures exhibited a unique ratio of dark/light pigments, which was displayed with the *L* values around 50. According to the results, a significant difference ($p<0.05$) between the lightness (*L* value) of the cocoa drink mixtures with 10–12% fat and cocoa mixtures prepared with cocoa having 16–18% fat was observed. The results indicate that, although cocoa butter is intrinsically almost colourless, it nevertheless affects the colour of the powder. The Hunter *a* scale results revealed the presence of red colour components in the experimental cocoa drink mixtures, which were significantly higher ($p<0.05$) in cocoa drink mixtures containing higher fat content (16–18%). Additionally, the cocoa powders used exhibited a substantial content of yellow colour components, which was confirmed by a high *b* value for all cocoa powders, ranging from 20.53 to 28.21.

The total colour difference (ΔE) is a combination of *L*, *a* and *b* values and presents a colorimetric parameter extensively used to characterize the variation of colour in food during processing. Since mixture A was considered as the standard (usual commercially available cocoa drink mixtures), a lower ΔE of a sample indicates a colour similar to the standard, while a higher ΔE of experimental cocoa drink mixtures indicates a product colour closer to plain cocoa powders. As can be seen in Table 3, although cocoa powder with lower fat content (10–12%) exhibits higher ΔE than cocoa powder containing higher fat content (16–18%), higher total colour difference was found in all cocoa powder drink mixtures prepared with cocoa powder containing higher fat content (16–18%). The lowest ΔE was found in mixture E (both with lower and higher cocoa fat content), which was composed of sucrose, isomaltulose and eritrythol, indicating that this cocoa drink mixture was the closest to standard (mixture A). A markedly high increase in ΔE was observed in mixture H, as well as in mixtures D and F, regardless of the cocoa fat content. These were the only cocoa drink mixtures prepared with glucose, which implies that this sugar significantly influences the overall colour of the final product. According to the results, the addition of sugars and sweeteners to cocoa powder reduced the red and yellow colour components, and the type of sugar or sweetener produced a notable difference in colour of the cocoa drink mixtures.

Conclusions

Mixing sugar and cocoa powders represents the first step in cocoa drink powder production. The physical properties of such mixtures differ significantly from the properties of sugars and cocoa separately. This change in properties affects the behaviour of the mixture, and thus industrial handling operations which follow mixing, such as conveying or agglomeration, have to be adjusted according to the mixtures' properties. This paper presents a characterisation of physical properties of non-agglomerated sugar mixtures and sugar/cocoa mixtures.

The addition of sugars to cocoa powders changes significantly the flow properties of the mixture. The median diameter of the mixture depends on the diameter of sugar and cocoa particles added to the mixture. A significant change has also been detected for bulk density values, which are higher than the sole cocoa powder bulk densities and lower than the sole sugar mixture bulk density. The maximum compression force

is higher than the maximum decompression force for all the samples. The compression forces of sugar mixtures diminish with the addition of cocoa particles, while the opposite trend has been found for the decompression force. The mixtures flow stability values all differed from 1, which indicates that all the mixtures have undergone changes during the PFSD test. They have also exhibited decreasing compaction coefficients, which indicate that they became more freely flowing with an increase in flow speed. Caking test has shown that all the mixtures are susceptible to caking. Flow properties of the mixtures in general were very poor, which indicates the need for agglomeration to improve the flow properties.

As for reconstitutional properties, the amount of insoluble compounds is rather high, which implies that instantization of these mixtures is needed.

According to the results of colour measurement, the addition of sugars and sweeteners to cocoa powder reduces the red and yellow colour components, but the type of sugar and sweetener does not result in a notable difference in colour of the cocoa drink mixtures.

The influence of cocoa powder fat content used in this study could not be determined since the cocoa powders used differed in particle size, which also affected the flow properties of the powders.

Acknowledgements The authors would like to thank the food industry "Zvečevo" for supplying the cocoa powder used in this study. This work was supported by the Ministry of Science, Education and Sports, Republic of Croatia, Projects 058-0581846-2810 and 058-0000000-3470.

References

Abu-hardan, M., & Hill, S. E. (2010). Handling properties of cereal materials in the presence of moisture and oil. *Powder Technology, 198*, 16–24.

Belščak-Cvitanović, A., Benković, M., Komes, D., Bauman, I., Horžić, D., Dujmić, F., & Matijašec, M. (2010). Physical properties and bioactive constituents of powdered mixtures and drinks prepared with cocoa and various sweeteners. *Journal of Agricultural and Food Chemistry, 58*(12), 7187–7195.

De Muijnck, L. (2005). Cocoa. In C. Onwulata (Ed.), *Encapsulated and powdered foods* (pp. 451–473). Florida: CRC.

Eduardo, M. F., & Lannes, S. C. S. (2007). Use of texture analysis to determine compaction force of powders. *Journal of Food Engineering, 80*, 568–572.

Fitzpatrick, J. J. (2005). Food powder flowability. In C. Onwulata (Ed.), *Encapsulated and powdered foods* (pp. 247–258). Florida: CRC.

Fitzpatrick, J. J. (2007). Effect of composition and storage conditions on the flowability of dairy powders. *International Dairy Journal, 17*, 383–392.

Galet, L., Vu, T. O., Oulahna, D., & Fages, J. (2004). The wetting behaviour and dispersion rate of cocoa powder in water. *Food and Bioproducts Processing, 82*(C4), 298–303.

Gerhards, C., Kael, C., & Schubert, H. (2004). Measurement of attrition of agglomerated cocoa beverage powders: a comparison of Friabilator and vibration tests. *Journal of Food Engineering, 65*, 101–108.

Ghosal, S., Indira, T. N., & Bhattacharya, S. (2010). Agglomeration of a novel food powder: effect of maltodextrin and gum Arabic dispersions on flow behaviour and compacted mass. *Journal of Food Engineering, 96*, 222–228.

Ilangantileke, S. G., Wahyudi, T., & Bailon, G. (1991). Assessment methodology to predict quality of cocoa beans for export. *Journal of Food Quality, 14*, 481–496.

Jain, R. K., & Bal, S. (1997). Properties of pearl millet. *Journal of Agricultural Engineering Research, 66*, 85–91.

Judd, D. B., & Wyszecki, G. (1967). *Colour in business science and industry.* New York: Wiley.

Kowalska, J., & Lenart, A. (2005). The influence of ingredients distribution on properties in agglomerated cocoa products. *Journal of Food Engineering, 68*, 155–161.

Minifie, B. W. (1989). *Chocolate cocoa and confectionery: Science and technology.* New York: Chapman & Hall.

Omobuwajo, T. O., Busari, O. T., & Osemwegie, A. A. (2000). Thermal agglomeration of chocolate drink powder. *Journal of Food Engineering, 46*, 73–81.

Özkan, N., Walisinghe, N., & Chen, X. D. (2002). Characterization of stickiness and cake formation in whole and skim milk powders. *Journal of Food Engineering, 55*, 293–303.

Rennie, P. R., Chen, X. D., Hargreaves, C., & Mackereth, A. R. (1999). A study of the cohesion of dairy powders. *Journal of Food Engineering, 39*, 277–284.

Shittu, T. A., & Lawal, M. O. (2007). Factors affecting instant properties of powdered cocoa beverages. *Food Chemistry, 100*, 91–98.

Straatsma, J., Van Houwelingen, G., Steenbergen, A. E., & De Jong, P. (1999). Spray drying of food products: 2. Prediction of insolubility index. *Journal of Food Engineering, 42*, 73–77.

Telis, V. R. N., & Martinez-Navarrete, N. (2010). Application of compression test in analysis of mechanical and colour changes in grapefruit juice powder as related to glass transition and water activity. *LWT- Food Science and Technology, 43*, 744–751.

Teunou, E., Fitzpatrick, J. J., & Synnott, E. C. (1999). Characterization of food powder flowability. *Journal of Food Engineering, 39*, 31–37.

Vissotto, F. Z., Jorge, L. C., Makita, G. T., Rodrigues, M. I., & Menegalli, F. C. (2010). Influence of the process parameters and sugar granulometry on cocoa beverage powder steam agglomeration. *Journal of Food Engineering, 91*, 283–291.

Vu, T. O., Galet, L., Fages, J., & Oulahna, D. (2003). Improving the dispersion kinetics of cocoa powder by size enlargement. *Powder Technology, 130*, 400–406.

Yanes, M., Duran, L., & Costell, E. (2002). Rheological and optical properties of commercial chocolate milk beverages. *Journal of Food Engineering, 54*, 229–234.