Effect of powdering on critical water activity estimate from dynamic dewpoint isotherm of a crispy starch-based snack: a case study with fish cracker

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Abstract The moisture sorption isotherm (MSI) and critical water activity ($a_{w,crit}$) of a dry food determine the moisture barrier properties required of packaging for desired shelf life of starchy dry food. These can be obtained with the novel rapid dynamic dewpoint isotherm method (DDI), but with such rapid measurement incomplete equilibration is of concern, and this relates to suitable particle size of the sample tested. Further, an MSI curve without clear inflection point can make it difficult to extract the $a_{w,crit}$. The objective of this work was to investigate the effects of particle size of a starch based snack on its MSI and on $a_{w,crit}$. A novel model to fit the MSI data was also created to obtain the $a_{w,crit}$. Fish cracker samples were prepared in three particle sizes ($< 180 \mu\text{m}$, $250\text{--}425 \mu\text{m}$, and $\sim 3000 \mu\text{m}$) and tested at 25 and 35 °C for MSI using DDI. The sample comminution by grinding had clear and consistent effects, with finer particles absorbing more moisture. For this crispy snack, the rapid dense measurements enabled estimating the critical point that was robust against a 10 °C temperature change with about 200 μm particle diameter. This suggests near complete equilibration by the lack of rate effects from temperature, which were seen with larger particles. The results indicate that powdering dry crispy foods enables proper DDI measurements, while without powdering the

isotherms can be degraded by particle size effects. The broken-stick type model fit the data extremely well and showed the critical transition clearly as a jump discontinuity in the derivative (slope).

Keywords Moisture sorption isotherm · Dynamic dewpoint isotherm · Critical water activity · Crispy snack food · Segmented regression

Introduction

Fish cracker or “keropok” is a popular puffed starch based snack product in ASEAN countries. It is made mainly from cassava starch or sago starch with some seasoning to form a dried gel, which is further puffed in hot oil or in a microwave oven. A recent review of keropok from Food Science perspective is available (Karrila 2011). This starch based snack typically contains fish (Kaewmanee et al. 2015), or shrimp or other protein sources. In a starch based crispy snack food, brittle materials are in glassy amorphous state and water typically acts as a plasticizer (Labuza et al. 2004), so on absorbing water the product tends to transition from brittle amorphous state to soft rubbery state losing its crispness. Controlling water permeability of the packaging becomes an essential factor affecting the shelf life (Robertson 2009) of this product.

The water activity (a_w) of a food substance is essentially that relative humidity (RH) of surrounding air at which the food neither absorbs nor releases moisture (Karel and Lund 2003). The MSI is the relation of a_w and sample moisture content at such equilibria. The level of a_w is related to various degradation phenomena that determine the shelf life (Barbosa-Canovas et al. 2007). In particular, the phase change or glass transition of a crispy cereal snack tends to

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occur at a specific a_w called $a_{w,crit}$ (Labuza et al. 2004). Sometimes estimates of $a_{w,crit}$ can be discerned from the MSI of a dry foodstuff, as has been done with for example milk powder in Carter and Schmidt (2012).

The estimation of shelf life is conceptually based on the following elements. The sample inside the package is assumed to constantly be in equilibrium with the water vapor inside, so the relative humidity (RH) inside follows the MSI, given sample moisture. The rate of moisture entering the package is proportional to the difference of RH outside and inside, i.e. the difference in vapor pressures: the packaging is assumed to be the rate-limiting barrier determining alone moisture entrance rate (given vapor permeability and area of that barrier). Assuming the sample is dominant in capacity to take up moisture, while the headspace within package is comparatively insignificant, all moisture entering is assigned to the sample whose moisture content now follows the rate of permeation through the package.

Under these assumptions the progress of sample moisture content with time can be calculated. The role of critical point on the MSI is that reaching it is equated with the end of shelf life: up to this point moisture may have been accumulated by surface adsorption, but now bulk absorption begins with the accompanying degradation phenomena (loss of crispness, phase changes, structural rearrangements, and possibly chemical reactions). This conceptual scheme explains the roles of both MSI and the critical transition in current practice of estimating the shelf life, given the packaging and the environmental conditions.

The association of adsorption isotherm with glass transition is experimentally observed for maltodextrin (Samuhasaneetoo et al. 2004). A comparison of infant food formulas also confirms the glass transition effects of moisture, in this case inducing crystallization of lactose whose crystallinity experiences a dramatic step-like increase between water activities 0.33 and 0.43 (Tham et al. 2016). These studies determined the MSI by the traditional salt solution method, at a sparse set of a_w .

Nowadays, the modern dynamic dewpoint isotherm method is available for rapid MSI measurements (Carter 2015; Romani et al. 2016). It gives a near continuous coverage of a_w , typically with around one hundred measurement points during absorption. While the definition of a_w implies equilibrium, the rapid DDI method may not give enough time for equilibration (Schmidt and Lee 2012). However, while the slow traditional measurements demand little in terms of equipment and provide time for equilibration, food tends to mold and spoil during the weeks or months of measurement (Penner 2013): the true equilibrium of unspoiled food remains elusive. Furthermore, the traditional measurements only reveal a few equilibrium points, as typically less than ten saturated salt solutions are

prepared to regulate relative humidity. From such sparse data, detecting a transition point can only give very rough estimates.

Selected most important MSI models in food applications are available in a review paper (Al-Muhtaseb et al. 2002). Any model with only a small number of parameters will have scope limitations: some isotherm types are not approximated well by that specific model. Guidance to selecting an isotherm model for a food substance can be gleaned from Iglesias and Chirife (1982), which contains a tabulation of the best fit models—from a small selection that was tested—to a wide variety of literature curated measured isotherms, along with plots of all these isotherms.

However, these traditional models of MSI are by their design smooth, not showing any transition or “knee” in the MSI. With sparse data this is reasonable, but the DDI gives enough data to potentially show when a transition occurs.

The MSI of a dry food product is affected by many factors, for example the temperature and various plasticizers or humectants. The particle size of the sample is also an important factor affecting equilibration rate, as it relates to the sample surface that absorbs water. A natural way to speed up equilibration is to comminute the samples. Reducing the particle size (diameter, characteristic linear dimension) d improves interfacial exchange of moisture with surrounding air, because the specific surface of a powder is ideally proportional to $1/d$. If the intraparticle diffusion were rate limiting, both the moisture gradient and the diffusion distance would contribute to equilibration rate with combined effect proportional to $1/d^2$. In general, for comparable results across a set of samples, any pre-processing before a_w measurements should be consistent, as stated in chapter 6 by Fontana (2007) in Barbosa-Canovas et al. (2007). However, the effects on isotherms of powdering samples by grinding have received surprisingly little attention. Clearly such effects have gained importance with the introduction of the rapid DDI method that might require comminution to reduce equilibration times; it is the equilibrium isotherm that is physically meaningful.

While the effects of comminution on water absorption during immersion have been studied, for example in food context by Strange and Onwulata (2002), this appears to be possibly the first study assessing comminution effects on sorption isotherm.

The brief account above gives background and general context to the current study that focused on crispy fish cracker or keropok. The goals of this research were to investigate the effects of comminution by grinding on MSI for fish cracker samples using the DDI method, and to fit models to the MSI data in order to reveal an abrupt transition (sudden change in derivative) at a $a_{w,crit}$.

Materials and methods

Fish cracker material

Fish cracker samples were obtained from a local producer in Pattani province, Thailand. Fish cracker production is currently a homestead or cottage industry, without tight standards or quality control, and with minimal investment in machinery and automation. In our case the product ingredients were fresh fish meat (14.79% db), mixed cassava and sago starches (36.49% db), salt (0.15% db) and sugar (0.3% db); and the rest was water. During production, in brief, all those ingredients were mixed, kneaded and rolled to cylindrical bars, then placed in boiling water until cooked to obtain a gelled intermediate product. After cooling the gel was sliced to about 4 mm thickness and these circular chips were dried under the sun to around 10% moisture content. The dried gel was puffed using an 800 Watts microwave (Sharp-R220, Sharp Manufacturing Co. Ltd., Naknon Pathom, Thailand) for 1 min, and packed in polypropylene plastic bags. The packed samples were stored at ambient air-conditioned room temperature and used in the experiments within 5 days.

Comminution to powders

Fractionating a ground or powdered sample to various size fractions could select to these fractions different compositions or different states of material (e.g., crystalline vs. amorphous). In the current study the whole sample was ground, sieved, and the coarse fraction retained on sieve was ground again, repeating until the entire sample had the desired particle size. This leaves the composition unaffected, but the grinding may alter the state of materials in the particles. The grinding was manual with a mortar and pestle, and the targeted particle size ranges 250–425 μm , and < 180 μm were screened with laboratory sieves. Otherwise sample chips were fractured to granules of approximately 3000 μm diameter, to allow the weighing of suitable sample amounts for measurement. These were the three levels of comminution to be tested experimentally.

Sample moisture determination

The initial moisture content of each ground sample was determined by the AOAC hot air oven method (AOAC 2000), and converted to %dry basis. The moisture in samples is here always expressed as the moisture ratio (*MR*), which is the mass ratio of moisture to dry solids with the unit % dry basis (db).

Isotherm measurement

The MSIs were measured using the Vapor Sorption Analyzer (Decagon Devices Inc., Pullman, WA, USA), with the DDI method. The sample loaded in a 4 cm diameter and 1 cm deep stainless steel pan was around 1–2 g by weight. The settings in the control software were as follows. The flow rate was 100 ml/min, and a_w resolution was set at 0.01. The two stages of each run were: desorption from initial to $a_w = 0.2$; and adsorption for a_w from 0.2 to 0.9. The second stage provided the adsorption data for analysis, covering a_w range 0.2–0.9. The MSIs for samples of each particle size were measured at two temperature set-points, 25 °C and 35 °C. Thus full factorial design was applied, and the columns in Table 1 match each of these six cases.

Theory/calculations: method development to fit isotherms

The approach is straightforward in an Excel spreadsheet. We have not tested the optimizers available for other spreadsheet programs. The main goal of this modeling effort was to enable detecting a transition point in each absorption isotherm, as this appeared impossible by subjective visual inspection. Such transition point is one of the key elements needed to determine the moisture (water vapor) barrier properties required of packaging.

Other secondary benefits of fitting isotherm models include the following. A single adsorption curve measurement can give tens or even hundreds of a_w values with matching (pseudo)equilibrium moisture contents, so it is preferable to report a model that fit these data well and its fitted parameters. This fit may also remove measurement noise in the original data and the model can even be differentiated. Simulations or other calculations with isotherms tend to require fitted models, or at least interpolating the data. Furthermore, the parameters in physics based models may give insights into the dominant phenomena and mechanisms.

Common criteria for a “good” model include: small approximation error, parsimony or small number of parameters fitted, and ability to fit multiple cases. Consistent trends of the model parameters across the cases are desirable, and corroborate good behavior of the model.

Initial data fitting experiments were done with only one case, namely fish cracker ground to particle size < 180 μm and measured at 25 °C. It was found by exploration that in two segments the absorption isotherm is well represented by

$$MR = A \log(C - a_w) + B \quad (1)$$

Table 1 Summary of water adsorption isotherm fits to the various cases of powdered or granular fish cracker

Size range (μm)	< 180	< 180	250–425	250–425	3000	3000
Temperature (°C)	25	35	25	35	25	35
C	0.9296	0.9271	0.9367	0.9274	0.9379	0.9289
A	− 8.8627	− 10.4979	− 7.8898	− 9.9397	− 6.8548	− 8.0944
B	3.8185	3.6324	3.1307	3.0285	2.2933	2.3137
E	− 23.7486	− 24.0329	− 24.5751	− 24.0389	− 27.9222	− 26.4641
F	− 0.4781	− 0.2996	− 1.8114	− 1.0431	− 5.1366	− 3.4462
$a_{w,crit}$	0.4151	0.4148	0.4311	0.4131	0.4940	0.4431
MR_{crit} (% db)	6.3767	6.6821	5.4676	5.8989	4.7109	4.8518
R^2	0.9997	0.9996	0.9997	0.9997	0.9997	0.9997
minerr (% db)	− 0.3657	− 0.6444	− 0.2918	− 0.3324	− 0.3855	− 0.5305
maxerr (% db)	0.2442	0.5951	0.2434	0.4048	0.2622	0.3795

The fitted parameters (*A* to *F*) are for 10-based logarithm function in the model Eq. (2)

after the constant *C* is properly chosen and then held fixed. Here *MR* is the moisture ratio; *A*, *B* and *C* are fitting constants; and a_w is the water activity. In other words, with appropriate choice of *C* the plot of *MR* vs. $\log(C - a_w)$ shows two segments of straight lines, with transition at their knee or joint.

Once *C* is known, the remaining fitting of two lines is known in statistics as broken-stick fitting, a special case of segmented regression. Our problem is slightly more difficult, since we need to also find a *C*-value with which the broken stick gives a good fit. All fitting was done by least squares, i.e. in the spreadsheet a column calculating $(MR_{measured} - MR_{model})^2$ was formed, and the sum of this column was taken as the objective to be minimized for fitting the model.

The model equation used is an ad hoc—type statistical fit, it was not derived from any physical or thermodynamic conceptual model. However, several earlier isotherm models have used the terms $\log(a_w)$ and $\log(1 - a_w)$, among those listed in chapter 1 by van den Berg and Bruin (1981) in the book by Rockland and Stewart (1981). The former term is very frequent, while the latter is (implicit or explicit) in the model formulas A36 (Peirce equation) and A37 (Peirce equation with correction term for evaporation), A38 (Smith equation), A52 (Henderson equation), A53 (Day and Nelson equation), A54 (modified Henderson equation), and A55 (Henderson and Thompson equation), in the numbering system of that compiled list. Apparently some physical justifications for both these terms exist.

One novelty then was to replace the “1” in the latter term by an adjustable constant, as if correcting the a_w that the measurement device is recording with a constant shift before transforming with $\log(1 - a_w)$. The other novelty, in the context of isotherms, was the segmented regression with a transition from one segment of data to the other; this gives a jump discontinuity in the slope.

In Fig. 1a, $\log(a_w)$ does not show linear segments or obvious transitions, $\log(1 - a_w)$ shows possibly two transitions or one sharp transition and a long curved segment, and finally a properly tuned $\log(C - a_w)$ gives two linear segments with a sharp transition. The adsorption isotherm is also shown in conventional view without any transformations in Fig. 1b, with the model fit included for comparison. While in the conventional view it is difficult to discern any clear abrupt transition, the broken-stick fit makes the point of transition unmistakable. This transition point was interpreted as the critical point, giving the critical moisture and a_w .

To fit the whole absorption data in one step, i.e. to fit the two line segments and the parameter *C* simultaneously, the constants from *A* to *F* in

$$MR_{model} = \max\{A \log(C - a_w) + B, E \log(C - a_w) + F\} \quad (2)$$

were determined by least squares. The fitted parameter values will be listed specifically for 10-based logarithms; parameters *A* and *E* need to be re-scaled if another base is used.

This allows fitting the whole absorption isotherm in a spreadsheet, in one shot. Maximum works in (2) because the graph of *MR* vs. a_w curves up (a convex function), while if the graph was curving down (a concave function) we would have to use minimum instead.

The Solver in Excel 2010 did not find the least squares solutions, despite its various user options, while the freely downloadable Direct Optimizer add-in performed flawlessly and solved the optimum in each case within a few seconds. The constraint $C \geq 0.91$ helped avoid logarithms of negative numbers during the optimization search, started from $C = 1$ with the other parameters set to 0. Despite no failures to converge, we recommend that the optimization should be run twice to see if the numbers

Fig. 1 The measured water absorption isotherm for fish cracker ground to particle size below 180 μm , measured at 25 °C temperature, is explored by plotting variously transformed water activities in **a**, and a comparison of the measured MR to two fitted models illustrates the excellent fit obtained with the novel segmented model in a conventional isotherm plot (**b**). The constant C has the value given in Table 1

change, as an iteration limit might stop the first run early. Various calculation and stopping criteria parameters can be set for the optimizer, but instead of relying on them to be well set, this is a simple and good practice. If the optimization already converged the next run will stop immediately; otherwise it is a push of a button and at most a few seconds to wait.

The intersection “knee” of the fitted lines is at

$$\log(C - a_{w,crit}) = (F - B)/(A - E) \quad (3)$$

from which

$$a_{w,crit} = C - 10^{(F-B)/(A-E)} \quad (4)$$

as the default logarithm in Excel is 10-based. The critical MR is given by

$$MR_{crit} = (EB - AF)/(E - A) \quad (5)$$

Data analysis

The adsorption data were processed in Excel 2010 worksheets, using the freely downloadable Direct Optimizer version 1.01 (2006) add-in to fit parameters by least squares. Statistical testing of the critical point results was run in the freely downloadable jamovi software (version 0.9.5.12).

Results and discussion

Subjective assessment of measured isotherms

The measured isotherms are shown in Fig. 2. Obviously the comminution had a consistent effect at each measurement temperature, increasing the adsorbed moisture at low and midrange a_w . Theoretically a_w at a given MR increases with temperature, following the Clausius–Clapeyron equation of thermodynamics, but the observed temperature trend was opposite to this: as temperature increased the curves moved “up and left”, while from theory we would expect “down and right”. However, similar observed behavior with temperature is seen in several plots of Iglesias and Chirife (1982), so our data are qualitatively quite reasonable despite conflicting with expectations from Clausius–Clapeyron equation.

As MSI curves with smooth appearance were obtained in all cases, determining a $a_{w,crit}$ with matching MR for each isotherm was not possible by subjective assessment of the isotherm graphs. Also in a recent study (Romani et al. 2016) of a biscuit snack, no subjectively obvious knee or transition could be detected in the MSI curves, and generally the MSI curves from DDI tend to appear smooth for crispy snacks. While determining the $a_{w,crit}$ would be very useful, it requires data analysis that can vary case by case.

Model fit summary

The water adsorption isotherm fits are summarized in Table 1 across all cases of fish cracker samples, and the implications of these results are now discussed in relation to the goals of this research.

Goodness of fit with the novel isotherm model

The novel isotherm model performed extremely well, as shown by the last three rows of Table 1. The R^2 value (coefficient of determination) was obtained from the trend line in Excel for a plot of $MR_{measured}$ vs. MR_{model} , and is better than 0.9995 in all cases.

The directional error bounds $minerr$ and $maxerr$ were calculated for each single isotherm so that

$$MR_{model} + minerr \leq MR_{measured} \leq MR_{model} + maxerr \quad (6)$$

Across all samples, the largest absolute error of fit is below 0.6% db. Moreover, these maximal errors are at high values of MR , while around the critical transition point the accuracy of fit is of the order 0.1% db.

This extremely good fit of measurement data by two straight line segments after the one-parameter transformation $\log(C - a_w)$ indicates that the measured data were mutually consistent. It does not imply that the data were precise or accurate. The results appear close to ideal for determining a transition point or a critical point and summarizing isotherms with a few parameters.

Figure 1b includes the least squares fit with the often practiced GAB model by Guggenheim, Anderson and de Boer, correctly given for example in Siripatrawan and Jantawat (2006), here achieving coefficient of determination $R^2 = 0.98$. The parameters in the GAB model were constrained to the ranges given in the Vapor Sorption Analyzer Operator’s Manual (Decagon Devices Inc., Pullman, WA, USA). The comparison obviously favors our novel isotherm model, and illustrates how the apparently good coefficient of determination 0.98 can mislead: the GAB model cannot reproduce the data with good accuracy. As seen in Fig. 2, all cases gave isotherms with similar

Fig. 2 Adsorption isotherms plotted for the various fish cracker cases. The lower temperature cases are shown with lines while the higher temperature cases are shown by symbols at the measured points (see the embedded legend for details)

characteristic shape, so an isotherm model fitting one of these well is expected to also describe the other cases with good approximation. Table 1 confirms this expectation.

This isotherm model has two linear segments after a simple transformation of the water activity. The knee or joint of these segments was interpreted as the critical transition point, at which surface adsorption transitions to bulk absorption. This novel isotherm model should only be considered a mathematical or statistical trick that might be helpful; it was not derived from known physics or thermodynamics.

It is worth emphasizing that traditional isotherm models are smooth, they will never display a jump discontinuity of the derivative or slope. To create such a jump it is natural to segment the data, so at some point the equation changes, which gives the jump. Segmented fitting of models would seem to require manual selection of the segments, essentially hand picking the approximate jump point first. However, suitable optimization software fully automated this task in our current case study, making segmented fitting easy to practice in a very pragmatic way using just a common spreadsheet. This makes the computational approach reproducible and user-independent.

In summary, to extract quantitative characteristics from measured isotherms, a new type of isotherm equation was devised. It fit the adsorption isotherms of fish cracker extremely well. This novel isotherm model is potentially useful also for other starch crispy snack foods. The practical data fitting in a common spreadsheet was described in detail.

Effects of sample comminution and isotherm temperature

The dependence of $a_{w,crit}$ estimates on comminution and temperature set-point is shown in Fig. 3. The critical points

Fig. 3 The critical water activities estimated by segmented model fits show consistent trends with the isotherm temperature as well as with the particle size of sample

or glass transition points in prior literature, such as Jakubczyk et al. (2008) and Carter and Schmidt (2012), tend to have a_w around 0.4 and $MR < 10\%$ db, so our estimates appear reasonable in magnitude.

The $a_{w,crit}$ consistently decreased both with particle comminution and with temperature. However, the temperature effect decreased as the particles got smaller, until this effect practically vanished. This suggests that the measurements had high precision: a mere coincidence would be unlikely. Also in prior published results, such as for spray dried milk powder, the $a_{w,crit}$ tends to decrease with temperature (Carter and Schmidt 2012).

On one hand this shows again that the grinding of fish cracker to a powder clearly and consistently affected its adsorption isotherm. On the other hand, such grinding made the $a_{w,crit}$ estimate robust against measurement temperature effects. This may indicate that the rapid dynamic measurement recorded pseudo-equilibria, i.e. with comparatively large particles the equilibration was far from complete. Then the rate-effects of temperature (Hébrard et al. 2003) were significant, and at the higher temperature the granular samples got closer to equilibrium and to the powdered samples, while at the lower temperature the granular samples lagged further away. An Analysis of variance (ANOVA) run with only the main effects from particle size and temperature (i.e., no interaction term, due to so few cases) showed no significant effects on $a_{w,crit}$.

A similar plot of the critical moisture ratio (MR_{crit}) is shown in Fig. 4. The trends with comminution and temperature are again consistent, so that MR_{crit} slightly increased with temperature and dramatically increased with comminution. The effect size of a 10 °C change in temperature was maximally about 0.5% db (for the case with 250–425 μm particles), while the effect size of powdering the sample was maximally about 1.8% db (at the higher of the two temperatures). ANOVA analysis (Table 2) showed

Fig. 4 The critical moisture ratios that match the critical water activities show consistent trends with the isotherm temperature and with the particle size of sample

Table 2 The ANOVA analysis of the main effects, particle size and temperature, on MR_{crit} (no interaction term in model)

Factor	Sum of squares	df	Mean square	F	p	H ² p
Size (μm)	3.0567	2	1.5284	144.1	0.007	0.993
Temp ($^{\circ}\text{C}$)	0.1284	1	0.1284	12.1	0.074	0.858
Residuals	0.0212	2	0.0106			

that particle size had a statistically significant effect on the MR_{crit} , and the last column after p value shows partial effect size estimates relative to standard deviation in the data. The post-hoc test with Tukey's correction (Table 3) shows that any two of the tested particle sizes differ mutually, statistically significantly as regards MR_{crit} .

Sample comminution increased the specific surface, reduced diffusion distances, and likely broke moisture barriers formed by oils or fats. Thus MR_{crit} was expected to increase with powdering, as it indeed did. This corroborates incomplete equilibration of the coarse particles. Because of the moisture barrier removal by comminution, the critical moisture does not inform about completeness of equilibration; and temperature effects on the moisture barriers are non-obvious.

The comparatively small effect size of temperature suggests that, in the temperature range from 25 to 35 $^{\circ}\text{C}$, measuring the water adsorption isotherm at a single temperature suffices for fish cracker. The observed temperature trend is opposite to expectations, as it was for the whole isotherms: both moisture and heating tend to plasticize, so less moisture should be required at a higher temperature for transition. However, as noted for the whole isotherms, unexpected behavior can still be reasonable. Various types of transition that correlate with each other and relate to crispness are discussed in Labuza et al. (2004), including the glass transition, and the moisture required typically decreases with temperature for these transitions.

There is no prior journal publication quantitating the effects of powdering samples on their moisture adsorption isotherms, although some prior work has inspected various size fractions in a sample. For semolina the equilibration (adsorption) rate increases with temperature in the range from 25 to 45 $^{\circ}\text{C}$, and for its size fractions the rate increases as the size decreases (Hébrard et al. 2003); both observations match basic expectations from physics and physical chemistry. Since fractionation can select for chemical composition or material state, its effects need not be the same as those of grinding a sample. In a study of

starch-protein extrudates made of potato starch with soybean and milk proteins, the isotherms were measured for the below 0.2 mm fractions of the extrudates, but the effects of actual grinding were not assessed (Włodarczyk-Stasiak and Jamroz 2008). However, according to Penner (2013) a poster by Shands and Labuza (2009) has described experiments with corn flakes, showing comminution effects on isotherms (we have had no access to that conference poster). Our results corroborate such effects that are quite reasonably expected; if not from dynamics of the measurement, then from moisture barriers.

Since comminution or powdering by grinding had a clear effect, we may ask which measurement results are more relevant to the crispy chips that are packaged. We can argue for the powdered samples as follows. First, their critical point estimates were only slightly affected by temperature, and possibly actual material characteristics were measured as opposed to particle size effects. Second, because the practical shelf life is comparatively long, the chip format snacks have ample time to equilibrate—they should get close to the true equilibrium, which is a physical material characteristic. Therefore the true equilibrium may be more relevant than the rapidly measured pseudo-equilibrium of granular samples. However, without actual dynamic models validated at the relevant time-scales this argument only provides a reasoned but unvalidated hypothesis.

We recommend that the moisture adsorption isotherms of crispy food products should be measured both in granular form and in finely powdered form ($\sim < 200 \mu\text{m}$ particle size). For shelf life estimates the best case is the finely powdered sample that can absorb significantly more moisture before reaching its critical point. The coarser granular sample can absorb less but it has slightly higher $a_{w,crit}$, which benefits only little in a high humidity environment: it is the difference in relative humidity outside and inside the packaging material that determines the vapor diffusion rate through this rate-limiting barrier. Thus the granular case is worse off with about similar rate of

Table 3 Post-hoc testing for particle size comparison as regards MR_{crit}

Size (μm) comparison	Mean difference	SE	df	t	p-tukey
< 180 vs. 250–425	0.846	0.103	2.00	8.22	0.026
< 180 vs. 3000	1.748	0.103	2.00	16.98	0.006
250–425 vs. 3000	0.902	0.103	2.00	8.76	0.023

receiving moisture but poorer capacity to tolerate it, and it gets the shorter shelf life estimate. (Under contrived unlikely conditions the difference in $a_{w,crit}$ can dominate over the difference in capacity to tolerate moisture. Namely, if the ambient humidity were between the two critical activities, then only the fine grained sample could gain moisture beyond its critical point.

The detailed theory of shelf life estimates, in terms of equations, is covered in prior literature both in theory (Taoukis et al. 1988) and with practical examples (Kulchan et al. 2010).

We also suggest that the isotherm model that was here successful might be useful more widely for crispy snack foods that are moisture sensitive. In particular, its segmented nature with a “knee” identifies the $a_{w,crit}$ and MR_{crit} , which often relate to the glass transition, provided that a good fit to the MSI is achieved with this model.

The powdering of puffed fish cracker, a snack food popular in ASEAN countries, had definite positive effects on the water adsorption isotherm measurements, as it stabilized the $a_{w,crit}$ results against temperature effects, indicating that equilibration may have been near complete during the dynamic measurements by DDI method. Thus actual material characteristics may be discerned from a powdered sample.

Conclusion

Measured dynamic dewpoint moisture sorption isotherms (DDIs) for a crispy dry starch based snack, fish cracker, were extremely well fit by segmented regression. The switch point between segments was interpreted as the critical transition with moisture accumulation, relevant to phase changes in the sample that cause loss of crispness. Subjectively the DDI curves appeared smooth with no clear transition point, while segmented regression provided critical point estimates with consistent behavior across the test cases. This approach could be widely applicable to DDI data, to provide the practically important estimates of critical transitions.

From the results we conclude that the particle size of a ground starch based snack, here specifically of fish cracker, clearly affected the moisture adsorption isotherm and the $a_{w,crit}$ estimated from the isotherm. Care needs to be taken if $a_{w,crit}$ is further used for shelf life estimates of this kind of product.

Analysis of the critical transitions indicates that powdering the sample at least reduced, possibly eliminated incomplete equilibration during the rapid DDI measurements. Therefore we recommend powdering samples to avoid corruption by particle size effects of DDI results. However, since powdering removes moisture barriers that

are intrinsic to many food products and strongly affect their moisture sorption, also granular samples should be measured: these are expected to give comparatively pessimistic shelf life estimates.

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Compliance with ethical standards

Conflict of interest The Authors' declares that they have no conflict of interest.

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