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Reduced and Low-lactose Powdered Milk Production and Determination of its Physicochemical and Microstructural Properties During Storage

Leite em Pó Reduzido e Baixo Teor de Lactose: Produção e Determinação das Propriedades Físico-químicas e Microestruturais Durante o Armazenamento

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The lactose hydrolysis-based production of powdered dairy products is a challenge faced by the food industry due to difficulty in drying these products, as well as in powder storage stages. Therefore, the aim of the current study is to feature lactose-free fat-reduced powdered milk during storage, based on using samples produced through spray drying and lyophilization processes. Samples of powdered milk produced through the two aforementioned drying methods were subjected to different storage conditions (temperatures at 21 °C and 50 °C). Subsequently, the following sample features were determined: spectral profiles (based on Raman spectroscopy), microstructure (based on scanning electron microscopy), particle size in solution (based on laser diffraction), and sorption isotherms; in addition, a Maillard reaction (5-hydroxymethylfurfural) indicator was measured. The powders obtained by freeze-drying had worse characteristics compared to the products dried via spray dryer, in addition, as the hydrolysis content of lactose increased, a worsening in the characteristics of the powders was again observed. Finally, it is possible to conclude that drying via spray-drying is the best alternative compared to freeze-drying, for products with and without lactose hydrolysis.

Keywords: Crystallization; lactose; powdered milk; lyophilization; Raman; spray dryer

1. Introduction

The development of dairy products with lactose hydrolysis has gained prominence in recent years since a considerable portion of the Brazilian and world population has some degree of intolerance (partial or total inability to digest lactose due to the lack of the enzyme lactase in the digestive system) to this carbohydrate .1-6 Dehydrated dairy products are also included within these lactose-free products, but there is a great discussion about the best way of production, aiming at better performance in the industrial process and stability of the product during storage.[1-6]

According to Zhu et al.,[7] hydrolyzed milk presents a large number of molecules (glucose and galactose) in amorphous state during the drying process; therefore, this product gets hygroscopic due to decrease in glass transition temperature, and it makes the production process challenging to this industry in terms of productivity, chambers' clogging and powder conservation. Glassy state maintenance during powdered milk production and storage stages is directly linked to its composition. Failure to maintain product's amorphous state can lead to changes, such as clusters, impaired rehydration, increased product color and changes in viscosity.[8,9,10]

The increase in the air temperature entering the drying chamber above the TTg of the milk causes this milk to change from a glassy state to a gummy one. Since milk with hydrolyzed lactose has a lower TTg compared to traditional milk, the drying parameters must be different from traditional milk in order to avoid agglomeration, adherence to the chamber, caking, darker coloration and increased hygroscopicity that can lead to occurrence of adhesion problems to the equipment, caking, darkening of the powder, and low industrial performance. [9,10]

Maillard reaction is the term used for a group of chemical reactions, initiated by a condensation of an amino group with reducing sugar and then followed by a cascade of reactions, leading to the formation of different intermediates, including aromatic components

and polymers of brown coloration and high molecular weight that leads to a darkening of the product. [10,11] Lactose hydrolysis accelerates Maillard reaction, which, in its turn, promotes casein cross-linking.[11] Products undergoing lactose hydrolysis have greater potential to present Maillard reaction, due to higher concentrations of reducing sugars in them.[12] The magnitude of Maillard reaction development affects lactose-free powdered milk stability and shelf-life.

Therefore, the aim of the current study was to produce, and to determine the features of, whole powdered milk types with low lactose content in order to assess their stability during storage, based on changes in their physicochemical and microstructural properties. Powders were produced via spray-dryer and products via freeze-dryer for different levels of lactose hydrolysis, aiming to understand how the production method of these powders could modify their physical-chemical and morphological characteristics. In addition, the variation in the percentage of lactose hydrolysis was also carried out in order to understand how this hydrolysis could result in some properties of the powders that were subjected to different storage conditions.

2. Experimental

2.1. Producing the powdered milk

Concentrated whole milk resulting from the reconstitution of control powdered milk in water added with approximately 40% of total solids was used to produce the investigated powdered milk (the whole milk powder used was purchased from provided companies). A portion of this milk was extensively hydrolyzed based on the addition of 0.2 % ($v \cdot v^{-1}$) of Maxilact enzyme (DSM®, São Paulo, Brazil), at mean temperature of 34 ± 1 °C. The extensively hydrolyzed milk (T100) was added to traditional milk at the following rates: 5%, 10%, 20% and 50 % ($v \cdot v^{-1}$); and it corresponded to treatments T5, T10, T20 and T50, respectively. All products (control, T5, T10, T20, T50 and T100) were dried in spray dryer (LM MSDi 1.0 model - LabMaq do Brazil, Ribeirão Preto, Brazil), based on the following mean drying parameters: drying air temperature at 160 °C, outlet air temperature at 86 °C and product flow rate of 1.16 $L \cdot h^{-1}$; as well as in LABCONCO Freezone 2.5 Plus freeze dryer at temperature of approximately -76 °C. Spray drying was carried out at the Federal University of Viçosa, while freeze-drying was carried out at the Federal University of Juiz de Fora. The analyzes were performed in triplicate.

2.2. Scanning Electron Microscopy

The herein investigated powdered milks were morphologically featured based on Scanning Electron Microscopy (Hitachi TM 3000, Hitachi Ltd., Tokyo, Japan) at different magnifications.

2.3. Physicochemical analyses and free HMF determination process

The water activity of milk powder was recorded for different storage conditions in Aqualab device (Decagon 3TE, Decagon Devices Inc., USA), whereas powdered milk moisture was determined in infrared thermogravimetric scale (Sartorius MA150).[10] The analyzes were performed in triplicate.

The samples were initially reconstituted in a 12% solids solution, then 10 mL of this sample solution was added with 5 mL of 0.3 mol. L^{-1} oxalic acid and 5 mL of 40% trichloroacetic acid ($m.v^{-1}$). The resulting solution was homogenized and then filtered. After complete filtration, a 4 mL aliquot of filtrate was removed and 1 mL of 0.05 mol. L^{-1} thiobarbituric acid was added. The sample was heated in a water bath at 40 °C for 30 minutes. Readings were performed on an Ocean Optics USB 200+XR1-ES spectrophotometer (brand: Ocean Insight). The absorbance value obtained at a wavelength of 433 nm was used in the equation of the straight line obtained by the analytical curve performed during the analysis process, thus obtaining free HMF values for each sample, according to Keeney & Bassette (1959).[13] The analyzes were performed in triplicate.

2.4. Sorption isotherms

Powdered milk samples were stored at five different relative humidity levels (11.1%, 33.1%, 43.2%, 54.4% and 75.5%) for 21 days, based on using saturated LiCl, $MgCl_2$, K_2CO_3, $Mg(NO_3)_2$ and NaCl solutions, respectively. Subsequently, sorption isotherms were determined for all products, by weighing the powders, before and after the aforementioned 21 days, in order to find variations in water content throughout storage time.[6] The analyzes were performed in duplicate.

2.5. Laser diffraction-based particle size analysis

Particle size distribution of the herein analyzed milk powders during the rehydration process was determined based on using the Beckman Coulter LS 13 320 laser diffraction analyzer (Beckman Coulter, Miami, FL, USA) coupled to liquid analysis module (Aqueous liquid module, Beckman Coulter, Miami, FL, USA). The number of samples necessary to generate the turbidity demanded for the readings was added to the reservoir of the liquid analysis module, which was filled with water, at room temperature. Samples were slowly added to it in order to avoid clusters' formation. The refractive index of 1.332 was used for the dispersing medium (water); 1.47, for fat globules; and 1.57, for casein micelles.[14] The analyzes were performed in duplicate.

2.6. FT-Raman spectroscopy

Raman spectra were recorded for powder samples,

under all storage conditions. It was done by using RFS 100 FT-Raman Bruker spectrometer equipped with Ge detector, and excitation line at 1,064 nm deriving from a solid state Nd:YAG laser. Samples were placed in aluminum capsules. The following parameters were used for data collection purposes: 125 mW of power, 512 scans and spectral resolution 4 cm^{-1} in the spectral region between 3,500 cm^{-1} and 50 cm^{-1}. OPUS 6.0 software (Bruker Optik, Ettlingen, Germany) was used to collect analytical data.

2.7. Chemometric analysis

Matlab software version 7.10.0 (R2010a) was used to assess Raman spectra for exploratory analysis purposes. Collected data were pre-processed based on using baseline correction to help minimizing and normalizing variations in the baseline. Second derivative based on Savitzky-Golay algorithm, with second-order polynomial and 15-point window, was applied to correct the baseline. Mean-centering pre-processing and principal component analysis (PCA) were used to centralize the mean. The number of principal components was determined based on using the eigenvalue graph, which enabled assessing the role played by Raman spectra in samples' distribution in the score chart. The spectral region from 2800 to 3100 cm^{-1} was used to separate the samples in chemometrics, according to studies already reported in the literature.[15,16]

3. Results and Discussion

3.1. Morphologically featuring milk powder based on Scanning Electron Microscopy

The Scanning Electron Microscopy (SEM) applied to powdered milk types produced through spray drying has mostly shown smooth-surface round-shaped granules. On the other hand, powdered milk types produced through lyophilization have shown particles with asymmetric flake shape. These differences observed in the morphology of the analyzed powders have already been reported in the literature, in a study conducted with dry camel powdered milk produced through spray drying and lyophilization processes.[17]

The comparison between control (A1) and T100 (A2) spray-drying treatments has evidenced that the non-hydrolyzed product presented smaller number of clusters than the one recorded for the extensively hydrolyzed treatment, which presented larger number of aggregates.[6] On the other hand, the morphology of both products dried by lyophilization (B1 and B2) did not show any changes.

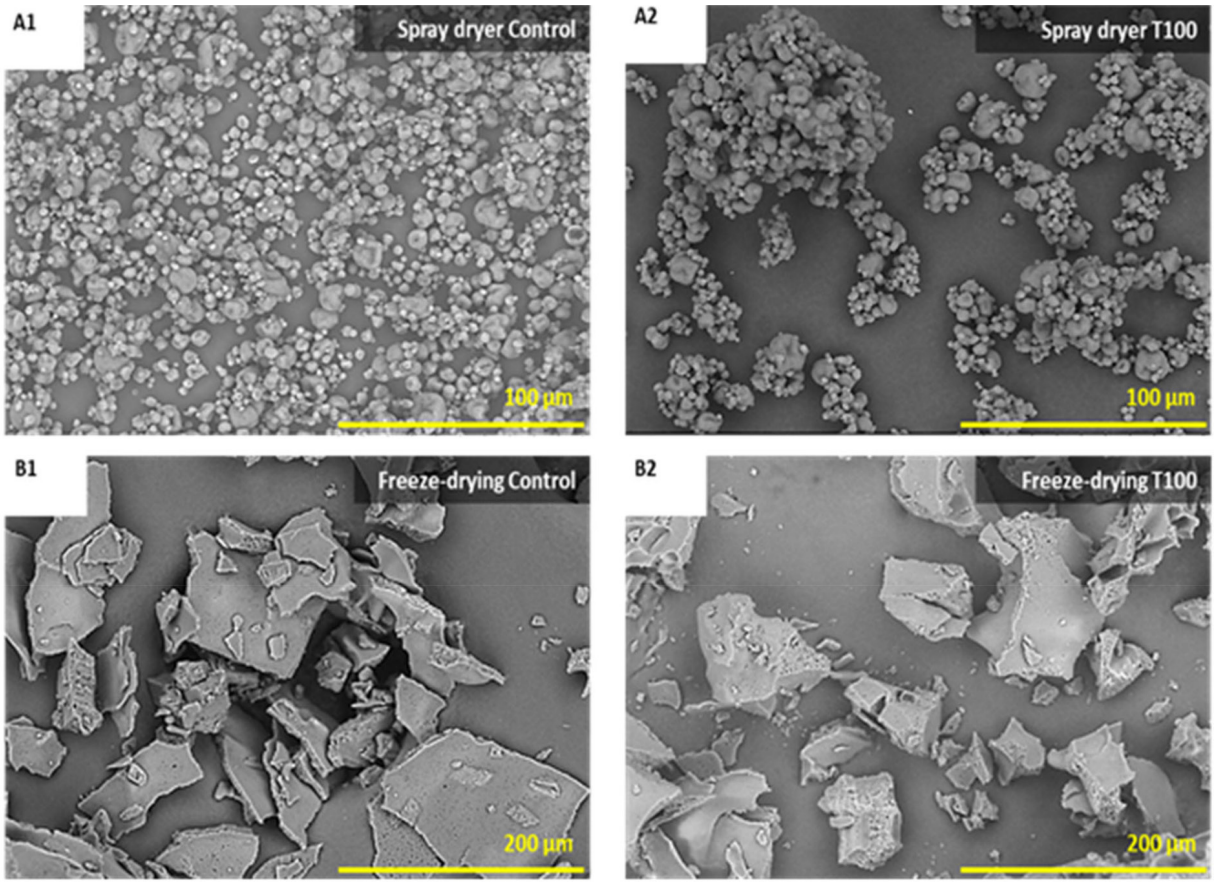

Figure 1. Scanning electron microscopy images of powdered milk types: (A1) control powder milk produced through spray drying; (A2) powdered milk produced through spray drying; (B1) control powdered milk produced through lyophilization; (B2) extensively hydrolyzed milk powder produced through lyophilization

3.2. Moisture and water activity (aw) analysis and free HMF determination

Physical-chemical data about water activity (aw), moisture, and free 5-hydroxymethylfurfural (HMF), after storage at 50 °C and relative humidity <10% for 21 days, are shown in Table 1.

Water activity values recorded for products dried based on the two aforementioned techniques were close to the expected value of 0.2; spray-dried powders recorded aw slightly higher than that observed for freeze-dried products. This value (0.2) is the one recommended for powdered milk, since this water activity presents the lowest rate of reactions capable of degrading the product, such as oxidation reactions, non-enzymatic hydrolysis and increased likelihood of microorganisms' development due to external contamination.[10] Two studies conducted with skimmed and whole spray-dried bovine powdered milk recorded mean water activity of 0.252 and 0.258, respectively.[18,19] On the other hand, one study recorded mean water activity of 0.155 for lyophilized milk.[20]

Given the difficulty in determining the moisture content of milk powder hydrolyzed through the conventional method, a graph was herein plotted to depict sample mass loss observed in analysis based on time and conducted with thermogravimetric scale, as shown in Figure 2. Curves in the aforementioned graph were subjected to derivation and the relative humidity of each powdered milk sample was found based on the value recorded for the inflection point of each curve.

Spray-dried products recorded moisture content ranging from 4.17 to 5.94 ($g.100g^{-1}$) in the control, T5, T10, T20 and T50 products, although they did not statistically differ from each other by Tukey's test ($p > 0.05$). On the other hand, the T100 product recorded moisture content of 10.18 ($g.100g^{-1}$), which was statistically different from contents recorded for the other products. The same correlation could be observed for freeze-dried products, since the highest moisture content was also recorded for T100. A study has shown that freeze-dried hydrolyzed milk presented moisture content of 3.96, whereas non-hydrolyzed milk presented moisture content of 2.63; this outcome corroborated data found in the current study.[21]

Comparison between dry methods enabled seeing that spray drying produced milk powders with lower moisture contents in all treatments, at the same extensively hydrolyzed milk addition level, than the lyophilization method. These results are consistent with the literature,

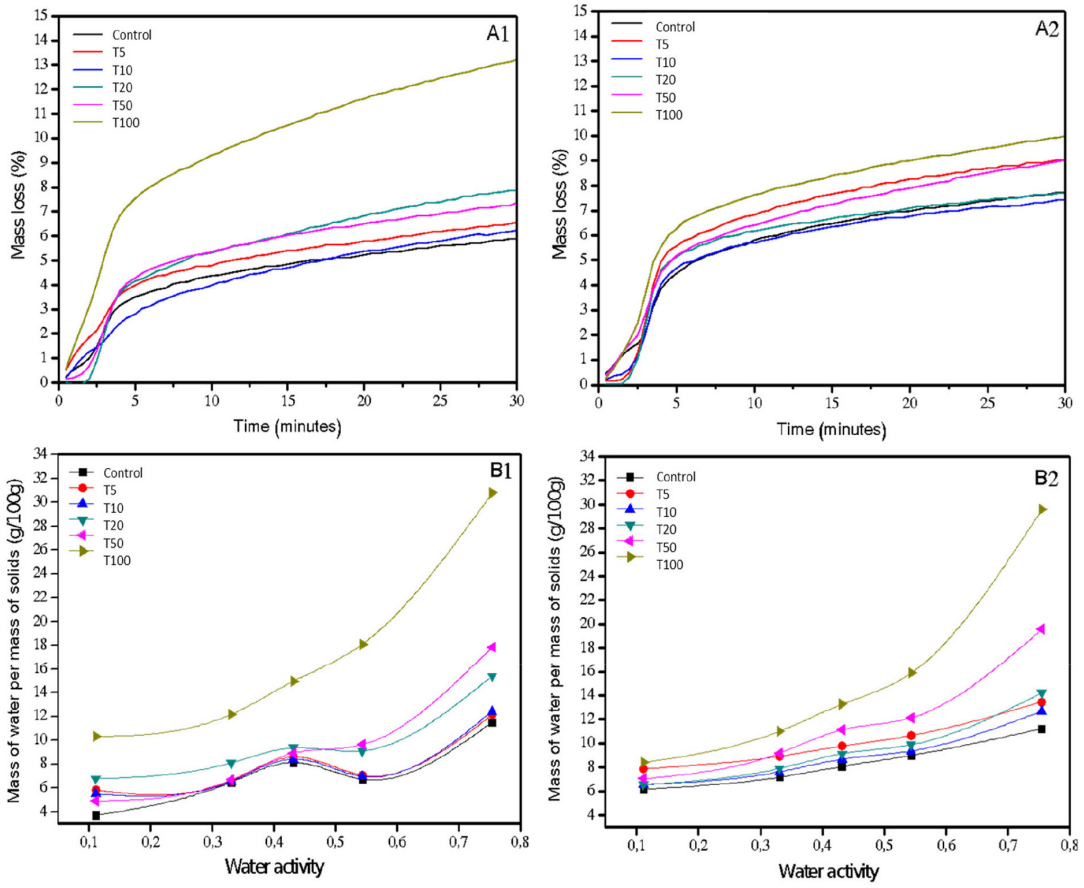

Figure 2. (A) Mass loss of powdered milk types subjected to 145°C, based on time: (A1) powdered milk types produced through spray drying; (A2) powdered milk types produced through lyophilization. (B) Sorption isotherms at 5 different relative humidity levels (11.1%, 34.4%, 45.3%, 54.2% and 75.5%); (B1) powdered milk types produced through spray drying; (B2) powdered milk types produced through lyophilization

Table 1. Physicochemical data about whole powdered milk types and free HMF determined in powdered milk types after 21-day storage at 50 °C. (n=3)

Treatment	Spray drying			Lyophilization		
	Moisture (g 100g^{-1})	Water activity	Free HMF concentration (µmol L^{-1})	Moisture (g 100g^{-1})	Water activity	Free HMF concentration (µmol L^{-1})
Control	4.74 ± 1.21^{a}	0.260 ± 0.021^{ab}	90.28 ± 26.37^{a}	5.52 ± 0.20^{a}	0.238 ± 0.002^{a}	59.79 ± 11.03^{a}
T5	4.33 ± 0.13^{a}	0.241 ± 0.044^{ab}	93.89 ± 39.73^{a}	6.14 ± 0.98^{a}	0.224 ± 0.013^{a}	86.97 ± 14.08^{a}
T10	4.17 ± 0.50^{a}	0.234 ± 0.015^{ab}	95.09 ± 31.54^{a}	5.48 ± 0.16^{a}	0.207 ± 0.020^{a}	113.73 ± 17.94^{a}
T20	5.02 ± 0.36^{a}	0.223 ± 0.019^{a}	96.74 ± 34.20^{a}	6.12 ± 0.64^{a}	0.233 ± 0.027^{a}	135.75 ± 14.45^{a}
T50	5.94 ± 0.98^{a}	0.289 ± 0.008^{b}	163.78 ± 33.64^{a}	8.88 ± 3.48^{a}	0.248 ± 0.047^{a}	249.39 ± 77.03^{b}
T100	10.18 ± 1.20^{b}	0.276 ± 0.027^{ab}	287.64 ± 73.62^{b}	10.52 ± 3.99^{a}	0.264 ± 0.072^{a}	369.34 ± 19.02^{c}

Control without the addition of extensively hydrolyzed milk, T5, T10, T20, T50 and T100; addition of 5%, 10%, 20%, 50% and 100% extensively hydrolyzed milk to the control. *Means followed by the same letter in the same column did not significantly differ from each other by Tukey's test (p >0.05)

according to which, camel milk subjected to the freeze-drying and spray-drying methods recorded moisture content of 2.81 and 2.43, respectively, on average.[17]

Based on the analysis of free HMF results (Table 1), powdered milk types subjected to the herein described storage condition recorded higher free 5-hydroxymethylfurfural concentration (one of Maillard reaction indicators) in powdered milks subjected to higher extensively hydrolyzed milk addition. Maillard reaction takes place in the presence of one reducing sugar and one amino group (amino acids, peptides and/or proteins); thus, since lactose hydrolysis releases glucose and galactose, the concentration of reducing sugars increases in products subjected to higher hydrolyzed milk addition.[12,22,23] Another factor capable of explaining high free HMF values lies on the fact that the Maillard Reaction development process is optimized when dairy products are subjected to heat treatments and to high storage temperature conditions. This non-enzymatic browning reaction triggers a cross-linking process among caseins that may be correlated to milk powder's decreased rehydration capacity.[24,25,26]

The free HMF concentration in products subjected to dry-spraying has increased from 90.28 µmol·L^{-1} to 287.64 µmol·L^{-1} in the control product up to T100, whereas freeze-dried products recorded free HMF concentration increase from 59.79 µmol·L^{-1} to 369.34 µmol·L^{-1} in the control product up to T100. Since the Maillard reaction can change products' color, it is possible drawing a parallel between increased free HMF concentration (one of its indicators) and products' darkening process. A study available in the literature has shown that freeze-dried products were darker than the spray-dried ones. This outcome corroborated data observed for T10, T20, T50 and T100; however, reverse data were recorded for both the control and T5.[17]

3.3. Sorption isotherms

After the centesimal composition and water activity of powdered milks were determined, sorption isotherms were set at 25 °C, for each powdered milk (Figure 2). Water activity values ranging from 0.35 to 0.50 are critical due to lactose transition from amorphous to crystalline state, since lactose crystallization within this range can boost deteriorating changes in the product.[27] Based on Figure 2B1, which refers to powdered milk produced through spray drying, all powdered milk samples have shown sigmoid curve depression within the aforementioned critical range, except for the T100 treatment - this depression indicates lactose crystallization. Crystallization was not observed in the extensively hydrolyzed powdered milk, since no depression was attributed to the curve generated for this product.[25] On the other hand, Figure 2B2 does not show any depression in isotherms' curves generated for powdered milk produced through lyophilization - this sorption isotherm curve profile was also reported in a study conducted with camel powdered milk.[17] Another study recorded similar curves for passion fruit pulp dried with maltodextrin or gum arabic and skim milk.[28]

3.4. Particle size analysis based on laser diffraction

Table 2 presents the size distribution of particles smaller than 1 µm (expressed in percentage) recorded for each sample. The distribution of raw milk particles shows two different populations: one refers to casein micelles showing size of approximately 150-200 nm and higher solubility in water, whereas the other one corresponds to fat globules showing size of approximately 5 µm and lower solubility in water.[29,30,31] According to Table 2, submicro-particles' volume (%) has decreased as hydrolysis level increased, both for powdered milks produced through spray drying and for those produced through lyophilization. The submicro-particles' volume (%) of samples stored at 50 °C got even smaller; T100 products reached submicro particles' volume of 0 %. Higher lactose hydrolysis levels enable glycosidic interactions between particles of reduced-fat and low-lactose powdered milks, and it decreases their rehydration capacity.[25]

Another interesting result of particle size analysis lies on the difference observed for rehydration capacity between products subjected to the two drying techniques (Table 2). Almost all products subjected to the freeze-drying technique have shown lower rehydration capacity than that observed for products subjected to the spray dryer technique, under both storage conditions. Similar results were reported in the literature: a study has shown that bovine milk samples subjected to spray-drying presented smaller particle sizes than samples subjected to lyophilization, based on parameters $d_{3,2}$ and $d_{4,3}$, which measure particles' mean surface area size and mean volume size, respectively.[32] Another study with similar results has shown that freeze-drying also led to particle sizes larger than those of products subjected to spray-drying, based on parameters such as d_{10}, d_{50}, d_{90}, $d_{4,3}$ and $d_{5,3}$.[17]

3.5. Raman spectroscopy and chemometric analysis

Figure 3 shows Raman spectra of powdered milk presenting different lactose conformations. Samples were subjected to five storage conditions, at relative humidity of 11.1%, 34.4%, 45.3%, 54.2% and 75.5 %. It was possible seeing that powders' crystallization degree has increased as relative humidity also increased; they changed from amorphous (Figura 3A) to glass transition profile (Figura 3B) and, finally, to crystalline profile (Figura 3C). However, this behavior was not observed for the T100 powdered milk. Although this sample was subjected to storage condition at high relative humidity, it presented spectrum profile similar to that of Figura 3A, i.e., it remained in its amorphous state.

Based on the FT-Raman analysis, powdered milk types produced through lyophilization have shown crystalline profile, except for the T50 and T100 products. This finding explains the fact that sorption isotherms of powdered milk types produced through lyophilization did not show depressions in the curves at the critical glass transition point, since they likely got crystallized during samples' freezing and/or lyophilization process. Consequently, they did not go through glass transition during the storage process.

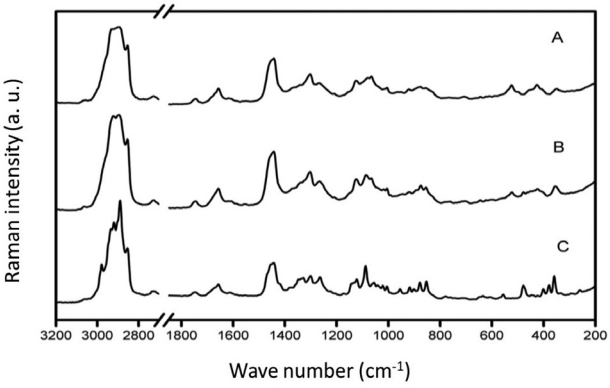

Figure 3. Raman spectra: spectrum typical of powdered milk at amorphous (A), glass transition (B) and crystallized (C) state

Principal component analysis was carried out to check cluster formations between powdered milk samples produced through spray-drying and lyophilization. Figure 4A presents the score chart referring to exploratory analysis based on PCA conducted with Raman spectroscopy data recorded for powdered milk produced through spray-drying. It is possible seeing samples' separation based on their crystallization degree: one cluster refers to powdered milks that got crystallized at 75.5% relative humidity in the control and T20 samples, the other cluster refers to glass transition in T50 powdered milk types stored at 54.4% and 75.5% relative humidity and, finally, another cluster refers to powdered milk types that remained in amorphous state after they were subjected to different relative air humidity conditions. It is worth emphasizing that extensively hydrolyzed powdered milks produced through spray-drying

Table 2. Particle size distribution analysis applied to powdered milk rehydrated in water.

	Treatment	Before storage at 50°C < 1,0 µm (%)	After storage at 50°C < 1,0 µm (%)
Spray drying	Control	45.8	14.8
	T5	41.0	5.5
	T10	42.6	4.5
	T20	32.5	3.8
	T50	11.2	1.2
	T100	0	0
Freeze-drying	Control	18.9	0
	T5	16.9	0
	T10	21.9	0
	T20	25.7	0
	T50	19.9	0
	T100	27.9	0

Control without the addition of extensively hydrolyzed milk, T5, T10, T20, T50 and T100; addition of 5%, 10%, 20%, 50% and 100% extensively hydrolyzed milk to the control

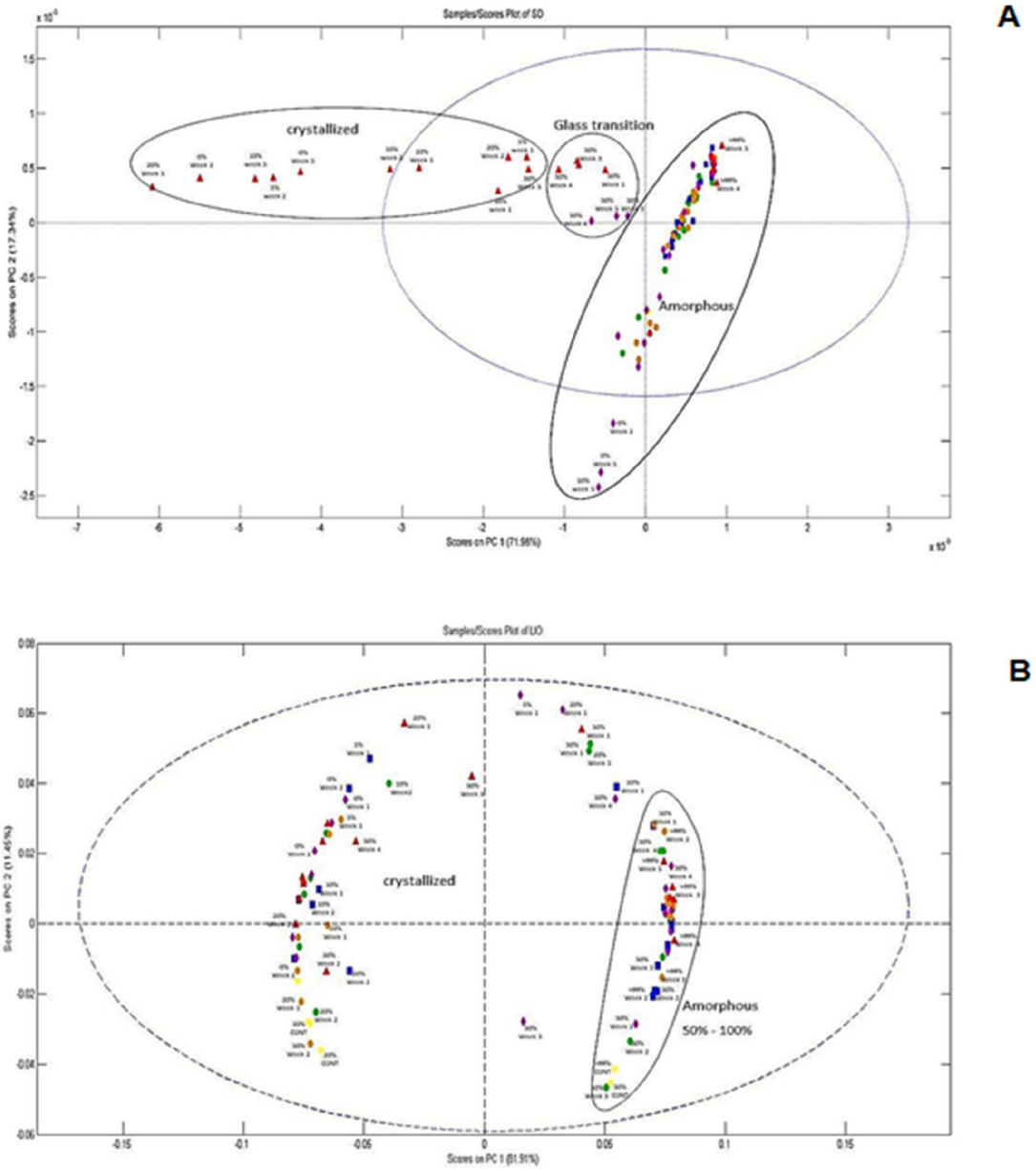

Figure 4. PC1 versus PC2 score plots of the 3,200-200 cm^{-1} spectral region: (A) Powdered milk samples produced through spray drying and stored under different relative humidity conditions for 40 days; (B) Powdered milk samples produced through lyophilization and stored under different relative humidity conditions for 40 days

remained in the amorphous state, even after 40-day storage at 75.5% relative humidity.

On the other hand, the score chart plotted for powdered milk types produced through lyophilization (Figure 4B) presents the formation of a cluster referring to treatments T50 and T100 - all samples remained in amorphous state after 40-day storage at 75.5% relative humidity.

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