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Role of α-Relaxation and Glass Transition in Understandings Stickiness of Milk Solids

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Abstract - **Stickiness of powder particles is often responsible for their impaired flow characteristics. Stickiness resulted from glass transition showing a relationship with mechanical α-relaxations, and stickiness occurred differently in dairy solids modified in their lactose and protein contents. Glass transition, α-relaxation and stickiness properties of milk solids systems were related to their solids composition and water plasticization. Lactose showed high magnitudes of mechanical α-relaxations, which were less pronounced at the lower lactose contents. There was a correlation with the magnitudes of mechanical properties above the glass transition and the steepness of the increase of torque values at sticky-point temperature (STP). The results indicated that mechanical α-relaxations were significant to understanding flow characteristics and the stickiness behavior of food solids. Stickiness can be reduced by mixing proteins to dairy solids. The present study provided useful information for the control of particle flow and powder stickiness in dairy and food powder industries.**

Keywords - **Glass transition temperature (Tg), Mechanical α-relaxation, Sticky-point temperature (SPT)**

I. INTRODUCTION

Flow characteristics of amorphous food solids are affected by the glass transition as a result of changes in molecular mobility coupled with α-relaxations found in mechanical measurements [1]. Amorphous lactose is often responsible for stickiness and caking of dairy solids produced by spray drying [2]. Lactose in dairy powders may exist as an amorphous component and its water plasticization is often responsible for powder stickiness and caking [2]. Impaired flow of amorphous powders may be observed at a temperature decreasing surface viscosity of particles to below a critical value referred to as a sticky-point [3]. The sticky point occurred around 10-20°C above the onset glass transition [4]. The decrease in viscosity is related to decreased relaxation times above the glass transition which can be observed from changes in α-relaxation [5]. Dynamic-mechanical analysis is sensitive for measuring mechanical relaxations occurring around and below the glass transition [6]. Although many studies have confirmed that stickiness was controlled by the glass transition [2, 3], no attempts have been made to relate changes in mechanical properties of food powders to stickiness above their glass transition. The objectives of the present study were to determine mechanical properties of modified milk solids systems with varying protein and lactose contents, to determine the effect of solids composition on thermal properties and stickiness behavior, and to establish relationships of glass transition, α-relaxations and stickiness.

II. MATERIALS AND METHODS

A. Samples of Powder

In the present study, lactose and milk powders with different lactose and protein proportions were used for the experiment [7]. Lactose, milk powder with high lactose content (MPC-25), skim milk powder (SMP) and milk powder with high protein content (MPC-55) were obtained by a spray drying method and supplied by Moorepark Technology Ltd., Fermoy, Co. Cork, Ireland. The composition of milk powders is given in Table 1.

TABLE 1 : GLASS TRANSITION (TG) AND WATER CONTENT OF LACTOSE AND MILK POWDERS WITH DIFFERENT PROTEIN AND LACTOSE PROPORTIONS STORED AT 24°C FOR 120 HOURS.

Composition (%)		Lactose	MPC-25	SMP	MPC-55
Protein		n/a	27	40	57
Ash		n/a	1	1	1
Fat		n/a	8	7	11
Water		2	5	4	5
Carbohydrate		98	59	48	26
(%) Relative amounts of sugars in carbohydrate fraction of powder	glucose	n/a	1.2	1.4	2.1
	galactose	n/a	1.4	1.8	2.3
	lactose	100	97.4	96.8	95.6

B. Differential Scanning Calorimetry (DSC)

Approximately 10-15 mg of each sample of powers was placed in DSC pans and stored for 72 h at different water activities (0.11-0.44 aw). These pans were sealed and scanned from well below to above the T_g regions at 5°C/min. The T_g was obtained by the onset temperature of glass transition according to Jouppila and Roos [8].

C. Dynamic-mechanical Analysis (DMA)

Approximately 1 g of each was transferred into a glass vial and stored at different water activities (0.11-0.44 a_w) for 5 days. The humidified powders (60 mg) were loaded into a pocket sample holder and scanned at a heating rate of 3°C/min from 40°C below to above the observed α-relaxation zone with frequencies of 0.5, 5 and 20 Hz [9]. The T_α was measured at a temperature of a drop in storage modulus at a constant frequency and a_w. The T_α is dependent on frequency of the applied stress; therefore, Arrhenius equation was used to analyze the relationship between the glass transition temperature and α-relaxations at different frequencies [6].

D. Stickiness Measurement

Sticky-point measurement was carried out by the method of zkan et al. [10] with some modifications. Powders were humidified at different water activities (0.11-0.44 a_w) until the steady-state water contents were obtained in powders. The powders were transferred to a water-jacketed cylinder and left in the water-jacketed cylinder connected to a temperature-controlled water bath for 20 to 30 min for stabilization at each measurement temperature. Isothermal measurements were carried out from 20 to 80°C at 10°C intervals. The torque values measured for rotation of the stirrer in the powders as a function of time were recorded every second for 40 s at 0.3 rpm controlled by the respective Brook- field RHEO 2000 version 2.7 software. The average torque value at each temperature was calculated using the last 20 data points (20 to 40 s). The stickiness parameters were taken from the initial and second slopes of the increase in torque against temperature [7].

III. RESULTS AND DISCUSSION

A. Glass Transition and Water Plasticization

Glass transitions of lactose and milk powders were determined using DSC. The T_g is a property of the amorphous phase and governed by the miscible amorphous phase components (Gordon and Taylor, 1952). The values of T_g and water content in lactose and milk powders with different protein and lactose proportions are given in Table 2. The anhydrous T_g values of lactose, MPC-15, MPC-25 and SMP were lower than those of MPC-55. The T_g of MPC-25 and SMP followed closely the T_g of amorphous lactose at all water activities, while MPC-55 showed a higher T_g suggesting that the T_g was determined by the lactose component and milk proteins perhaps increased the T_g of milk solids in agreement with the study of Haque and Roos [11]. The DSC T_g data indicated the typical water plasticization of lactose and milk powders similar to lactose and milk powders reported in several studies [11, 12, 13]. Milk powders showed a significant water lasticization at high water contents. This sensitivity to water may have resulted from its higher amorphous monosaccharides content as compared to lactose. The lower T_g and significant water plasticization could be accounted for the presence of monosaccharides [4, 14, 15] in the amorphous solids phase.

TABLE 2 : GLASS TRANSITION (TG) AND WATER CONTENT OF LACTOSE AND MILK POWDERS WITH DIFFERENT PROTEIN AND LACTOSE PROPORTIONS STORED AT 24°C FOR 120 HOURS.

Water activity	Lactose		MPC-25		SMP		MPC-55	
	m	T_g	m	T_g	m	T_g	m	T_g
0	0	105	0	101	0	105	0	124
0.11	2.3	65	2.9	56	3.1	52	3.5	63
0.23	4.2	47	4.7	40	4.6	38	4.8	46
0.33	6.6	30	6.7	23	6	24	6.5	36
0.44	9.6	13	9.5	7	8.8	6	7.8	16

B. Mechanical relaxations

Storage modulus decreased dramatically around the glass transition. The magnitude of a drop in storage modulus (⊗E′) decreased with increasing protein content (Fig. 1). T_α increased with increasing protein content and frequency. The frequency of α-relaxation corresponding to T_g was 1.9x10^{-5} Hz as explained by Arrhenius plots (Fig. 2).

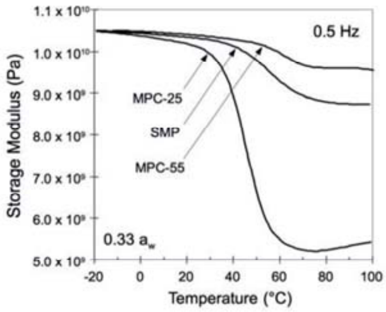

Fig. 1 Changes in mechanical relaxations (storage modulus) of lactose and milk powders with different protein-lactose ratios around glass transition.

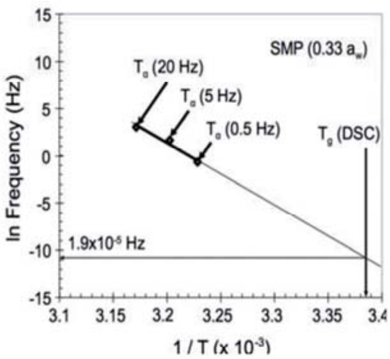

Fig. 2 Arrhenius plots of α-relaxation temperatures of dairy solids as measured by DMA at frequencies of 0.5, 5 and 20 Hz corresponding to Tg.

C. Stickiness Measurement

Stickiness behaviour of milk powders was measured by a sticky-point tester. Sticky-point temperature (SPT) was determined by temperatures that the torque values used for turning the spindle in milk powders increased. In the study, we found that flow properties of milk powders were affected by their lactose-protein ratio, glass transition and water activity. Torque values of milk powder with high lactose contents increased significantly around the glass transition (T_g) with increasing temperature (Fig. 3). The steep increase in the torque value (SPT) for each powder occurred around the glass transition which was largely governed by lactose fraction of amorphous solids. The increase in MPC-55 showed a lower slope than in lactose and lactose containing milk powders suggesting less rapidly developing stickiness in high protein milk powders with increasing temperature above the SPT. The SPT increased with increasing protein content. This was probably a result of the higher protein content of MPC-55 reduced the mobility of the lower concentration of lactose molecules as a result of protein-lactose hydrogen bonding [16]. This study can be assumed that the carbohydrate and protein fractions may exist as partially or fully phase separated components and the quantities of water sorbed by the amorphous lactose-protein fraction contributing to SPT at varying total water contents may differ. However, torque values, flow characteristics and stickiness behaviour of the powders were also affected by water content and water activity (a_w) resulting in water plasticization and the liquid bridging between particles in agreement with powder stickiness measured by a particle gun technique [17].

Although the T_g of the milk powders increased with increasing protein content, the increased protein content decreased the observed torque values around the glass transition more substantially suggesting the increasing cohesion and sensitivity to temperature and water with decreasing protein content (increasing lactose content) and a_w (Fig. 4). Since lactose was the major component of milk powders (MPC-25 and SMP), lactose and its plasticization behaviour contributed significantly to the formation of liquid bridges between particles preceding cohesion [2, 3, 18, 19].

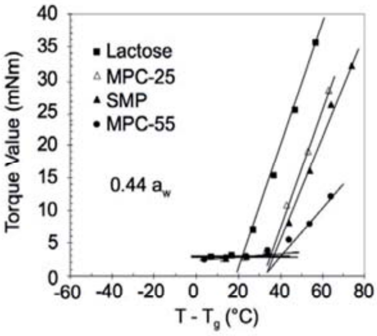

Fig. 3 Torque values for lactose and milk powders with different lactoseprotein ratios at 0.44 aw as a function of temperature difference to the Tg (T - Tg).

Increasing protein content in milk powders (MPC-55) may decrease the mobility of the lactose molecules on particle surfaces as a result of lactose–protein interactions [16]. This may be accounted for by the lower lactose content and different plasticization behavior of proteins at particle surfaces. At a higher T-T_g more rapid flow compensated for the smaller quantity of amorphous carbohydrates and led to the formation of liquid bridges between particles [2, 4, 13]. In the low lactose systems, stickiness could be observed above the T_g with relatively small increases in the torque values as compared to milk powders with high lactose contents. Therefore, changes in the lactose–protein ratio in milk powders could be used to control powder characteristics for decreased particle stickiness during processes and storage. The results of this study indicated that an increase in the protein content of milk powders could be used to reduce the particle adhesion and wall deposition in spray drying and to retard stickiness in powder storage.

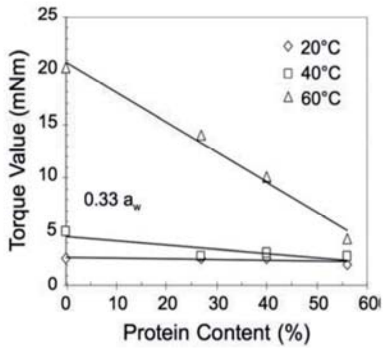

Fig. 4 Torque values of milk powders at 0.33 a_w against protein content measured at 20, 40, and 60°C. Solid lines show trends of torque values with protein content.

D. Comparison of Glass Transition, Mechanical Relaxation and Stickiness

The relationship of stickiness of sugar-containing powders and their surface viscosity was reported by Downton et al.[3] and its dependence on the glass transition was established by Roos and Karel [4]. The comparison of T_g, T_α and SPT indicated that SPT occurred above the T_g and were closed to T_α measured at 0.5 Hz (Fig. 5). An increase in water content and a_w decreased the temperatures, at which the T_g, T_α and SPT were recorded for the milk powders. Water plasticization of lactose at the higher a_w increased its mobility and liquidlike properties at particle surfaces and could retard powder flow more efficiently at lower temperatures [3, 5, 19]. At a constant a_w, the SPT of milk powders was related to the amorphous lactose–protein fraction in milk powders showing a decrease in SPT of milk powders with decreasing protein content (Fig. 6). An increase in protein content of milk powders may increase the protein content at the particle surfaces and change the flow and stickiness behaviour of particles [20].

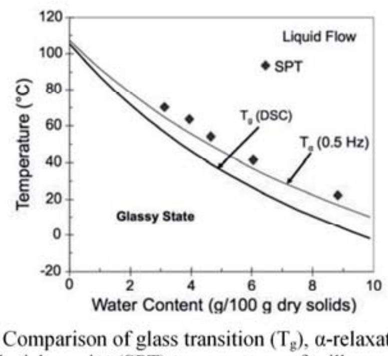

Fig. 5 Comparison of glass transition (T_g), α-relaxation (T_α) and sticky-point (SPT) temperatures of milk powders.

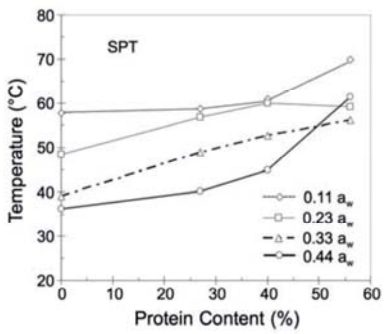

Fig. 6 Sticky point temperatures (SPT) of milk powders at various water activities (a_w) against protein content.

CONCLUSIONS

Stickiness was related to glass transition and were affected by milk solids composition. Glass transition of lactose was responsible for T_g and stickiness for milk powders. Increasing protein content improved flow characteristics and contributed to decreased stickiness of milk powders around glass transition. Mechanical α-relaxation can be used to describe time-dependent stickiness. Increasing protein content decreased molecular mobility of lactose and increased T_α contributing to reduce powder stickiness. These data are useful in setting guidelines for the control of temperature and water content to reduce the powder stickiness in different stages of drying processes, powder handling and storage. This study suggested that stickiness is decreased for high protein milk powders with lower levels of adhesion on particle surfaces in drying equipment and less rapidly developing stickiness during storage. The α-relaxations can be also used to predict flow characteristics and stickiness of milk powders.

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