Sorption behaviour, glass transition and flowability of powdered orange co-product

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ABSTRACT

The aim of this study was to contribute to the valorization of orange juice co-product in order to offer it as a natural, versatile, high quality, and stable powdered food ingredient for human nutrition. To ensure its efficient use for this purpose, co-product powder was characterized from a technological point of view in terms of the physicochemical aspects related to the presence of water and its ability to remain free-flowing and non-agglomerated, allowing for easy handling. The results of this study ensure the flowability of the freeze-dried orange co-product powder according to both the angle of repose (40º) and porosity (83%) values. However, it was also characterized as a hygroscopic product; therefore, specified conditions for a proper storage of the powdered co-product should be defined. In this case, both the refrigeration temperature and a relative humidity of under 35% should be established in order to avoid glass transition, thus remaining a free- flowing powder.

Keywords: angle of repose, porosity, hygroscopicity, orange juice co-product

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INTRODUCTION

Most countries, especially their urban areas, face a huge problem when it comes to the disposal of the by-products generated by the food industries. As an example, Spanish citriculture produces around 7 million tonnes of citrus fruit per year, of which more than 50% is biomass made up of peel and endocarp membranes that is generally destined for the animal feed sector. Specifically, during orange juice production, around 50% (w/w) of the oranges are discarded, generating residues mainly composed of peels, pulp, seeds and leaves, among other things (Rezzadori et al. 2012). This biomaterial, despite being rich in water and dietary fiber, contains proteins, minerals, essential oils and other bioactive compounds, such as vitamins, flavonoids, and carotenoids, which are of great interest due to the fact that they are beneficial for human health (Helkar et al. 2016; USDA 2018).

In the last few decades, there has been huge interest in foods rich in dietary fiber (DF), which is a well-known constituent of a healthy diet. The high DF intake has been related to a reduced risk of suffering diverticular disease, a healthy gut microbiome, a reduced risk of developing cardiovascular disease and thus a lower mortality rate, and a reduced risk of both local and systemic chronic inflammation (Aune et al. 2019; Barber et al. 2020). For that reason, the recommended daily intake of dietary fiber is 25-35 g (EU 2017). In fact, there are studies proposing to apply the fiber obtained from the citrus by-product for the development of biscuits (Nassar et al. 2008) or meat products (Fernández-López et al. 2004), for example. In addition, the scientific community has carried out a great deal of research into the recovery of vitamins, phenols, carotenoids, etc. and their encapsulation for nutraceutical purposes (Attanzio et al. 201; Dugmore el al. 2017). However, each of the above-mentioned uses involves a partial recovery of the by-product that does not contribute 100% to the circular economy models of the agri-food industry. For this reason, and in the interest of contributing to a healthy and sustainable diet, what may be proposed is the valorisation of the orange juice co-product in its entirety for use in foodstuffs. Turning it into a cost-effective innovative product, with added value due to its high content of bioactive compounds, would lead to an increased competitiveness of the industrial sectors working with natural fibers.

To ensure the successful use of the co-product as a food ingredient, it is necessary to stabilize it in order to reduce its water content, which is in the order of 70-75 %; this, in turn, will lead to a reduction in its weight and bulk, favoring the logistics and lowering the costs incurred by its distribution and storage. On the other hand, offering it as a powdered product may contribute to its commercial success due to this format's ease of handling and the popularity already enjoyed by many other powdered food ingredients. As the composition and treatments applied to fruit peels could condition their properties, and thus their technological applications (Tejada-Ortigoza et al. 2017), a key aspect in the development of this product is the selection of the drying process and the subsequent crushing/milling methods. However, it is essential to know, in the first instance, whether powder is really a viable format for the orange juice co-product. Food powders will exhibit different physical properties dependent on the properties of the particle as an individual entity, the properties of the assembly of particles, and the interaction between those assemblies and the fluid matrix in which they are contained (Barbosa-Cánovas et al. 2005). For that reason, the measurement of the physical properties is relevant in order to define the powder and provide information about its handling and the processing characteristics (Teunou et al. 1999). For a powdered food product, the most interesting properties from a technological point of view are its flowability and its ability to be mixed with water. In this context, the aim of the present study was to determine the glass transition temperature-water content-water activity relationships of the freeze-dried powder orange co-product and its ability to remain free-flowing and non-agglomerated, allowing easy handling throughout storage, as well as its wettability.

MATERIAL AND METHODS

Raw material

The co-product obtained from the extraction of orange (*Citrus sinensis* var. Salustiana) juice was obtained from the cafeteria located in the Fine Arts Department of the Polytechnic University of Valencia (Valencia, Spain) in February 2020. Before processing, the epidermis was rinsed with water to remove any traces adhering to it.

Sample preparation

The co-product was crushed and emulsified with water in a 1:1 ratio for 60 seconds per kg mix (Eurofred, Barcelona, Spain). The mix was distributed in aluminium plates, 30 cm in diameter and 1 cm thick. The sample was frozen at -45 ºC (Liebherr MedilineLGT 2325; Liebherr, Kirchdorf an der Iller, Germany) for 24 h and freeze-dried at 5 Pa and a shelf temperature of 50 ºC for 20 h (Telstar Lyo-Quest -55; Telstar, Terrassa, Spain). 40 g batches of the obtained cakes were crushed (Thermomix TM 21; Vorwerk, Madrid, Spain) at 3700 rpm for 20 s to obtain a powder with a particle size of < 500 µm (sieving machine RP 200 N CISA and sieves CISA 200/50, Spain).

Sorption isotherm

The powder was distributed in 5 aluminum plates which were placed at 20 ºC in hermetic chambers containing saturated salt solutions (ClLi, CH_3COOK, $MgCl_2$, K_2CO_3, $Mg(NO_3)_2$), whose corresponding relative humidity (RH) ranged between 11% and 53% (Greenspan 1977). The samples were kept in each environment for two months, during which time they reached equilibrium with the surroundings. At this moment, the water activity of each powder was assumed to be equal to that of the saturated salt solution. The water content of the powder and the water activity values were obtained as explained in the next section.

Water content and water activity

The water content (x_w, g water/ 100 g powder) of the powder was obtained with an automatic Karl Fisher titrator (Compact Coulometric TitratorC10S; Mettler Toledo, Worthington, OH, USA). The water activity (a_w) was evaluated with a dew point hygrometer (Aqualab 3TE, Meter Group, Munich, Germany). Three replicates were carried out for each analysis.

Glass transition temperature

The glass transition temperature (Tg) of the powdered sample conditioned at different RH was determined by differential scanning calorimetry (Q2000, TA-Instruments Crawley, UK, equipped with an RCS 90 cooling system). Approximately 14 mg of powder was placed into DSC pans (P/N SSC000C008, Seiko Instruments Inc., Japan). The heating rate was 5 ºC/min and the temperature range varied between -80 ºC and 80 ºC, according to the water activity of each powder. The midpoint of the glass transition was obtained from each thermogram and considered as the Tg.

Fitted models

The BET model and the Gordon and Taylor model were used to predict the water sorption and the relation Tg - x_w, respectively. The experimental x_w - a_w and Tg - x_w were fitted to the linearized BET model (Eq. 1) and to the linearized Gordon and Taylor (1952) equation (Eq. 2), respectively.

$$\frac{a_w}{(1-a_w)\,W_e} = \frac{1}{W_0\,C} + \frac{C-1}{W_0\,C}.\,a_w \qquad (1)$$

Where We is the equilibrium water content (g water/g dry solute), Wo is the monolayer water content value (g water/g dry solute), C is the energy constant related to the sorption heat, and a_w is the water activity.

$$T_g = T_{g(s)} + k\frac{x_w\,.(T_{g(w)}-T_g)}{(1-x_w)} \qquad (2)$$

Where Tg is the glass transition temperature (ºC), $Tg_{(s)}$ is the glass transition temperature of the anhydrous solids (ºC), k is the Gordon and Taylor constant model, x_w is the mass fraction of water (g water/g product), and $Tg_{(w)}$ is the glass transition temperature of amorphous water: -135 ºC (Roos 1995).

Hygroscopicity

The hygroscopicity was obtained from the water content that the powder gained after its exposure in an environment with a specific relative humidity (RH). To that end, 1 g of powder was exposed for 2 h in a hermetic container with a RH of 75% at 20 ºC using a dissolution of saturated NaCl (a_w=0.75). The hygroscopicity was expressed as g water gained / 100 g dry product. Three replicates were carried out.

Wettability

The wettability is inversely proportional to the time required to wet all the particles of the powder when poured over water. 10 g of powder was discharged over 250 mL of distilled water at 25 ºC ± 1 contained in a 500 mL glass beaker with an internal diameter of 85 mm. The time (s) at which all the particles were completely sunk and disappeared from the surface was recorded (IDF 2014). Three replicates were carried out.

Angle of repose

The angle of repose (αº) is a powder flowability parameter which is calculated from the angle formed between the slope of the cone of the product when the powder is dropped down onto a horizontal surface and the latter (Gallo et al. 2018).The methodology proposed by Silva-Espinoza et al. (2021) was followed to determine αº. 10 g of the powdered product was poured into a funnel (top diameter = 80 mm, stem =11 mm, steam length = 29 mm, approx. Overall height =85 mm), placed at a height of 5 cm from the horizontal surface covered with 80 g/m2 DIN-A4 (Apli Paper S.A.U., Barcelona, Spain). The height and the diameter of the powder cone were measured to calculate αº (Eq. 3). Three replicates were carried out.

$$\alpha^{\circ} = \tan^{-1}\left(\frac{2h}{D}\right) \quad (3)$$

Where h = height from the top of the product cone to the horizontal surface (cm); dD = maximum cone product diameter (cm), taken as an average of at least 6 values.

Density and Porosity

True and tapped bulk densities were characterized to calculate porosity. True density (ρ) was calculated based on the sample composition following Eq. (4). The tapped bulk density (ρ_T) was obtained by pouring up to 10 mL of powder into a graduated tube and subjecting it to a vibration process in a vortex (Advanced Vortex Mixer, ZX3, VELP® SCIENTIFICA, Italy) for 10 s at 1200 rpm. The ρ_T was calculated from the relation between the weight of the powder and the volume that it occupied after the vibration process. Porosity (ε %) was calculated following Eq. (5).

$$\rho = \frac{1}{\frac{x_w}{\rho_w} + \frac{x_{CH}}{\rho_{CH}} + \frac{x_L}{\rho_L} + \frac{x_P}{\rho_P} + \frac{x_A}{\rho_A}} \quad (4)$$

Where x_w, x_{CH}, x_L, x_P, and x_A are the mass fractions of the components of the sample (water, carbohydrate, lipids, proteins, and ashes, respectively; x_w, determined as previously described, and the rest of the components were calculated by taking into account the experimental water content of the obtained powder and the mean orange coproduct composition referred to by USDA (2018); ρ_w, ρ_{CH}, ρ_L, ρ_P, and ρ_A are their densities, respectively (ρ_{CH} = 1,4246 g/cm^3, ρ_w = 0,9976 g/cm^3, ρ_L = 0.9164, ρ_P = 1.2894 g/cm^3, and ρ_A = 1.7434 g/cm^3, Choi and Okos 1986).

$$\varepsilon(\%) = 100\frac{\rho - \rho_T}{\rho} \quad (5)$$

RESULTS AND DISCUSSION

Physical Properties

Table 1 shows the powdered coproduct proximate composition. It was calculated by taking into account the experimental water content of the obtained powder and the mean orange coproduct composition referred to by USDA (2018). As can be observed, this biomaterial is an important source of carbohydrates, of which approximately 40-45 % is natural dietary fiber (USDA, 2018). According to Tejada-Ortigoza et al. (2018), the insoluble fraction accounts for 88.5 % of this fiber content. Natural carbohydrate biopolymers from plant sources provide a broad range of functional properties (Mirhosseini and Amid 2013). They are appropriate alternatives to the synthetic biopolymers to be used as carriers for the distribution of drugs

around the body, as emulsifiers or as thickeners among others. In this case, the results suggest a contribution of 38 g of dietary fiber /100 g of powdered co-product. The composition shown in Table 1 and the density of the pure components (Choi and Okos 1986) were used to calculate the true density of the co-product (Table 1). The ρ value is 6 times higher than the ρ_T, which involves high values of ε (Table 1) due to the air contained both inter and intra-particles. The ε and αº were selected as parameters for powder flowability characterization (Silva-Espinoza et al. 2021). According to the Royal Spanish Pharmacopoeia (RFE 2015), an αº value of 40 corresponds to the powder group considered to have regular flowability, which is above the values corresponding to acceptable flowability. So, it could be classified as being transitional between cohesive and free flowing. Similar values of αº and ε were obtained by Silva-Espinoza et al. (2021) for powdered orange puree pulp although in this case, stabilizers, such as gum Arabic and bamboo fiber, were needed to be added to make an otherwise sticky and agglomerated powder manipulable and easy to handle. In this case, the good result in terms of the orange co-product powder flowability may be due to the high content in dietary fiber. The fiber content of the orange co-product itself acts as a stabilizer and fille, enhancing the powder flowability without needing the addition of any additional biopolymer. This suggests that, among its diversity of applications, the orange co-product can be used as a stabilizer for those food industries working with dehydrated products. On the other hand, the fact that it is close to acceptable flowability makes it a good candidate for being compacted in order to obtain, or help to obtain, tablets of interest to the pharmaceutical or nutraceutical industry (Gallo et al., 2011). In every case, there would be an increase in the physiological health implications related to the presence of both fiber and the other bioactive compounds.

As regards the hygroscopicity, the powdered co-product showed 6.5 g gained water / 100 g dry product, which apparently indicates a hygroscopic product. This is a consequence of it being a fruit product, as similar results have been obtained in studies carried out on different fruit powders (Goulas and Adamopoulos 2008; Goulas and Adamopoulos 2010). In fact, the aforementioned authors point to the high content in sugars as being responsible for the high degree of hygroscopicity of this kind of product. As regards the wetting time, the value was high and in the order of that shown by orange pulp powders formulated using starch modified with octenylsuccinic groups (OSA, Silva-Espinoza et al., 2021). The structure of the OSA contains hydrophobic groups that worsened the wettability. In this case, the composition of the co-product, including both high molecular weight solutes and insoluble dietary fiber as commented on before and the presence of lipids in the peels, could be worsening the wettability. In this sense, a better application for this powdered co-product may be as an emulsifier in foods containing water and oil or perhaps as an excipient in medicines, a field of interest that seems to require further research.

Glass transition temperature-water content-water activity relationships

Food dehydration processes often lead to the formation of an amorphous matrix which will be in a glassy or rubbery state depending on its composition and the temperature at which it is found. Glass transition is the change of state responsible for the change in the amorphous matrix from glassy to rubbery or vice versa. The stability problem of many powdered foods is related to the development of stickiness and caking phenomena that start to occur in the rubbery state. The temperature at which this glass transition occurs (Tg) rises as the water content decreases and the average molecular weight of the solutes present increases. In this sense, controlling the water content and temperature changes related to the surrounding conditions is crucial to ensure the glassy state of powdered products. The high degree of hygroscopicity of the orange co-product will lead to a rapid water gain when subjected to an environment with a RH higher than its a_w (Ross 1995). The stability map, which relates Tg-x_w-a_w, is the right tool with which to discover the stability of powdered foods in different environments.

The water sorption isotherm provides the relationship between water content (in dry basis) and a_w at a given temperature and is useful for the purposes of investigating the long term hygroscopicity of the material which would condition many other techno functional properties. Any food will gain or lose water depending on its environment, until it reaches thermodynamic equilibrium. When this equilibrium is reached, the water activity of the product coincides with RH/100. In this sense, the water sorption isotherm permits the prediction of the final water content of a product when exposed to different RH. The result of the sorption experiment carried out with the orange co-product is presented in Fig 1. The BET model is the one of the best-known mathematical models for predicting a sorption isotherm in the low water activity range. As an

be observed, the modelized isotherm is typical sigmoid in shape (type II isotherm) according to the BET classification (Brunauer et al. 1938), which corresponds to biological and food materials. The R^2 of the fit value corresponds to 0.946. The C constant value, one of the parameters of the BET model, was 15.1, which confirms the isotherm as a type II given C > 2 (Timmerman, 1982). The BET monolayer water content, W_o, is the other parameter of the model which is of use for the purposes of estimating the amount of water bound to specific polar sites in dried foods. W_o showed a value of 0.0722 g water/dry solid. This result coincides with similar values obtained for some fruit products, such as orange pulp powder (Silva-Espinoza et al. 2020) and dried pomegranate peels (Al-Rawahi et al. 2013).

As has been mentioned, it is necessary to maintain a powdered food in the glassy state so as to avoid a loss of flowability. As the Tg of a concrete product changes depending on the water content, it is crucial to know the relationship between Tg and x_w. The Gordon-Taylor equation (Eq. 2) has been described as a reliable predictor that allows these experimental values to be related (Roos et al. 1996). The prediction contributes to an understanding of the plasticization effect of water which leads to the agglomeration of food powders. The experimental data obtained in this study were well fitted to this model, with a R^2 of 0.9556 (Fig. 2). Anhydrous solids Tg ($Tg_{(s)}$) and K, parameters of the model, showed values of 126.55 and 9.16, respectively. As expected, it can be observed that the Tg of the orange co-product powder decreases as the x_w increases. This plasticizing effect of water leads to a reduction in the inter- and intra-macromolecular forces, reducing the Tg (Matveev et al. 2000). If we look at Fig. 2, at room temperature (20 ºC) the glass transition will occur when the powder reaches 10 g water content/100 g co-product. This value agrees with water content values of 5% and 18 % for the glass transition at 20 ºC obtained for orange pulp powder and inulin, respectively (Silva-Espinoza et al. 2020; Zimeri and Kokini 2002). The fiber content is much lower (approximately 2%) in the orange pulp powder than the orange co-product powder, since the former did not contain the peel. And the inulin is considered dietary fiber in itself, while the fiber content in our product is 40%. Therefore, it can be assumed that, at a given water content, the higher the fiber content, the higher the Tg.

As shown in Fig. 2, both temperature and water content play major roles in the glass transition. As the Tg decreases in line with an increase in water content, the glass transition of a material in the very stable glassy state may stem from an increase in its water content or temperature (Telis and Martínez-Navarrete 2012). As a product may be stored and managed at different temperatures and RH, the latter conditioning its final water content, the stability map of the orange co-product will make it possible to know what are the best conditions for its handling. From the BET and Gordon and Taylor fitted models, the Tg-a_w-x_w relationships can be obtained to build the stability map (Fig. 3).

The stability map has been described as a useful tool that permits an easy identification of the critical processing or storage conditions (temperature and RH) for the glass transition (Fabra et al. 2009). Critical water activity (CWA) and critical water content (CWC) are the limiting values of a_w and x_w, respectively, above which the glass transition would take place at a given temperature. In this case, the CWA and CWC values were approximately 0.220 and 0.07 g water/g product, respectively, at 20 ºC (room temperature). However, due to the low CWA and the hygroscopicity of the co-product (Table 1), storage at 4°C rather than at room temperature may be recommended to ensure powder flowability, which increases its CWA so that in environments with a RH of approximately 35 %, its glassy state would be guaranteed (Fig. 3).

CONCLUSIONS

The flowability of orange juice co-product powder and its behaviour when mixed with water seem to be related to its composition. The powdered co-product showed good flowability, which is likely due to its high fiber content acting as a stabilizer/filler. However, the insoluble part of the fiber and the lipid content hinder its rehydration in water. Despite the powdered co-product being hygroscopic given the sugar content, it shows a high glass transition temperature value as compared with other fruit powders. The high fiber content of this product seems to contribute to an increase in the Tg, delaying the stickiness and, therefore, powder agglomeration, at a given environment relative humidity. To ensure the glassy state of the powder, and thus its flowability, its storage is recommended at refrigeration temperature in order to increase the critical water content to 35%.

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Figure captions

Fig. 1 Water sorption isotherm of orange juice co-product powder at 20 ºC. Equilibrium water content (We) at different water activities (a_w).

Fig. 2 Glass transition temperature (Tg) of the orange co-product powder at different water contents (x_w)

Fig. 3 Glass transition temperature (Tg)-water activity (a_w)-water content relationships of the freeze-dried powder coproduct. Critical water activity (CWA) and critical water content /CWC) for the glass transition at 4 ºC

Table 1. Proximate composition of orange co-product and values of measured physical properties.

Water (w/w)	0.016 ±0.004	ρ_T (g cm^{-3})	0.238 ± 0.019
Carbohydrate (w/w)	0.8948	ε (%)	83.1 ± 1.3
Protein (w/w)	0.0537	α^o	40.4 ± 0.2
Lipid (w/w)	0.0072	Hygroscopicity (%)	6.5 ± 0.2
Ash (w/w)	0.0286	Wettability (s)	1390 ± 138
ρ (g cm^{-3})	1.409		

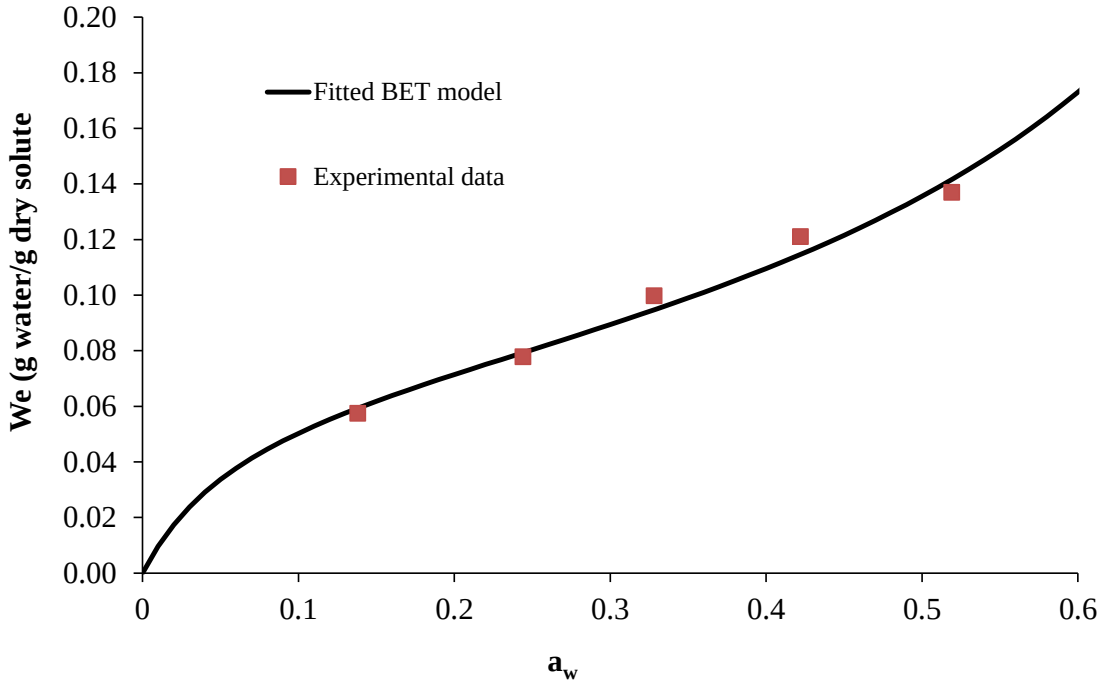

Fig. 1

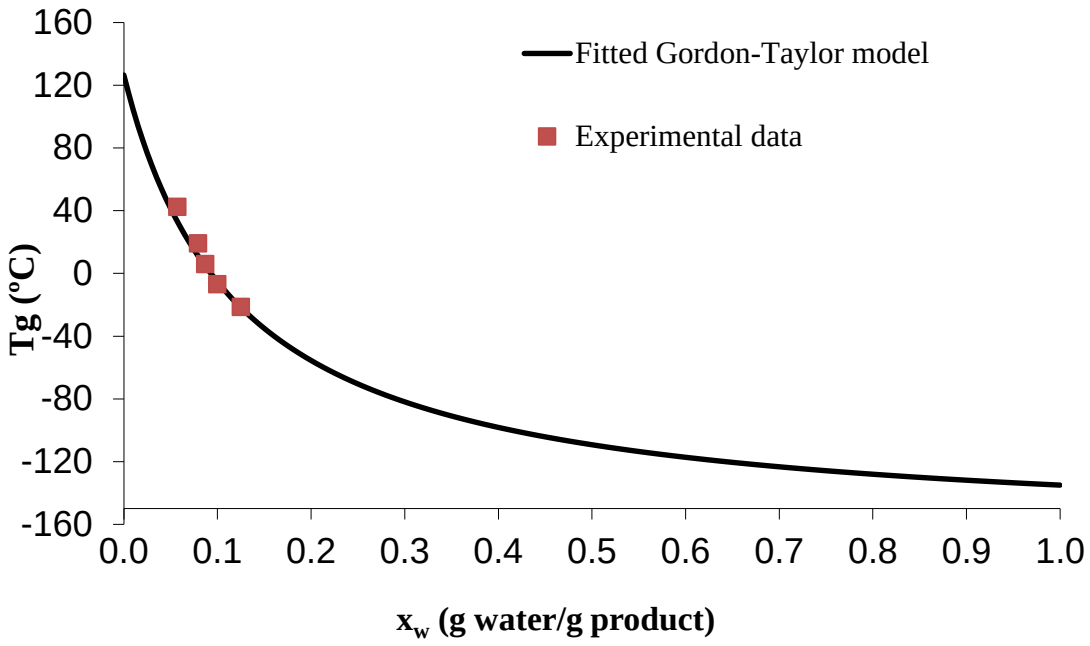

Fig. 2

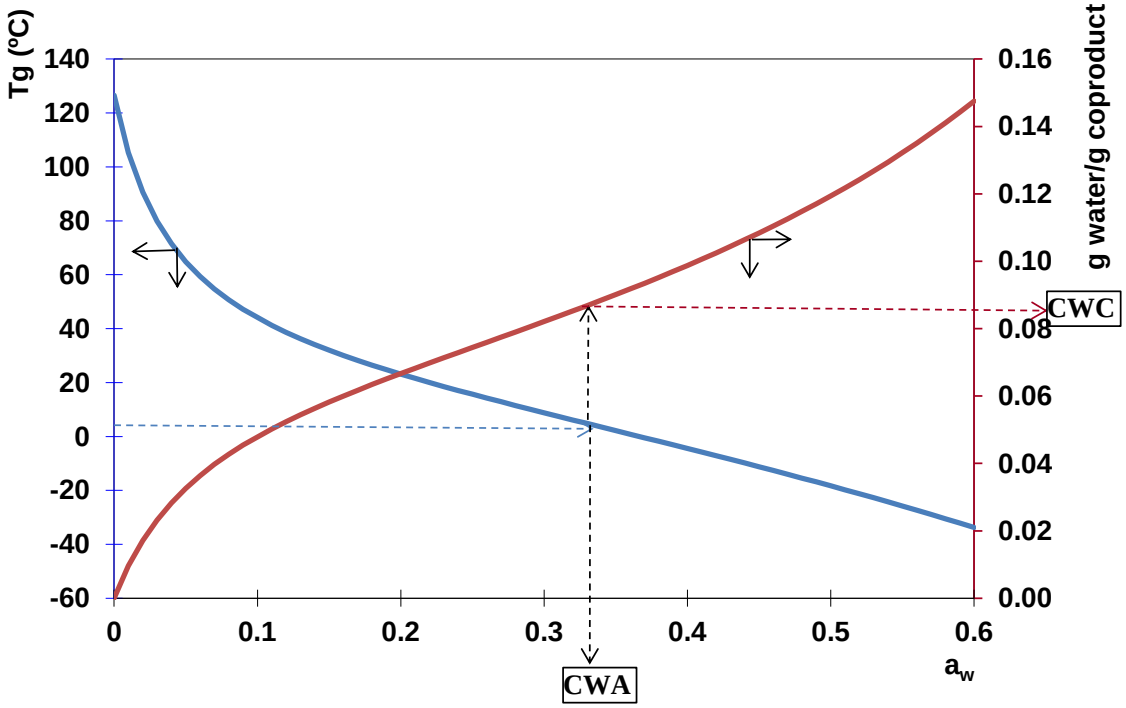

Fig. 3