STICKINESS AND THERMAL PROPERTIES OF SKIM MILK SOLIDS

Nattiga Silalai,[1,*] Yrjö H. Roos[2]
[1]Department of Food Technology, Siam University, Bangkok, Thailand
[2]School of Food and Nutritional Sciences, University College Cork, Cork, Ireland
*e-mail: nattiga.silalai@gmail.com

Abstract: Dielectric and mechanical properties of skim milk powders were determined by dielectric (DEA) and dynamic-mechanical (DMA) analysis, respectively. DEA and DMA were used to observe relaxations around the glass transition of skim milk solids. The α-relaxation temperature (T_α) was determined from dielectric (ε') and mechanical (*E'*) properties. The Guggenheim-Anderson-de Boer (GAB) model was used to model water sorption. T_α shifted to higher temperatures with increasing frequencies but decreased steeply with increasing water content. The sticky-point temperatures as determined by a viscometer technique were close to the T_α measured by DEA (0.5 kHz) but were slightly higher than the T_α value measured by DMA (0.5 Hz). The critical water activity and water content at 24°C for stickiness was 0.35 and 6.4 g/100 g dry solids, respectively. Changes in skim milk powder such as stickiness and crystallization were influenced by water plasticization and glass transition. The results suggested that DEA and DMA can be used to observe parameters to set the guidelines for temperature and water content to reduce and control stickiness of skim milk powders during process and storage.

Introduction: Stickiness is a surface phenomenon caused by plasticization of particle surfaces which allows a sufficient decrease in surface viscosity for adhesion of powders[1]. Dairy powders containing hydrolyzed lactose were more susceptible to stickiness and caking since lactose components are galactose and glucose which were hygroscopic and act as plasticizers causing a decrease in glass transition temperature.[1] DSC is technique can observe a heat capacity change over glass transition (second-order transition).[2] Correlation of glass transition and stickiness was studied by several researchers.[3,4,5] Sticky points were found around 10-20°C above T_g.[6,7,8] In addition to DSC, changes in mechanical and dielectric properties associated with glass transition which can be followed by using dynamic-mechanical (DMA) and dielectric (DEA) analysis.[6] However, no information of correlation between changes in relaxation behavior and stickiness of dairy powders has been reported. Therefore, the objective of the present study was to observe dielectric and mechanical properties of skim milk solids around glass transition and to establish relationships of glass transition, α-relaxation and stickiness of skim milk solids.

Methodology:

1. Milk Powder Preparation

In this study, spray-dried skim milk was produced by a Niro tall form drier with pressure nozzle atomisation at Moorepark Technology Ltd, Fermoy, Co. Cork. Skim milk powder (SMP) was evaporated to ca. 45% solids and underwent low heat treatment (72°C for 14 seconds) prior to spray drying. The powders were dried using inlet and outlet temperatures of ca. 185°C and 85°C, respectively, and were spray dried in agglomerated form only. Spray-dried skim milk were kept immediately in plastic bag and then hermetically sealed at room temperature. The powders further were dried in a vacuum oven at 50°C for 24 h prior to analysis.

2. Water Sorption Behavior

Powder samples dried were equilibrated in evacuated desiccators over saturated salt solutions of LiCl, CH_3COOK, $MgCl_2$, and K_2CO_3 at corresponding relative humidities (RH) of 11.4%, 23.1%, 33.2%, and 44.1%, respectively at room temperature (23-24°C). Water

activity (a_w) values were 0.01 x RH at equilibrium.[9] Water content at each a_w was determined from the mean weight of triplicate samples. The Guggenheim-Anderson-de Boer (GAB) model was used to model water sorption according to Haque and Roos [10]. The relative percentage Root Mean Square (RMS value) was used as an indication of the fit of the GAB models. Triplicate sample of skim milk powder was analyzed.

3. Dynamic-Mechanical Analysis (DMA)

A Triton dynamic mechanical analyser (Tritec 2000 DMA version 1.43.00 software, Triton Technology Ltd, Loughborough, UK) was used to determine mechanical relaxations of amorphous components of the powders by observing the storage modulus (*E'*), loss modulus (*E″*) and tan δ (ratio of loss and storage modulus; *E″/E'*) as a function of temperature. In this study, a temperature location of drop in storage modulus (*E'*) was taken as the onset temperature of α-relaxation (T_α). The samples were humidified in vacuum desiccators over a range of relative humidities (0 to 44.1%) before measuring. Approximately 50 mg of humidified powders were loaded into a metal pocket fabricated from a sheet of stainless steel (Triton Technology Ltd, Loughborough, UK). The powder pocket was formed by folding the sheet along a pre-scored line and then was crimped closed to form a thin sandwich. The closed pocket was clamped directly into the DMA instrument. The pocket was subjected to a bending oscillatory motion in and out of the plane, forcing horizontal shearing of the powders between the two plates of the pocket as reported by Royall *et al.*[11] The humidified samples were scanned first 40°C above the α-relaxation temperature region at 3°C/min, then cooled at 5°C/min to 40°C below the α-relaxation, and the second heating scan at 3°C/min was run to well above the α-relaxation at which DMA data was recorded. Frequencies used were 0.5, 1.0, 5.0, 10.0, and 20.0 Hz. Triplicate sample of skim milk powder was analyzed.

4. Dielectric Analysis (DEA)

A dielectric thermal analyser (Triton DS6000 DETA, Triton Technology Ltd, Loughborough, UK) was used with the LCR meter. Dielectric properties of dairy powders can be derived from dielectric constant or permittivity (ε'), dielectric loss (ε''), and tan δ (ε''/ε'). DEA α-relaxation temperature (T_α) was taken from the onset temperature of molecular motions. The samples were humidified in vacuum desiccators over a range of relative humidities (0 to 44.1%) before measuring. Approximately 50 mg of humidified powders was placed between parallel plate capacitors with a diameter of 33 mm. The humidified samples were scanned first 40°C above the α-relaxation temperature region at 3°C/min, then cooled at 5°C/min to 40°C below the α-relaxation, and the second heating scan at 3°C/min was run to well above the α-relaxation at the DEA data were recorded. Frequencies used were 0.5, 1.0, 5.0, 10.0, and 20.0 kHz. The thickness of samples in the plate electrodes should less than 2 mm**.** Triplicate sample of skim milk powder was analyzed.

5. Stickiness Measurement

A rotational viscometer (Brookfield viscometer model R/S Rheometer, Harlow Essex CM195TJ, England) was used to determine the sticky-point temperatures of the dairy powders according to method of Özkan *et al.*[8] Powder samples were kept in desiccators over saturated solutions[10] so that powders were humidified and obtained water content as required. Temperature was of water jacket was set to a constant temperature of approximately 0, 10, 20, and 30°C above T_g. The humidified 50 g powder sample was transferred to a cylinder cup connected to water jacket. Then, these powders were left in the water jacket for 20-30 min until the powders achieved the set temperature investigated by a thermocouple. Then, the stirrer was inserted into these powders and torque values as a function of time were recorded by a rheometer programme (Brookfield RHEO 2000 Version 2.7). The torque values were recorded at 0.3 rpm for 40 seconds (one data point was recorded at every second). The average torque values were calculated using the last 20 data points (20-40 second). A new

sample was used for each torque measurement. Triplicate sample of skim milk powder was analyzed.

Results and Discussion:

1. Water Sorption Isotherm of Skim Milk Solids

Water sorption is a property that can be used to determine changes in physical properties and stability of dairy powders. The release of water sorbed by dairy powders resulted in dairy particle surfaces which were plasticized by water due to the formation of liquid bridges between particles causing stickiness and crystallization. [12] The water sorbed by amorphous lactose was released as a result of crystallization and it occurred more rapidly in lactose than in skim milk powders as shown in Figure 1. The present study indicated that water sorption by milk proteins delayed the release of water sorbed by amorphous lactose in skim milk powders. This was consistent with the findings of several studies.[1,12]

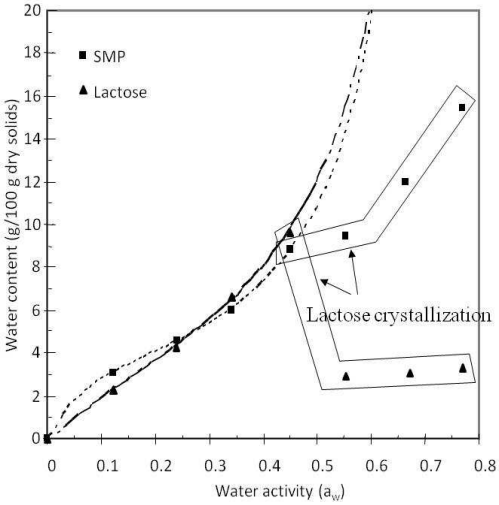

Figure 1: Water sorption isotherms for spray-dried skim milk solids and lactose

2. Mechanical Properties

Generally, the α-relaxation can be observed from change in *E'*, *E''* and tan δ associated with glass transition. In this study, a dramatic change in mechanical properties occurred at temperature above glass transition (Figure 2; left). Above the glass transition, a material becomes softened as a result of thermal plasticization resulting in high molecular mobility.[13] Therefore, storage modulus of SMP decreased dramatically with increasing temperature as shown in Figure 2 (left). Above the glass transition, the storage modulus of skim milk solids decreased considerably in relation to a decrease in T_α with increasing water content. This was due to an increase in molecular mobility by water plasticization.[13,14] Kouassi and Roos[15] indicated that the broadness of the transition was related to the composition of the systems and water content at various water activities. The effect of water on mechanical properties was discussed by several studies.[13,14,16]

3. Dielectric Properties

Glass transition is often considered as an α transition and the onset temperature of long-range motions in amorphous materials. Polar groups in the sample respond to the alternating electrical field and an absorption maximum is obtained at the frequency that equals the molecular motion. Detection of α-relaxation temperature from DEA spectra used locating the onset temperature of α-relaxation (ε') which appears when molecules are rotating in phase with the applied frequencies.[17] A significant change in dielectric properties occurred at temperature above glass transition temperature similarly to a change in mechanical properties (Figure 2; right). Increasing molecular mobility above T_g affects dielectric

properties.[16] Over the glass transition, the magnitudes of changes in dielectric properties (ε') of skim milk solids increased with increasing water content as well as decreasing T_α. This could be explained by water plasticization effect[4] and increasing dipoles.[18,19] Ryynänen[18] indicated that water is a dipolar compound that couples electromagnetic energy in electric fields more efficiently than most other food components; therefore, increasing water content increased the dielectric constant in accordance with the findings of Shinyashiki *et al*.[19]

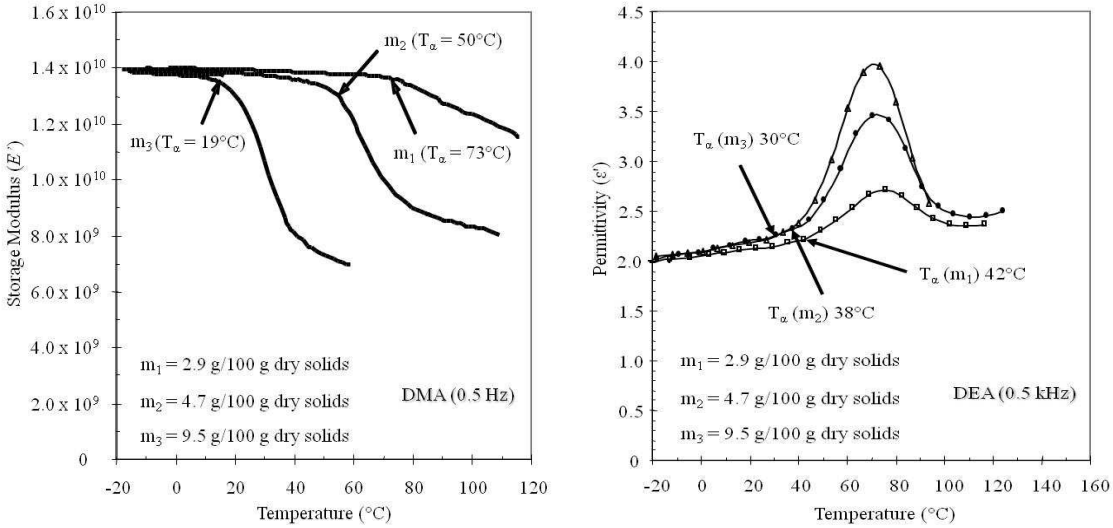

Figure 2: Mechanical (Left) and dielectric (Right) properties for spray-dried milk solids as measured by DMA at frequency of 0.5 Hz and DEA at frequency of 0.5 kHz, respectively.

4. Stickiness Measurement

The torque measurements using a viscometer allow a quantitative description for the stickiness behavior of the milk powders as shown in Figure 3. The basic principal of this technique is that when viscosity of food materials is depressed, contact time of particle surfaces decreases as well as liquid bridges are formed between particles in a shorter time[20] causing high torque forces for rotating spindle.

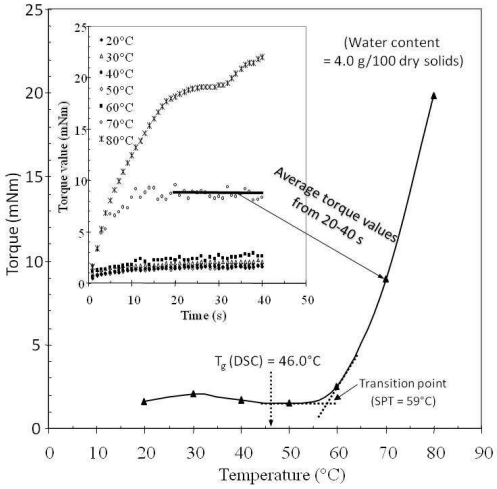

Figure 3: Stickiness of skim milk powder as determined by torque measurement at different temperatures.

Therefore, this technique was useful for direct determination of the stickiness in dairy powders. In this study, the torque values of SMP were higher with increasing temperatures because when temperature of the powders increased to above the T_g, the viscosity decreased

to below a critical level of 10^7 Pa s, which may occur at temperatures 10-20°C above glass transition.[21] As a result of glass transition, the amorphous lactose was transformed to the rubbery state which exhibits sufficient mobility of lactose molecules for contributing to the formation of liquid bridges between the powder particles.[22,23]

5. Storage Stability

The glass transition, α-relaxation and sticky-point temperatures decreased with increasing water content due to water plasticization. Plasticization behavior can be observed from detection of changes in mechanical and dielectric properties occurring over glass transition.[17] As studied previously, stickiness was related to glass transition which was associated with changes in mechanical and dielectric relaxations;[16,17,21] thus, changes in relaxation behavior in relation to stickiness of SMP was investigated in the present study.

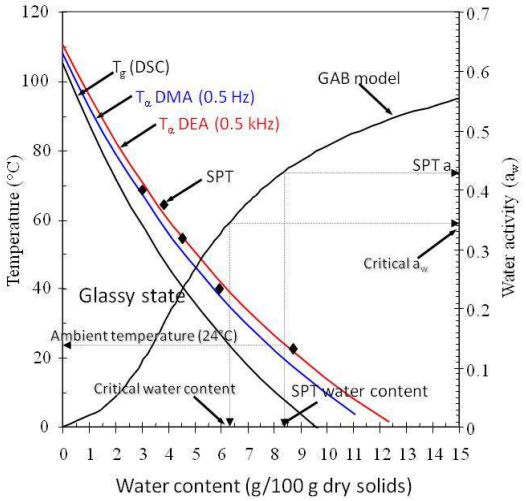

Figure 4: State diagram showing a critical water activity and water content of milk powder stored at ambient temperature (24°C).

The effect of water on α-relaxations and sticky points was studied by establishing the stability diagram to show critical values for water content and water activity resulting in stickiness of dairy powders at ambient temperature. Sticky-point temperatures were found to be close to DMA T_α curve, but they were on the DEA T_α curve as shown in Figure 4. Therefore, DEA T_α curve was assumed to be a sticky line to determine the critical water activity and water content for the occurrence of stickiness of dairy powders at ambient temperature. The critical water activity and water content for the occurrence of stickiness of skim milk powders at 24°C were found to be 0.43 and 8.4 g/100 g dry solids, respectively. This indicated that the occurrence of stickiness was influenced by plasticization by water and temperature, and change in mechanical and dielectric properties was also related to stickiness behavior.

Conclusion:

In the present study, the rates of changes in dairy powders such stickiness, collapse and crystallization were influenced by water sorption and glass transition associated with relaxation behavior. Dynamic-mechanical analysis (DMA) and Dielectric analysis (DEA) can be used to observe relaxations around the glass transition. At above T_g, significant changes in mechanical and dielectric properties of powders were found. The T_α shifted to a higher temperature with increasing frequency, whereas T_α decreased steeply with increasing water content as a result of plasticization. The sticky points were found to be nearly to DMA T_α curve but they were on the DEA T_α curve. The critical water activity and water content at 24°C for the occurrence of stickiness was 0.43 and 8.5 g/100 g dry solids, respectively. This

indicated that changes in dairy powders such as stickiness, collapse and crystallization were influenced by water sorption and glass transition associated with relaxation behavior. Therefore, DMA and DEA are complementary techniques that can be used to determine changes in mechanical and dielectric properties related to glass transition and stickiness.

References:

1. Thomas M.E.C., Scher J., Desobry-Banon S., Desobry S., Crit Rev Food Sci and Nutri, 2004, 44, 297-322.
2. Roos Y.H., Karel M., Biotechnology Progress, 1990, 6, 159-163.
3. Downton G.E., Flores-Luna J.L., King C.J., Ind Eng Chem Fund, 1982, 21, 447-451.
4. Roos Y.H., Karel M., J Food Sci, 1991, 56(1), 38-43.
5. Chuy L.E., Labuza T.P., J Food Sci, 1994, 59, 43-46.
6. Roos Y.H., Phase Transitions in Foods, San Diego, Academic Press, 1995.
7. Ozmen L., Langrish T.A.G., Drying Tech, 2002, 20(6), 117-1192.
8. Özkan N., Walisinghe N., Chen X.D., J Food Eng, 2002, 55, 293-303.
9. Jouppila K., Roos Y.H., J Dairy Sci, 1994, 77, 1797-1808.
10. Haque M.K., Roos Y.H., J Food Sci, 2004, 69(8), 384-391.
11. Royall P.G., Huang C., Tang S.J. Duncan J., Van-de-Velde G., Brown M.B., Int J Pharma, 2005, 301, 181-191.
12. Berlin A., Anderson B.A., Pallansch M.J., J Dairy Sci, 1968, 51(12), 1912-1915.
13. Kalichevsky M.T., Blanshard J.M.V. A study of effect of water on the glass transition of 1:1 mixtures of amylopectin, casein and gluten using DSC and DMTA. Carb Polym, 1992, 19, 271-278.
14. Kalichevsky M.T., Jaroszkiewicz, E.M., Ablett, S., Blanshard J.M.V., Lillford P.J., Carbo Polym, 1992, 18, 77-88.
15. Kouassi K., Roos Y.H., Food Res Int, 2002, 34, 895-901.
16. Roudaut G., Simatos, D., Champion D., Contreras-Lopez E., Le Meste M., Inn Food Sci and Emerg, 2004, 5, 127-134.
17. Talja R.A., Roos Y.H., Thermo Acta, 2001, 380, 109-121.
18. Ryynänen S., J Food Eng, 1995, 26, 409-429.
19. Shinyashiki N., Shinohara M., Iwata Y., Goto T., Oyama M., Suzuki S., Yamamoto W., Yagihara S., Inone T., Oyaizu S., Yamamoto S., Ngai K.L. Capaccioli S., J Phys Chem B, 2008, 112, 15470-15477.
20. Bhandari B.R., Howes T., Drying Tech, 2005, 23, 781-797.
21. Roos Y.H., Karel M., Biotech Prog, 1991, 7, 49-53.
22. Bhandari B.R., Howes T., J Food Eng, 1999, 40, 71-79.
23. Roos Y.H., Lait, 2002, 82, 475-484.

Acknowledgements: This study was carried out with the financial support from the Food Institutional Research Measure (FIRM), the Department of Agriculture and Food under the project of 'Investigation of stickiness of milk powder for the purpose of improved process control in milk powder manufacture' (06RDTMFRC443).

Keywords: stickiness, dynamic-mechanical analysis (DMA), dielectric analysis (DEA), skim milk solids (SMP), thermal properties