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ScienceDirect
Food Chemistry 106 (2008) 1417–1427
Food Chemistry
www.elsevier.com/locate/foodchem

Review

Antiplasticization effect of water in amorphous foods. A review

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Received 16 October 2006; received in revised form 28 March 2007; accepted 30 March 2007

Abstract

Water is the most effective plasticizer in food matrices, decreasing glass transition temperature (T_g) and mechanical resistance and determining a softening effect with the increasing of its concentration. However an opposite effect (i.e. hardening, toughening) could be observed in some food and in specific moisture or a_w range and this is referred to an anti-plasticization effect. Several are the possible causes for this phenomenon and various are the factors that have been recognized to affect its occurrence in a food matrix: mechanical testing method, mechanical parameter tested, type of food (composition and micro-macrostructure).

In this paper, several studies on anti-plasticization effect of water are reviewed by focusing the attention on the interactions water–food matrix and in particular to those occurring in amorphous cell foods. The different chemical and physical factors that affect this phenomenon are also discussed.

The simultaneous occurrence of a plasticization and anti-plasticization effect of water, even if in different a_w range, and the results of studies on amorphous food matrices may suggest an important effect of water–matrix interaction on the textural properties.

Keywords: Anti-plasticization; Plasticization; Water; Water activity; Texture; Mechanical properties

Contents

1. Introduction

Mechanical properties of foods are determinant to their behaviour in processing, storage, distribution and consumption and the importance of the factors that affect them has been recognized (Roos, 1995). The perceived texture of a food is a more complex concept, as it comprises all physical characteristics sensed by the feeling of touch that are related to deformation under an applied force and thus to the mechanical properties. From a sensorial point of view texture is an important quality attribute and contains

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doi:10.1016/j.foodchem.2007.03.077

features liked and disliked by consumers (Szczesniak, 1988). In dry cereal products, crunchiness and crispness are considered by consumers as indices of freshness, proper technology and good quality, while gumminess, plasticity or sogginess caused by increased moisture disqualify the products (Hsieh, Hu, Huff, & Peng, 1990; Knorr & Kleemair, 1975).

Mechanical properties of foods depend on several compositional, physical and processing parameters and arise from the arrangement of various chemical species (molecules) by physical forces into distinct micro- and macrostructures (Aguilera, 2002). The relative concentrations of chemical species, the physical forces involved in their interactions, the manner in which these elements are spatially arranged as well as the physico-chemical properties exhibited at each successive level, could determine different physical state and structural characteristics of food matrix and, thus, different mechanical behaviour.

Water and temperature are, by far, the most investigated factors in texture studies due to their relevance both in processing and storage of foods and in affecting their quality and stability. Moisture and temperature increase, in fact, could significantly influence the physical state of foods, inducing phase transition that could contribute to define their mechanical properties. In many solid products an increase of temperature and/or moisture could determine a softening effect by inducing the so-called plasticization. This phenomenon is of great relevance in the food field as it could influence processing, shelf life and sensorial acceptability of products.

In the past decades many studies have been carried out on the effects of water and low molecular weight components that, for their effect on the mechanical properties of the food systems, have been defined as plasticizers. From a mechanical point of view, the primary effect of a plasticizer is to increase the workability, flexibility, ductility and extensibility of a polymer by decreasing its mechanical resistance (Sears & Darby, 1982). The free volume theory recognizes as plasticizer the component able to impart a greater free volume per volume of material due to an increase in the proportion of end groups and to its lower glass transition temperature (T_g) in comparison with that of the material (Sears & Darby, 1982; Slade & Levine, 1991). Intermolecular bonds could be weakened or broken by the plasticizer, thus leading to a general reduction in elastic modulus (Seow, Cheah, & Chang, 1999).

Besides water, a plasticization effect has been recognized in food matrices due to the presence of monosaccharides, such as fructose (Peleg, 1996), sorbitol (Gaudin, Lourdin, Forssell, & Colonna, 2000), polyols, among which glycerol (Lourdin, Bizot, & Colonna, 1997; Shogren, Swanson, & Thomson, 1992) and liquid fats. Some of these compounds are able to shift the T_g of the system even at equal moisture content, whilst others (e.g. liquid fats) could simply contribute to increase the fraction of the fluid component able to weaken the intermolecular interactions.

As water is concerned, despite its well recognized and studied plasticizing effect, it has been observed that in some glassy polymer-plasticizer systems, at temperatures below T_g, the increase of plasticizer concentration leads to a harder and tougher structure despite T_g decrease. This has been recognized as 'anti-plasticization' effect and it occurs over a concentration range below the 'plasticization threshold' (Sears & Darby, 1982; Seow et al., 1999; Vrentas, Duda, & Ling, 1988). As well indicated by Seow et al. (1999) the anti-plasticization effect here discussed has a meaning different from that used by Slade and Levine (1991) to indicate the enhancement of the T_g of a material due to the addition of a compound with an higher T_g.

Different are the hypothesis about the causes of the anti-plasticization effect of water on the mechanical properties of food matrix and increasing is the interest of scientists on this phenomenon as documented also by the most recent literature (Gondek & Lewicki, 2006; Marzec & Lewicki, 2006; Moraru, Lee, Karwe, & Kokini, 2002). However, limited are the studies aimed to better understand the relationship between the state of the water, structural (micro- and macro-) and compositional properties and anti-plasticization effect of water in a food matrix.

In this paper several studies on anti-plasticization effect of water are reviewed by focusing the attention on the interactions water–food matrix and in particular to those occurring in amorphous cell foods. The different chemical and physical factors that affect this process are also discussed.

2. Effect of water on textural properties

Water is an important constituent of foods which affects their quality, stability and physical properties. Its concentration could range from values close to zero, as in baked and dry foods, to 98%, as in fresh or liquid foods. Water influences rheological properties of food in liquid and solid state as well. In liquid state it is implied in viscosity and consistency changes, while in solid food matrices water affects their response to force (Lewicki, 2004). In fresh plant foods and vegetables, texture can be attributed to the structural integrity of the primary cell wall and the middle lamella and to the turgor generated within cells by osmosis (Jackman & Stanley, 1995) whilst in some processed products, like cereal extrudates and snacks, the reaching of low water content is determinant for their characteristic brittleness, crispness or crunchiness. In the latter case the moisture increase during storage could affect the starch/protein matrix altering the strength and lowering the sensorial acceptability of the product (Katz & Labuza, 1981).

2.1. Plasticization effect

Water is considered to be the most effective plasticizer in food matrices, decreasing T_g and mechanical resistance (Brent, Mulvaney, Cohen, & Bartsch, 1997; Moraru et al., 2002; Roos & Karel, 1991; Slade & Levine, 1991). Water acquires properties of solvent and promotes mobility of polymer chain (Lewicki, 2004) and crisp, hard or tough materials become soft, extensible and flowable upon hydration.

Water plasticization is a process of great importance mainly in low moisture, cell or porous foods, such as seeds, breakfast cereals or snacks of cereal origin, that in their original or native state are characterized by a crispy and brittle texture, which is relevant for their sensorial acceptability and/or processing.

Textural change in low moisture food materials as a result of water plasticization can be considered as a collapse phenomenon which is often governed by glass transition (Levine & Slade, 1988; Roos, 1995). Removal of water during processing of many products often results in the formation of an amorphous state, which is a non-equilibrium state with time-dependent properties (Beckett, Livings, & Schroeder, 1994; Piazza & Masi, 1997). The physical state of amorphous materials could change from a solid glassy state to a liquid-like rubbery one when the glass transition temperature (T_g) is reached. In formulated foods, as well as in cereal based products, T_g depends on product composition, thermal history as well as on water content. The increase of moisture triggers the decrease of the glass transition temperature, T_g, to below the ambient temperature and a phase transition occurs in the food matrix (Slade & Levine, 1991). Support for this mechanism comes from the known plasticizing effect of water on a variety of bio- and synthetic polymers, which is indeed manifested by lowering the T_g (Fig. 1).

The effect of a plasticizer on synthetic polymers has been explained in terms of two mechanisms: (a) the plasticizer molecules screen off attractive forces between polymer chains and/or (b) the plasticizer molecules enlarge the spaces between polymer chains allowing chain segments greater freedom movement (Alfrey, 1948; Platzer, 1965).

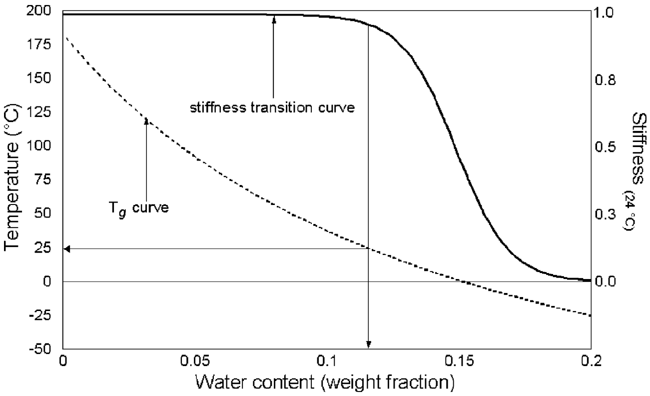

Fig. 1. Modified state diagram showing the decrease of the onset temperature of the glass transition temperature range (T_g) and its prediction with the Gordon–Taylor equation against the water content, and a textural (stiffness) change as described by a transition curve. The critical moisture value depressing the T_g to 24 °C and the corresponding stiffness value are shown with arrows (from data presented by Roos et al., 1998).

Even if plasticization is dependent on the water content or moisture of a food matrix, in studies focused on technological aspects and shelf-life, it has been also related to water activity. This physico-chemical parameter accounts for the state of water in the matrix as affected by the water–matrix interactions and is an index of the freedom of water molecules. Its relationship with the texture of solid foods has been investigated and many studies demonstrated that in specific foods and environmental conditions (e.g. temperature) the a_w changes are related to the mechanical properties and mouthfeel and, in particular, with crispness (Katz & Labuza, 1981; Valles Pamies, Roudaut, Dacremont, Le Meste, & Mitchell, 2000).

Water uptake above a critical moisture content, higher than BET monolayer value, is reflected by the consumer perception of a textural change; this because water causes a decrease in the macromolecular interactions that contribute to the crunchiness sensation due to water–matrix and water–water interactions (Katz & Labuza, 1981). The critical moisture content above which texture is dramatically affected by moisture changes has been expressed in terms of water activity and reported as critical water activity 'a_{wc}' (Sauvageot & Blond, 1991).

The effect of water plasticization on the textural properties of a solid system could be determined by mechanical evaluations. Plasticization of a hard and brittle food could induce a softening effect which is well described by the modification of textural parameters derived from force–deformation curves. Hardness, stiffness, crispness, toughness (Gondek & Lewicki, 2006; Katz & Labuza, 1981; Martinez-Navarrete, Martinez-Monzo, Pedro, & Chiralt, 1998; Roos, Roininen, Jouppila, & Tuorila, 1998; Wollny & Peleg, 1994), as well as the Young's modulus, pseudo modulus or initial slope are among the textural indices more used to evaluate water induced plasticization as they reflect the changes in visco-elastic properties above glass transition in amorphous foods (Roos, 1995). The plasticization phenomena could be also described by an increase of deformability (distance at fracture point) or by extrusion force (Martinez-Navarrete, Moraga, Talens, & Chiralt, 2004; Sacchetti, Pittia, Biserni, Pinnavaia, & Dalla Rosa, 2003). Plasticization dramatically affects the shape of the force–deformation curve by lowering the hardness/stiffness and compression modulus and increasing the deformability; sample failure is evidenced as an event more related to a structural collapse than to a material fracture (Attenburrow, Goodband, Taylor, & Lillford, 1989).

Plasticization is also described by a more smooth and regular trend of the force–deformation curve (Peleg & Normand, 1993a, 1993b; Sacchetti et al., 2003). The peculiar texture of low moisture, crispy and brittle food is characterized by jagged force–deformation curves, irregular and irreproducible, that could be obtained during mechanical testing (Barrett, Normand, Peleg, & Ross, 1992; Borges & Peleg, 1997; Harris & Peleg, 1996; Wollny & Peleg, 1994). The force–displacement relationship can be mathematically treated to yield fairly reproducible mechanical measures of their stiffness (Peleg & Normand, 1993a) or brittleness (Barrett et al., 1992; Peleg & Normand, 1993b). The degree of jaggedness of their force–deformation curves could be also quantified in terms of apparent fractal dimension, mean magnitude of the Fourier power spectrum or by standard deviation of the force or stress fluctuations (Peleg, 1995) and used to give an index of crunchiness. Upon moisture sorption, this characteristic jagged mechanical behaviour is generally lost and a material that is hard and brittle (or crunchy and crispy) when dry become soft and ductile.

Plasticization was also investigated by sensory analysis and generally described as a loss of crispness or stiffness (Hough, Buera, Chirife, & Moro, 2001; Katz & Labuza, 1981; Roos et al., 1998; Valles Pamies et al., 2000).

Changes of mechanical or textural properties are indices of the transition of the food matrix from a glassy to a rubbery state due to the plasticization effect of water and occur when the food reaches and overcomes a moisture or a_w value higher than the material critical value. In the transition region itself the curve depicting the stiffness-moisture is characterized by a sigmoid shape showing downward concavity (Fig. 1).

In the attempt to describe the mechanical properties at and around the transition, a model able to fit the changes of the textural parameters as a function of the main factors affecting the glass transition (temperature, moisture content) or water activity has been developed (Peleg, 1994a, 1994b, 1994c; Peleg, 1995; Wollny & Peleg, 1994). This model could be applied to describe the loss of stiffness or of any other textural parameter (strength, brittleness, etc.) and to characterize the specific influence of water on the food material. The most frequently encountered type has a characteristic sigmoid shape that could be described by the simple Fermi's equation (Peleg, 1994a, 1994b, 1994c).

$$Y_{(X)} = \frac{Y_0}{1 + e^{\frac{X - X_c}{b}}}, \quad (1)$$

where $Y_{(X)}$ is the magnitude of the mechanical parameter (stiffness, crunchiness); Y_0 is the magnitude in dry state; X is the factor causing glass transition (moisture, temperature) or a_w; X_c is a characteristic X value where $Y_{(X)} = Y_0/2$; b is a constant that accounts for the steepness of the relationship around X_c. This model fits a graph in which at low X levels, before plasticization, the $Y_{(X)}$ is parallel to the x-axis and, after plasticization, the textural parameter tends to zero value (Fig. 2a). This model could be modified by the addition of a term which account for residual stiffness after plasticization and assumes the form of Eq. (2) that describes the trend reported in Fig. 2b.

$$Y_{(X)} = \frac{Y_0 - Y_r}{1 + e^{\frac{X - Xc}{b}}} + Y_r, \quad (2)$$

where Y_r can represent a true residual magnitude of the mechanical parameter at high X values.

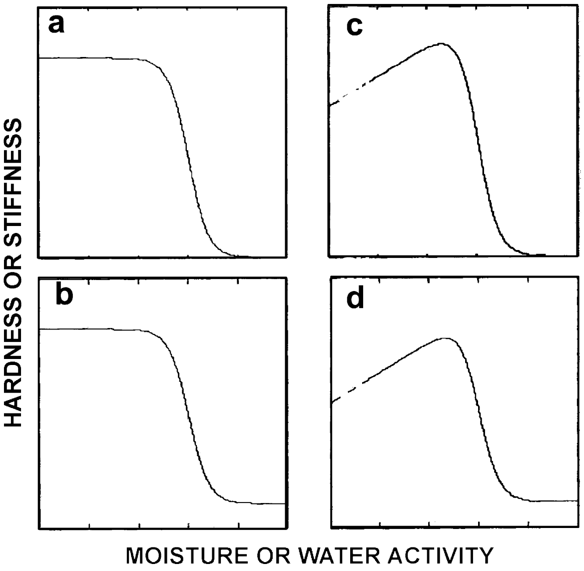

Fig. 2. Schematic view of four types of relationship between stiffness or hardness parameters and water content or activity (adapted from Harris and Peleg, 1996).

In Table 1 are summarized the regression parameters calculated on different food matrices using a_w as independent variable and different mechanical parameters as dependent ones. It is evident that, within the same food matrix, different mechanical properties do not change in the same way upon moisture sorption and different a_{wc} could be determined. The analysis of the a_{wc} values of different food matrices permits to evidence that the plasticization occurs at various a_w or moisture content and, thus, glass transition temperature. Since different composition and structure of food matrix could significantly influence the changes due to plasticization, it could be suggested that plasticization could be considered as a general phenomenon with different manifestations in different materials (Borges & Peleg, 1997).

2.2. Anti-plasticization effect

In the last decades some studies reported that in some dried solid food matrices small amounts of sorbed water led to increased rigidity and firmness with behaviour similar to the anti-plasticization effect observed in synthetic polymers. This effect has been observed in food systems different for nature, composition and production process: precooked and freeze–dried beef (Kapsalis, Walker, & Wolf, 1970; Reidy & Heldman, 1972); corn meal extruded (Halek, Paik, & Chang, 1989), starch extruded (Shogren et al., 1992), gluten and tapioca starch films (Chang, Abd Karim, & Seow, 2006; Gontard, Guilbert, & Cuq, 1993), air-dried apples (Bourne, 1986), coffee beans (Pittia, Nicoli, & Sacchetti, 2007), extruded flat bread (Fontanet, Davidou, Dacremont, & Le Meste, 1997; Marzec & Lewicki, 2006), breakfast cereals (Gondek & Lewicki, 2006) as well as other more complex starch–meat extruded matrices (Moraru et al., 2002).

Table 1
a_w critical values (a_{wc}), calculated by Eq. (1), above which plasticization occurs in different food matrices with regard to the textural parameter used to investigate it

Product	Regression parameters of Eq. (1)				R^2	Textural parameter	Reference
	Y_0	a_{wc}	b	Y_r			
Zwieback	78	0.65	0.0028	27	0.911	Force ($\varepsilon = 0.1$)[a]	Wollny and Peleg (1994)
	1.55	0.64	0.084	1.06	1.00	Apparent fractal dimension	
Cheese balls	21	0.69	0.050	2.5	0.989	Force ($\varepsilon = 0.1$)[a]	
	1.42	0.44	0.024	1.17	1.0	Apparent fractal dimension	
Cheese balls	0.35	0.62	0.087	–	0.998	Force (N) ($\varepsilon = 0.2$)[a]	Harris and Peleg (1996)
	1.40	0.33	0.058	1.04	0.999	Apparent fractal dimension	
Cheese puffs	0.65	0.58	0.110	–	0.985	Force (N) ($\varepsilon = 0.2$)[a]	
French bread	4.9	0.78	0.040	–	0.990	Force (N) ($\varepsilon = 0.2$)[a]	
Pumpernickel	5.2	0.84	0.005	–	0.980	Force (N) ($\varepsilon = 0.2$)[a]	
Kidney beans	150	0.75	0.003	40	0.990	Toughness (mJ)	Borges and Peleg (1997)
Chickpeas	475	0.58	0.15	100	0.991	Breaking force (N)	
	510	0.70	0.052	72	0.987	Toughness (mJ) ($\varepsilon = 0.2$)[a]	
	660	0.52	0.11	0	0.997	Pseudo-modulus (N mm^{-1})	
Almonds	240	0.67	0.22	1	0.993	Pseudo-modulus (N mm^{-1})	
Hazelnuts	70	0.58	0.17	20	0.992	Pseudo-modulus (N mm^{-1})	

a_{wc} values are reported together with other regression parameters and goodness of fit.

[a] ε is strain.

In general the anti-plasticization effect of water has been mainly observed in systems that, for their chemical composition and low moisture content, are characterized by a glass transition temperature (T_g) higher than ambient temperature. T_g of reduced moisture foods is generally higher than the range of temperatures over which they are normally stored and their quality is determined. In such conditions these food matrices are generally glassy, amorphous solids and present a brittle and fragile texture. Upon hydration, a maximum of certain mechanical properties have been found over the low to intermediate moisture content or water activity range above which, upon further water increase, a plasticization effect occurs (Fig. 2c and d).

The moisture or the corresponding a_w ranges in which anti-plasticization and the eventual plasticization effect occur could be defined using a modified form of the Fermi's equation (Harris & Peleg, 1996; Peleg, 1995) that describe the trends reported in Fig. 2c and d.

$$Y_{(X)} = \frac{Y_0 + CX}{1 + e^{\frac{X - X_c}{b}}}, \tag{3}$$

$$Y_{(X)} = \frac{Y_0 - Y_r + CX}{1 + e^{\frac{X - X_c}{b}}} + Y_r, \tag{4}$$

where Y_r can represent a true residual magnitude of the mechanical parameter at high X values and C is a rough measure of the slope of $Y_{(X)}$ before the drop of the mechanical parameter.

The type of system and the measured physical property greatly affect both the anti-plasticization range and the 'plasticization threshold'. Moreover, the exact range of moisture and the corresponding water activity in which the anti-plasticization occurs and reaches its maximum could vary depending on the type of food. In cheese balls and French bread croutons Harris and Peleg (1996), observed an increase in stiffness as the a_w rose from 0.11 to 0.5 and 0.6, respectively, and only at higher hydration degree the same food matrices showed a steep decrease in the mechanical properties. They suggested that at moderate levels of a_w the partially plasticized matrix becomes more cohesive, a higher resistance is offered upon force application and higher energy is needed to disintegrate it. Not only the different composition but also structural characteristics are, obviously, implied in the different anti-plasticization and plasticization range observed by the two food products.

The phenomenological observations, however, do not explain why starting from an almost dry or low moisture content matrix, at increasing hydration degree a plasticization effect does not occur. It could be suggested that the first and earlier water sorbed by a water compatible glassy polymers causes a mechanical anti-plasticization effect independent of its kinetic effect in lowering the T_g of the polymer–water blend below the T_g of the neat polymer (Slade & Levine, 1995).

Different and not well defined are the possible factors implied in anti-plasticization which have been identified by studies carried out in synthetic polymers as well as food matrices (Seow et al., 1999): a reduction of the free volume of the plasticized system (Anderson et al., 1995; Vrentas et al., 1988), polymer–diluent interactions that create steric hindrance and decrease segmental mobility, stiffening action due to the presence of the rigid plasticizer molecules adjacent to polar groups of the polymer (Anderson et al., 1995) or decreased friction (Simon & Ploehn, 2000). Some authors suggested also a crystallization effect on the increased mechanical properties but this hypothesis did not found confirmation (Guerrero, 1989). However, until now, anti-plasticization appears as a complex phenomenon in which several causes are interrelated.

Since the plasticizer properties and polymer–diluent interaction are retained to be a possible cause of the anti-plasticization effect, it should be taken in consideration that the interactions water–matrix affect the mobility and the physico-chemical properties of water. Thus, changes in water properties resulting from such interactions were hypothesized as possible causes of mechanical anti-plasticization effect in foods (Seow et al., 1999).

3. Anti-plasticization as described by textural or physical tests

Some textural tests could be more or less sensitive than other to anti-plasticization, thereby affecting the magnitude of the effect observed in a given system.

Limited is the literature on experiments performed to compare the results of different types of mechanical test (fracture, tensile, compressive) applied to food materials undergoing water anti-plasticization. In a study carried out on hot-pressed pullulan–starch blends containing 10% sorbitol or xylose, the maximum stress, determined by flexural and tensile test, was increased by water uptake, while Young's modulus was decreased (Biliaderis, Lazaridou, & Arvanitoyannis, 1999). In tapioca starch films, tensile strength, strain at breaking and toughness were increased upon hydration but tensile modulus and T_g were decreased (Chang, Cheah, & Seow, 2000a). Chang, Cheah, and Seow (2000b) measured the fracture behaviour of dried bread by three point bend test and compression test and evidenced an anti-plasticization effect of water by analysing the compressive fracture stress but not by analysing the compressive and flexural modulus as well as flexural strain.

The possible causes of these results are of different nature. At first, some authors hypothesized that the variations in the response to textural testing may arise due to differences in sensitivity of the different methods which could influence the detection of certain changes in mechanical behaviour (anti-plasticization–plasticization) of food matrices at different a_w (Chang et al., 2000b). This could be true if we consider that different are the forces that act on a material when a tensile, bending or compressive uniaxial test, is applied. The same authors, however, suggested that opposite effects induced by water sorption as evaluated by similar textural tests could reflect the different macro-structural properties of the food matrices under study. Upon application of the same force, relatively compact materials could show different fracture behaviour than highly cellular or porous material. In dry porous materials with relatively thin cell walls that undergo rapid brittle fracture upon mechanical stress, the moisture-induced anti-plasticization leads to a more rapid brittle fracture at similar, or even lower, strain while these cell walls are still in the glassy state (Fig. 3a). On the contrary, stiffening of compact glassy materials induced by water seems to alter the fracture mechanism from an unstable brittle fracture at low strains to an elastoplastic fracture at higher strains (Fig. 3b). The uniaxial compression, rather than three-point-bending test could be better used to detect anti-plasticization in cellular glassy product, whilst flexural experiments seems more useful in more compact glassy starch materials (Attenburrow, Davies, Goodband, & Ingman, 1992; Nicholls, Appelqvist, Davies, Ingman, & Lillford, 1995).

Not only the type of test could affect the manifestation of the anti-plasticization but also the type of parameter used to investigate it. In fact, by the application of the same testing method to a material undergoing hydration, certain parameters could evidence an immediate plasticization effect, whilst other remain practically unaffected or show an anti-plasticization effect. Katz and Labuza (1981) evidenced an anti-plasticization effect of water on snack foods by measuring compression work and cohesiveness but not when the initial slope of compression curve was measured. Martinez-Navarrete and Chiralt (1995) evidenced an anti-plasticization effect of water on turron by TPA analysis of hardness and chewiness but not by measuring cohesiveness or elasticity. Valles Pamies et al. (2000) analysed the texture of extruded cereals by puncture test and evidenced water anti-plasticization on hardness and crackliness but only plasticization on crispness. Martinez-Navarrete et al. (2004) tested wafer texture by three point bend test and evidenced an anti-plasticization effect of water by taking into account the firmness and firmness to strain parameter but not by taking into account the strain at fracture. Other authors (Battacharya, Narashima, & Battacharya, 2005) applied a compressive test on dhal and evidenced an antiplasticization effect of water by firmness testing but not by testing the limit of linear strain. Pittia et al. (2007) found that fracture force and energy of green coffee beans tested

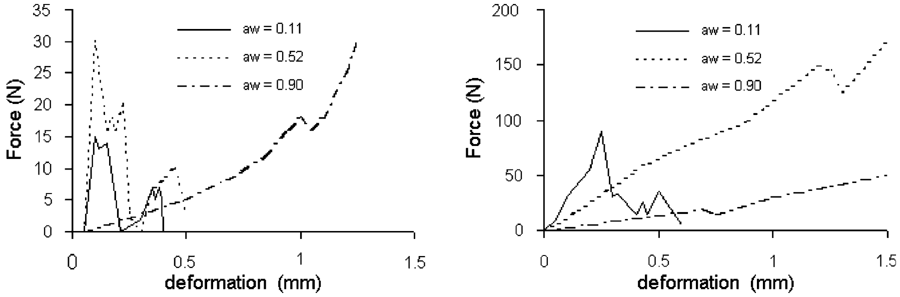

Fig. 3. Evolution of the force–deformation profile of coffee beans undergoing anti-plasticization with the increasing of water activity: (a) dark roasted coffee beans; (b) green coffee beans (from data presented by Pittia et al., 2007).

by compression evidenced an anti-plasticization effect of water upon hydration whilst compressive modulus and deformability did not. Moreover, in the same anti-plasticization range, fracture and deformability showed a progressive increase but above the critical a_w value, where a plasticization effect was observed, deformability showed to reach a plateau level.

These results seem to evidence that in general anti-plasticization is better manifested when force (fracture, breaking, compression, tensile), energy or work (stiffness, toughness) are used to describe the textural characteristics of a product, whilst other mechanical properties, such as deformability, modulus (Young's or pseudo) and initial slope, evidence a plasticization effect in the same experimental conditions. Other physical parameters used to describe crispness or brittleness of food such as the jaggedness of force deformation curve and acoustic emission are not able to describe an anti-plasticization effect of water even when the stiffness or hardness did it (Attenburrow et al., 1992; Borges & Peleg, 1997; Harris & Peleg, 1996; Van Hecke, Allaf, & Bouvier, 1998).

In some cases, in brittle materials undergoing anti-plasticization upon moisture uptake (Fig. 4), the characteristic stress–strain or force–deformation curve described by a peak stress at the first main fracture anticipated and/or followed by a series of fractures at lower stresses and characterized by an irregular and jagged profile shows a progressive change towards a smoother curve in which fracture occurs at higher deformation (Hsieh et al., 1990; Martinez-Navarrete & Chiralt, 1995; Martinez-Navarrete et al., 2004; Pittia et al., 2007). The smoothening of the force–deformation curve upon hydration is typical of foods undergoing plasticization (Peleg & Normand, 1993a, 1993b; Sacchetti et al., 2003). In other cases (Fig. 3b), with the increasing of hydration within the anti-plasticization range, the stress deformation curve shows an evolution from the characteristic curve of a brittle material to a curve in which stress continues to increase after a bio-yield point with increasing deformation, due to compression or densification of the material, and the jaggedness of the profile is reduced (Borges & Peleg, 1997; Harris & Peleg, 1996; Martinez-Navarrete & Chiralt, 1995; Pittia et al., 2007). These behaviours suggest an evolution of the fracture mechanism towards a plastic failure, usually associated with polymeric materials in the leathery or rubbery state, even in foods undergoing anti-plasticization.

Food texture could be measured not only by mechanical tests but also by sensory analysis and, from a sensory standpoint, anti-plasticization is perceived as an hardening of the foodstuff (Valles Pamies et al., 2000) which becomes less crispy (Katz & Labuza, 1981; Valles Pamies et al., 2000).

Both mechanical and sensory data may confirm the idea that in most cases the anti-plasticization effect could be considered as a mere hardening or 'toughening' effect where sorbed water simply increases the energy and force required to fracture or break a foodstuff. The most plausible explanation for this phenomenon is that plasticization, which stems from the ability of the molecules to reorient themselves, reduces the material brittleness and inhibits the ability of cracks to propagate; this allow the material to absorb more mechanical energy and to develop higher stresses (Peleg, 2002). This explanation is also in accordance with that given by Attenburrow and Davies (1994) which observed that the hardening effect severely limited the number of fractures as described by the number of acoustic emission events.

4. Physico-chemical properties of food matrix affecting antiplasticization effect

4.1. State of water in food

The effect of the state of water on the anti-plasticization effect as described by mechanical changes has not been extensively discussed in the literature. In general it could be observed that the anti-plasticization effect of water, similarly to the plasticization, was always observed at a moisture content, or the corresponding a_w value, higher than the respective monolayer values (Hsieh et al., 1990; Kapsalis et al., 1970; Martinez-Navarrete & Chiralt, 1995;

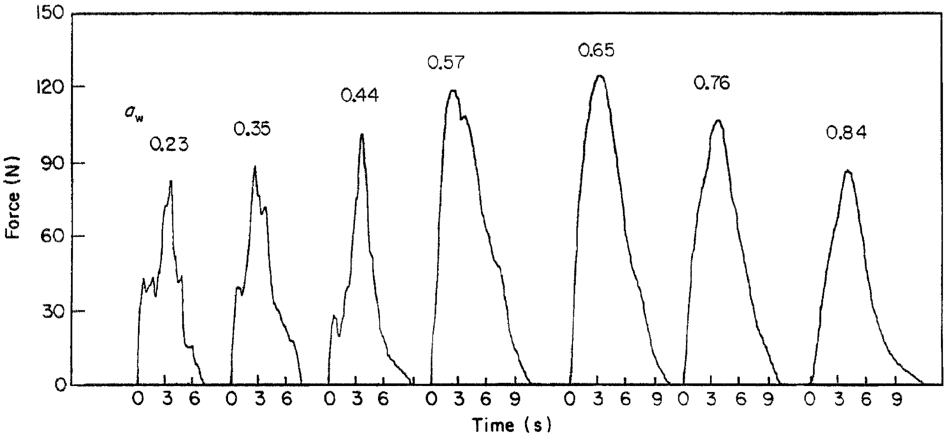

Fig. 4. Evolution of the force–time profile of a rice cake undergoing anti-plasticization with the increasing of water activity (adapted from Hsieh et al., 1990).

Martinez-Navarrete et al., 2004; Marzec & Lewicki, 2006; Pittia et al., 2007) even if, in some cases, for given textural parameters, an anti-plasticization effect was observed at lower moisture content (Martinez-Navarrete et al., 2004; Marzec & Lewicki, 2006).

The anti-plasticization threshold could be thus identified as a moisture value higher or around the BET value. This could confirm the hypothesis that the first and earlier sorbed water molecules are more likely to cause mechanical anti-plasticizing effect independent of their kinetic effect in lowering the T_g of the polymer–water blend below the T_g of the neat polymer (Seow et al., 1999). The anti-plasticization effect of water could be, thus, discussed by taking into account polymer–water interactions which could affect the state of water in food such as: the formation of supplementary hydrogen bonds between water and the polymeric food matrix (Gontard et al., 1993), the binding of water to the absorbent surface of polymeric structures (Benado & Rizvi, 1985; Leung & Steinberg, 1979), and the more 'structured' effect of water in the propinquity to macromolecular surfaces (Etzler, 1991).

The anti-plasticization effect which has been observed in adsorption studies was also evidenced in desorption conditions during coffee dehydration (Pittia, Dalla Rosa, & Lerici, 2001) and in this case the hardness and fracture energy of the samples decreased despite of the increase of normalized density which, in turn, was determined by structural collapse (Fig. 5).

In the case of roasted coffee beans textural changes were studied as a function of moisture and a_w and it was evidenced an anti-plasticization effect of water above the BET monolayer value (Pittia et al., 2007) whilst the plasticization thresholds for differently roasted beans were calculated to occur around an a_w value corresponding to the upward concavity of the sorption isotherm, when the monolayer is completely hydrated and the state of water changes from hydration water to physically entrapped water (Fig. 6). The critical moisture content for plasticization was calculated from the sorption isotherm and, in turn, corresponded to the moisture content at which T_g of roasted coffee occurs at ambient temperature.

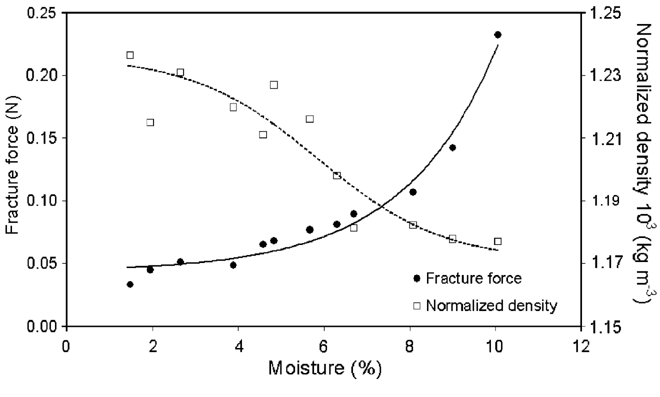

Fig. 5. Variation of normalized density and fracture force of raw coffee beans during water desorption at 95 °C in air forced oven (from data presented by Pittia et al., 2001).

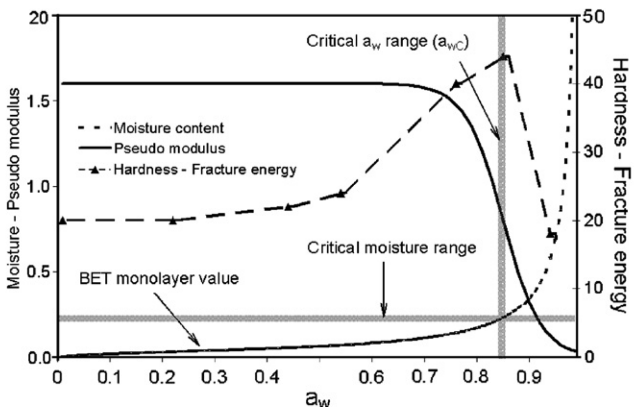

Fig. 6. Schematic view of hardness and pseudo modulus relationship with water activity and moisture sorption isotherm in roasted coffee beans (from data presented by Pittia et al., 2007).

The anti-plasticization effect of water in food occurs in the glassy state at temperature lower than T_g. Hardening effects observed in food at high moisture, above the corresponding T_g values (Hsieh et al., 1990; Kapsalis et al., 1970), may be due to crystallization or to association of polymer chain which is facilitated by enhanced molecular mobility in the rubbery state and do not depend on the effect of water as anti-plasticizer (Seow et al., 1999).

4.2. Food composition

Food composition could dramatically affect the anti-plasticization effect of water; this because the functional groups of molecules present in food as well as the spatial conformation of the molecules themselves could affect the food–water interactions (Lewicki, 2004).

The anti-plasticization effect was observed in wheat starch gels heated at 90 °C but not in gluten gel heated at the same temperature (Attenburrow et al., 1992). While gelatinized starch is highly hydroxylated and very hydrophilic, gluten proteins are water insoluble amphiphilic compounds rich in non-polar amino acid, moreover the hyper-aggregation of protein to form the gluten structure could completely change the protein conformation by favouring the formation of hydrophilic and hydrophobic interactions and the eventual formation of structures physically segregated from water such as bubbles and oil droplets (Eliasson & Larsson, 1993). Since segregated physical structures could hardly interact with any absorbed water they could limit the water effect whether it is a plasticization or anti-plasticization one. This different behaviour of starch and protein determines low water binding energy of starch–gluten mixtures rich in gluten and higher binding energy in mixtures rich in starch (Xiong, Narshimham, & Okos, 1991).

As far fats are concerned, Borges and Peleg (1997) showed that nuts rich in oils evidenced a more moderate plasticization upon moisture uptake than legumes and water did not determine any anti-plasticization effect in nuts. The limiting effect of fat content on water induced plasticization was also observed by Saleem (2005) in a study on biscuit cracking at different water content.

Cereal extrudates containing 20% sugar, which is hygroscopic and limit water availability due to competition with starch for available water, underwent anti-plasticization at an a_w higher than 0.7 which is much higher than that of a sugar-free extrudate ($a_w > 0.2$) (Valles Pamies et al., 2000).

The relationship between water activity and textural parameters (hardness or breaking energy) was also investigated in extruded wheat and rye flat bread. At low water activity the anti-plasticization effect was more evident in wheat bread than in rye bread; this difference was attributed to the chemical composition of the two types of bread. Rye bread, in fact, contains pentosanes which strongly bind water and hinder the anti-plasticization effect due to restricted interaction of water with food macromolecules such as starch and protein. At higher water activity the effect of composition was no more important because the amount of water was sufficient to influence the mechanical behaviour of the bread matrix and to determine an anti-plasticization effect (Marzec & Lewicki, 2006).

In consideration of literature data, it could be suggested that hydrophobic compounds, which show very weak interaction with water could limit the anti-plasticization effect of water in foods, whilst highly hygroscopic compounds, which strongly bind water, could limit the anti-plasticization only at low a_w values by shifting the anti-plasticization threshold at higher water activities.

4.3. Structure and physical properties

Food structure and physical properties could affect the mechanical properties as well as water state in food. In fact, the effective water diffusivity in foods, as well as free water content, highly depend on pore structure and particle size distribution (Peppas & Brannon-Peppas, 1994; Xiong et al., 1991).

The anti-plasticization effect upon moisture sorption is more evident in dense samples which show lower values of ‘free’ water and less pronounced in samples with low density (Halek et al., 1989). This result confirms the hypothesis that the state of water plays a fundamental role in the determination of the plasticization effect. Even if the results of Halek et al. (1989) did not permit to evidence different anti-plasticization thresholds in foods with different porosity, the data suggest that the plasticization effect of water occurs at higher water contents for high density samples probably due to their higher water binding properties.

The response of a food material to compression force in the anti-plasticizing range of water activities could be influenced by the internal microscopic structure of the material. Gondek and Lewicki (2006) studied the plasticization effect on breakfast cereals and observed that corn flakes underwent a hardening and toughening effect with the increasing of water content over a critical water activity value around 0.4, while in wheat bran flakes anti-plasticization was not so evident. In corn flakes, which present a rather homogenous porous structure with continuous air cell walls matrix, the anti-plasticization effect was little affected from water content at low water activities. At $a_w > 0.4$ the water strengthened the cell wall matrix and increased resistance to compression. This anti-plasticization effect was not evidenced in wheat bran flakes which have a not homogenous and rather of agglomerate structure with open porosity.

The anti-plasticization effect of water in highly porous roasted coffee occurs at higher a_w values than in dense green coffee (Pittia et al., 2007). Both the high water binding capacity of green coffee (due to higher sugar content) and its cellular structure could limit the anti-plasticization effect of water at low moisture content, thus the anti-plasticization threshold was at a_w values much higher than the BET monolayer value. In roasted coffee the anti-plasticization threshold was expected to occur at lower a_w values but, on the contrary, it occurred at higher a_w and the anti-plasticization effect was more limited. In the light of the results obtained by Gondek and Lewicki (2006), the non-homogeneous open porous structure of roasted coffee induced by toasting could play a major role in the manifestation of this textural behaviour.

Anti-plasticization effect largely depends on the type of physical structure. Dried cellular structures with rather intact cell walls could undergo to an anti-plasticization effect upon moisture content (Bourne, 1986; Borges & Peleg, 1997; Pittia et al., 2007) and the same behaviour was showed by cell foods such as extruded or puffed foods (Hsieh et al., 1990).

In fresh plant tissues, besides cell wall structure, an important role on tissue strength and macroscopic fruit firmness is played by turgor pressure. It is exerted by intracellular liquids on the cellular membrane and cell wall and imparts turgidity, rigidity, crispness and a fresh appearance to the plant tissue. Turgor is lost when fruits or vegetables are dehydrated, through transpiration, or when they cease to respire (Aguilera & Stanley, 1999). During transpirational dehydration the elastic modulus decreases rapidly with decreasing water potential and increasing water deficits. When the water deficits increases beyond the turgor loss region the rate of this decrease is largely reduced (Herppich, Herold, Landahl, & De Baerdemaeker, 2003). Water addition to partially dehydrated plant tissues could further exert an anti-plasticization effects due to additional water effects on turgor.

Foods without a cell or a close porous structure could show or not anti-plasticization and this could depend not only on structural characteristics but also on the interactions between water and the polymeric food structure (e.g. gluten is porous but do not undergo anti-plasticization upon moisture uptake).

5. Conclusion

The role of water on the textural properties of cellular amorphous food matrices has generally viewed as plasticizer exerting a softening effect upon moisture sorption, even if on some amorphous matrices plays also an opposite effect which is generally defined anti-plasticization. In most cases this is a substantial hardening or stiffening effect since it is accompanied by an evolution of the fracture mechanism from a brittle to an elastoplastic failure.

Even if the scientific community has given much attention to plasticization, also the anti-plasticization effect of water could influence food quality. Sensorial acceptability of anti-plasticized foods could be diminished by the hardening effect and/or their adequacy to processing could be reduced as in case of grinding of cereals and seeds.

The hardening or toughening effect upon hydration generally occurs in certain materials below or around the T_g, in a moisture (or a_w) range and with a maximum depending on food composition and structure. It seems that the interactions water–food matrix components play a relevant role as they are strictly related to both chemical and structural properties of the material. The contemporaneous occurrence of a plasticization and anti-plasticization effect of water even if in different moisture or a_w ranges may suggest an important effect of water–matrix interaction on the textural properties.

To achieve a better comprehension of the anti-plasticization effect of water in amorphous cellular matrices it is necessary a deeper investigation on the state of water in the material by calorimetric and/or NMR analyses as well as on the macro- and micro-structural changes induced by water upon hydration.

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