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THE USE OF GLASS TRANSITION TEMPERATURE IN FORECASTING WHEY POWDER STORAGE STABILITY OBTAINED BY ELECTRO-SPARK TREATMENT

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Abstract: *This study investigated the behavior during storage of dry whey obtained using different approaches that prevent caking (by adding silicon dioxide, electro-spark treatment of whey). Forecasting the stability of quality whey powder was carried out based on a glass transition temperature.The glass transition temperature of whey powder was measured by differential scanning calorimetry.We showed that the highest glass transition temperature (+18.5 °C) and,subsequently, the smallest difference between product temperatures and glass transition temperature were discovered in dry whey, obtained with the use of electro-spark treatment, which proved to be stable during storage.We have found that the other samples of dry whey under normative storing conditions (from 0 till 20 °C) are predominantly in rubbery state, which can influence negatively the stability of the product during storage. Based on the glass transition temperature we determined that electro-spark treatment used in the technology of whey powder allowed reaching anti-caking effect due to physico-chemical processes resulting from electro-spark charges. This was proved by calculating the stickiness and caking sensibility index and the degree of caking (to 2 %). It was experimentally proved that the dry milk whey produced with electro-spark treatment differed positively from other samples by absence of non-fermentative darkening.Whey powder produced from whey treated with electro-spark charges was characterized by the highest degree of whiteness, which did not significantly change in 8 month storage.*

Keywords: *wheypowder, electro-spark treatment, glass transition temperature, caking, stickiness and caking sensibility index.*

1. Introduction

Dry milk whey belongs to amorphous metastable products, which is very sensitive to temperature and humidity changes. Spoiling of low humidity products during storage is determined by chemical, biochemical or/and physical changes, including migration and loss of humidity which can cause caking, fermentative and non-fermentative reactions displayed by product darkening.
Conditions of outer environment (temperature, moisture content) have big influence upon these processes, as well as product structure, active acidity, water activity index etc.
In order to increase quality, avoid spoiling of food products and to increase their shelf life, various technological measures are used, as well as nontraditional treatment measures, processing methods and storage techniques. At the same time for long shelf life products, including dry whey concentrate, important issue is the choice of qualities and characteristics used for objective and reliable forecasting of quality index changes during storage.
In a range of works [1-5] correlation was proved between some qualities of dry

products (such as stickiness, caking) and glass transition – phase transition of separate nature, particular to amorphous material.

The process of glass transition is a process of material transition from glass-like to rubber-like state and vice versa which is accompanied by changes in its thermodynamic and mechanical qualities, molecular mobility and dielectric penetrability[6]. The range of temperatures at which this transition is observed is called the glass transition temperature (*Tg*). The concept of glass transition together with the concept of water activity is lately widely used to forecast stability of food products under drying and storage[7].

It is considered that stability of organoleptic, chemical and physicochemical qualities of dried food products depends on storage temperatures. At temperatures higher than glass transition temperature may occur oxidation, crystallization and recrystallization processes, and increase in adhesive qualities, because is increasing in molecular mobility and lowering viscosity of the material. This in turn leads to changes in chemical and physical state, sticking of particles on the solid surface and caking of the product. The speed of such changes is determined by the difference in product temperatures (*T*) and *Tg* [2, 7, 8]. Itisknownthatthelowerthedifferencebetweenproductstoragetemperatureandglass transition temperature, thebetterisitsstorage [2, 3, 6].

Humidity content of the product has a decisiveinfluenceupontheglass transition temperature [8, 9, 14, 18, 22]. The change in chemical content, phase state of sugars and biopolymers (casein, whey proteins) has its influence upon dependence of *Tg*from product humidity content [13-22].

Scientific sources predominantly pay attention to glass transition temperature of vegetative origin products, separate components (including various carbohydrates) and model samples of dry products. At the same time, not much data is available on multicomponent products, produced in industrial conditions with the use of modern technological approaches, including demineralization of whey, use of electrophysical treatment procedures and anti-caking agents. However, this data is necessary to determine or prove storage regimes of dry products and to forecast stability of their quality indexes.

Theaimoftheworkwastodetermineglass transition temperature ofdrymilkwhey, obtained with the use of various approaches that prevent caking (adding silicon dioxide, electro-spark treatment of whey); tostudythebehaviorofexperimentalsamples duringpackaging, transportationandstoragebyparametersdiapasonchange [*T* – *Tg*].

2. Materials and Methods

2.1. Objects of research.

Demineralizedwheypowder(WPD) wasderivedbydemineralizationofcheesewheyatnanofilterutility(GEA, Denmark), thickening(end up with mass fraction of milk solidsto 50-52 %), coolingofthethickenedmilkwheyandcrystallizationoflactose (10-12 hours, under 15 °C) and further drying at spraying drier (Vzduchotorg, Slovak Republic).

Whey powder enriched with particles of magnesium and manganese (*$WPEP_{MgMn}$*)wasobtainedbytheabovementionedscheme,butdemineralized whey wastreatedatexperimentalelectro-sparktechnologicalinstallationbeforethickening.Thelatter consisted of charge impulse generator, control panel, running charge chamber, measuring and supplementary tools[10]. Electro-spark treatment was conducted under such conditions of charge contour: recharge condenser voltage – (75 ± 5) V; condenser volume – 100 uF;

resistance of granules layer in charge chamber – 0.15–1.5 Om; interval between metal granules – to 0,1 mm; impulse frequency – 0.2–2.0 kHz; exposition – 1 min for magnesium electrode system; 0.5 min – for manganese electrode system. In result of volumetric electro-spark dispersion of metal granules (Mg and Mn), whey was enriched by these components (Table 1).

Content of Mg and Mn in whey samples was determined at atomic-absorption spectrometer AAS1N (Carl-Zeiss Jena, Germany), equipped with burner for acetylene-air flame and lamps with hollow cathode for magnesium and manganese.

Table 1

Content of magnesium and manganese inwheypowders

Whey powders	ContentMg, g/kg	ContentMn, mg/kg
WPD	0.94±0.03	1.1±0.04
$WPEP_{MgMn}$	2.9±0.15	12.9±0.5

Demineralized whey powder with anti-caking agent (WPD_{ACA}) 1.0% of anti-caking agent was added to demineralized whey powder and thoroughly mixed. Silicon oxide SiO_2 (E-551 Silicon dioxide amorphous) was used as an anti-caking agent.

2.2. Chemical and physical analysis

Glass transition temperatures and heat capacity changes (Δ*Cp*) were determined using differential scanning microcalorimeter (DSC-2M) made at Special design office of biological instrument making in Pushchino (Russia) and equipped with a ThermCap data acquisition and processing program written in the Delphi programming language.

Micro calorimeter temperature scales were graded by to two benchmark points: -95.0 °C (melting temperature of chemically pure toluene) and 0 °C (melting temperature of water after double distillation). Cooling of calorimeter block was performed with the use of liquid nitrogen. Accuracy of temperatures measurement was not worse than ±0.1 °C.

The samples were hermetically canned in aluminum containers. Weighting was performed at microanalytical scales VLM-1 with accuracy ±0.01 mg. Overall content of water in samples was determined after measurements by dehydration till constant mass in the drying box at 104-105 °C.

In order to avoid artifacts connected to humidity condensation in calorimeter chambers, measurement block was filled with dried gas-like helium, which flow was controlled during measurements.

Samples were cooled at –50 °C at scanning rate 16 K/min. Temperature intervals (Δ*Tg*), beginning temperatures T_g^s and end temperatures of glass transition T_g^f were determined by DSC-curves, obtained under heating of samples at scanning rate 16 K/min from –50 till +35 °C. Typical DSC heating curve is presented at fig.1. *Tg* was determined as Δ*Tg*/2. The change in heat capacity under glass transition ΔCp was obtained by the difference in heat capacity at T_g^f and T_g^s. Each sample had undergone at least three measurements.

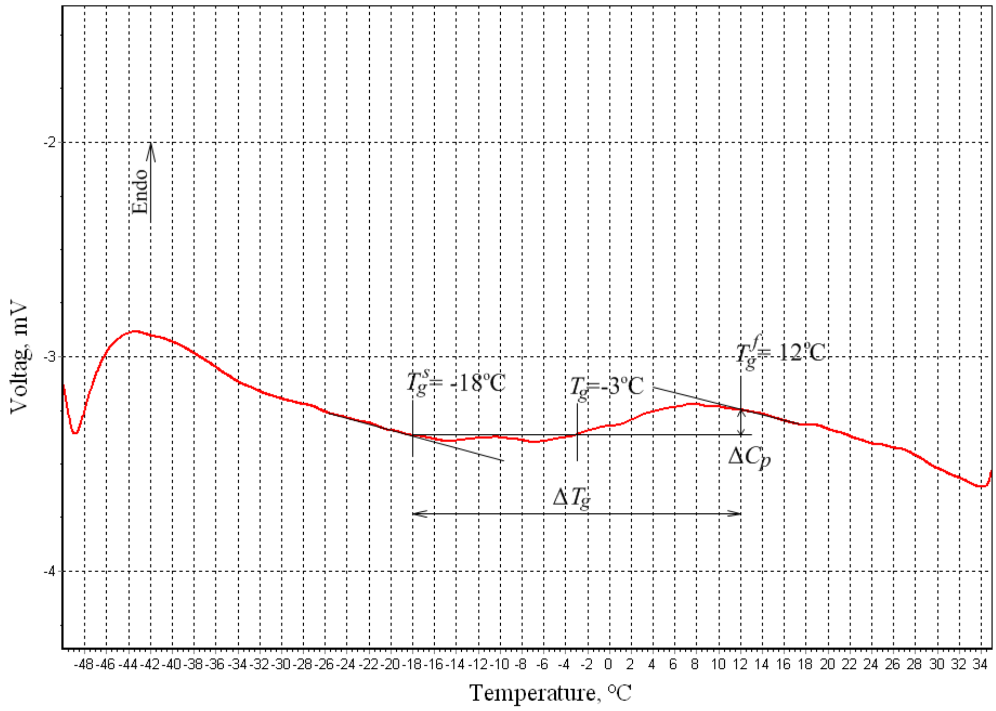

Fig. 1 Typical DSC heating curveforwhey powder showing the glass transition

The degree of caking was measured using the method described by Pisecky [11]. In the beginning amount of whey power (5 g) was kept in desiccators under artificially created conditions of high humidity (above 80 %) until the mass increase stopped. Afterwards samples were dried in drying box during 1 hour at 104±2 °C. After cooling in a desiccators, the sample was weighed, quickly transferred to a stainless steel sieve (250 µm), and shaken for 5 minutes in a shaking apparatus. The powder that passed through the sieve was weighed, and the caking index was determined by the equation 1.

$$C3 = \frac{M_1 - M_2}{M_1} \times 100 \qquad (1)$$

where$M_1$is the total mass of powder (g) and $M_2$is the mass of fines that passed through the sieve (g).

Ability of dry product particles to stickiness and/or caking during treatment and storage was forecasted under a stickiness and caking sensitivity index (SCSI). SCSI (in diapason from 0 to 10) was determined by equation 2 according to parameters changes diapason [*T* – *Tg*] (*T* – temperature of dry product) and Δ*Cp* [3].

SCSI = Number of points [T – Tg] + Number of points [ΔCp], (2)

where*Tg* is the glass transition temperature, °C; *T* – dry product temperature (at the exit from drier, in the dry powder batch mixer and under storage), °C; Δ*Cp* – change in heat capacity, J/(g·K).

This index simultaneously integrates the values of [*T* – *Tg*] (ranging between 0 and 5) and Δ*Cp* (ranging between 0 and 5) (Tab. 2) [3].

Table 2

Calculation of stickiness and caking sensitivity index [3]

T – Tg, °C	ΔCp, J/(g·K)	Number of points
[T – Tg]≤5	ΔCp<0.1	0
5<[T – Tg]≤10	0.1≤ ΔCp<0.2	1
10<[T – Tg]≤15	0.2≤ ΔCp<0.3	2
15<[T – Tg] ≤20	0.3≤ ΔCp<0.4	3
20<[T – Tg]≤30	0.4≤ ΔCp<0.5	4
30<[T – Tg]	0.5≤ ΔCp	5

Non-fermentative darkening of dry milk whey was determined by the change of product whiteness during storage. Whiteness of the product was estimated in relative points at Blik-P3 (Russia) instrument for measurement of directed zonal reflection index and determining whiteness.

3. Results and discussion

For research objects DSCcurves of heating were determined (fig.2), according to which characteristic temperatures of glass transition were found out (Table 3).

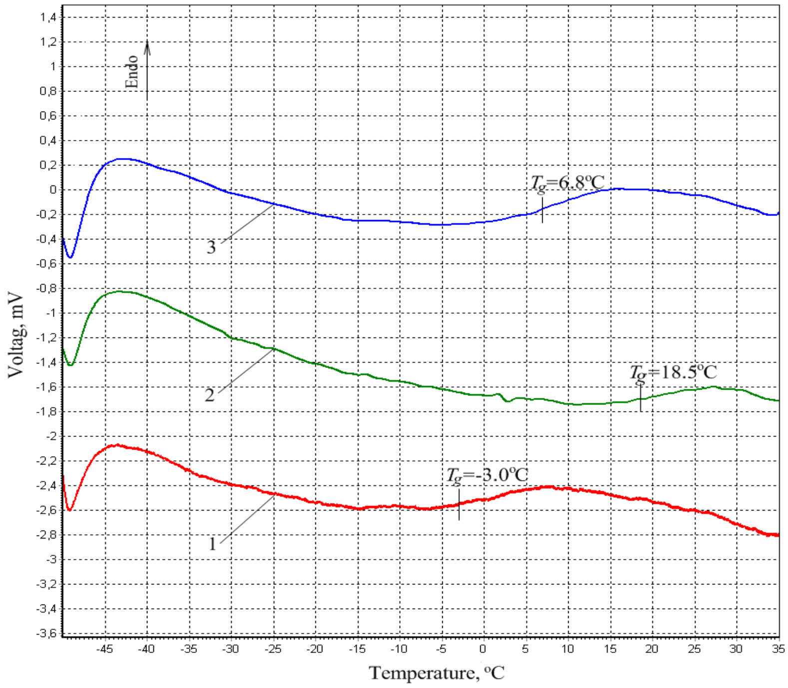

Fig.2 DSC heating curvesforwheypowder: 1 – WPD, 2 – WPEP$_{MgMn}$, 3 – WPD$_{ACA}$.

Results obtained showed the difference in studied samples by glass transition temperatures. The control sample of demineralized whey powder had the lowest *Tg* level. Addition of silicon dioxide as an anti-caking agent to WPD leads to increaseglass transition temperature on 10 °C. It was observed highest *Tg* value for whey powder enriched with magnesium and manganese particles.

Significant Tg grow in whey powder, produced with the use of electro-spark treatment, and most likely is explained by physicochemical processes taking place in whey components, as a result, of electro-spark charge. Among them: accumulation of magnesium and manganese particles in colloidal form in case of their transition from electrodes to solution; their interaction with water and whey components (including proteins and thus increasing its molecular mass); transition of lactose and creation of its derivatives (lactulose, lactobionic acid) [12].

Table 3

Wheypowdersampleshumiditycapacityandtemperaturesofglasstransition

Sample	Moisture content, g/gdrywhey	T_g^s, °C	T_g^f, °C	Glass transition temperature, Tg, °C
WPD (control)	0.044	−18.0±0.2	+12.0±0.2	−3.0±0.2
$WPEP_{MgMn}$	0.031	+10.0±0.2	+27.0±0.2	+18.5±0.2
WPD_{ACA}	0.034	−6.0±0.2	+19.0±0.2	+6.8±0.2

The conduct of researched whey powder samples during packaging, transportation, mixing with other components (sticking of particles to hard surfaces) and storage (caking) was forecasted by the change in index diapasons [*T* – *Tg*] and Δ*Cp*, established by DSC-curves. The SCSI value calculated from equation 2. It is known that SCSI allows to forecast the dry product behavior during drying, transportation and storage, from the most favorable case (SCSI ≤ 4: no stickiness and/or no caking) to the most unfavorable (SCSI ≥ 6: high to very high stickiness or caking hazard) [3].

For measurements with the aim of forecasting product behavior during packaging, transportation (stickiness) and storage (caking), such temperatures were taken for the dry product (*T*): on the exit from dryer – +30 °C; storage – +20 °C. Calculated results are presented in Table 4.

Table 4

Wheypowderbehaviorduringpackaging, transportationandstorage as a functionof [*T* – *Tg*] andΔ*Cp* values

Sample	ΔCp, J/(g·K)	Stickiness		Caking		Degree of caking, % (experimental data)
		[T – Tg], °C	SCSI (calculated data)	[T – Tg], °C	SCSI (calculateddata)	
WPD (control)	0.38	33.0	8	23.0	7	16.4±0.7
$WPEP_{MgMn}$	0.23	11.5	4	1.5	1	2.0±0.04
WPD_{ACA}	0.32	23.2	7	13.2	5	13.4±0.4

The analysis of received values showed that the highest ability to caking and high stickiness was particular for control sample of whey powder. Adding silicon dioxide decreased product caking risk, which was proved by SCSI and level of caking, measured experimentally.

Based on the glass transition temperature measurement and change of specific heat capacity, it was determined that including electro-spark treatment in technology of whey powder allowed reaching anti-caking effect due to physicochemical processes resulting from electro-spark charges. This was proved by stickiness and caking sensibility calculation index (SCSI =2) as well as experimental data of the degree of caking (to 2 %).

Research results and SCSI levels, calculated on their basis fully correspond to observations over research samples in the process of storage under 18±2 °C temperatures and relative humidity not more than 80 %.
It is worth mentioning that besides stability to caking of whey powder particles produced with the use of electro-spark treatment, these samples positively differed from other samples by the absence of non-fermentative darkening.
Researchsamplesproducedfromthewheytreatedwithelectro-spark charges was characterized by highest degree of whiteness, which did not significantly lower in 8 months storage (Table 5). Other samples suffered from lowering whiteness index by 8.8-10.5 conventional units depending on the type of product.Lossofwhitenesstestifiestheflowof Maillardreaction, whichasknowncannotretardevenunderlowhumidityunlikeotherbiochemicalprocesses.Nevertheless,its speed decreases by reducing the difference between the storage temperature andTg[2, 3]. It was observed in whey samples prepared using electric spark treatment.

Table 5

Change of whiteness in whey powder research samples during storage

Sample	Whey powder whiteness, conventional units, in storage		
	1 month	6 months	8 months
WPD	90.6±2.0	83.6±2.3	80.1±1.7
$WPEP_{MgMn}$	97.4±1.0	95.7±1.1	95.1±0.8
WPD_{ACA}	90.9±1.6	85.4±1.0	82.1±1.2

4. Conclusions

This study investigated the behavior during storage of dry whey obtained using different approaches that prevent caking (adding silicon dioxide, electro-spark treatment of whey). Forecasting the stability of quality whey powder was carried out based on a glass transition temperature.
We showed that the highest glasstransitiontemperature (+18.5 °C) and,subsequently,smallestdifferencebetween product temperatures and glass transition temperaturewere discovered in dry whey, obtained withtheuseofelectro-sparktreatment, which proves its stability while in storage.
We found that the other samples of dry whey under normative storing terms (from 0 till 20 °C) are predominantly in rubbery state which can negatively influence on stability of the product while in storage.
Based onthe glass transition temperaturewe determinedthatincludingelectro-sparktreatmentintechnologyofwheypowder allowed reaching anti-caking effect due to physicochemical processes resulting from electro-spark charges. This was proved by calculation stickiness and caking sensibility index and thedegreeofcaking(to 2 %).
Itwasexperimentallyprovedthat the drymilkwheyproducedwithelectro-sparktreatmentpositivelydifferedfrom other samples byabsenceofnon-fermentativedarkening.
Whey powderproducedfromthewheytreatedwithelectro-spark charges was characterized by highest degree of whiteness, which did not significantly lower in 8 months storage. Other samples suffered from lowering

whiteness index by 8.8-10.5 conventional units depending on the type of product.

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