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An assessment of various powdered baby formulas by conventional methods (DSC) or FT-IR spectroscopy

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Abstract Milk components are assumed to be uniformly distributed in a concentrate whilst it is being dried. During milk powder production, these components are redistributed in the drying droplets and the powder surface composition is significantly different from that of the bulk of it. The objective of this article was to analyze and compare phase transitions of powdered baby formulas as well as to make a study of their FT-IR spectra. Food powders of different composition were tested by a differential scanning calorimeter (DSC, TA Instruments Q 200) with a normal pressure cell and a System 2000 spectrophotometer. Significant differences were observed in the shape of curves of the mixtures and the agglomerates. The observed phase transitions in powders depended on fat content. Characteristic peaks of melting lactose were observed in the curves of the powdered baby formulas. The IR spectra proved to be useful in determining adulteration of baby formulas. Both methods were complimentary during a thorough evaluation of these food powders.

Keywords Baby formulas · Phase transitions · DSC · FT-IR

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Introduction

Powdered food is durable, convenient and easy to use [1]. The property of amorphous sugar to first absorb considerable moisture [2, 3] and then to release moisture is probably one of the key reasons for physical instability in a variety of food powders even though sugar crystallization is frequently inhibited by other chemical components [4]. Milk components are assumed to be uniformly distributed in a concentrate whilst it is being dried. During milk powder production, these components are redistributed in the drying droplets and the powder surface composition is significantly different from that of the bulk of it [5]. The product properties may be substantially affected by the form of the solid produced, particularly whether it is in amorphous or crystalline form.

Amorphous and crystalline products possess different properties [6, 7]. Powdered baby formulas are of multicomponent composition, and therefore vary in powder structure. Many food powders contain amorphous glassy components, such as amorphous sugars. Many spray-dried dairy powders contain lactose in its amorphous state. Amorphous components are thermodynamically unstable and there exists a driving force for them to crystallize. However, crystallization requires that the molecules must be able to move [8]. Crystallization process is usually divided into three phases [9].

Differential scanning calorimetry (DSC) is an established thermal analytical technique that can measure phase and glass transition properties because glass transition induces a change in the specific heat of the material due to molecular mobility [8, 10].

The use of thermal analytical techniques and the information obtained is useful in controlling quality changes in food during processing and in storage [10, 11]. IR

spectroscopy, on the other hand, serves as an established method to determine types and number of chemical bonds present in a sample and therefore it can be used to study any chemical changes occurring in a processed powder.

The objective of this study was to analyze the phase transitions of ingredients and their influence on the thermokinetic properties of powder milk baby formulas using DSC as well as using Fourier transform infrared spectroscopy (FT-IR) to differentiate samples with various chemical compositions with a view to establishing evidence for milk powder adulteration.

Materials and methods

Materials

The powders used in this study were both skimmed milk (SM) and whole milk (WM) powders produced by Dairy Cooperative in Koło, Poland. Commercially available powders containing essential polyunsaturated fatty acids were studied: Ropufa"10" n-3 Food Powder S/SD and Ropufa"10" n-6 Food Powder—both distributed by DSM Nutritional Products Co. Ltd. in Mszczonów, Poland as well as lecithin powder distributed by Hortimex Co. Ltd., Konin Poland, and cocoa powder were distributed by Grekens Cocoa Bv Wormer, Holland.

Two mixtures were prepared, M-1 and M-2. The first consisted of SM plus essential polyunsaturated fatty acids (n-3; n-6) and the second consisted of WM plus essential polyunsaturated fatty acids (n-3, n-6), and cocoa and lecithin. The rationale behind choosing the studied ingredients was as follows: cocoa was chosen as the most popular flavour on the Polish market; lactose was chosen as it is an ingredient of milk powder. The choice of maltodextrin was dictated by the fact that it was present in capsules containing unsaturated fatty acids used in this study. It can be said that inclusion of lactose and maltodextrin is in a way a by-product of working with milk powder and unsaturated fatty acids. The practical result was to study the effects of not only these ingredients which were our primary focus (milk powder, unsaturated fatty acids) but also those which presence was necessary and unavoidable (lactose, maltodextrin).

Agglomeration

Technological processes involved in the production of powdered mixtures with n-3 and n-6 essential polyunsaturated fatty acids were mixing, wet agglomeration and drying. These processes were carried out in a fluidized bed agglomerator of the STREA 1 type produced by Niro-Aeromatic A.G., Bubendrof, Switzerland. The wet agglomeration process in the fluidized bed used 20 mL water, 15% lactose solution and 10% maltodextrin solution as the wetting liquid (binder solution). A sample of food powder weighing 300 g was placed in the product container, and fluidized by means of an upward flowing air stream. The temperature of the inlet fluidizing air entering the bed was set at 50 °C. During agglomeration it was necessary to increase fluidizing air flow regularly to maintain correct fluidization of enlarged agglomerates. Process of agglomeration lasted for 15 min. When the binder solution had been used up the product was dried for 15 min at 50 °C [12, 13].

The inside part of each agglomerate was chemically identical with the mixture M-1. The outsides varied depending on the agglomerating agent used: water (sample A-1), 15% lactose (sample A-2), 10% maltodextrin (sample A-3). Altogether six samples were studied (A-1, A-2, A-3, M-1, M-2 and SM—skimmed milk).

Differential scanning calorimetry

Before the calorimetric experiments, all samples were dried for 24 h in a vacuum, under pressure of 13 kPa and at a temperature of 40 °C. The food powders were stored in a desiccator at until measurement. Water activity of SM powder was 0.017, A-1—0.083, A-2—0.052, A-3—0.062, M-1—0.055 and M-2—0.060. Low water activity was close to the value of water activity of $CaCl_2$ at 25 °C—0.001.

The milk powders were studied by DSC (DSC, TA Instruments Q 200) in a normal pressure cell. The cell was purged with dry nitrogen at 50 mL/min and calibrated for baseline on an empty oven and for temperature using standard pure indium. Specific heat capacity was calibrated using a sapphire. The powders were cooled with a mechanical refrigeration cooling system (intracooler). An empty sealed aluminium pan was used as a reference in every test. The food powders (10–15 mg) were non-hermetically sealed in aluminium pans (volume 30 μL). The samples were heated from −60 °C up to 300 °C with the heating rate of 5 °C/min. The DSC technique was used to obtain curves of heat flow (W/g) versus temperature curves [14, 15]. A second DSC test was performed by cooling the samples from 20 to −90 °C with the cooling rate 2 °C/min [15]. The samples weighed between 10 and 15 mg. All analyses were completed in triplicate.

FT-IR spectroscopy

IR spectra were registered in the classic range of 4,000–400 cm^{-1} (25 scans) and 1 cm^{-1} resolution using a System 2000 Perkin Elmer spectrophotometer connected to PC software PeGrms running on Windows 98 platform. KBr matrix pellets were prepared by mixing 300 mg of

dried KBr with 1 mg of a sample in a ball mill, for 3 min. The powder was then pressed in a hand hydraulic press Graseby Specac with a compression pressure of 10 tons. All measurements were completed in triplicate [16].

Results and discussion

Differential scanning calorimetry

Figure 1 shows the DSC curves obtained for the studied samples: SM as well as the mixtures and the agglomerates. Characteristic peaks, generated by phase transitions running within the studied sample of SM during heating were observed. The first endothermic peak was observed in SM curve at the temperature of 104.23 °C. This signal indicated denaturation of specific milk proteins, e.g. peptides, polypeptides and globulin peptides, depending on exact location [15]. Zhang et al. [17] obtained similar results studying with DSC the effects of heat treatment on soymilk protein denaturation. According to their data, the temperature of endothermic peaks ranged from 90 to 100 °C, whilst the denaturation temperature increased with the increase of content of soymilk protein.

Two distinct endothermic peaks located at the temperatures of 155.52 °C (water evaporation) and 183.13 °C (beginning of melting of lactose) were observed. However, according to literature data [18] the temperature of melting point of pure lactose is higher and depends on the state of the sugar. Gombas et al. [18] studied temperatures of phase transitions of both amorphous and crystalline lactose and observed the endothermic peaks on DSC diagrams at 144 °C (water evaporation) and 213 °C (genuine melting of lactose), respectively. The temperature of melting of lactose (183.13 °C) measured in our experiment differed from that obtained by Gombas et al. [18], mainly due to effect of complex ingredients of SM. DSC diagram of 100% crystalline α-lactose has an endothermic peak at

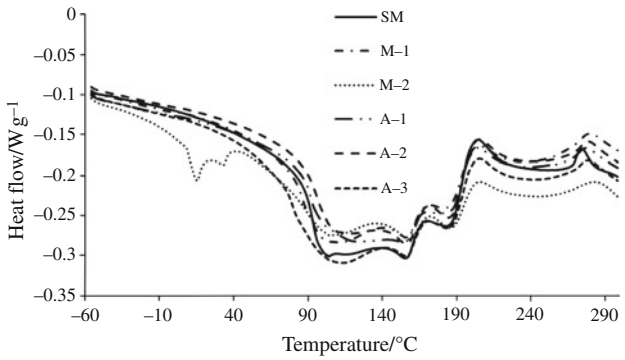

Fig. 1 DSC curve of SM powder, mixtures and agglomerates

144 °C, which represents the loss of crystalline water [18]. Obtained here DSC curves of SM powder and the mixtures had an endothermic peak at 155.52 °C. Since, the temperature of this peak was higher than that representing the loss of crystalline water; it appears that it was not connected with this phenomenon. Melting temperatures of 100% crystalline α and β lactose were observed by Gombas et al. at 213 and 224 °C, respectively. In our study, the endothermic peak indicating the melting temperature of lactose was observed in DSC diagrams of SM and the mixtures at 183.13 °C. The temperature of melting was lower compared to that of pure lactose. Other ingredients of SM and mixtures could be responsible for this change in melting temperature.

Within higher temperatures, ranged from 200.57 to 271.63 °C, two additional exothermic peaks were observed. Our suggestion is that those peaks are generated by phase transitions of fatty ingredients of milk powder, as the oxidation process starts within this range of high temperatures [19]. As it is well known that ingredient composition of various samples impacts on temperature of such phase transitions of fats, it is no surprise that slightly different locations of peaks on curves are provided by various authors [19]. The exothermic peak observed here was akin to peaks representing phase transitions in fat oxidation. But since the observed peak was registered in the atmosphere of nitrogen, fat oxidation cannot be involved. According to literature [20], the peak was a result of sample decomposition.

The curve of WM (data not presented here) contains two endothermic peaks of phase transitions, located at 7.22 and 52.86 °C, which are very typical for milk fat. Their exact location also depends on milk powder composition. Fitzpatrick et al. [8] who studied thoroughly the influence of water content on milk powder, lactose and whey permeate powder properties (e.g. flowability or glass transition temperature) found similar peaks in the curves of their samples. They also proved that the composition of a powder has significant influence on the location of peaks in its DSC curves.

The samples M-1 and M-2 were mixtures; the main ingredient of M-1 was SM whilst in M-2 it was WM. The curves of M-1 and M-2 trace a similar course starting from the temperature of 50 °C upwards. In the lower temperatures, two characteristic endothermic peaks appear in the curve of M-2 at 13.94 and 33.56 °C. Two characteristic endothermic peaks represented phase transitions of fatty acids, contained in milk fat, which melt within this range of temperatures. WM was the main ingredient of mixture M-2. Unfortunately, although essential polyunsaturated fatty acids (n-3; n-6) were added to both samples M-1 and M-2, no peaks generated by phase transitions of those additives were observed. Characteristic peaks of phase transitions for n-3 and n-6 fatty acids are presented in

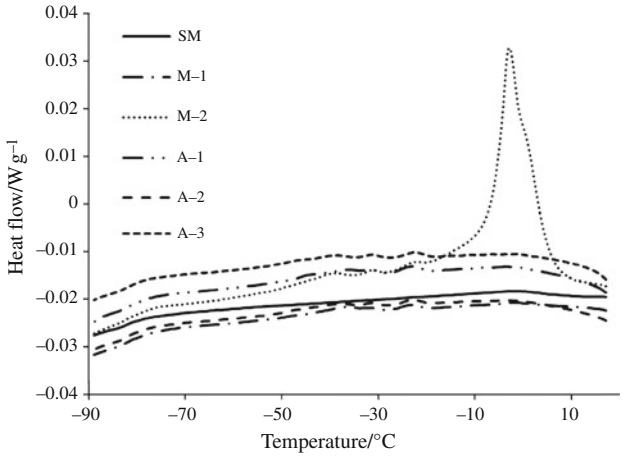

Fig. 2 DSC curve of cooling of SM powder, mixtures and agglomerates

Fig. 2. The range of temperatures in the experiment and the heating rate of 5 °C/min were not adequate to detect phase transition of n-3 and n-6 fatty acids which accounted for only a few percent of mixtures content.

M-1 was a starting mixture for the preparation and the study of the agglomerates (A-1 to A-3). The endothermic peak responsible for milk proteins was observed in the curves of all the studied agglomerates, as in the case of SM. Its location depended, however, on the outside part of the agglomerate. In the case of the agglomerate A-1, where water was used as wetting liquid, the peak was observed at 122.83 °C, whilst for the other agglomerates it appeared at lower temperatures, e.g. 119.58 °C for A-2. These values were significantly higher compared to those for the samples M-1 and M-2 (110.57 and 104.40 °C, respectively) indicating that agglomeration process influenced phase transition. Similar results were obtained by Zhang et al. [17] who proved dependence of protein concentration in solution on the shape of soymilk curves. The endothermic peaks of protein denaturation were located between 90 and 100 °C depending on protein content.

Three specific peaks of melting of lactose, one of main ingredients of baby formulas, were determined in the curves of the agglomerated powders. The first, endothermic peak of melting at 145 °C corresponds to the temperature at which α-lactose monohydrate loses its crystal water. The second, exothermic peak at 175 °C was specific for amorphous form of lactose. The poorly resolved third peak above 200 °C was related to melting of lactose [7, 21]. In the thermograms of the samples A-2 and M-1, the first, endothermic peak, related to loss of water by α-lactose monohydrate, was located at higher temperatures (M-1—155.52 °C and A-2—157.44 °C). On the other hand, the second peak, related to transition of amorphous form of lactose, was located at lower temperatures in the case of A-1 compared to M-2 (172.36 and 167.71 °C for M-2 and M-1, respectively). At the higher temperatures, the curves were similar and several characteristic exothermic peaks occurred. The samples of agglomerates A-1, A-2 and A-3 were prepared during agglomeration at high temperature. Lactose was the ingredient of mixtures which underwent phase transitions. Phase transition of amorphous lactose (exothermic peak) was not observed on the DSC diagram of SM in that range of temperatures, and so the interpretation was different.

The signals generated by milk fat and essential unsaturated fatty acids (EUFA) were only observed in the sample M-2 (see Fig. 1) but not in others, although EUFA were added to every studied sample. This was probably caused by too high heating rate and a relatively low temperature at the beginning of the process; since, according to [22], only an extremely low heating rate allows for demonstration of the presence of added fats.

The effect of cooling the SM, the mixtures and the agglomerates are shown in Fig. 2. Although the content of milk fat (0.5%) in SM was quite low, its presence was observable in the cooling curve. Small, mild exothermic peaks occured in the range of 8.42–9.18 °C. Fat was present in composition of all the baby formulas. Three exothermic, mild peaks were observed in the cooling curves of the mixture M-1 and the agglomerates A-1, A-2 and A-3 in the temperature range from −17.47 to −46.12 °C. An exothermic distinct peak at temperature of 2.99 °C was observed in the cooling curve of the M-2 sample. Lopez and Ollivon [22] investigated crystallizing properties of a mixture of triacylglycerols, cocoa butter/miglyol, cooled at 0.5 °C/min using DSC and X-ray diffraction (XRD) and proved that application of both methods can enrich our knowledge of mechanisms of crystallisation in emulsions. An exothermic peak, at about 12 °C, was observed on the cooling curve of triacylglycerols, which obviously were pure fat without food powder, and therefore their peak was located at a higher temperature compared to the obtained in our study (for the M-2 sample it was 2.99 °C).

The phase transitions observed for the fats in our study were most probably due to polymorphism. Polymorphism in TAGs and fats as well as phase transitions among various polymorphic forms have been studied by calorimetry before [23].

We did not study crystallization kinetics of bulk lipids or formation and stability of their various polymorphs as a function of time and temperature. For such measurements, a lipid sample has to be heated first to at least 20 °C above the melting point of its stable polymorph to erase all memory effects [24, 25].

IR spectroscopy

IR spectra presented in Fig. 3 were registered in the classic range (4,000–400 cm^{-1}) and used to differentiate the six samples of powdered baby formulas (different compositions due to different content of the added fat). The

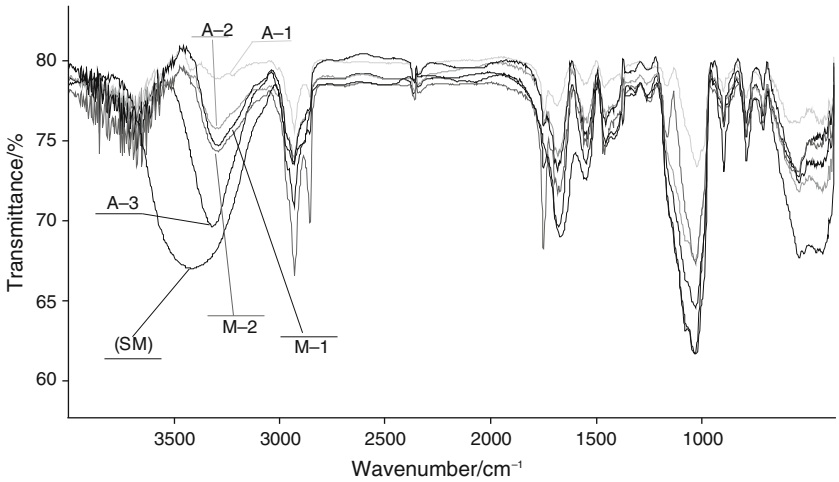

Fig. 3 Spectra of all studied powders in whole registered spectral range 4,000–400 cm^{-1}. *Bold black lines* denote reference spectrum (SM)

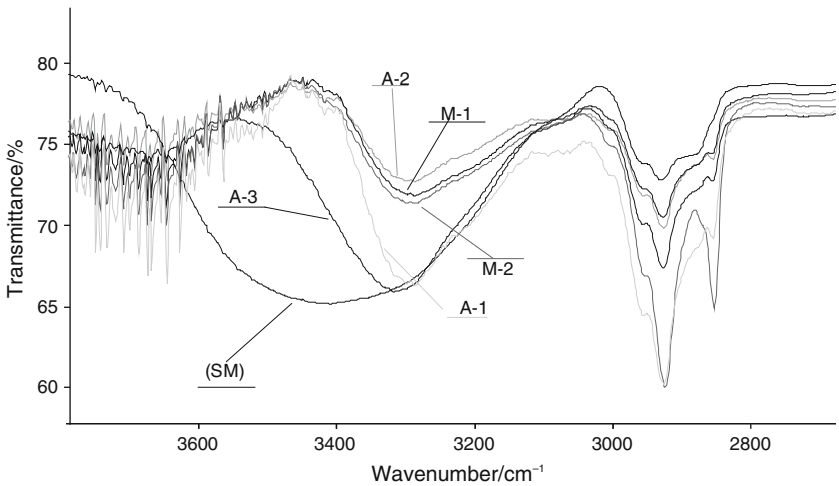

Fig. 4 Extension of spectral range (4,000–2,800 cm^{-1}) of spectra of all studied powders. *Bold black lines* denote reference spectrum (SM)

wavenumbers of the characteristic bands located in selected spectral regions, namely 3,500–3,200, 2,900–2,800 and 1,800–1,600 cm^{-1}, allowed discrimination of the samples containing added fat from the original ones. All the spectra in the whole registered spectral range are presented in Fig. 3. The bold black-coloured spectrum registered for the SM is treated as a reference spectrum and reflects all molecular vibrations occurring in a low-fat powder. This figure is provided to make the reader aware that it is possible to notice differences occurring in the studied spectra in various spectral ranges with the naked eye.

In the highest frequency region, around 3,500–3,300 cm^{-1} (Fig. 4), a wide and intense band generated by stretches of O–H bond of water molecule is present. The location of this band depended on whether agglomeration process was conducted or not. In the spectrum of the low-fat sample, for which no agglomeration process was applied (SM), the intensity of this band is very high and the band maximum is located at 3,428 cm^{-1}, which is in contrast to the significantly less intense band generated by vibrations of the same atoms (O–H) in the spectra of the other samples, with a slightly distinct band located at around 3,310 cm^{-1}. The intensity of the band in the region 3,600–3,200 cm^{-1} is related to the number of water molecules. As the content of water in SM sample is higher than in other samples, the intensity of this band in this case is also higher. In the case of samples M-1 and M-2 the content of water is at a similar level and lower than in the SM sample and therefore the intensity of bands registered for those samples are similar to each other and lower than that for SM.

To avoid ambiguity caused by different path lengths due to different thicknesses of pellets, the intensity was evaluated as a ratio of the intensity of a given band to the intensity of the band generated by C–H vibration occurring in the neighbouring region of 3,000–2,800 cm^{-1}. Aforementioned differences in shape, intensity and location of O–H stretches are due to a different way of distribution of water molecules in different powders. In the samples of the agglomerated powders, water molecules are trapped between other molecules forming mixture, and therefore vibrate with different energy which, in turn, is reflected in the spectrum as a different wavenumber and intensity. Different strength of interaction of a hydrogen atom with

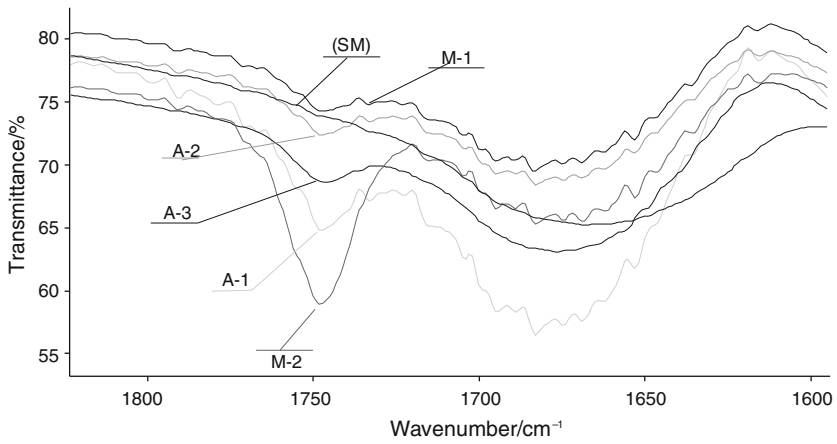

Fig. 5 Extension of spectral range (1,800–1,600 cm^{-1}) of spectra of all studied powders. *Bold black lines* denote reference spectrum (SM)

an electronegative oxygen atom of a neighbouring water molecule (hydrogen bond) might also be a reason for the mentioned differences.

In the region of 3,000–2,800 cm^{-1} where symmetric and asymmetric stretches of C–H bonds of saturated hydrocarbon chains generate their bands, the set of four characteristic bands occured in every studied spectrum, except the reference spectrum (SM) in which only three bands occured. Four bands are located at the same wavenumbers (within the experimental error): 2,957 (weak), 2,927 (strong), 2,875 (very weak) and 2,855 cm^{-1} (strong) for every other sample. Those bands are due to $–CH_2$ vibrations of saturated hydrocarbon chains of fatty acids. On the other hand, a weak band present in every spectrum located at 3,015 cm^{-1} is an evidence for stretches of $–CH_2$ of unsaturated hydrocarbon chains. In the case of the reference spectrum, the band at 2,855 cm^{-1} did not exist; moreover, the band at 2,875 cm^{-1} was of weak but not very weak intensity. The strong band at 2,855 cm^{-1} absent in the reference spectrum is generated by $–CH_2$ stretches of hydrocarbon chain of the added fat, which is of a different structure compared to the fat present in the reference sample. Data from this spectral region allow discriminating the genuine SM powder from those with added fat. If unwanted fat is added spectral data change significantly.

The next spectral region 1,800–1,600 cm^{-1} (see Fig. 5) contained two characteristic bands at 1,747 cm^{-1} (band 1) and 1,676 cm^{-1} (band 2) for every studied sample, except the reference sample (SM), for which only one band located at 1,665 cm^{-1} was present. This fact differentiated the reference sample from the others. The lack of band at 1,747 cm^{-1} (band 1) and the different location of band 2 is a proof of purity of the sample and confirm that no fat was added.

The ratio of intensity of the two above-mentioned bands (band 1 to band 2) depended on the sample composition and was highest for the sample M-2. In this case, lecithin and cacao additives were used and those compounds provided significantly more intense band at 1,747 cm^{-1}, generated most probably by C=O vibrations of aldehydes, ketones or, less probably, free fatty acids. The ratio of band 1 to band 2 decreased for the reference sample, whilst for the remaining samples it was the same and at its lowest level. In the case of the sample agglomerated with maltodextrin or protein, bands generated by C=O stretches of esters became more intense.

Conclusions

1. Both studied methods are complimentary in a thorough evaluation of powdered milk.
2. The phase transitions observed in the studied agglomerates and mixtures differ, which proves that the preparation method plays a significant role in determining final physicochemical properties of the formula.
3. The presence of lactose and proteins can be determined by DSC.
4. The presence of additional fat can be determined by FT-IR.
5. Application of both methods enables detecting adulteration, e.g. identifying if nutritionally important n-3, n-5 fatty acids were added as claimed on a label or not. Addition of unwanted artificial fat can also be detected.

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