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STRUCTURAL COLLAPSE OF PLANT MATERIALS DURING FREEZE-DRYING

V. T. Karathanos[*], *S. A. Anglea*[**] *and M. Karel*[***]

Rutgers University, Cooc College, Food Science Department, P.O. Box 231, New Brunswick
NJ 08903, USA

Abstract

Structural collapse of plant materials, which affects quality of foods, was studied. Fresh and osmotically dehydrated plant materials were freeze-dried at several chamber pressures, to achieve initial sample temperatures that were below (–55°C), near (–45°C), or above (–28°C) their glass transition temperature (T_g =–45°C). Freeze-drying at –55°C resulted in products retaining their original volume. When the initial sample temperature was increased above T_g, the resulting freeze-dried samples collapsed. When the initial sample temperature was increased above the temperature of ice melting (T_m'), the samples collapsed further.

Keywords: apple, celery, glass transition, plasticize, potato

Introduction

Production of high quality products through dehydration processes, such as freeze-drying [1] and osmotic dehydration [2], is an active area of research. Both processes have the potential to maintain desirable quality characteristics such as high bulk volume and porosity, giving better rehydration properties, compared to those of air-dried materials. It may be possible that one of these processes, in combination with air-drying, would help improve upon an air-dried product, while still maintaining cost efficiency.

A process combining osmotic dehydration and air-drying utilizes the osmotic dehydration step to reduce the water content, prior to air-drying, which then further reduces the amount of water to 5 to 15%. The physical state of the material during the dehydration process is important in determining final product quality. In air-drying, the bulk volume decreases significantly as water is

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[*] Present address: Agricultural University of Athens, Dept. of Food Science and Technology, Iera Odos 75, Athens 11855, Greece.

[**] Present address: Campbell Soup Company, Campbell Place, Camden, NJ 08103.

[***] Author to whom all correspondence should be addressed.

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removed, resulting in poor rehydration properties. Low temperature air drying results in some improvement. Karathanos *et al.* [3] found that air-drying of fresh celery at 5°C resulted in a product having improved physical properties, compared to that dried at 60°C.

Freeze-drying offers ideal product volume and porosity in a finished product dried under ideal conditions. This results because the ice sublimes, and no unfrozen water is available to plasticize the material matrix. Frozen systems are composed of a pure ice phase co-existing with a phase of concentrated amorphous solution (CAS) [4, 5], in which the solvent is the unfrozen water. The amount of unfrozen water in the maximally freeze-concentrated CAS varies with its composition. The concentrations of the maximally freeze-concentrated solute, for glucose, fructose, and sucrose, are 79.2, 78.6 and 79.5% by weight, respectively [6]. The onset$^{(o)}$ and corresponding endset$^{(e)}$ temperatures, of the glass transition of the maximally freeze-concentrated CAS (T_g') for glucose, fructose, and sucrose, measured by DSC, are $-57^o(-52^e)$, $-58^o(-53^e)$, and -46^o (-40^e)°C, respectively [6]. The T_g' increases with increasing molecular weight of the carbohydrates in the CAS [7, 8]. The glass transition temperature (T_g') determined by mechanical spectrometry has been shown to correspond to the 'endset' temperature of the transition measured by DSC [9]. The T_g values obtained by mechanical spectrometry were –44, –48, and –43°C for 80% solute concentrations of glucose, fructose, and sucrose, respectively [6].

Materials may collapse during and after freeze-drying, resulting in changes in product quality [10]. The collapse temperature is of great importance in food processing since it represents the temperature at which structural mobility in-

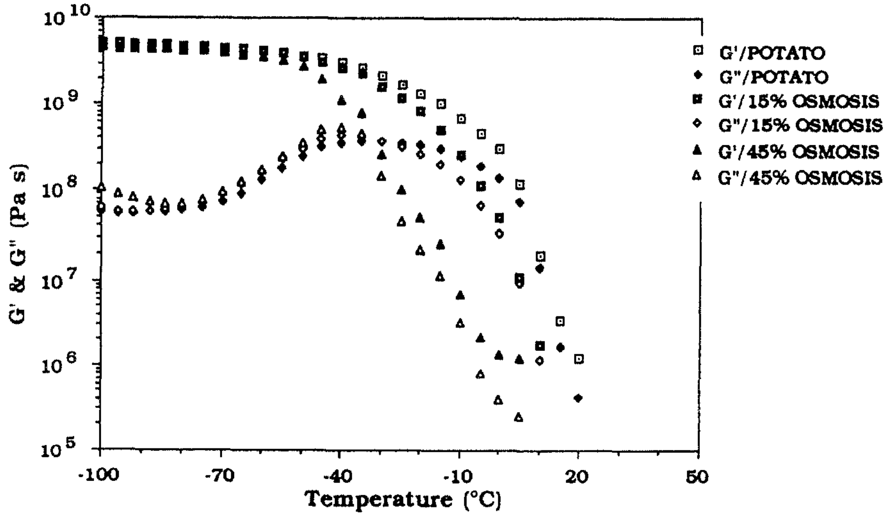

Fig. 1 Dynamic mechanical properties (G' and G'') of fresh potato and potato osmotically dehydrated in 15, 30 and 45% sucrose solutions [16]

creases [8] and quality decreases [11]. Collapse during freeze-drying has been related to the collapse temperature of the CAS [4]. Increased plasticization of the CAS by unfrozen water occurs above the temperature at which the ice begins to melt (T'_m), thus decreasing the CAS viscosity and causing acceleration of collapse during freeze-drying. Bellows and King [12] proposed physical relationships that predicted that collapse occurs when the viscosity of the CAS is in the range of 10^4 to 10^7 Pa s.

The collapse temperature is related to, but higher than, the T_g [10]. Above T_g, the viscosity of the amorphous matrix decreases steeply with temperature [13]. A useful relationship between viscosity and the temperature difference above T_g is the Williams-Landel-Ferry equation [14], which can be applied from T_g to about T_g+100°. This equation predicts very large viscosity changes within a few degrees above T_g. In freeze-drying, the removal of ice through sublimation creates pores, the walls of which may collapse due to surface forces or gravity. The viscosity of the CAS, which is usually the major component of pore walls, prevents or retards collapse.

Plant materials are viscoelastic, and this allows the evaluation of their physical state by mechanical spectrometry as well as by differential scanning calorimetry (DSC) [9, 15, 16]. Anglea *et al.* [16] showed, by mechanical analysis of fresh and osmotically dehydrated apple and potato, that the T_g is –45°C (Fig. 1). Apparent crystallization of unfrozen water was detected during mechanical analysis, suggesting that maximum freeze-concentration had not occurred previously (Fig. 2). DSC analysis of fresh and osmotically dehydrated potato showed similar results. Because the T_g for all samples was similar, it was

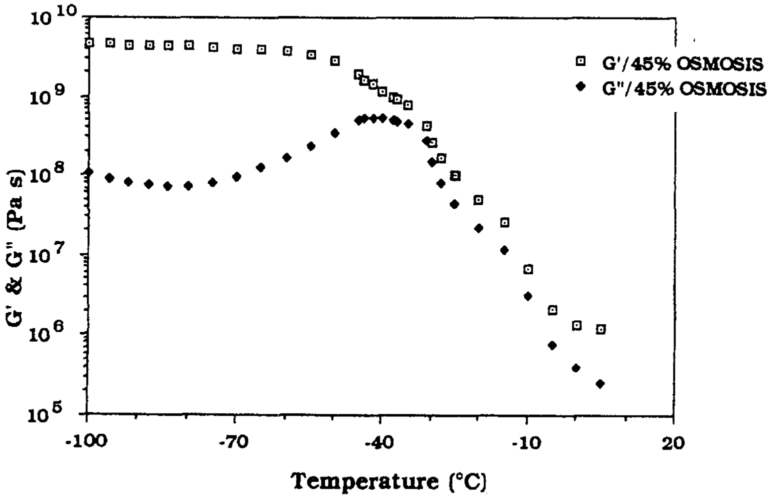

Fig. 2 Dynamic mechanical properties (G' and G'') of fresh potato osmotically dehydrated in a 45% sucrose solution, emphasizing the crystallization/recrystallization zone in the region from –40 to –30°C [16]

assumed that all samples froze to approximately the same amorphous solution concentration. In complex systems, such as plant tissues, maximum freeze-concentration is impossible to achieve, at least within reasonable annealing times. However, even in simple model systems, where maximum freeze-concentration has been achieved, it is evident that the two methods give similar but not identical correlations of T_g at the same maximally concentrated solute concentration, because the thermal event (detected by DSC) must occur before any mechanical changes can be realized within the plant material.

The objective of this investigation was to determine the effect of product temperature, as it relates to viscosity of the CAS and to the unfrozen water content, on structural collapse during the initial stages of freeze-drying.

Materials and methods

Plant tissues

Red Delicious apples, celery, and Russet potatoes were purchased at a local supermarket. The water content and sugars content, as percentage of the total solids, for these plant tissues are shown below [17].

Red Delicious apple: water – 81 to 86%; sugars – 63 to 82% of total solids, with an average of 69% (comprised of 10% glucose, 55% fructose, and 35% sucrose).

Celery: water – 92 to 94%; sugars – 11.5 to 18.4% of total solids, with an average of 15% (comprised of 40% glucose, 35% fructose, and 25% sucrose).

Russet potato: water – 78 to 82%; sugars – 0.5 to 23.5% of total solids, with an average of about 10% (comprised of 44% glucose, 30% fructose, and 26% sucrose).

The water contents of our experimental materials were determined for representative samples, using an oven method (24 h drying at 105°C), and were found to be 89, 95 and 79% (on a wet basis) for apple, celery and potato, respectively.

Table 1 Materials exchange resulting from osmotic dehydration

	Weight change/%		
Osmotic sucrose solution/%	Apple	Celery	Potato
15 net solids change	+2.4	–8.6	–26.6
15 water change	+1.2	–11.7	–27.0
45 net solids change	–26.5	–40.0	–44.2
15 water change	–36.5	–55.0	–49.6

Although it is evident that the monosaccharide levels in these plant tissues vary (Table 1), the T_g's of the tissues, at the same freeze-concentration of CAS, are the same [16]. This suggests that in frozen systems, the total sugar content determines T_g at concentrations close to that at T_g'. This is consistent with the observation that C_g' is approximately 0.8 g solute/g solution for mono- and disaccharides. Therefore, in designing freeze-drying methodology for the present work, the temperatures evaluated were the same for all plant tissues.

Osmotic dehydration

Plant materials, cut into rectangular shapes, were weighed and their outside dimensions were measured using a micrometer. They were kept in a slowly stirred solution of sucrose (Sigma Chemical Co.; anhydrous, grade II) (15% or 45% w/w) in distilled water, at room temperature overnight. The samples were removed, weighed and their dimensions measured. The final moisture content was measured using the oven method.

Prepared tissues, $4\times1\times1$ cm^3, were frozen at –35°C for 48 h, tempered for 2 h at –80°C, and freeze-dried for 48 h using a Virtis (Benchtop 31) laboratory freeze-dryer. Freeze-drying was performed under high (0.53 Pa) or reduced vacuum conditions (90.64 Pa and 209.28 Pa), to obtain varying initial sample temperatures that were below (–55°C), near (–45°C), or above (–28°C) T_g of the tissues (–45°C). It was not possible to analyze celery using RMS, due to the configuration of the sample required for the measurement. However, the sugars content of celery is very similar to that of potato, and thus it was assumed that collapse during freeze-drying would depend on T_g in the same manner. The vacuum was reduced by leaking the pressure release valves. Needles, containing thermocouple wires, were inserted in the center of the samples before freezing. The temperature of the sample during freeze-drying was monitored using a digital thermometer. After freeze-drying, the final weight and bulk volume were measured.

Collapse

The specific bulk volume, V_{bs}, was calculated from the measured outside geometric dimensions of the sample, or by a glass beads-displacement method [18], when the geometry of the sample made calculation from outside dimensions impractical. The volume change, which occurred after freeze-drying at different temperatures, was measured relative to V_o, the specific bulk volume of the fresh material after freeze-drying at 0.53 Pa (–55°C). The specific bulk volume is the volume of solids, water and air per gram of sample. The ratio used to compare plant tissues freeze-dried under varying conditions was:

$$V_{bs}/V_o \cdot 100$$

Mechanical spectrometry

Mechanical spectrometry was employed to study transitions in fresh plant materials at temperatures below the melting point of ice. A Rheometrics mechanical spectrometer (RMS-800, Rheometrics Inc., Piscataway, NJ), employing the rectangular torsion test fixture in the oscillatory dynamic mode, was used to characterize the viscoelastic properties of these materials. G' and G'' were measured. G' represents the elastic character of the material and is called the storage modulus (since elastic energy is stored and can be recovered). G'' represents the viscous character and is called the loss modulus (since viscous energy is dissipated or lost).

Fresh and osmotically dehydrated plant materials were cut into strips of approximately 58 mm×11 mm×2 mm for all measurements made using the rectangular torsion test fixture. Temperature sweeps were accomplished using the RMS oven, from initial sample temperatures of –100 to –150°C to ice melting, at a heating rate of 2°C min^{-1} under a fixed strain of 0.1% and at a frequency of 1 Hz. Liquid nitrogen (137.9 Pa) was employed to lower the oven temperature below ambient. G'' and G' were evaluated to determine the T_g of the unfrozen phase (as the maximum of the loss modulus peak [19]), the recrystallization temperature of water, and the melting temperature of ice. When the G'' maximum was not sharp, but rather reached a maximum, leveled off, and then decreased, the T_g was taken as the temperature at the beginning of the plateau region. Three replicate measurements were performed and their average reported.

Results and discussion

Structural collapse of plant materials during drying

Vegetables do not collapse significantly (less than 10%) during freeze-drying at low temperatures, and therefore have very high bulk volumes. Collapse can, however, be significant when freeze-drying occurs at reduced vacuums and consequently at higher temperatures. Figures 3, 4, and 5 show collapse of apple, celery and potato at various freeze-dryer pressures, corresponding to different sample temperatures that were below, near, or above the sample T_g. The temperature was measured during the initial hour of freeze-drying. T_m' (–32°C), the onset temperature of ice melting, follows T_g in these plant materials [16]. Detrimental effects occurred above T_g, as the initial sample temperature during freeze-drying increased. Above T_g, the viscosity of the CAS decreases. Above T_m', ice melting resulted in increased plasticization of the tissue matrix and a further decrease in viscosity.

Collapse is dependent on sugar content, only insofar as sugar content affects the T_g of the concentrated amorphous solution. In these experiments, T_g was the same for all tissues, and therefore this factor was not expected to contribute to any differences in collapse in the experiments for celery, apple, and potato. However, the moisture content, and therefore the amount of unfrozen water above T_m', is different. This factor was expected to contribute to differences in collapse.

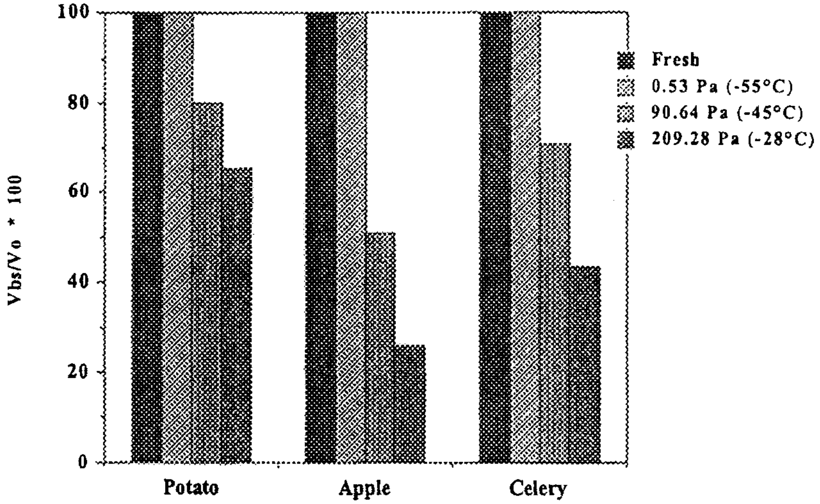

Fig. 3 Shrinkage of fresh tissues during freeze-drying. Sample temperatures investigated were below, near, or above T_g

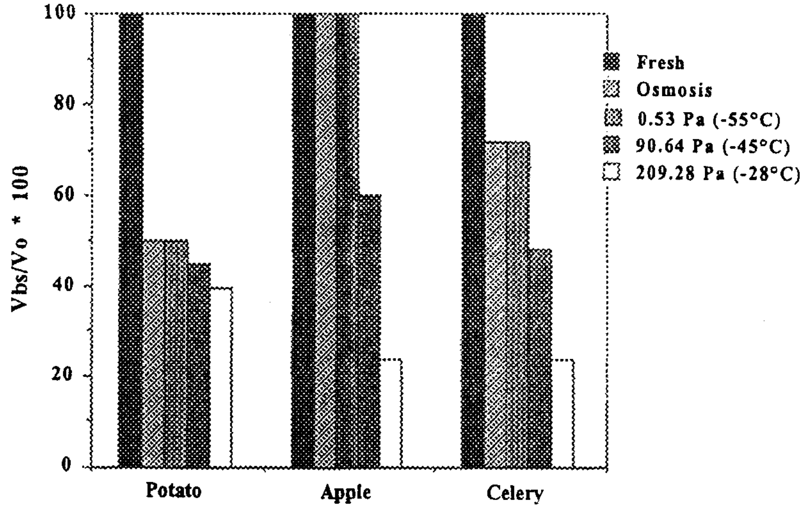

Fig. 4 Shrinkage of plant tissues during osmotic dehydration in a 15% sucrose solution and subsequent freeze-drying. Sample temperatures were below, near, or above T_g

Collapse during osmosis

Figures 4 and 5 show the shrinkage during osmosis of fresh plant tissues in 15 or 45% sucrose solutions, as well as the subsequent collapse during freeze-drying. Table 1 shows the materials exchange during osmosis for apple, celery, and potato, under both osmosis conditions. Table 2 shows the final moisture content after the osmosis step, compared to that of the fresh tissues.

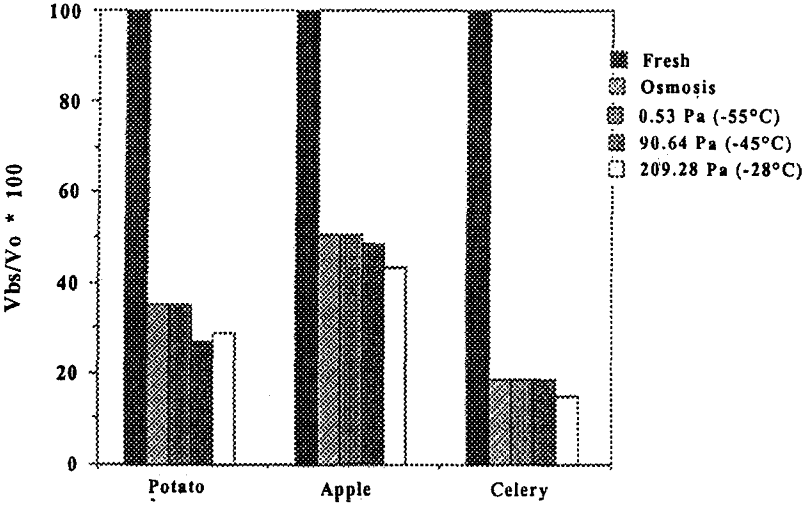

Fig. 5 Shrinkage of plant tissues during osmotic dehydration in a 45% sucrose solution and subsequent freeze-drying. Sample temperatures were below, near, or above T_g

Table 2 Moisture content of fresh and osmotically dehydrated plant tissues

		Moisture content (g H_2O/g solids)		
Osmotic sucrose solution/%		0	15	45
	Potato	3.72	2.40	1.10
	Apple	7.90	7.18	2.44
	Celery	18.96	10.35	2.02

Consideration of the materials exchange during osmosis in a 15% sucrose solution leads to the expectation that potato, having lost the greatest percentage of total weight, would have collapsed the most. Results shown in Fig. 4 are in agreement with this expectation. Potato lost almost 50% of its original volume, whereas apple and celery lost 0 and 30%, respectively.

From a similar analysis of the 45% osmosis tissues,the results in Table 1 suggest that celery would lose the most, with potato following closely, and apple showing the least collapse. Figure 5 shows these results. Celery lost about 80% of its original volume, potato decreased by 65%, and apple lost only 50% of its original volume.

Collapse of plant tissues during freeze-drying at –55°C

During freeze-drying of fresh and osmotically dehydrated plant tissues at –55°C, no collapse was evident. This is an ideal freeze-drying condition, where water sublimation occurs below T_g and the CAS viscosity remains at a maximum.

Collapse of fresh tissue during freeze-drying at –45°C

During freeze-drying at –45°C, no unfrozen water resulting from ice melting would be expected. Since T_g was determined to be the same for these tissues, differences in collapse should be at a minimum. Figure 3 shows that celery and potato lost 25 and 20% of their original volume, respectively, whereas apple decreased by 45%, more than expected. These differences may be due to factors other than differences in CAS viscosity, since the T_g's of the three tissues were the same. It is possible that other structural factors that differ among these tissues, such as cell wall make-up, play a role in collapse.

Collapse of tissue osmotically dehydrated in 15% sucrose solution

Treated celery collapsed 20% during freeze-drying at –45°C. Collapse during osmosis and drying, compared to that of fresh tissue, totalled 50%. Apple collapsed 40% and potato collapsed 3% during freeze-drying at –45°C. Although large differences among the tissues were seen in collapse during osmosis, approximately the same overall volume loss was evident for all tissues, when product shrinkage after osmosis and subsequent freeze-drying at –45°C was evaluated.

Figure 4 also shows the extent of collapse of these treated tissues during freeze-drying at an initial sample temperature of –28°C. In this case, one would expect the water content to dictate collapse, since the greater the amount of unfrozen water available, the more volume reduction would occur. Thus, one would expect potato, having the lowest moisture content, to collapse the least. In fact, it collapsed only 10% during freeze-drying at –28°C, for a total volume loss of 60%. Apple, having an intermediate moisture content, collapsed 75% during freeze-drying, compared to that of the fresh tissue. Celery, having the greatest amount of unfrozen water available, collapsed an additional 50% from the osmosis state, for a total of 75% volume reduction. Based on moisture content, celery should have collapsed more than apple. However, the natural structure of celery may have contributed to preventing some volume loss.

Collapse of tissue osmotically dehydrated in 45% sucrose solution

Differences in collapse are not expected to be great during freeze-drying at –45°C, except for those due to differences in tissue structure. Apple collapsed about 2%, compared to its osmotically treated counterpart, and 50% compared to its fresh state. Celery collapsed 0%, compared to treated celery, for a total of 80% collapse overall. Potato collapsed an additional 10% beyond the osmotically treated sample, for a total of 75% volume reduction (Fig. 5). It is evident that because extensive collapse occurred during the osmotic dehydration step, further volume reduction was not probable. It seems that tissue structure may have just as significant a role in affecting collapse as does viscosity of the CAS.

Based on the amount of available water and its effect on collapse, greater collapse would be expected in apple, less in celery, and the least in potato. Figure 5 shows that 5% reduction occurred in apple, 3% in celery, and 8% in potato, compared to that of their osmotically treated counterparts. However, moisture contents were very low in all these tissues (Table 2), perhaps leading to only slight differences in collapse.

The results of freeze-drying at –28°C, when only individual plant tissues are considered, do support the validity of the theory that available water affects matrix viscosity, which in turn affects collapse.

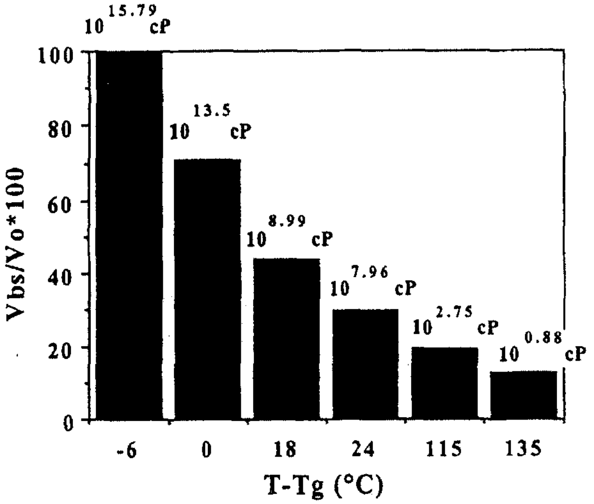

Fig. 6 Shrinkage of celery during drying at different T–T_g values. The viscosity (cP) corresponding to each T–T_g value is shown. The viscosity was estimated using the WLF equation with the universal constants (C1=–17.44, C2=51.6)

Figure 6 shows the variation of structural collapse of fresh celery with dehydration temperature. Although the mechanism of dehydration is different for freeze- drying and air-drying, both processes are governed by pore collapse upon water evaporation and matrix plasticization by water. The extent of collapse increased with increasing dehydration temperature. Because viscosity decreases greatly within a few degrees above T_g (–45°C), significant changes in V_{bs}/V_0 were evident when drying at –55, –45 and –28°C was compared. Above –28°C, additional changes in V_{bs}/V_0 were minimal because the viscosity was already very low.

Conclusions

The effectiveness of freeze-drying depends on the sample temperature during processing. For any given material, collapse occurred above T_g and was dependent on $T-T_g$. For tissues that had the same T_g after freezing, collapse was dependent on the amount of unfrozen water available above T_m'.

This was evident in all experiments conducted at –28°C. The unfrozen water plasticized the matrix, reducing its viscosity, thereby increasing its mobility and causing collapse. Osmosis did not aid in preventing collapse during subsequent freeze-drying.

Differences in the structural nature of plant tissues were not studied in this work. However, it is realized that, along with the impact of unfrozen water content on collapse, the difference in tissue structure between celery, apple, and potato probably also impacted the results.

Future work could include studying the differences in plant tissue composition as they contribute to prevention of collapse. This might point to further means of collapse prevention in more complex food systems.

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