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Water activity and the preservation of plant foods

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Abstract

The general constitution of plant foods, namely of vegetables and fruits, may be described as a watery solution of low molecular weight species, mainly sugars, salts and organic acids and of high molecular weight hydrocolloids, contained in a water insoluble cellular matrix of macromolecules, mostly carbohydrates, including insoluble pectic substances, hemicelluloses and proteins. All of these constituents, to different extents, interact with water and have the ability to lower its vapour pressure; with small molecules this is mainly through polar binding, and with large biopolymers, through surface interactions and capillary effects. For a long time, scientists have realised that the relative vapour pressure, i.e. the water activity, could be much more important to the quality and stability of food than the total amount of water present. Over the past few decades, the glass transition temperature, as well as its dependence on moisture content has also gained interest, as it could become the main determinant of the dynamic of changes in many non-equilibrium, low moisture systems. Processed fruits and vegetables are often low moisture, sugar-rich foods, characterised by colour, flavour and structural properties. The relationships between both a_w and T_g and some important chemical, physical and structural changes which can occur during processing and preservation of fruits and vegetables and their derivatives, are presented.

Keywords: Water activity; Glass transition; Plant foods; Fruits; Vegetables; Ingredients

1. Introduction

For half a century scientists have realised that relative vapour pressure, i.e. water activity, could be much more important to the quality and stability of food than the total amount of water present. The choice of water activity (a_w), rather than moisture content (MC), as the reference parameter in most applications of food processing and storage, is based on a number of widely recognized effects:

- a_w is a determinant for the growth of microorganisms;
- a_w is well related with most degradation reactions of a chemical, enzymatic, and physical nature;
- moisture migration in multidomain foods obey a_w not MC;
- The "monolayer" derived from water vapour sorption isotherm gives an indication of the optimum moisture content in dried foods;
- a_w is easier to measure than MC, and the measure is non-destructive.

Over the past decades, the concepts related to water activity have been enriched by those of glass transition (T_g) (Slade & Levine, 1991), thus providing an integrated approach to the role of water, with special reference to non-equilibrium, reduced moisture food systems. In such foods, the dynamics of changes may be influenced by kinetic properties and may be better predicted by glass transition temperature rather than by water activity.

As a matter of fact, there can be dramatic differences in viscosities at equal a_w for solutions of different molecular weights and complexities. Depending on the solute(s), very high "glass-like" viscosities can hinder diffusion at relatively high water activities, while very low viscosities can allow diffusion, even at a_w close to zero (Fig. 1). When mobility and diffusion are key factors, it is quite evident that the water activity may not be, on its own, a reliable reference parameter, while useful information can be extracted from the glass transition relationships.

On the other hand, T_g is not as easy to measure as a_w, and may not be a representative parameter in multicomponent, multidomain complex foods, where it is often undetectable. The wide range of fruit and vegetable derived foods, includes extremely simple systems, such

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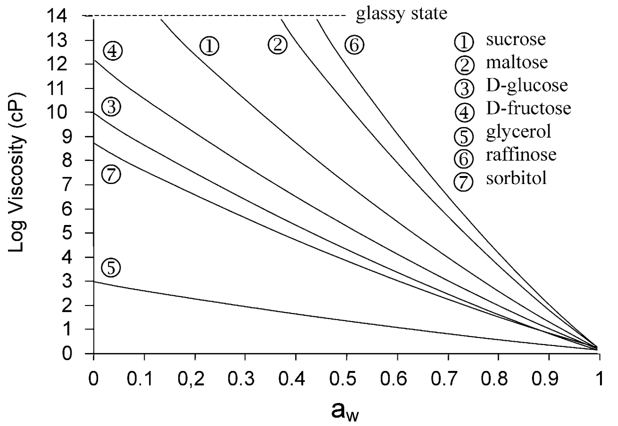

Fig. 1. Estimated viscosity of model solutions as a function of water activity (adapted from Anese, Shtylla, Torreggiani, & Maltini, 1996).

as clarified fruit juices, but also highly complex structures, such as plant tissues, and both the a_w and T_g approach may be required.

The general constitution of plant foods, namely of vegetables and fruits, may be described as a watery solution of low molecular weight species, mainly sugars, salts and organic acids and of high molecular weight hydrocolloids, contained in a water insoluble cellular matrix of macromolecules, mostly carbohydrates, including insoluble pectic substances, hemicelluloses, proteins and, sometimes, lignins. Intracellular air spaces are present in parenchymous tissue and these may be considered as true structural elements, having a very characteristic influence on the perceived texture.

All of these constituents, to different extents, interact with water and have the ability to lower its vapour pressure; with small molecules this is mainly through polar binding and, with large biopolymers, through surface interactions and capillary effects.

Similarly, some constituents will have a strong effect on phase transition temperatures, while others will not. As observed by Aguilera, Cuadros, and del Valle (1998), the T_g of fruits and vegetable tissues almost coincides with that of the juice, and no T_g appears for the cellular matrix alone. While most of the components have a significant effect, either on the water activity, and/or on the T_g, some components, namely hydrocolloids such as soluble pectins, will have only a negligible effect on T_g and on water activity. Nevertheless, they can strongly increase the macro viscosity of the soluble fraction and reduce the tendency of fruit and vegetable extracts to collapse. A scheme of the interactions with water, of these components, and their contribution to a_w and T_g is depicted in Fig. 2.

2. Chemical and enzymatic reactions

The relationships between water activity and reactions of both enzymatic and chemical nature may be rather complex, due to the different ways that water can react in foods (Labuza, 1975), among these are:

- hydrating of polar or ionic groups, which can affect their reactivity;
- dissolution and mobilization of chemical species, allowing them to react;
- hydrating and swelling of biopolymers, exposing new reactive sites;
- increasing diffusion of reactants (plasticization effect);
- decreasing reactant concentration at high water contents (dilution effect).

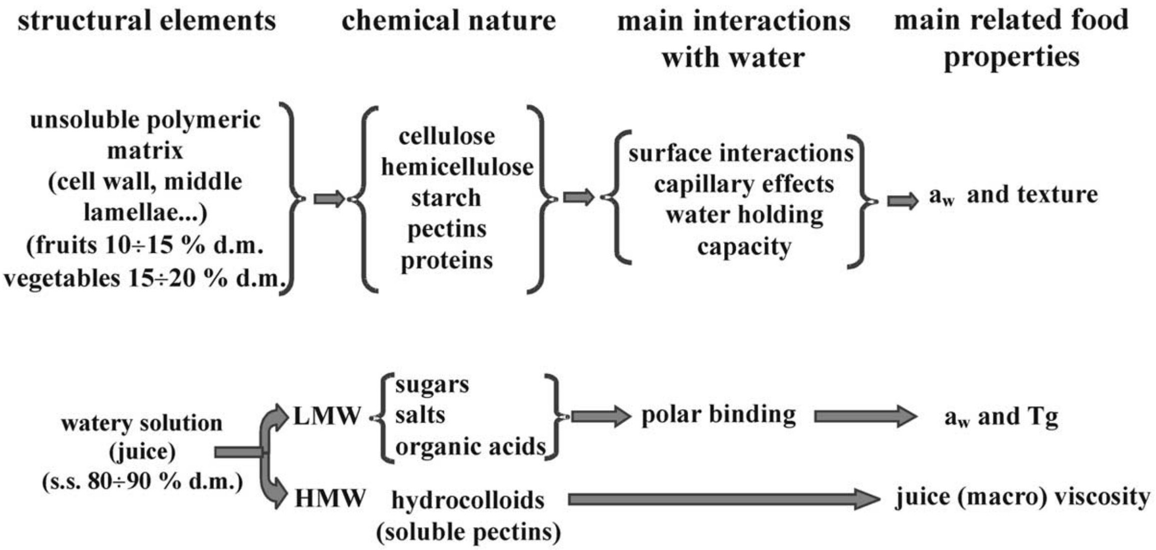

Fig. 2. Basic structural elements of fruits and vegetables.

In addition, water itself can act as a reactant (e.g. hydrolysis), or be a product of the reaction (e.g. condensation of water molecules in the Maillard reaction).

2.1. Oxidative changes

Water may show both anti and pro-oxidant effects, when a system passes from low to high water content. The protective effect of a ''monolayer'' water on foods containing oxidable sites was first observed by Salwin (1962) during storage of dehydrated food items. He suggested that water attached to the sensitive sites should protect them from reaction with oxygen, possibly by excluding absorption of oxygen directly, and possibly by coordinating trace metals or by decomposing free radicals.

According to Labuza (1975) water may act as an antioxidant at low a_w by:

- hydration of trace metal ions
- h-bonding of hydroperoxides
- promoting free-radical recombination,

and act as a pro-oxidant at high a_w by:

- plasticization effect promoting mobility
- dissolution of precipitated catalysts
- matrix swelling, exposing new catalytic surfaces.

As would be expected, a minimum-maximum type curve should result from these effects. While the antioxidant effects mainly affect foods of animal origin, they are also relevant to fruits and vegetables where oxidative bleaching of carotene and lycopene can lead to degradation of colour, flavour and nutritional quality. According to Salwin (1962), degradation of quality was most rapid at water contents below 6.5% for potatoes, 3–4% for shelled walnuts, 1.9% for round red bell peppers and green peppers, and 1.8% for precooked carrots, while a water content close to zero was required for peach juice, where caking, rather than oxidation, is the main degradation mechanism.

2.2. Non enzymatic (Maillard) browning

Non-enzymatic browning occurs mostly in intermediate moisture fruits, fruit concentrates and purees, and dehydrated vegetables, such as potatoes, where undesirable flavour and colour changes can occur. Maillard browning can also lead to desirable effects, as in coffee roasting, cocoa beans, corn flakes, french fries.

Among the most familiar expressions of Maillard browning is the bell-shaped curve which relates the rate of the reaction to water activity, as shown in Figs. 3 and 4 for dried apple slices and an apricot puree, respectively. Maximum browning has been observed in most cases at water activities 0.3–0.7; however, in systems where a low water activity is not associated with a strong increase in viscosity, e.g. in an ethylene glycol-based model (Loncin, 1975), a maximum does not appear and the reaction rate continuously decreases from low to high a_w.

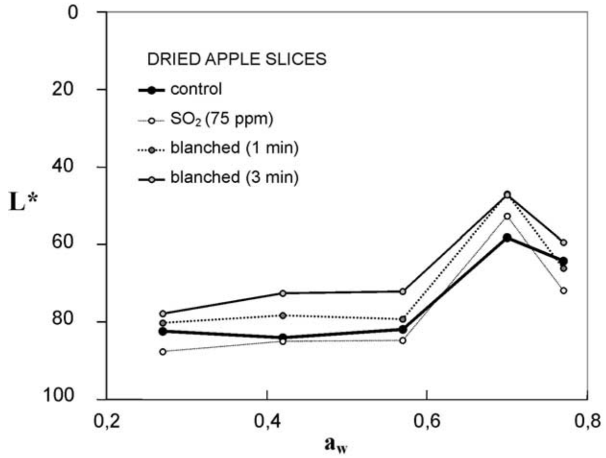

Fig. 3. CIE chromaticity value L^* after 8 weeks of storage at several a_w values. Brown colour development is indicated by lower L^* (adapted from Beveridge & Weintraub, 1995).

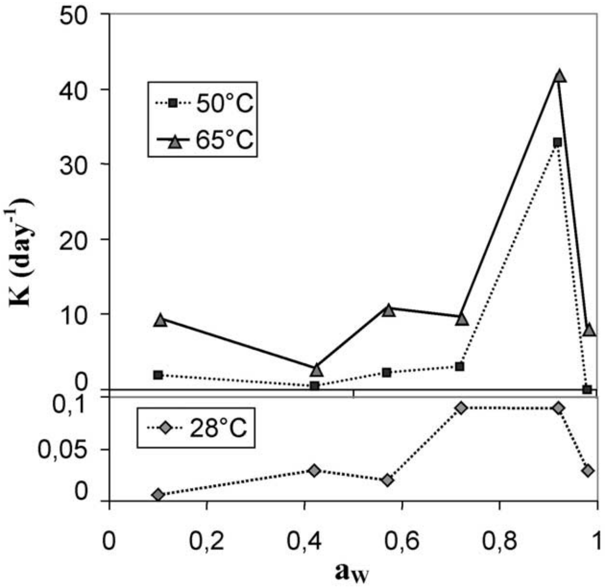

Fig. 4. Reaction rate constant for browning of apricot puree (Piva, Lerici, & Dalla Rosa, 1986).

Since the earliest investigations, an accepted interpretation for the bell-shaped curve in Maillard browning was that, on the low moisture side, the rate is limited by diffusion resistance, which lowers the mobility of reactants and reaction products (Labuza, Tannenbaum, & Karel, 1970; Loncin, 1975). It was considered that diffusion, but also solubilization of reactants, can only occur at a water content above the monomolecular layer on the sorption isotherm, although browning could also develop, to some extent, even below this moisture level. At high water contents and water activities, the rate decreases due to the effect of dilution of the reactants.

Ideally, both the shifting of the bell-shaped curve along the water activity (or the water content) axis and the height of the browning maximum, could be graphically represented with a model where the reaction rate is virtually limited by two independent variables: (a) reactant concentration—the rate increases as the a_w decreases and, (b) reactant diffusivity within the matrix—the rate decreases with the decrease of a_w, and has a tendency towards zero for viscosities above c.a. 10E 12 Pas, i.e. in the glassy state, as is schematically depicted in Fig. 5.

In systems with different reactant concentrations and different ratios of viscosity to a_w, the browning maximum will increase with increasing concentration and shift toward higher a_w in systems with high ratio viscosity/a_w, i.e. with higher molecular complexity (or glass transition temperatures) (Maltini & Anese, 1994). Similar trends can be recognized in many experimental data, such as those from Eichner and Karel (1972), shown in Fig. 6. In the model solutions, both reactant concentration and the ratio of viscosity to a_w decrease, due to increased proportions of glycerol in sugar–amino acid–polyvinylalcohol solutions equilibrated at different water activities. As noted by Eichner and Karel (1972), "on increasing the amount of glycerol, the reaction rate was increased at low water activities and the browning maximum shifted to lower water activities". Even if reactant concentration and diffusivity may be the main controlling parameters, in real foods many additional physical, physico-chemical and structural factors can have an influence on the dynamic of browning in real foods. Some of these parameters are presented in Table 1. Among these are the different roles of water as a solvent, as a plasticizer, as a diluent and as a product of the reaction.

3. Physical and structural changes

Physical and structural changes affecting quality and stability of processed fruits and vegetables include collapse during drying, sticking and caking of dry powders, agglomeration, crystallization, loss of volatiles, loss of crispness and other forms of texture degradation. These changes are strongly related to the glass transition temperature and may occur, in principle, when the T_g drops below the storage or processing temperature, with a rate depending on the difference ($T-T_g$). For such changes, state diagrams become an elective tool for prediction (Fig. 7), while a "critical a_w" may be identified as an operative parameter from a diagram relating sorption isotherm with glass transition curve (Fig. 8) (Roos, 1995). The T_g line on the state diagram poses an upper limit, below which physical changes are avoided. However, these changes can also be prevented or delayed to a considerable extent, when some structuring elements are present. In fruit tissues, although the sugar solution may represent 85–90% of the total weight, cell walls accounting for only 1–3% are responsible for the rigidity and solid like behaviour (Aguilera et al., 1998). When a cell wall skeleton is present, as in whole plant

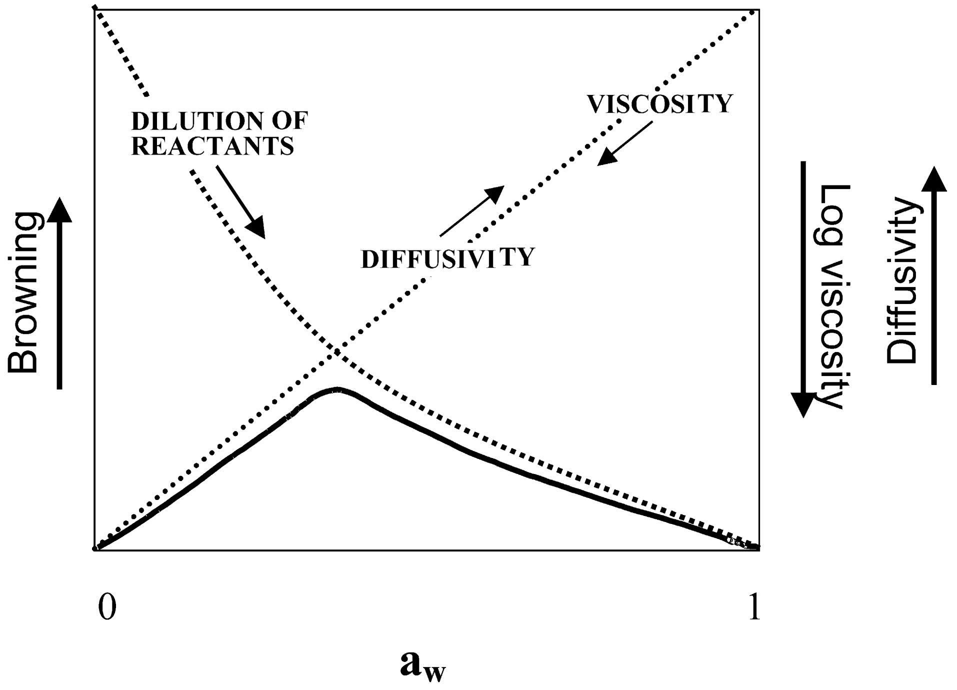

Fig. 5. Schematic representation of diffusivity and dilution of reactants vs. a_w as rate-limiting factors of non-enzymatic browning.

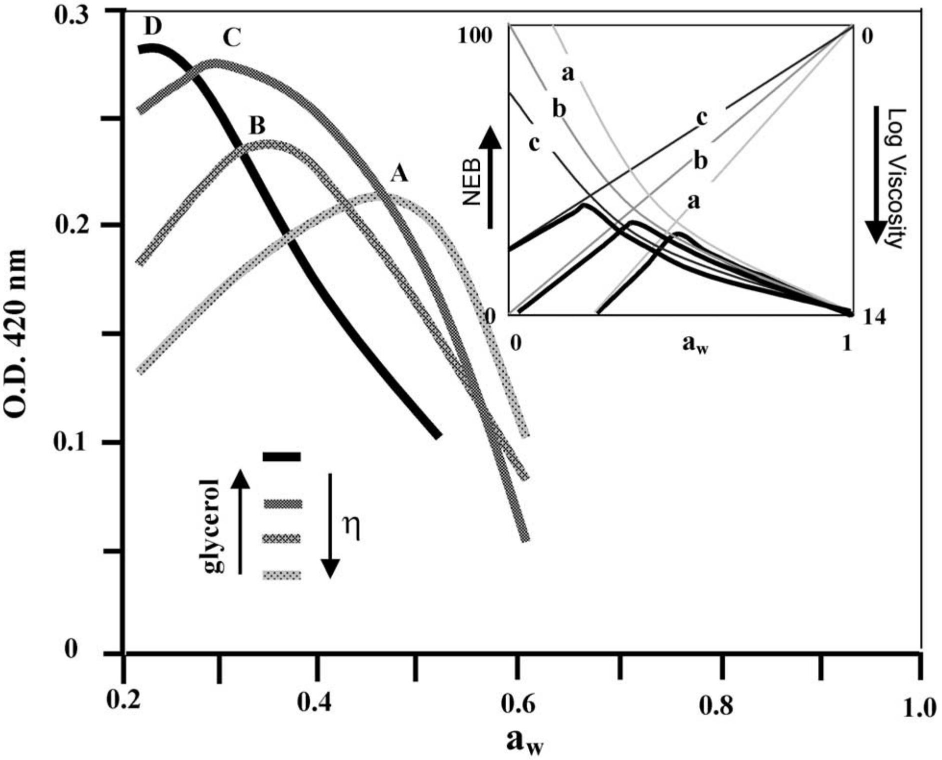

Fig. 6. Changes in optical density, at 420 nm, of glucose–fructose–glycerol–polyvinyl alcohol as a function of water activity. Inset: schematic representation as in Fig. 5. In the figure, when the amount of glycerol increases, both reactant concentration and viscosity decrease ($a > b > c$) (adapted from Eichner & Karel, 1972; Maltini & Anese, 1994).

Table 1
Some physical, physico-chemical and structural factors influencing the rate of non-enzymatic browning

Rate enhancing	Rate limiting
• Reactants concentration (law of mass action) • Diffusivity within the matrix • Water content as a matrix plasticizer (enhances diffusivity) • Solubility in the matrix (affects reactant concentration in the liquid phase) • Shrinkage (collapse) of the matrix (affects diffusion paths for reactants) • Porosity (increases the potential for shrinkage) • Glass-viscous transition (allows reactants to diffuse) • Crystallisation of the matrix (increases reactants concentration in the non-crystalline volume) • Phase separation in non-crystallising systems (increases reactant concentration in the liquid volume) • Water non-miscible components (increases reactant concentration in the water phase) • Possibly, water binding ability of the substrate (subtracts water from the system)	• Reactant solubility • Water content as a diluent • High viscosity (affects mobility and diffusivity) • Water content as a product of the reaction (shifts backwards the equilibrium of the reaction)

tissues, possible physical changes may shift at temperatures much above the apparent T_g. Actually, no T_g has been detected for the cellulose matrix in apples, which may exist in the crystalline state, as pointed out by Newman, Ha, and Laurence (1994), or it may have a T_g higher than thermal degradation (Roos, 1995). Other than cell walls in plant tissues, soluble hydrocolloids and suspended particles can also improve the mechanical properties of fluid extracts and reduce the rate of physical changes during processing and storage. It is noteworthy that neither a_w nor T_g give reliable information on this aspect.

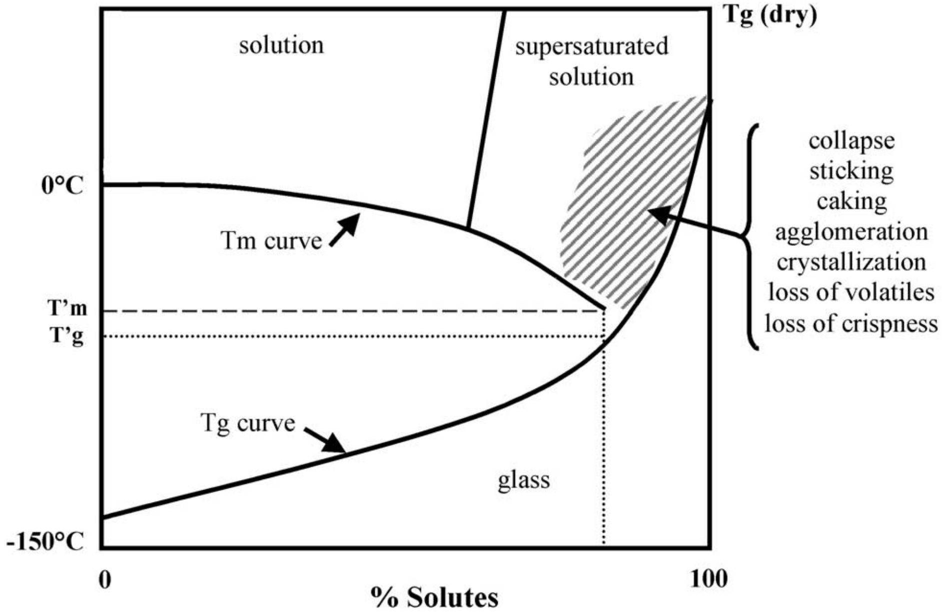

Fig. 7. Glass transition related changes in low moisture non equilibrium foods.

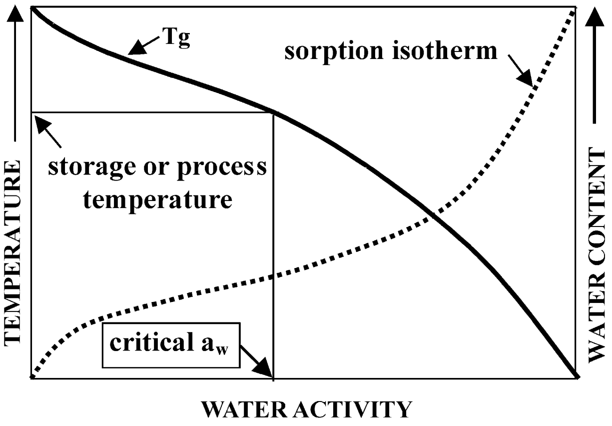

Fig. 8. ≪Critical a_w≫ at which product's $T_g \leqslant$storage/process TC.

3.1. Collapse, sticking and caking

Collapse during drying is due to the viscous flow of the semisolid network which is formed in the initial stages of drying processes. The loss of a porous structure is associated with an irreversible occlusion of the pores and with the formation of a thick viscous body. Reduction of drying rates, loss of volatiles, high residual moisture and poor storage and rehydration properties are among the consequences. Collapse is time-dependent, and its occurrence and prevention depends on the drying technique. In the freeze-drying of depectinized fruit juices, the collapse temperature almost coincides with the T_g' (the T_g of the concentrated unfrozen phase), but the strong macroviscosant effect of both suspended insoluble phases (e.g. pulp filaments) and soluble pectins can increase the critical temperature to well above the T_g' of the juice (Maltini, 1980). In the spray-drying of sugar-rich foods, such as fruit juices, sticking of particles occurs when the chamber wall temperature is 20–30 °C above the T_g of the juice (Bhandari & Howes, 1999). As the T_gs of juices are very low, the spray-drying of pure product is generally not economically feasible, and high molecular weight additives are required. In the vacuum band drying of pure fruit concentrates, a high consistency index of the soluble fraction of the juices (i.e. a high soluble pectin content) was required to avoid collapse, while the presence of suspended pulp had no effects (Maltini, Nani, & Bertolo, 1992). Conversely, both fractions, but mainly the pulp content, were able to improve the drum-drying of fruit puree (Dall'aglio, Carpi, & Versitano, 1990).

Caking is a degradation phenomenon in which a low moisture, free-flowing amorphous powder is first transformed into soft lumps, then into an agglomerated solid, and finally into a sticky material, with a strong reduction of porosity and bulk volume. Collapse, caking and stickiness are related phenomena and are among the most deleterious changes, which irreversibly affect spray dried and freeze dried fruit powders (Aguilera & Stanley, 1999).

From a practical standpoint, caking and collapse differ because the time scale for caking is usually much longer than that for collapse, so that caking during long term storage is much more difficult to prevent. Actually, fruit powders are mainly composed of sugars and organic acids, which are structurally stable in the metastable solid "glassy" state below their glass transition temperature. While vegetables show relatively high T_g dry values, the T_g temperatures of fruit juices are closely related to their sugar/acid compositions, as shown in Table 2. In most cases, the T_g of dry juices is below room temperature, and caking can not be avoided unless the storage temperature is reduced below T_g, or high T_g components, such as sucrose or maltodextrins, are added to the juice.

3.2. Volatiles release

During drying of fruit and vegetable juices, volatiles are entrapped in microregions and both retention and

Table 2
Glass transition temperatures of some sugars, organic acids, and fruits and vegetables

Solutes (T_g°C)		Fruits (T_g°C)				Vegetables (T_g°C)	
Sucrose	67	Apricot	18	Raspberry	41	Celery	58
Glucose	31	Pear	5	Blackberry	22	Cabbage	43
Fructose	5	Apple	18	Orange	45	Carrot	57
Citric acid	6	Strawberry	29	Lemon	11	Potatoes	71
Malic acid	−21	Blueberry	15	Peach	20		

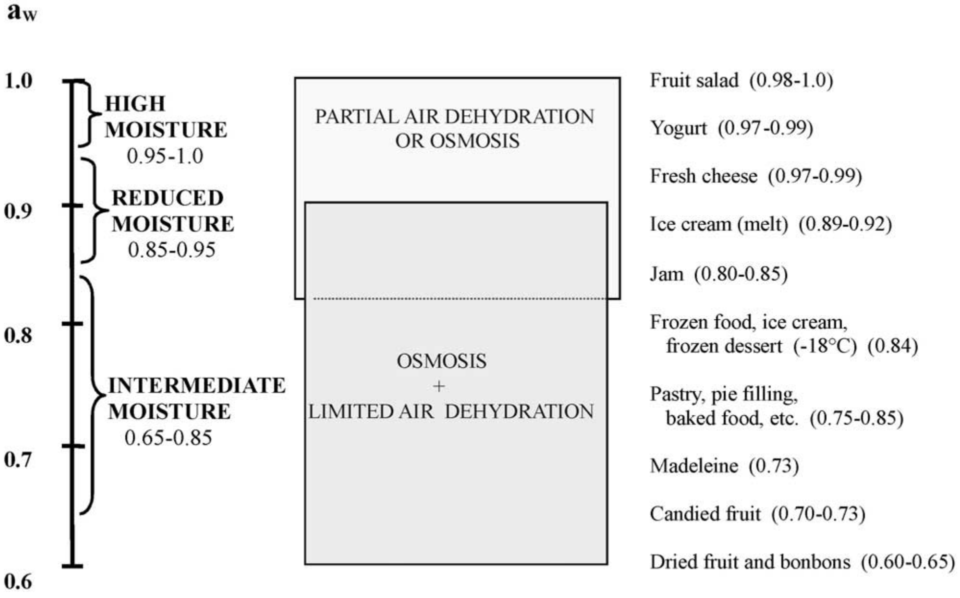

Fig. 9. a_w of fruit ingredients required for some food products.

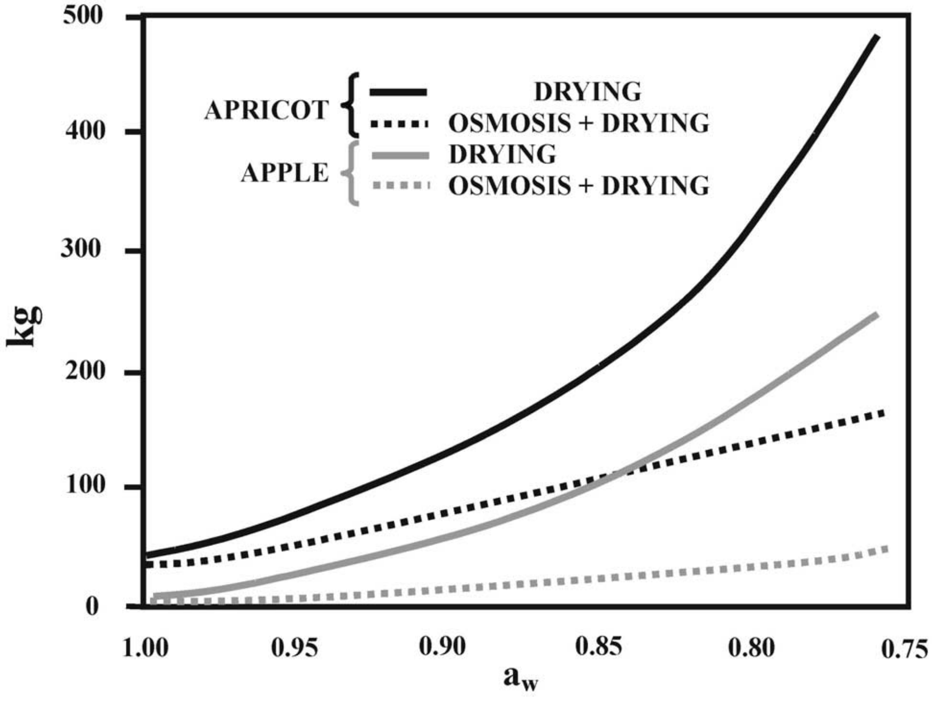

Fig. 10. Texture (maximum force, Kramer shear-press cell) after air-drying or osmosis (45 min, 25 °C, fructose syrup 70° Bx) + air-drying of apple and apricot cubes.

release are considered to be kinetically-governed phenomena. In dry systems, entrapped volatiles are released when T_g drops below the storage temperature (Goubet, Le Quere, & Voilley, 1998; Levi & Karel, 1995; Roos, 1995). In contrast, during moistening of freeze-dried apple cubes, a sharp increase in the release of volatiles have been observed only at about $T-T_g = 50$ °C (Venir, Munari, & Maltini, unpublished data), just before macrostructural collapse (shrinkage). The insoluble structural elements of the fruit tissues may constitute a further physical barrier to the release of volatiles, in addition to the glass transition effect at a microstructural level.

4. Role of a_w in fruit–vegetable ingredients for composite foods

Fruits and fruit pieces are frequently used as basic materials or as additional components in many composite foods and food formulations. In such systems the water activity of the ingredients must be controlled in order to avoid moisture migration. As shown in Fig. 9, water activities in the range 0.6–1 may be required, according to the type of food. For use as ingredients, the fruit a_w is usually reduced by controlled dehydration, but, below a critical value, excess hardening generally occurs. An alternative is to depress the a_w by an osmotic treatment, i.e. by soluble solid intake rather than by loss of water (Torreggiani, 1995). For a_w below 0.9, the combination of osmosis and a limited air-dehydration is usually the best choice. The combination of the thermodynamic effect of solutes on a_w lowering and of the kinetic effect of water content on consistency, can allow texture at a given water activity to be controlled to a considerable extent. An example of such effects is shown in Fig. 10, where the influence is shown of an osmotic step, applied prior to drying, on texture at equal a_w values of apple and apricot cubes.

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