

Role of Water State and Mobility on the Antiplasticization of Green and Roasted Coffee Beans

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ABSTRACT: The effect of water on “antiplasticization” and plasticization of green and roasted coffee was studied by textural analysis, sorption isotherms, differential scanning calorimetry (DSC), and nuclear magnetic resonance (NMR). From BET monolayer value to $a_w = 0.61$ and 0.75 for green and roasted coffee, respectively, the solid matrix hydration occurred and water induced hardening. Very short NMR T_2 values and the concomitant absence of any DSC endothermic peak assignable to water freezing were observed at these a_w values. When solid matrix hydration was completed, water started to act as a plasticizing agent, the compressive modulus started to decrease, and NMR revealed the appearance of a new proton pool with increased mobility. According to DSC, only when the plasticizing effect became important did water present enough mobility to freeze. Above this moisture value ($a_w = 0.78$ and 0.86 for green and roasted coffee, respectively), water determined a decrease of bean hardness and a further decrease of the elastic modulus.

KEYWORDS: coffee beans, texture, antiplasticization, plasticization, sorption isotherm, freezable water, transverse relaxation time

INTRODUCTION

Coffee beans are hygroscopic matrices and can readily take up moisture when exposed to the environment during storage. The increase of moisture, however, determines undesired textural changes, among which are the loss of the characteristic brittleness and fragility of the roasted coffee beans¹ and a hardening effect occurring on both green and roasted beans² that could increase the energy necessary to apply during grinding.

In many glassy foods an increase of moisture determines a phase transition, which induces a softening effect defined as “plasticization”.^{3,4} Water acts as a plasticizer by increasing the workability, flexibility, ductility, and extensibility of the polymer matrix and by decreasing its mechanical resistance.⁵ Intermolecular bonds could be weakened or broken by the plasticizer, thus leading to a general reduction of the elastic modulus.⁴

As far 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 its concentration leads to a harder and tougher structure despite the T_g decrease. This effect, often defined as “antiplasticization”, has been observed in polymeric systems of different nature, composition, and production process, and in food systems it occurs within a moisture range below the plasticization threshold.^{4–6} Various hypotheses have been developed to explain this phenomenon: stiffening action due to the formation of stable bridges between water and polymer polar groups; increased crystallinity induced by an increase in free volume; polymer–plasticizer interactions that cause the relaxation of low-density regions in a glass and enable the rearrangement of the polymer chains, thus resulting in the densification of the material; “hole filling” by the solvent, resulting in the reduction of free volume and suppression of motion; solvent

effect leading to the disappearance or decrease in the amplitude of sub- T_g relaxation processes and concomitant reduction of free volume.^{4–6} Among these theories, much attention has been recently given to the free volume reduction.⁶

In foods, the so-called antiplasticization occurs in a moisture range above the Brunauer–Emmet–Teller (BET) monolayer value, and the plasticization threshold could vary over a wide range of moisture levels depending on the type of matrix.^{4,6} Even if the term antiplasticization has been widely used to describe a hardening/toughening upon moisture absorption, in some cases, plasticization effects (i.e., decrease of elastic modulus) were observed in the moisture range in which the so-called antiplasticization occurs; thus, this phenomenon could be better depicted as a moisture hardening/toughening effect,⁴ which could be probably caused by a reduced ability of fracture to propagate.⁷

The occurrence of moisture toughening and plasticization effects in different moisture ranges may suggest an important effect of water–matrix interaction on the textural properties.^{4,6} To the authors' knowledge, there is a lack in studies aimed to better understand the relationship between the status of the water and the hardening effect of water in coffee beans through a multianalytical approach based on sorption isotherms, thermal analysis, and nuclear magnetic resonance (NMR).

The approach of combining different techniques to better investigate the status of water in several food systems has been recently adopted. Sorption isotherms, thermal analysis, such as differential scanning calorimetry (DSC), and NMR can offer

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different but complementary points of view in the study of the dynamics of the water binding process as well as the water status in food matrices.^{8–10} If sorption isotherms describe the degree of freedom of water molecules in a system by the study of the relationship between water content and water activity,¹¹ from a calorimetric point of view, “bound” water has been traditionally determined by DSC as the amount of unfreezable water within a sample cooled at low temperature (e.g., $-70\text{ }^{\circ}\text{C}$).¹² DSC has been widely used to monitor the gross phase changes of water in food systems.^{9,10}

Compared to DSC, foodstuff analysis via LF-NMR yields an additional degree of detail for the description of the embedded water because the measure of the transverse relaxation times (T_2) often reveals a multicomponent behavior that reflects the existence of different proton pools within the sample (e.g., protons from the macromolecular matrix, fat, or arising from water contained in different food compartments).¹³

In the present study the toughening and plasticization effects of water on coffee were studied by texture analysis, and the water status in coffee was investigated by the joint use of sorption isotherms, DSC, and LF-NMR techniques. The results obtained by this multianalytical approach were combined to better understand the role of water status in the determination of the toughening and plasticization effect.

MATERIALS AND METHODS

Materials. Green coffee beans (*Coffea arabica*) var. Santos from Brazil were provided by Saquella caffè (Pescara, Italy). Coffee aliquots ($140 \pm 1\text{ g}$) were roasted in a rotary laboratory roaster (model PRE 1, Probat, Emmerich, Germany) with hot air circulation. Green beans were roasted for 10 min using a time–temperature combination characterized by an initial hot air temperature of $210\text{ }^{\circ}\text{C}$ and an average temperature of $190\text{ }^{\circ}\text{C}$ (weight loss = 19%). This roasting process resulted in a dark-roasted coffee suitable for espresso extraction. The mean water contents of green and roasted coffee beans were 5.27 and 2.26%, respectively.

Texture analysis was performed on single coffee beans, whereas sorption isotherm, DSC, and NMR analyses were performed on sample beans ground in a mill, model Super Junior S (Moulinex, Paris, France), sieved to obtain particle size of about $1000\text{ }\mu\text{m}$ Ø.¹⁴

Texture Analysis. Coffee beans were transferred into glass desiccators, containing phosphorus pentoxide (P_2O_5), to perform complete sample drying. Moisture equilibration took place at $24\text{ }^{\circ}\text{C}$ inside seven sterilized glass jars (hygrostats), each containing one different saturated salt solution in the range of 10–91% relative humidity ($a_w = 0.10, 0.33, 0.44, 0.52, 0.76, 0.86, \text{ and } 0.91$). Dried samples of about 1 g were inserted into previously cleaned and oven-dried glass bottles, 10 mL in volume. Each hydration experiment comprised nine bottles. The bottles were kept half-open on a plastic net inside the hermetically closed hygrostats containing, on the bottom, different saturated salt solutions at the required a_w .¹¹ The bottles were periodically taken (three times a day) and weighed after closing, until they reached a constant weight for three consecutive weighings ($\Delta w < \pm 0.0005\text{ g}$). The a_w of the equilibrated samples was controlled by a dew point hygrometer, model Aqualab (Decagon Devices Inc., Pullman, WA).

Uniaxial compression on a single bean was carried out at $22 \pm 2\text{ }^{\circ}\text{C}$ by using an Instron (High Wycombe, U.K.) UTM dynamometer, model 4301, equipped with a 1 kN load cell, at a rate of 50 mm/min until failure occurred.^{1,2} Measurements were performed between two parallel plates of the dynamometer, at least on 25 beans randomly taken, on their longest side and with the flat side up. Fracture force (N), corresponding to the force at the major failure event on the force-displacement curve, was considered to be a measure of strength; fracture energy (J),

corresponding to the area under the force-displacement curve until the first breaking event occurred, was considered to be an empirical index of toughness.¹⁵ To highlight the effect of water on textural properties, data are reported as normalized fracture force and energy (adimensional), which were calculated by dividing the fracture force and energy of the sample rehydrated at a specific a_w value (F_{awj} and E_{awj}) by the respective values of the dried ones (F_{aw0} and E_{aw0}).

Compressive modulus (N/m^2) was computed using the following equation $[N/\Delta Y] \times (h/A)$, where N and ΔY correspond to the force and deformation at failure, respectively, h is the height of the specimen, and A is the sample area exposed to stress.¹⁶ The height, width, and length of each bean were measured by a caliper, and the area exposed to compression was assumed to be elliptical for calculation purposes. The mean value of bean height and area exposed to stress was evaluated on 25 specimens of the raw and roasted coffee samples at the different levels of moisture content and used to this purpose.

The compressive modulus was modeled as a function of a_w using the general form of Fermi's distribution that is described by eq 1¹⁷

$$Y_{(a_w)} = \frac{Y_0}{1 + e^{a_w - a_{wc}/b}} \quad (1)$$

where $Y_{(a_w)}$ is the compressive modulus, Y_0 is the compressive modulus in the dry state ($a_w = 0.1$), a_{wc} is the a_w value where a drastic textural change takes place, e is the exponential, and b is a dimensionless constant.

Water Sorption Isotherms. Ground and sieved coffee beans were completely dehydrated and rehydrated at different a_w values, with the same procedure used for samples realized for texture measurements. Raw and roasted ground coffee samples at different a_w values (0.24, 0.47, 0.58, 0.73, 0.84, 0.89, and 0.94) were obtained. The a_w of the equilibrated samples was controlled by an Aqualab dew point hygrometer (Decagon Devices Inc.). The dry matter content was determined by drying in a vacuum oven.¹⁸ Water content percentages are hereafter expressed on a dry matter basis.

The GAB equation (eq 2) was used to fit water sorption isotherms¹¹

$$X = \frac{X_m C_G K a_w}{(1 - K a_w)(1 + (C_G - 1)K a_w)} \quad (2)$$

where X is the water content (g water/100 g solids or %_{db}), a_w is the water activity, X_m is the water content of the monolayer (g water/g solids), C_G is the constant related to monolayer sorption heat, and K is the constant related to multilayer sorption heat.

The BET equation (eq 3), which corresponds to the GAB equation with $K = 1$, was used to determine the monolayer moisture contents¹¹

$$X = \frac{X_m C_b a_w}{(1 - a_w)[1 + (C_b - 1)a_w]} \quad (3)$$

where C_b is a constant related to the net heat of sorption.

DSC Measurements. Freezable water content on samples at different a_w values was evaluated by a Pyris 6 DSC (Perkin-Elmer Corp., Wellesley, MA). The DSC was equipped with a low-temperature cooling unit Intracooler II (Perkin-Elmer Corp.). Temperature calibration was performed with ion-exchanged distilled water (mp $0.0\text{ }^{\circ}\text{C}$), indium (mp $156.60\text{ }^{\circ}\text{C}$), and zinc (mp $419.47\text{ }^{\circ}\text{C}$). Heat flow was calibrated using the heat of fusion of indium ($\Delta H = 28.71\text{ J/g}$). For the calibration, the same heating rate as used for sample measurements was applied under a dry nitrogen gas flux of 20 mL/min. Each sample (about 20 mg) was weighed in a 50 μL aluminum pan, hermetically sealed, and then loaded onto the DSC instrument at room temperature, using an empty pan of the same type for reference. Samples were then cooled at $5\text{ }^{\circ}\text{C}/\text{min}$ to $-60\text{ }^{\circ}\text{C}$, held for 1 h, and then scanned at $5\text{ }^{\circ}\text{C}/\text{min}$ to $20\text{ }^{\circ}\text{C}$. Unfrozen water was evaluated as the maximum water content for which no enthalpic peak was detected¹⁹ and obtained from the intercept at

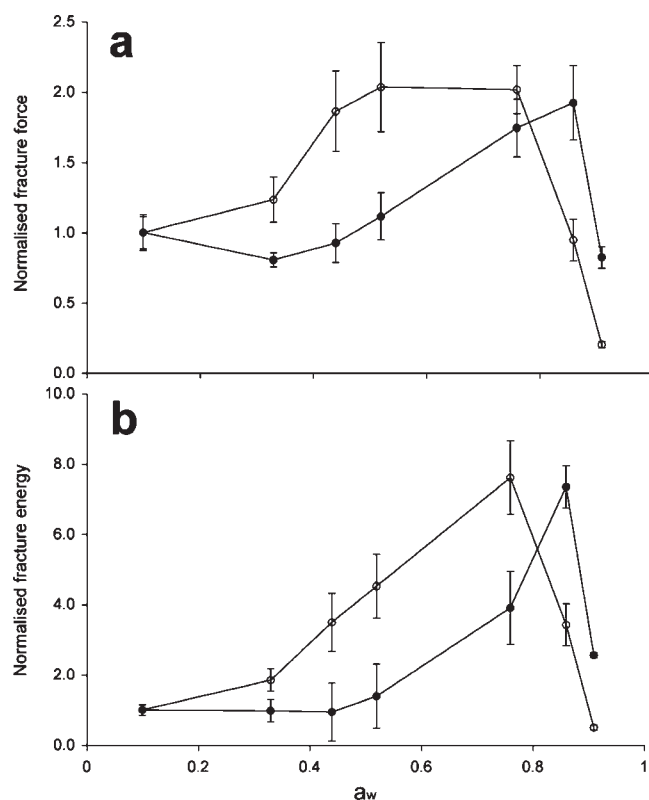


Figure 1. Normalized fracture force (a) and energy (b) of green (○) and roasted (●) coffee samples equilibrated at different a_w .

$\Delta H = 0$ of a linear fit of the melting enthalpies versus water content percentages.⁹

NMR Relaxation Measurements. The transverse relaxation time (T_2) of water protons was measured in triplicate for each ground sample rehydrated at different moisture levels. Samples were analyzed at 24 °C with the Carr–Purcell–Meiboom–Gill (CPMG) pulse sequence using a Bruker Minispec PC/20 spectrometer (Bruker, Germany) working at 20 MHz. The exponential decay comprised 5000 echoes, an echo time (TE) of 80 μ s, and a recycle delay of 3.5 s. The number of scans, as well as the amplification factor, were adjusted according to the moisture content of the samples analyzed to maximize the S/N ratio and to prevent signal clipping.

The raw CPMG decays were normalized to the dry matter weight of the samples before being inverted by the UPEN program.²⁰ UPEN lead to a continuous T_2 distribution interpretable in terms of different proton pools. The intensity of an NMR pool spanning a certain range of T_2 values on the relaxogram was obtained from the fraction of the “cumulative signal percentage” provided by UPEN in that range, multiplied by UPEN total extrapolated NMR signal (XSig).

Statistical Analysis. The sorption isotherms and Fermi equations were fitted to experimental data by nonlinear regression using the Marquardt algorithm.²¹ This is a search method to minimize the sum of the squares of the differences between predicted and measured values. The algorithm calculates the set of parameters with the lowest residual sum of squares (RSS) and their 95% confidence interval. The goodness of fit was checked by the estimation of the determination coefficient R^2 and the associated residual squares sum (RSS) values.

RESULTS AND DISCUSSION

Texture Analysis. Textural properties of raw and roasted coffee samples equilibrated at different a_w values, and thus having

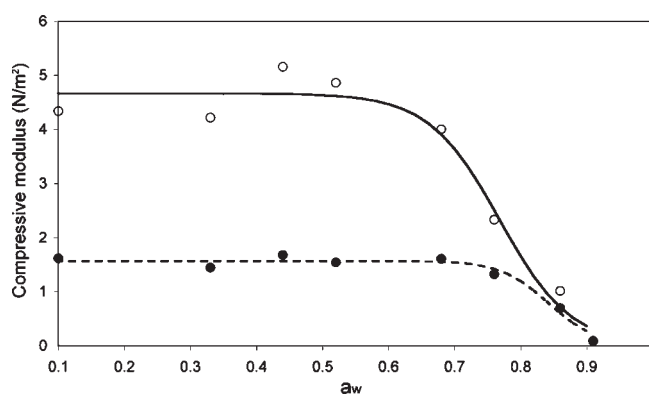


Figure 2. Compressive modulus of green and roasted coffee at different a_w values. Experimental values: (○) green; (●) roasted. Calculated values according to the Fermi model: (—) green; (---) roasted.

different moisture contents, were studied by uniaxial compression.^{1,2} A hardening and toughening effect due to water uptake (antiplasticization) was observed in the a_w ranges of 0.11–0.76 and 0.52–0.86 for green and roasted coffee beans, respectively (Figure 1). The hydration degrees at which the increase of strength and toughness started as well as the reaching of the maximum were different for green and roasted coffee beans. These results may be attributed to meaningful differences in chemical, physical, and microstructural properties. In particular, green beans, showing a dense structure characterized by a reduced porosity with micropores, underwent hardening/toughening at lower a_w value than roasted beans, the microstructure of which consists of a complex macropore system of excavated cells.^{22,23} This result confirms that moisture hardening/toughening is positively affected by the density of the food matrix.^{2,4,6}

At high a_w values, dried coffee beans, which are hard and brittle, become soft and ductile upon moisture adsorption. The force-deformation curve of brittle and fragile dried beans, described by a peak stress at the first main fracture followed by a series of fractures at lower stresses, gradually lost its characteristic jaggedness upon moisture content and changed its shape toward the typical smoother curve of plastic and viscous materials in which fracture occurs at higher deformation.^{2,4} Changes in the shape of the force-deformation curve were studied by the compressive modulus, which has been used by other authors to evaluate plasticization in food matrices undergoing moisture adsorption.^{2,15,16} The relationship between the compressive modulus and a_w in raw and roasted coffee samples was described by a sigmoidal curve (Figure 2). The compressive modulus did not evidence any increase upon hydration of coffee beans but did evidence the hydration degree at which the water plasticization effect occurs. This result confirms, thus, that, in cases like this, the so-called antiplasticization is merely a hardening/toughening effect caused by water uptake.⁴

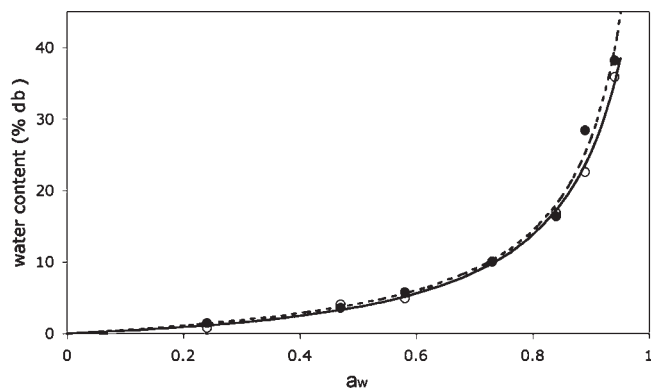
The compressive modulus data were fitted using Fermi's distribution function,^{2,3,15,17} and the estimated values of the model constants are reported in Table 1 for each coffee sample under study.

The Fermi model satisfactorily fitted the experimental data because the coefficient of determination was around 0.97 and the RSS values were, respectively, 0.799 and 0.068 for green and roasted coffee bean samples. The critical water activity values above which plasticization started were 0.64 and 0.77 for green and roasted coffee, respectively, whereas the a_w values above which a

Table 1. Regression Parameters of Fermi's Equation Applied to Compressive Modulus Changes Caused by Hydration

coffee sample	Y_0^a (N/m ²)	a_{wc}^a	b^a	R^2	RSS
green	4.660 ± 0.201	0.768 ± 0.016	0.054 ± 0.013	0.967	0.799
roasted	1.571 ± 0.053	0.843 ± 0.012	0.036 ± 0.010	0.971	0.068

^a Mean ± SD.

**Figure 3.** Moisture sorption isotherms of green and roasted coffee at 24 °C. Experimental values: (○) green; (●) roasted. Calculated values according to the GAB model: (—) green; (---) roasted.

50% decrease in stiffness occurred (a_{wc}) were 0.77 and 0.84 for green and roasted coffee, respectively. The estimated a_{wc} values are in the a_w range at which fracture force and energy started a steep decrease for both raw and roasted coffee (Figure 1). Furthermore, the a_w range over which stiffness was lost is, in general, relatively narrow as indicated by the low b values.

The mechanical behavior of foods undergoing plasticization seems to be determined by phenomena at molecular and structural levels and by their interactions.^{4,7} Roasted coffee beans, as a consequence of the severe heat treatment, present a significantly different composition and structure with respect to green coffee beans due to changes in the concentration of hydrophilic macromolecules (low and high molecular saccharides, proteins) and the formation of Maillard reaction and pyrolysis products, as well as the modification of the cellular characteristics of the matrix (porosity, cell size distribution, cell wall thickness).^{2,22,23} All of these factors are implied in the different textural behaviors of the green and roasted beans upon moisture adsorption and determine significantly different critical a_{wc} values.^{2,4}

Water Sorption Isotherms. The water sorption isotherms of green and roasted coffee beans at 24 °C were fitted by GAB model and are shown in Figure 3. In Table 2, the calculated parameters of the GAB equations together with R^2 and RSS values are reported.

The GAB model satisfactorily fitted the experimental data because the coefficients of determination were, respectively, 0.989 for green and 0.998 for roasted coffee samples and RSS values were very low. The isotherms for green and roasted coffee did not show the characteristic S-shaped curve of water adsorption isotherm of type II according to the BDDT classification²⁴ evidenced in previous studies,^{2,26,27} because of the lack of experimental points at $a_w < 0.24$. However, the calculated monolayer values, 5.28 and 4.23%_{db} for green and roasted coffee,

Table 2. Regression Parameters of GAB Equation Applied to Sorption Isotherms

coffee sample	X_m^a	C_G^a	K^a	R^2	RSS
green	5.28 ± 0.26	0.70 ± 0.18	0.93 ± 0.01	0.989	9.060
roasted	4.23 ± 0.52	1.13 ± 0.43	0.96 ± 0.01	0.998	2.431

^a Mean ± SD.

respectively, were consistent with previously reported literature data.^{25,26}

Even if it is largely argued whether the X_m parameter really represents the monolayer value or not, because it is not dependent on surface area,^{27,28} the estimation of this parameter is important because the so-called antiplasticization effect generally occurs above the X_m value.⁴ According to the literature,^{26,29} the values estimated using the GAB equation are largely approximated because the parameters X_m , C_G , and K are highly correlated. In our experimental conditions, the linear correlation coefficients among the estimated parameters through the GAB model were always >0.801. In this case, the BET equation, which corresponds to the GAB equation with $K = 1$, is widely used to determine X_m .²⁵ The X_m values of coffee samples calculated using the BET model were 3.99 ± 0.13 and $2.90 \pm 0.10\%$ _{db}; these values were less variable and slightly lower than those estimated by GAB model and consistent with previous research.^{2,25,26}

With the increase of a_w above 0.84, roasted coffee was able to adsorb more water than green coffee, in agreement with previous investigations.² Since the upper part of the isotherm corresponds to bulk water that fills large pores by causing swelling and solute dissolution,¹¹ it has been suggested that the higher porosity of the roasted bean could be responsible for the higher quantity of water when a_w values are equal.² However, this interpretation should be considered with care because other authors have indicated that porosity and particle size distribution do not influence the sorption isotherm of foods, which is only affected by modifications in chemical composition.^{27,30}

Differential Scanning Calorimetry. Heating scans of the same coffee samples used for sorption isotherm are shown in Figure 4. Below a_w values of 0.84 it is possible to observe the presence of a complex endothermic peak between about −12 and 15 °C, probably caused by unsaturated fatty acid melting, in both green and roasted coffee. This is consistent with previous research³¹ evidencing the occurrence of a complex endothermic peak between about −15 and 9.5 °C during coffee oil heating at 5 °C/min, ascribable to fat crystal melting. By increasing the level of hydration from 0.24 to 0.73, the peak area did not change significantly and the enthalpy (ΔH_f) values were, respectively, 8.73 ± 0.78 and 9.80 ± 1.14 J/g_{fw} for green and roasted coffee samples, in agreement with previous findings.³¹ In raw and roasted coffee, the lipid content is around 10–15%_{db}, and it is constituted principally by linoleic acid (about 45%) and other unsaturated fatty acids such as oleic (about 10%) and linolenic (about 1.5%).^{31,32} These unsaturated fatty acids have a typical melting point respectively at −11, −5, and 13.4 °C³³ that is congruous with the T range of the detected endothermic peak. This finding has to be taken in consideration because the mean fat melting peak enthalpy has been subtracted from the endothermic peak enthalpy found out at high a_w values (0.84, 0.89, and 0.94), when water started to freeze, to find accurate values of ice melting enthalpies.

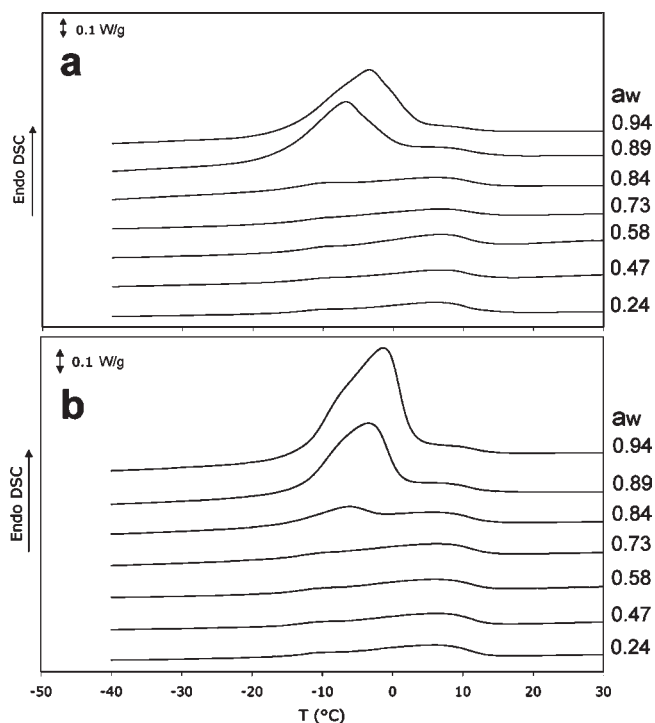


Figure 4. Normalized thermograms of green (a) and roasted (b) coffee samples equilibrated at different a_w values.

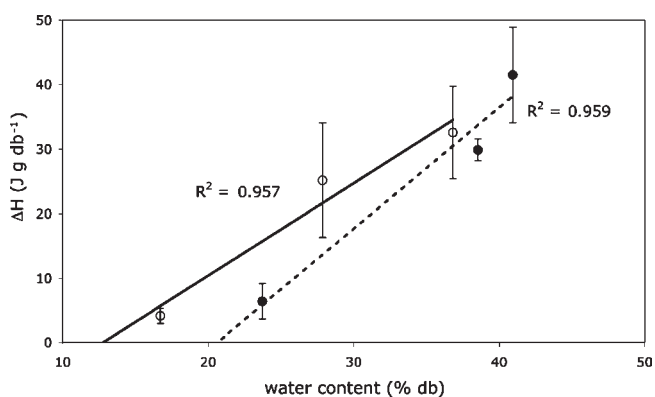


Figure 5. Linear fit of the freezable water melting enthalpies (in triplicate) versus water content.

Figure 4 shows that in both green and roasted coffee samples the magnitude of the endothermic peak started to increase from the a_w value of 0.84 due to the contribution of the ice melting phenomenon during heating. Until this value, only “unfreezable water” (usually considered as water bound to the macromolecular matrix with a mobility so limited that it cannot freeze) exists in coffee samples.

Total bound water, corresponding to the maximum water content, for which no enthalpic peak is detected, was calculated from the intercept at $\Delta H = 0$ of a linear fit of the melting enthalpies versus water content (expressed as %_{db}). In Figure 5, the results of linear regression of ΔH data (minus ΔH_i) versus water content are reported. The obtained fitting equations ($\Delta H = 1.431X - 18.21$ and $\Delta H = 1.431X - 18.21$ for green and roasted samples, where ΔH is the melting enthalpy per gram of

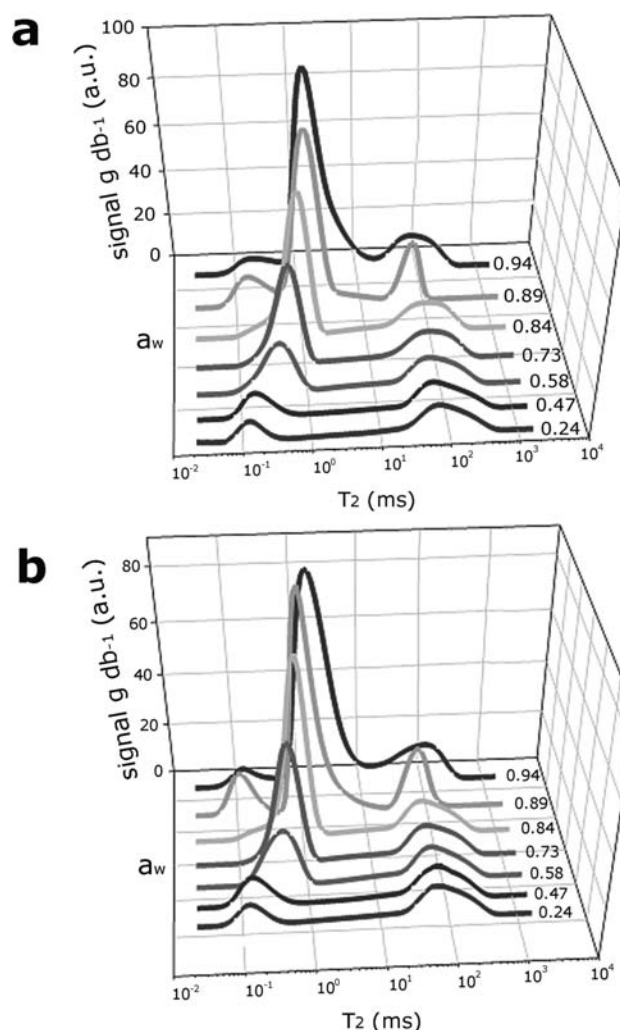


Figure 6. UPEN T_2 relaxograms of raw (a) and roasted (b) coffee samples equilibrated at different a_w values.

dry weight and X is the moisture percentage on dry basis) showed that, in our experimental conditions, the unfrozen water contents of green and roasted coffee were, respectively, 12.73 ± 0.73 and $20.59 \pm 0.91\%$ _{db}. These data are similar to those of other studies which reported that nonfreezable water in roasted coffee is about 15%¹⁴ and confirm the higher ability of roasted coffee to bind more water when moisture is equal. According to the GAB model, the a_w values at which the freezable water peaks appeared were 0.78 and 0.86 for green and roasted coffee, respectively.

Nuclear Magnetic Resonance. The continuous T_2 relaxograms of green and roasted coffee samples evidenced the presence of three different proton populations (hereafter named T_{2a} , T_{2b} , and T_{2c}) characterized by an increased level of mobility (Figure 6).

The major population (T_{2b}) showed an average T_2 starting from about 0.1 ms at low hydration levels, which gradually reached final values of 1.5 and 1.7 ms for green and roasted coffee, respectively. The extrapolated signal per gram dry base of this pool shows a linear increase with the moisture content to demonstrate that it can be assigned to the water progressively added to the matrix. By plotting the T_{2b} peak relaxation rate ($R_2 = T_2 - 1$) versus moisture (expressed as g H₂O/g db), there were observed a break point corresponding to a dramatic slope change

and a sudden jump toward longer relaxation rates, which occurs after a certain level of hydration (data not shown). The slope break point has been calculated to occur at a different hydration degree corresponding to a_w values of 0.61 and 0.75 for green and roasted coffee, respectively. Furthermore, this peculiar shift in the R_2 rate approximately occurs along with a width narrowing of the T_{2b} population revealing a shoulder (T_{2a}) at about $T_2 = 0.15$ ms, diagnostic of the presence of a new fast-relaxing proton pool. The slowest relaxing component T_{2c} can be assigned to the apolar phase in coffee as previously reported for other studies.⁹ In fact, the T_{2c} population seems not to be influenced by hydration because its signal per gram of dry base as well as its T_2 value are constant along all of the hydration process. In agreement with DSC results, this proton pool can be mainly attributed to the fat fraction present in both green and roasted coffee beans, the composition of which does not meaningfully change upon roasting.

Overall, our results suggest the presence of a relatively low mobility water population (T_{2b}) probably located inside the cell and interacting with the cell wall biopolymers at low and medium hydration degrees of coffee beans. This water can be thought as tightly associated with macromolecules, acting as a toughening agent because of the semisolid nature of its signal. The solid population decreased with water content according to other studies.³⁴ The sudden jump of T_{2b} toward longer relaxation rates occurring at $a_w = 0.61$ and 0.75 for raw and roasted coffee, respectively, might be indicative of the beginning of a different water–matrix interaction, which could affect the mechanical properties. This interpretation could be confirmed by the appearance of the T_{2a} population that can be ascribed to the solid matrix (whose NMR signal decays too quickly to be detected by CPMG experiments in our conditions) which, after being hydrated by water, is gradually more and more detectable in the low- T_2 region as its mobility is enhanced at these levels of hydration.

Water Status and Textural Changes. With the increase of the level of hydration, the first phenomenon detected was the completion of the BET monolayer (Figure 7) in both green and roasted coffee beans. The hardening/stiffening effects started around or above the a_w value at which the monolayer completion occurred (Figure 1), in agreement with results reported in other studies.⁴ This is the water that, after monolayer completion, builds up multilayers and begins to fill small pores,¹¹ and it is more likely to cause a mechanical toughening effect independent of its kinetic effect in lowering the T_g of the polymer–water blend below the T_g of the net polymer.

At higher water activity values (0.64 and 0.77 for green and roasted coffee, respectively) that correspond, according to Fermi's model, to the onset of the compressive modulus decrease, the NMR analysis revealed the appearance of a new proton pools with increased levels of mobility, respectively, at $a_w = 0.61$ and 0.75 . This result suggests that the NMR technique permits detection of the water responsible for the plasticization effect. This plasticization effect, however, does not determine a hardness/stiffness decrease because at this hydration level water is still filling the pores by decreasing porosity.¹¹

At higher hydration level ($a_w = 0.77 \pm 0.02$ and 0.84 ± 0.01 for green and roasted coffee, respectively), the plasticizing effect of water becomes important and, according to Fermi's model, there is a 50% decrease in compression modulus. At the same hydration level ($a_w = 0.78$ and 0.86 for green and roasted coffee, respectively), water exceeding the amount bound to the

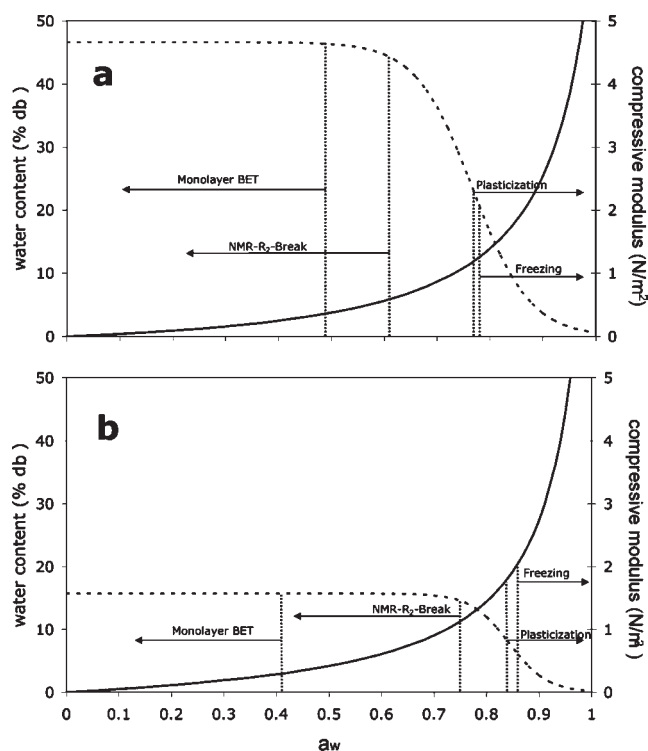


Figure 7. Schematic view of compressive modulus (---) relationship with water activity and moisture sorption isotherm (—) in green (a) and roasted (b) coffee beans.

macromolecular matrix had a sufficient mobility to freeze according to DSC experiments. According to a previous study,³⁵ at ambient temperature (20–25 °C) roasted coffee beans have a phase transition from glassy to rubbery state when the beans reach a moisture content of about 18–20%, which corresponds to the water content at which freezing water becomes detectable.

In general, freezable water and T_g values detected by DSC seem not to match the water mobility increase obtained by NMR, because the latter detects mobile water when it is not freezable and it has no translational mobility according to DSC analysis. Similar phenomena have been noted in starch and cellulose systems and are ascribable to the presence of “metastable” water.³⁶

The moisture contents that permit the detection of freezable water by DSC correspond to a_w values placed within the region of the upward concavity of the sorption isotherm, where the water begins to fill large pores and cause swelling and solute dissolution;¹¹ thus, above this a_w value, the compressive modulus, the hardness, and the stiffness decreased in both green and roasted coffee (Figures 1 and 7). In green coffee the softening effect started at a moisture content of about 11%_{db}, and above this value water exhibits only the slow-relaxing component in accordance with other studies.³⁷

The joint use of sorption isotherms, DSC, and NMR techniques permitted the identification of different types of water causing hardening/stiffness, plasticization, and softening effects in two food systems such as green and roasted coffee beans. The changing status of water affects the evolution of mechanical properties of these food systems independent of their dramatic difference in terms of chemical composition and physical characteristics.

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