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Dispersion Characteristics of Oil-in-Water Emulsions with Modified Starches

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Running title: **Droplets Size and Distribution of Reduced-Fat Emulsions with Modified Cassava Starch**

Abstract
Most food emulsions are characterized by high fat content and the development of reduced-fat food emulsions with the same physicochemical, rheological and organoleptic properties as the full-fat emulsions has been a considerable challenge. Reduced-fat food emulsions with modified cassava starches were prepared and the dispersion characteristics were analyzed by their microscope digital images. The results showed that the control sample had colloidal particles with the largest average volume and average surface. The modified cassava starches were used to making better dispersion characteristics of reduced-fat emulsions. From the results for the median diameter (Md) the highest values were obtained for the emulsion with 12 % cassava maltodextrin (CM), followed by the sample with 6% CM.

Practical applications
All studied emulsions show properties that may be used by the development of food emulsions with reduced fat content. The addition of modified cassava in reduced-fat emulsions improved the dispersion characteristics of the analyzed model emulsions. The average diameter of the oil globules decreased with increasing the amount of the used modified starch. There were no substantial differences in dispersion characteristics between the emulsions with two types of modified cassava starches, so both of them can be used like a fat mimetics.

Key words: reduced-fat food emulsions, cassava starch, dispersion characteristics

Introduction

The trends in food industry are focused on the development of new eating habits and new knowledge about functional foods and reduced-fat food product (Al-Sayea et al., 2012; Liu et al. 2007). The consumer attitude towards healthy foods is increasing which leads to the decreased consumption of some fats (Choudhary & Grover, 2012). The food emulsions are traditionally with a high fat content. The main difficulty and challenge facing food industry is to select ingredients that "mimic" properties of the oil phase in food emulsions. The oil content has influence on the appearance, taste, aroma, structure-mechanical characteristics and shelf life of food emulsions (McClements & Demetriades, 1998).

One of the important features of an emulsion is its droplet size distribution. The droplet size influences many characteristics, for instance the rheology and the stability of an emulsion (Abu-Jdayil et al., 2001; Opedal et al., 2009). Reducing the size of the fat droplets and adding the thickening ingredients can influence the appearance, flavor, texture and rheological characteristics of the product.

Generally, nonfat ingredients such as gums, starches, and proteins with different functionalities are incorporated into fat-reduced products. Many of these result in loss of quality and attributes in low-fat products compared to full-fat products (McClements & Demetriades, 1998).

Cassava starch has various applications in food industry, including as a thickening and gelling product. Globally, the price of cassava starch is lower than the other starches. The cassava starch forms a colorless gel, without taste and with high viscosity (Tonukari, 2004).

The control sample is emulsion with 70 wt. % oil phase (OP). The reason of this research is to produce products with functional properties and better characteristics. It was replaced the part of the OP in control sample and was used two types of modified cassava starches. It was produced low-fat emulsions with closely rheological characteristics, reported in Dzhivoderova et al., 2015 a, and dispersion characteristics of the samples were analyzed.

The objective of this study was to determine the influence of type and concentration of cassava starch on the dispersion characteristics, like an explanation of the stability and rheological properties of the low-fat emulsions. A further objective was to investigate both of the used starches like a fat replacers.

Materials and Methods

Materials

Starches

It was used two types of modified starches: Pregelatinized functional cassava starch - Novation Indulge 3920 without E number and Special cassava maltodextrin - N-Dulge CA1 from the Ingredion Incorporated, delivered by KUK – Bulgaria Ltd. The modified starches are cold gelatinized.

Additives

It was used sunflower oil from "BISER OLIVA" JSC – Bulgaria.

Like an emulsifier was used dry egg mélange from RoYAL V- Argentina.

The experimental arrangement

Reduced-fat food emulsions with cassava starch were prepared and their dispersion characteristics were analyzed by microscope. Capturing of the digital images of the samples was made with a microscope BOECO BM-180 (Germany), with digital camera MDCE-5 USB 2.0 (China). The digital images were computer analyzed.

Methods for the analysis

Preparing of the samples

Sunflower oil was used as oil phase (OP) in investigated model oil-in-water (O/W) emulsions. The emulsions were formulated with pregelatinized cassava starch (PCS), cassava maltodextrin (CM) and mixture of the two types of modified starch in a ratio of 1:1. The reduced-fat emulsions were prepared with 30 wt. % and 50 wt. % OP and different concentration of starch - from 4 to 12 wt. %.

Egg mélange was used as an emulsifier (6 wt. %). It is known that the egg mélange is used like a natural emulsifier in oil-in-water emulsions, mainly of mayonnaise type. Amount of the components in model emulsions were specified in Table 1. Notations indicated each of the emulsions and they were used in the text below. The starch and the egg mélange powder were mixed, and then the quantity of necessary water was added. The mixture was stirred until complete dissolution. The water phase was mixed with homogenizer Disho-Labor, Koruma`s V 60/10 for 1 min, with rotation frequency 3600 min^{-1}. The oil was added by slowly emulsification, in vacuum about 3-4 kPa. It was homogenized again for 1 min.

Computer analysis of the digital images
From every visual field were measured 70-150 objects. The numbers of analyzed objects (particles) for every sample were 1098.
It was used the method to analyzed the digital images and to determined dispersion characteristics of colloidal particles (oil droplets) in the analyzed samples – Image Analysis (Alava et al., 1999; Schubert et al. 2006). The computer determination was made with software program, analyzing the microscope images „UTHSCSA Image Tool – Version 3.0" made by The University of Texas Health Science Center – USA.
Recognition of objects was done by manually marking them with each colloidal particle image emerges circle - a new object (oil droplets are approximated to sphere whose projection in two-dimensional space was a circle). The added new sites were registered automatically by the software to measure their area based on the number of pixels of predetermined size. The results were imported for subsequent mathematical and statistical processing and analysis.

Sauter Diameter
One of the indicators, which were used to evaluate the characteristics of dispersed particles (oil droplets) of the samples, was Sauter diameter - d_{32}. It observed the volume and total surface of colloidal particles in a fixed volume of the sample. The Sauter diameter is inversely proportional to the specific surface of the colloidal particles investigated. Thus the less d_{32} means much less particles, because their total surface area is larger and opposite - the larger values of d_{32} means a large number of colloidal particles having a less total surface area. The Sauter diameter defined by:

$$d_{32} = \frac{\sum_{i=1}^{k} n_i d_i^3}{\sum_{i=1}^{k} n_i d_i^2}, \quad (1)$$

where: n_i is the number of the droplets of diameter d_i.

Statistical analyzes
The statistical analyzes were made with ANOVA, one- and two-factorial dispersion analyze with more observations for each level of the relevant factors and a confidence level of 0,05.

Results

Determination of dispersion characteristics of oil-in-water emulsions
Dispersion characteristics of the emulsion products were an important characteristic influences of the structural and mechanical properties and stability of products. The major indicator for the quality of emulsions is the determination of the oil droplets size and their distribution. Proteins, polysaccharides, surfactants can be used like a thickening agent in emulsion food products. They have a specific impact on the dispersion characteristics, helping to conurbation of oil droplets (McClements, 2005). The dispersion characteristics of the model oil-in-water emulsions with pregelatinized cassava starch, cassava maltodextrin and a mixture of the two types of modified starch in a ratio of 1:1 were presented in Tables 2 to 5. The results of the dispersion characteristics of the model oil-in-water emulsions with different quantity and type of modified cassava starch were supplemented by results which were shown the nature of the polydispersity of the analysed systems. The median diameters distribution of the oil droplets were presented in the histograms (Fig. 1).

Discussion
There were found differences between the dispersion of the model oil-in-water emulsions and the control. Table 2 showed that the average diameters of the oil droplets decrease with increases of the modified starch quantity. There were no substantial differences between dispersion characteristics of the low-fat emulsions. The emulsion with 12 % CM has the highest median diameter (Md) of oil droplets, followed by the sample with 6 % CM. With the larger number of smaller sized particles and larger total surface area is the sample with 14 % PCS. The control sample has the most of large-sized colloidal particles and small overall surface area. Table 5 showed that the control sample has the largest average volume and average surface of colloidal particles. Model oil-water emulsion with 14 % PCS has the smallest.
The size of the oil droplets decreases with addition of modified cassava starch. Other authors demonstrated that higher contents of starch were resulted in smaller particle size (Rahmati N. et al., 2015). The control sample chiefly has oil droplets with sizes 6 and 15 µm. The oil droplets sizes in the

low-fat emulsions are from 3 to 6 μm (Fig.1.), which determined higher emulsion stability (Dzhivoderova et al., 2015 b). For samples with CM and a mixture of the two types of modified starches were observed more influence of the quantity of the starches.

The previously analyses show that increase of the starch quantity brings together the oil droplets and theirs density increase too (Dzhivoderova et al. 2015 b). In support of this, the increase of the starch quantity increases the polydispersity too and the average diameters of the oil droplets. This results influence of the emulsion stability, reported in Dzhivoderova et al., 2015 b. Fig.1. -D) and E) showed that in the sample with CM there was more expressed polydispersity.

Conclusion

The addition of modified cassava in reduced-fat emulsions improved the dispersion characteristics of the analyzed model emulsions. The average diameter of the oil globules decreases with increasing the amount of the used modified starch. There are no substantial differences of dispersion characteristics between emulsions with the two types of starches.

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Table 1. Notations of model emulsions and the starch content in each sample

OP,%	**PCS,%**			**CM,%**			**PCS+CM (1:1), %**
70	–	–	–	–	–	–	–
50	**4**	**6**	**8**	**4**	**6**	**8**	**6**
30	**12**	**14**	**16**	**12**	**14**	**16**	**12**

Table 2. Dispersion characteristics of model oil-in-water emulsions with pregelatinized cassava starch

Parameters	**Control sample**	**6% PCS/50% OP**	**12% PCS/30% OP**
Dispersity (D), μm^{-1}	0,14	0,18	0,22
Average diameter, μm	6,99±0,01	5,43±0,02	4,51±0,01
Median diameter (Md), μm	19,95	14,92	19,63
Sauter diameter (d_{32}), μm	9,78	7,61	6,43
Average volume, μm^3	302,96±0,46	141,399±0,22	81,28±0,22
Average surface, μm^2	185,80±0,18	111,54±0,09	75,79±0,09

Table 3. Dispersion characteristics of model oil-in-water emulsions with cassava maltodextrin

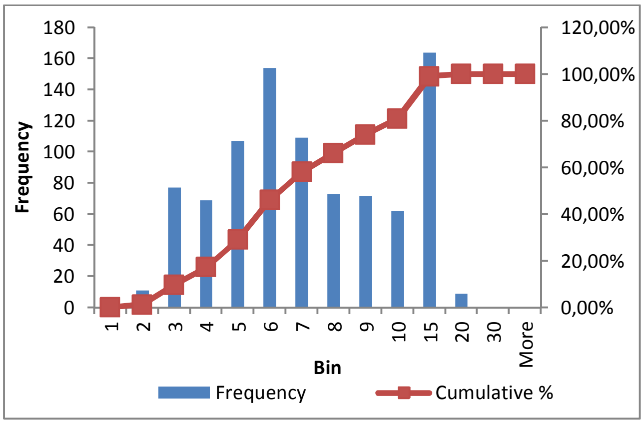
Parameters	**Control sample**	**6% CM/50% OP**	**12% CM/ 30% OP**
Dispersity (D), μm^{-1}	0,14	0,19	0,23
Average diameter, μm	6,99±0,01	5,33±0,01	4,40±0,01
Median diameter (Md), μm	19,95	30,08	198,31
Sauter diameter (d_{32}), μm	9,78	8,62	5,6
Average volume, μm^3	302,96±0,46	156,45±0,75	65,54±0,09
Average surface, μm^2	185,80±0,18	108,86±0,18	70,00±0,06

Table 4. Dispersion characteristics of model oil-in-water emulsions with mix of pregelatinized cassava starch and cassava maltodextrin (1:1)

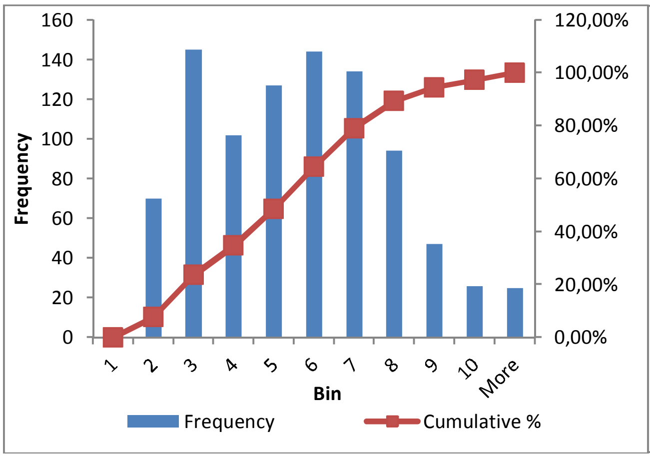
Parameters	**Control sample**	**6% CM+PCS/50% OP**	**12% CM+PCS/30% OP**
Dispersity (D), μm^{-1}	0,14	0,19	0,21
Average diameter, μm	6,99±0,01	5,13±0,01	4,84±0,01
Median diameter (Md), μm	19,95	14,40	14,47
Sauter diameter (d_{32}), μm	9,78	7,06	6,66
Average volume, μm^3	302,96±0,46	115,81±0,17	98,05±0,15
Average surface, μm^2	185,80±0,18	99,12±0,09	88,31±0,08

Table 5. Dispersion characteristics of model oil-in-water emulsions with 14% pregelatinized cassava starch and 14% cassava maltodextrin

Parameters	14% PCS/30% OP	14% CM/30% OP
Dispersity (D), μm^{-1}	0,27	0,23
Average diameter, μm	3,66±0,01	4,30±0,01
Median diameter (Md), μm	11,23	15,93
Sauter diameter (d_{32}), μm	4,62	6,80
Average volume, μm^3	36,90±0,05	83,21±0,2
Average surface, μm^2	47,92±0,038	73,43±0,1



A)



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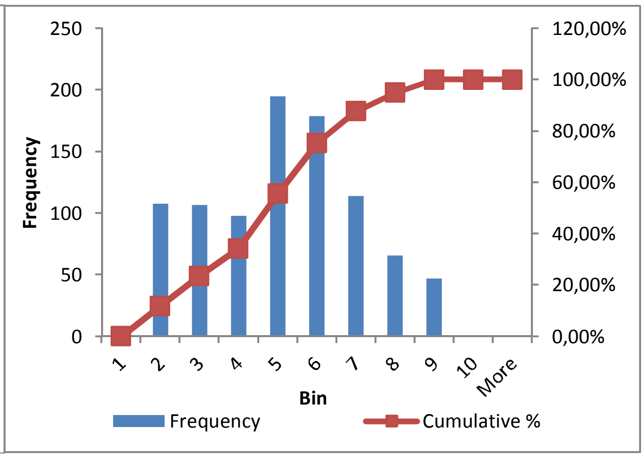
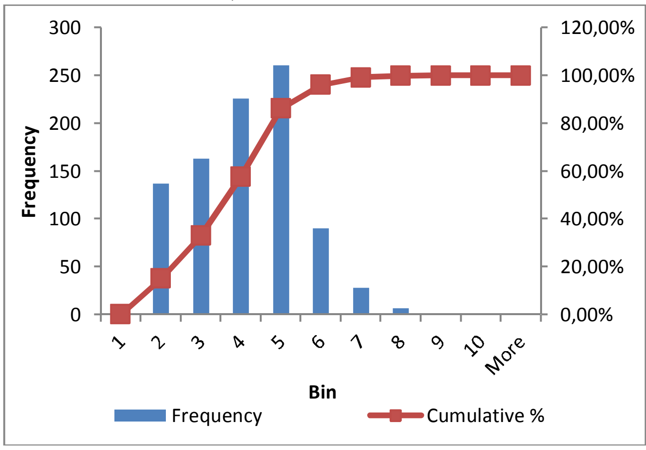
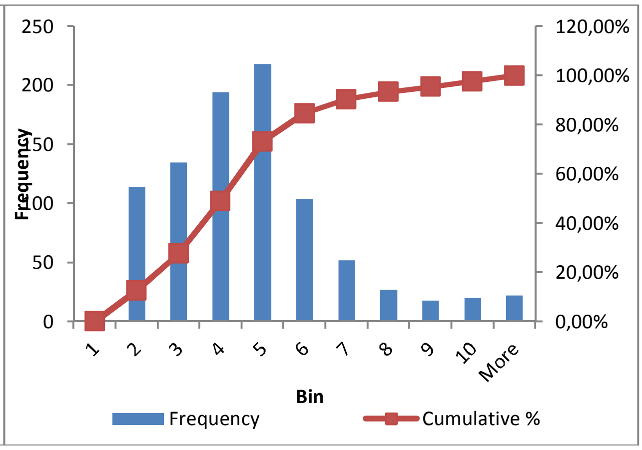


C)





D) E)

Fig. 1. Histograms of: emulsion with 70% oil phase – control sample – A), , emulsion with 50% oil phase and 6% mix of pregelatinized cassava starch and cassava maltodextrin (50/50) - B) and emulsion with 30% oil phase and 12% mix of pregelatinized cassava starch and cassava maltodextrin (50/50) - C), emulsion with 30% oil phase and 14% pregelatinized cassava starch - D) and emulsion with 30% oil phase and 14% cassava maltodextrin - E)