Review

Importance of glass transition and water activity to spray drying and stability of dairy powders

Yrjö H. Roos

Department of Food Science, Food Technology and Nutrition,
University College, Cork, Ireland

Abstract – Spray-drying is a rapid dehydration method allowing production of high quality dairy powders. In dehydration and subsequent powder handling and storage, however, both chemical and physical changes, such as caking, lactose crystallisation, and nonenzymatic browning, may impair powder characteristics and result in loss of powder quality. Many of these changes are related to the physical state of lactose, as rapid removal of water in spray drying results in the formation of low-moisture, amorphous, noncrystalline structures of lactose and other milk components. The amorphous components may exist as solid-like glasses or highly supercooled, viscous liquids. The formation of amorphous, glassy lactose during spray drying allows production of a free-flowing powder. High temperatures or residual water contents at the later stages of the drying process, however, may cause stickiness, caking, browning, and adhesion of the powder particles to the processing equipment. The glass transition of amorphous lactose occurs in the vicinity of room temperature at a water content of about 6.8 g $(g \times 100)^{-1}$ of lactose corresponding to an equilibrium relative humidity of 37% and 0.37 a_w (water activity). At higher water contents, as the glass transition of amorphous lactose is well below storage temperature, dairy powders become sticky and the amorphous lactose may exhibit time-dependent crystallisation. Crystallisation of amorphous lactose may also release sorbed water from the amorphous material, which enhances other deteriorative changes, such as the nonenzymatic browning reaction. Amorphous lactose in dairy powders encapsulates milk fat, which, as a result of lactose crystallisation, is released and becomes susceptible for rapid oxidation. The glass transition and water activity are, therefore, important factors controlling processability, handling properties and stability of dairy powders.

Glass transition / dairy powder / spray drying / stability / water

Résumé – Importance de la transition vitreuse et de l'activité de l'eau pour le séchage par atomisation et la stabilité des poudres de lait. Le séchage par atomisation est une méthode de déshydratation rapide permettant la production de poudres de lait de première qualité. Cependant, au cours

de la déshydratation puis de la manipulation et du stockage ultérieurs de la poudre, des changements à la fois chimiques et physiques tels que l'agglomération, la cristallisation du lactose et le brunissement non enzymatique, peuvent cependant altérer les caractéristiques de reconstitution et entraîner une perte de qualité de la poudre. Plusieurs de ces changements ont trait à l'état physique du lactose, puisque le retrait rapide d'eau au cours du séchage par atomisation conduit à la formation de lactose et des autres composants du lait à faible teneur en eau, amorphe, aux structures non cristallines. Les composants amorphes peuvent exister sous forme de verre très solide ou de liquides hautement sous-refroidis et visqueux. La formation de lactose amorphe vitreux au cours du séchage par atomisation permet la production d'une poudre très fluide. Des températures élevées ou des teneurs en eau résiduelle aux derniers stades du procédé de séchage, peuvent cependant provoquer le collage, l'agglomération, le brunissement et l'adhésion des particules de poudre à l'équipement de séchage. La transition vitreuse du lactose amorphe a lieu à température proche de la température ambiante, à une teneur en eau d'environ 6,8 g $(100 \text{ g})^{-1}$ correspondant à un équilibre entre l'humidité relative de 37 % et une a_w (activité de l'eau) de 0,37. À des teneurs en eau plus élevées, puisque la température de transition vitreuse du lactose est bien en dessous de la température de stockage, les poudres de lait deviennent collantes et une cristallisation du lactose amorphe dépendant du temps peut se produire. La cristallisation du lactose amorphe peut aussi larguer l'eau adsorbée du matériel amorphe, ce qui entraîne d'autres changements détériorants tels que la réaction de brunissement non enzymatique. Le lactose amorphe dans les poudres de lait encapsule la matière grasse lactique, qui, en raison de la cristallisation du lactose, est libérée et peut rapidement s'oxyder. La transition vitreuse et l'activité de l'eau sont donc des facteurs importants de contrôle de la fabrication, des propriétés de manutention et de stabilité des poudres de lait.

1. INTRODUCTION

The solids of dehydrated dairy products include lactose, lipids, proteins, and minerals. Lactose, proteins, and minerals are miscible with water or water-soluble while lipids have fairly little interactions with water [10]. The physical state of the non-fat solids (SNF) is highly dependent on water content [2, 3, 10] and, therefore, of great importance in defining drying behaviour and stability of dehydrated dairy foods [4, 9].

Lactose in liquid dairy products is dissolved in a continuous water phase, which also contains dispersed fat and proteins. When desired, lactose may be crystallised before dehydration, but preconcentrated liquids may also be spray dried without precrystallisation of lactose. Although the preconcentrated liquids may become supersaturated with lactose, crystallisation may not occur before spray drying if only a short time is allowed between evaporation and drying. A rapid removal of water in subsequent spray drying does not allow lactose crystallisation and while water is removed, lactose is transformed to a solid-like, amorphous, glass directly from the dissolved state [11, 12]. Therefore, the physicochemical properties of supersaturated, amorphous lactose are important in defining appropriate spray drying conditions and storage stability of many dairy powders [9, 15].

Several physicochemical changes of dairy powders are directly or indirectly related to the glass transition of amorphous lactose. The glass transition is a state transition of amorphous materials occurring between the solid, glassy and supercooled liquid states [9, 17, 18]. The amorphous materials are nonequilibrium systems and many of the changes, including the glass transition itself, have time-dependent characteristics [9]. In general, molecular mobility in the glassy state is limited to molecular rotations and vibrations while above the glass transition, translational mobility

appears [18]. Therefore, many amorphous glasses are fairly stable, but long-term stability is lost above the glass transition. For example, amorphous, glassy lactose is fairly stable, but as molecular mobility becomes significant above the transition, the solid-like properties are lost [4, 9, 11]. There is also a driving force towards the thermodynamically equilibrium crystalline state and the glass transition also results in time-dependent crystallisation [11–13]. Furthermore, stickiness and caking of powders, and rates of diffusion-controlled chemical reactions may be controlled by the glass transition [9, 17].

The significance of the glass transition in the spray drying process has received fairly little attention although the glass transition related changes of dairy powders have been well recognised. The present article discusses the role of glass transition in spray drying and in the control of stability of dairy powders.

2. GLASS FORMATION IN SPRAY DRYING

Spray drying involves atomisation of the liquid and subsequent evaporation of water as the material passes through the drying chamber. Although a number of different spray driers may be used, corresponding principles of glass formation apply according to Figure 1.

Dehydration of the atomised liquid particles proceeds from the particle surface to the inner core. A layer of concentrated solutes is formed on the particle surface and there may be a decrease in the particle temperature due to evaporative cooling. The extremely rapid removal of water increases the viscosity of the remaining solids and the particle surface approaches the glassy state before colliding with other particles or drier walls. It has been found that a critical surface viscosity resulting in stickiness and caking is $> 10^7$ Pa·s [1] and the generally
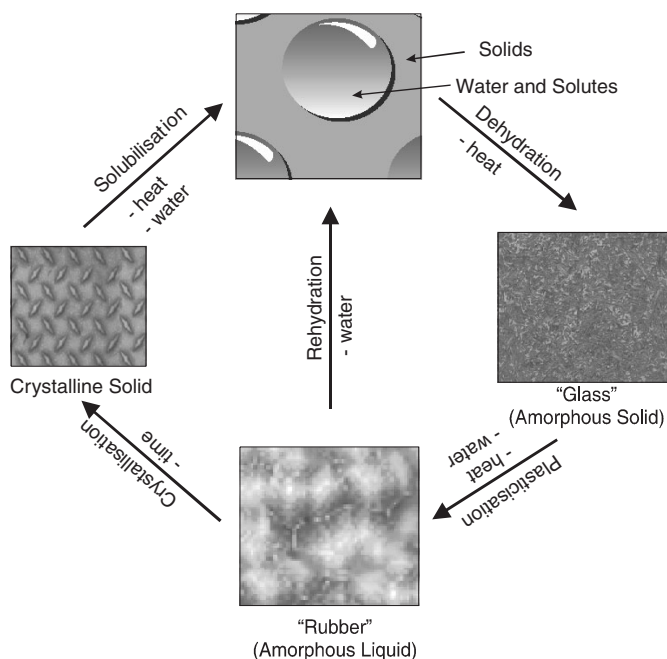

Figure 1. Formation of amorphous structures in dehydration and the relationships between equilibrium (solution, crystalline solid) and nonequilibrium (amorphous solid and liquid) states.

accepted value for the viscosity of glassy materials is $> 10^{12}$ Pa·s [18]. Such a high surface viscosity of drying particle surfaces allows the formation of solid, individual particles that can be exposed to further treatments in subsequent drying stages, e.g., agglomeration on a fluidised bed drier or a belt.

The vitrification of the particle surface in spray drying is essential in allowing free flow of the particles through the drying chamber and avoiding caking of particles with each other and on the drier surfaces. At the end of the drying process, the particle temperature and water content should support the solid, glassy state.

3. PROPERTIES OF AMORPHOUS MILK SOLIDS

The main amorphous components in dairy solids are carbohydrates and proteins. These components are both miscible with water and at least partially miscible with each other. However, it is likely that most proteins exist at least partially phase separated from carbohydrates in dehydrated dairy powders [6].

It is well known that melting temperatures of crystalline, water-soluble materials decrease with increasing water content [11, 12]. Both amorphous carbohydrates and proteins are also plasticised or softened by water [17], i.e., their glass transition occurs over a water content dependent temperature range decreasing with increasing water content [3–5]. The amorphous carbohydrates, however, often dominate the observed changes in dairy solids and their transition temperatures correspond to observed changes in physicochemical properties [2, 3]. Unfortunately, fairly little information is available on the protein transitions and the miscibility and transitions of carbohydrate-protein mixtures.

The glass transition of lactose and dairy solids has been observed using differential scanning calorimetry (DSC) [3, 11–13]. DSC measures a change in heat capacity that occurs over the glass transition temperature range. DSC is also the most common method in the determination of glass transition temperatures, which are taken from the onset or midpoint temperature of the change in heat capacity [9]. Other changes associated with the glass transition are changes in thermal expansion coefficient and mechanical and dielectric relaxations [9, 18]. The viscosity of the glassy state is often considered as constant and sufficiently high to maintain the solid-like properties. However, the liquid-like properties appear over the glass transition and there is a dramatic decrease in viscosity at and above the transition. Many sugars, including lactose are transformed rapidly from the solid glassy state to a syrup-like, sticky liquid.
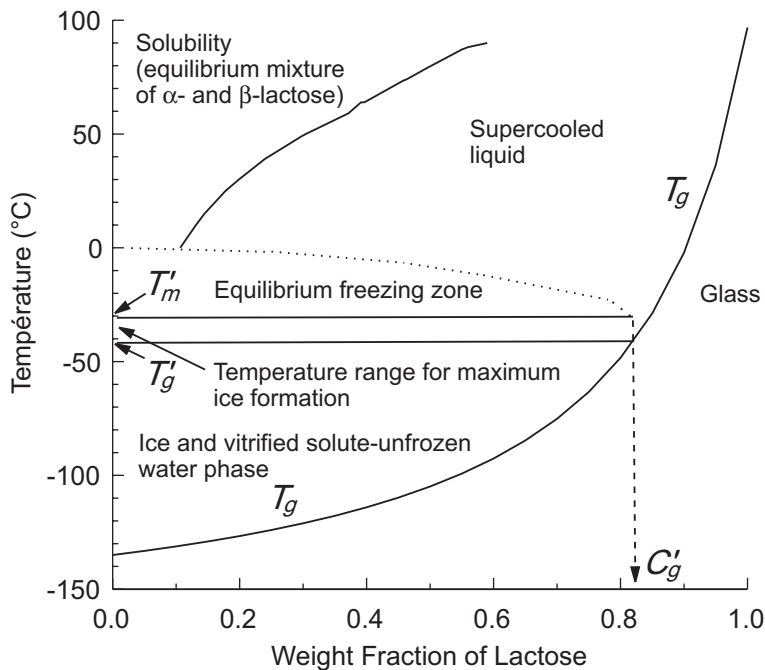
The glass transition of anhydrous lactose, as observed using DSC, has an onset temperature of 101 °C [12], which is one of the highest temperatures measured for "anhydrous" disaccharides [9]. Glass transition temperatures for anhydrous milk components and solids are given in Table I. The glass transitions observed in milk solids correspond closely to those of pure lactose [3, 4]. However, if lactose is hydrolysed, the observed T_g decreases dramatically, because of the much lower T_g of the galactose and glucose components [3]. This also results in significant changes in the spray drying behaviour and storage stability of lactose-hydrolysed milk solids [9].

Amorphous carbohydrates, including lactose and its hydrolysis products are significantly plasticised by water, which is observed from a rapidly decreasing T_g with increasing water content. The effect of water on the T_g of milk solids may be predicted using the Gordon-Taylor equation (1) [3, 9],

$$Tg = \frac{w_1 T_{g1} + kw_2 T_{g2}}{w_1 + kw_2} \qquad (1)$$

Table I. Anhydrous glass transition temperatures, T_g, of milk components and solids. Data from Jouppila and Roos [3] and Roos [9].

Material	Glass transition temperature (°C)
Galactose	30
Glucose	31
Lactose	101
Skim milk	92
Skim milk with hydrolysed lactose	49

Figure 2. State diagram of amorphous lactose showing lactose solubility, the glass transition temperature, T_g, glass transition of maximally freeze-concentrated lactose solutions, T_g' and the corresponding solids content, C_g', and onset of ice melting in the maximally freeze-concentrated solutions, T_m'.

where T_g is glass transition temperature of a mixture of solids with a weight fraction of w_1 and anhydrous T_{g1} and water with a weight fraction of w_2 and glass transition of T_{g2} for pure water. The T_{g2} is often taken as –135 °C and k is a constant.

The effects of water on the state and phase transition temperatures of amorphous food materials is often described us-

ing State Diagrams, which show the transition temperatures over a wide temperature range and in maximally freeze-concentrated systems [9, 17]. The state diagram of lactose is shown in Figure 2. The diagram of lactose is useful in explaining the effect of water on lactose properties in dehydration and dehydrated dairy products. The information of water plasticisation can also
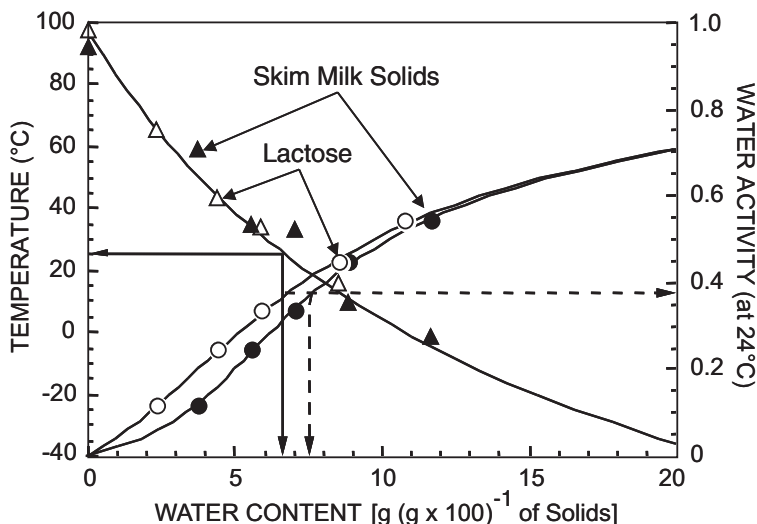
Figure 3. Glass transition temperature and water sorption properties of amorphous lactose and skim milk solids. The glass transition is depressed to 24 °C at a critical water activity of 0.37 (corresponding to critical storage relative humidity of 37%). The corresponding critical water content for lactose is 6.8 and skim milk solids 7.6 g (g × 100)$^{-1}$ of solids. Data from Jouppila and Roos [3].

be shown with water sorption properties (Fig. 3), which allows evaluation of the extent of water plasticisation of dairy powders in various storage conditions.

4. GLASS TRANSITION IN SPRAY DRYING

Several studies have shown that stickiness of dehydrated powders occurs as a result of particle surface plasticisation and concurrent decrease in viscosity allowing the formation of liquid bridges between powder particles [7]. It may be assumed that similar mechanisms control particle properties in the spray drying process. However, the process involves removal of the solvent and plasticiser, which has to occur with a rate competing with particle velocity and formation of a dry surface to allow free flow of individual particles throughout the dehydration process.

The glass transition temperature of skim milk solids showing the stickiness and caking zone at about 10 °C or higher above the T$_g$ measured by DSC is shown in Figure 4. Although the water content within drying particles and between individual particles may vary significantly, the particle temperature may be assumed to decrease during initial dehydration. Lactose exists most likely as highly supersaturated syrup in the solids phase. The particle surface may approach the glassy state when the inner particle core remains within the stickiness and caking zone providing the free flowing properties at the end of the drying. At the later stages, the surface properties may be altered to allow agglomeration in a fluidised bed drier or a separate agglomeration step. After dehydration the moisture distribution within the particles becomes more even and the water content is reduced to a sufficiently low level to maintain the solid, glassy state at typical storage conditions of dairy powders.

Figure 4. Glass transition of skim milk solids with a hypothetical particle temperature during water removal in spray drying, and formation of the glassy solid particles at the end of drying.
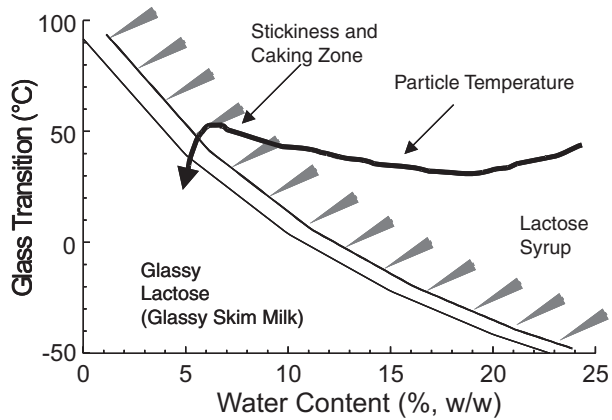
The surface properties of the drying particles are related to surface viscosity [1]. The viscosity as a result of water removal increases rapidly as the glass transition is approached. The viscosity changes of amorphous materials are often described using the Williams-Landel-Ferry (WLF) equation (2),

$$\log a_T = \log \frac{\tau}{\tau_s} = \log \frac{\eta}{\eta_s} = \frac{-C_1(T - T_s)}{C_2 + (T - T_s)}$$

(2)

which relates relaxation times above glass transition to a reference temperature, T_s [19]. If the T_g is taken as a reference temperature, the relaxation time, τ, and viscosity, η are related to their values at the glass transition (τ_g and η_g) and plasticisation, and are defined by the temperature difference, $T - T_g$, as shown in Figure 5.

Although, the WLF relationship is often used to describe changes in relaxation times above the glass transition, it does not follow changes over the transition temperature range. The changes in relaxation times at and around the transition are better described by the Fermi relationship [8].

The viscosity changes resulting from the glass transition can also be used to control agglomeration of fine particles and in the manufacturing of instant powders [9]. In such processes, it is essential to allow
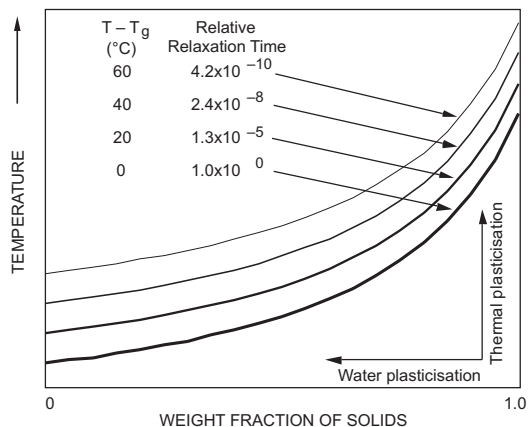

Figure 5. Relative relaxation times above the glass transition, as predicted by the WLF relationship.
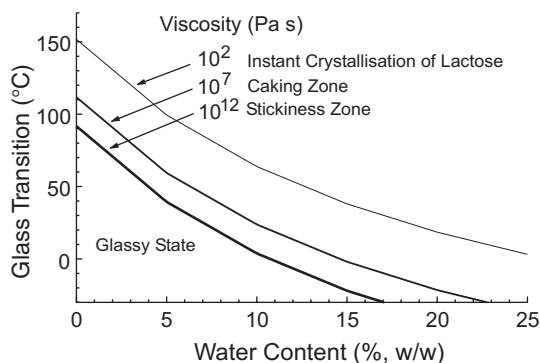
Figure 6. Glass transition related changes in mechanical properties and crystallisation in skim milk with amorphous lactose.

controlled stickiness on particle surfaces and adhesion of particles to clusters. The formation of clusters is followed by removal of water and cooling to solidify the surfaces into the glassy state. Therefore, the powders will have large particle sizes and remain free flowing and stable at appropriate storage conditions.

5. GLASS TRANSITION AND POWDER STABILITY

Several properties of powders with amorphous lactose or even some amounts of amorphous lactose can be related to its glass transition [2–5, 9, 13]. These include surface stickiness and caking [11], time-dependent lactose crystallisation [13] and release of encapsulated lipids [16], and increasing rates of nonenzymatic browning [15] and lipid oxidation [16]. The changes in mechanical properties and diffusion are responsible for stickiness, caking and lactose crystallisation, but the changes in the reaction rates are more complicated and affected by other factors, including pH, heterogeneities in water distribution, and miscibility of proteins and carbohydrates.

5.1. Stickiness, caking and crystallisation

Stickiness and caking are common problems in handling of powders containing amorphous carbohydrates. Stickiness and

caking appear as the viscosity of the amorphous components decreases and powder particles adhere [7]. Further plasticisation is often followed by collapse of structure as a result of increasing flow and lactose crystallisation, which may occur instantly at a high level of thermal and water plasticisation [9]. The development of stickiness, caking and crystallisation as a result of plasticisation is shown for skim milk in Figure 6. The crystallisation of lactose is highly time-dependent following the typical crystallisation rate behaviour of amorphous solids. The time-dependent lactose crystallisation in dairy powders is often observed in water sorption studies [3, 9]. These have shown that above a
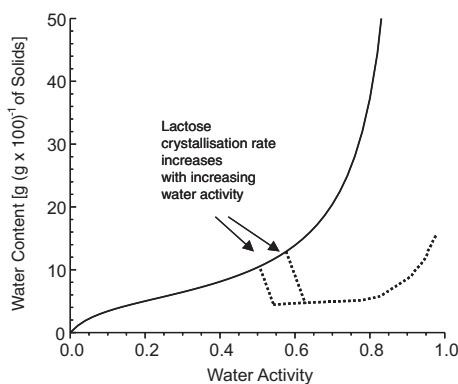

Figure 7. Sorption isotherm of skim milk solids. Crystallisation of amorphous lactose results in time-dependent loss of sorbed water.

Figure 8. Stability map for dairy powders containing amorphous lactose. The critical water activity corresponds to the glass transition depression of amorphous lactose to 24 °C, which may enhance deteriorative changes and loss of quality.
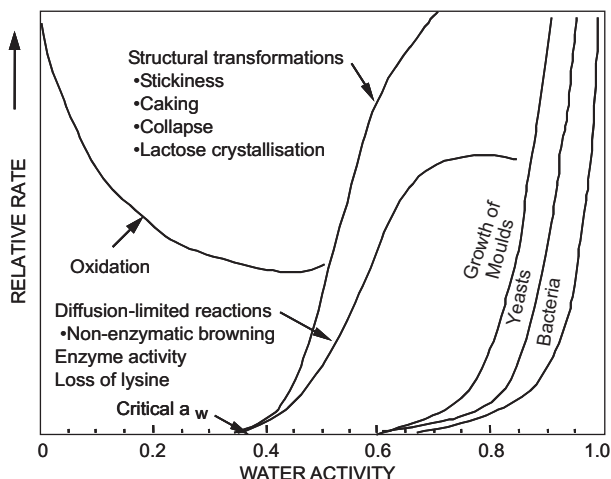
critical storage relative humidity, there is a loss of sorbed water (Fig. 7). The loss of sorbed water in dairy powders corresponds to the difference in water sorption by amorphous and crystalline lactose. However, it should be noticed that the loss of sorbed water is time-dependent and the crystalline form of lactose produced is dependent on the crystallisation conditions [3–5]. Most crystals formed are anhydrous, but at the higher storage humidities increasing amounts of α-lactose monohydrate is formed. Crystallisation of amorphous lactose in sealed packages and in bulk storage results also in an increase in water activity and acceleration of most deteriorative changes, such as browning reactions and oxidation [14–16].

5.2. Molecular mobility and stability maps

The glass transition in dairy powders with amorphous components is related to molecular mobility. The amorphous solids in the solid glass are frozen in a high viscosity state and they exhibit only molecular vibrations and side chain rotations. As the material undergoes the glass transition, the molecular mobility increases and translational motion of the molecules appears. This has been related to increasing rates of bimolecular reactions and enzyme activity in low moisture food systems [9, 17].

A hypothetical stability map for dehydrated skim milk with amorphous lactose is shown in Figure 8. At low water contents, free fat is accessible to oxygen and may undergo rapid oxidation. Increasing water activity may provide protection of free lipids as a result of water sorption on solid surfaces. Plasticisation by an increasing water content results in the decrease of the glass transition. At the critical water activity, the glass transition is decreased to storage temperature and further increases in water activity result in a decrease in viscosity of particles, stickiness, caking, and rapid increases in rates of lactose crystallisation and diffusion controlled reactions [4, 9]. Lactose crystallisation is responsible for release of encapsulated lipids and subsequent rapid oxidation in dairy powders [16]. The nonenzymatic browning reaction has also been observed to proceed at increasing rates above glass transition and it is substantially accelerated by an increase in water activity following crystallisation of amorphous lactose in dairy powders [14].

6. CONCLUSIONS

Phase and state transitions, including glass transition, have an important role in a proper control of the spray drying process of dairy materials and the quality of the products obtained. Furthermore, the transitions are important in understanding the stability of dehydrated dairy products. The glass transition of amorphous lactose affects the development of the particle properties during spray drying and subsequent agglomeration processes. Further knowledge of particle temperature and water content in dehydration is required to understand and reduce undesired stickiness and caking of particles in different stages of the drying process and powder handling. Moreover, such understanding is essential in controlling stability of spray dried dairy powders and to avoid deterioration resulting from lactose crystallisation or chemical and enzymatic reactions.

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