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A thin film dryer approach for the determination of water diffusion coefficients in viscous products

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Abstract

A thin film dryer (TFD) device has been used to study the drying behavior of viscous products and their water diffusivities. The thin product film was dried convectively using different air velocities, air temperatures, air humidities, initial solid concentrations, initial film thicknesses and optional addition of agar.

A mathematical model was developed based on the external and internal heat and mass transfer with ideal shrinkage. A coordinate system attached to the solids was used and later transformed to the initial height to facilitate the numerical implementation. The diffusion coefficient of the product was expressed as a function of water content and temperature by fitting the model to the experimental drying kinetics (for different conditions) obtained for a given product. The diffusion coefficients obtained for maltodextrin and PVP show good agreement with literature. They are significantly reduced when the material changes from the rubbery to the glassy state and can be well expressed by the Williams–Landel–Ferry (WLF) equation. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Diffusion; Modeling; Shrinkage; Thin film dryer; Maltodextrin

1. Introduction

Spray drying is often used in industry for dehydration of viscous foods. Although it is well known and implemented since decades, it is still partially based on empirical assumptions. In order to improve predictions for scale up or product change, it is important to investigate the limiting mechanisms governing the drying process.

The behavior of droplet drying is described by its external and internal mass and heat transfer. The internal mass transport is limited by the diffusion. This limitation is the focus of this work. The diffusion described by the diffusion coefficient, D, increases with the temperature and decreases sharply with decreasing water content. However, the values given in literature vary strongly, especially in the range of low water content. Most results consider drying kinetics of a droplet in an airflow, despite the presence of undesired phenomena affecting the results. One method to determine the drying kinetics is the filament method influenced by thermal conduction and asymmetric drying. Another method is acoustic levitation, showing however artificial deformation and enhanced convection. These side effects are difficult to determine and are often not taken into account. Due to this limitation we propose thin film drying for the validation of drying kinetics and the resulting diffusion coefficients.

A mathematical model was developed to describe the drying of a shrinking film using a coordinate system attached to the solids, which allows an easier numerical implementation of product shrinkage. The diffusion coefficient as a function of the water content and temperature is computed by fitting the model to the experimental drying results.

2. Theory

2.1. Ideal shrinkage

As no porosity develops during experimental drying, ideal shrinkage can be assumed and the diffusion of water (concentration C_w) must be exactly counter-balanced by diffusion of solids (concentration C_s). Volume additivity, therefore implies:

$$V_w + V_s = \frac{m_w}{\rho_w} + \frac{m_s}{\rho_s} \tag{1}$$

or after division by the volume:

$$\frac{C_w}{\rho_w} + \frac{C_s}{\rho_s} = 1 \tag{2}$$

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Nomenclature

a, b, c, d	parameters of diffusion coefficient
C	concentration (kg/m^3)
C_1, C_2	parameters in WLF equation (K)
D	diffusion coefficient (m^2/s)
E_a	activation energy (kJ/mol)
h	coordinate attached to the solids (m)
H_0	initial height of the film (m)
J	relative mass flux (kg/(m^2 s))
m	mass (kg)
n	mass flux relative to stationary coordinate (kg/(m^2 s))
T	temperature (K)
v	velocity (m/s)
V	volume (m^3)
x	coordinate in stationary system (m)
X	water content in dry basis (kg/kg)

Greek symbols

ρ	density of compound (kg/m^3)
ξ	new coordinate (m)

Superscripts

*	volume averaged
$\circ$	relative to solids
0	initial (time = 0)

Subscripts

air	air
bulk	bulk (solid + water)
g	glass transition
s	solid
w	water

It may be rewritten as:

$$\frac{n_w}{\rho_w} + \frac{n_s}{\rho_s} = 0 \tag{3}$$

with the mass flux n_w and n_s relative to the stationary coordinate, x.

2.2. *Mass flux in a shrinking system*

The water flux in a shrinking system can be expressed relative to a stationary coordinate described with n_w or relative to the *mixture* (solid and water) with J_w. The solid flux is respectively expressed as J_s and n_s. For calculating the water velocity, v_w (in relation to the stationary coordinate, x), the relative water velocity, $v_{rel,w}$ has to be coupled with the bulk mass average velocity, v_{bulk} (Fig. 1):

$$v_{rel,w} = v_w - v_{bulk} \tag{4}$$

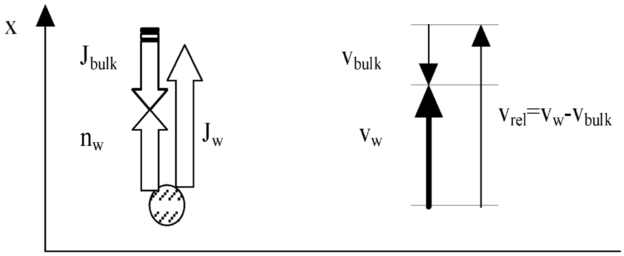

Fig. 1. Mass flux and velocities in a shrinking system.

The relative water velocity, $v_{rel,w}$, the velocity v_w, v_s, and mass average velocity, v_{bulk} are given by the ratio of flux to the concentration [1]:

$$v_{rel,w} = \frac{J_w}{C_w} \tag{5}$$

$$v_w = \frac{n_w}{C_w} \tag{6}$$

$$v_s = \frac{n_s}{C_s} \tag{7}$$

$$v_{bulk} = \frac{n_s + n_w}{C_s + C_w} \tag{8}$$

Combination of these equations leads to:

$$n_w = J_w + v_{bulk} C_w \tag{9}$$

The relative mass flux, J_w of water may be expressed the following way [1]:

$$J_w = -D\rho \frac{\partial (C_w/(C_w + C_s))}{\partial x} \tag{10}$$

Combining Eqs. (9) and (10) leads to Eq. (11):

$$n_w = -D\rho \frac{\partial (C_w/(C_w + C_s))}{\partial x} + v_{bulk} C_w \tag{11}$$

which is implemented by several authors [6,11,14]. Eq. (11) may be reduced to a simplified form utilized by [2] under the assumption of constant density, $\rho = C_w + C_s$:

$$n_w = -D \frac{\partial C_w}{\partial x} + v_{bulk} C_w \tag{12}$$

However, for a shrinking system, this assumption is only valid if $\rho_w = \rho_s$.

The simplification of Eqs. (9) and (10) show the well-known equation of mass transfer:

$$n_w = -D \frac{\partial C_w}{\partial x}, \qquad n_s = -D \frac{\partial C_s}{\partial x} \tag{13}$$

Instead of calculating the flux relative to bulk mass averaged velocity as shown, we can also define a bulk velocity, v^* averaged over the volume:

$$v^* = \frac{n_w}{\rho_w} + \frac{n_s}{\rho_s} \tag{14}$$

which is also mentioned in [1]. The mass flux with the volume averaged velocity becomes:

$$n_\mathrm{w} = J^*_\mathrm{w} + C_\mathrm{w} v^* \tag{15}$$

as mentioned in [8,15]. Note that, in an ideal shrinking system, Eq. (3) implies $v^* = 0$ and $n_\mathrm{w} = J^*_\mathrm{w}$.

Let us introduce a 4th coordinate system linked to the solids. The solids do not move relative to this new coordinate system, which allows us to maintain the same amount of solids in the slices obtained by discretisation. Let us name the relative mass flux, J°_w and velocity, v°_w:

$$v^\circ_\mathrm{w} = v_\mathrm{w} - v_\mathrm{s} \tag{16}$$

With the definition of velocities from Eqs. (6) and (7), we obtain the same equation as [5,14]:

$$J^\circ_\mathrm{w} = n_\mathrm{w} - \frac{C_\mathrm{w}}{C_\mathrm{s}} n_\mathrm{s} \tag{17}$$

2.3. Fick's second law

The change of water concentration, C_w is commonly described in literature with Fick's second law, illustrated in Eq. (18):

$$\frac{\partial C_\mathrm{w}}{\partial t} = \frac{\partial}{\partial x}\left(D\frac{\partial C_\mathrm{w}}{\partial x}\right) \tag{18}$$

However, this approach is calculating the change of concentration at a fixed point along the stationary coordinate system, x (shown in Fig. 2A), which creates numerical difficulties due to the shrinkage of the boundary layer. Therefore, a shrinking coordinate h, which is attached to the solids, is proposed (shown in Fig. 2B).

Eq. (17) can be transformed with Eqs. (3) and (13) in an equation as a function of concentration gradient:

$$J^\circ_\mathrm{w} = -D\frac{\rho_\mathrm{s}}{C_\mathrm{s}}\frac{\partial C_\mathrm{w}}{\partial h} \tag{19}$$

The change of mass in a certain position in the new coordinate, h (Fig. 2B) can be described by the difference of mass flux relative to the moving boundaries (Eq. (19)):

$$\frac{\partial}{\partial t}(C_\mathrm{w}\,\Delta h) = -\rho_\mathrm{s}\left[\left(\frac{D}{C_\mathrm{s}}\frac{\partial C_\mathrm{w}}{\partial h}\right)\bigg|_h - \left(\frac{D}{C_\mathrm{s}}\frac{\partial C_\mathrm{w}}{\partial h}\right)\bigg|_{h+\Delta h}\right] \tag{20}$$

Partial differentiation of the left-hand side and substitution of $\mathrm{d}(\Delta h)$ from mass conversion [10] with

$$\mathrm{d}(\Delta h) = \Delta h\,\frac{\rho_\mathrm{s}}{\rho_\mathrm{w} C_\mathrm{s}}\,\mathrm{d}C_\mathrm{w} \tag{21}$$

results in Eq. (22), which is equivalent to the equation of [14]:

$$\frac{\partial C_\mathrm{w}}{\partial t} = C_\mathrm{s}\frac{\partial}{\partial h}\left[\frac{D}{C_\mathrm{s}}\frac{\partial C_\mathrm{w}}{\partial h}\right] \tag{22}$$

Introducing a new, virtual coordinate system, ξ (see Fig. 2C), which keeps the same amount of solids (C_s as solid concentration) in each section:

$$C^0_\mathrm{s}\,\mathrm{d}\xi = C_\mathrm{s}\,\mathrm{d}h \tag{23}$$

results in

$$\frac{\partial C_\mathrm{w}}{\partial t} = \frac{C^2_\mathrm{s}}{(C^0_\mathrm{s})^2}\frac{\partial}{\partial \xi}\left[D\frac{\partial C_\mathrm{w}}{\partial \xi}\right] \tag{24}$$

With the transformation of the diffusion coefficient

$$D_\xi = D\left(\frac{C_\mathrm{s}}{C^0_\mathrm{s}}\right)^2 = D\left(\frac{\mathrm{d}\xi}{\mathrm{d}h}\right)^2 \tag{25}$$

and the substitution of the water concentrations as a function of the dry basis water content, X (kg H_2O/kg solids) Eq. (24) simplifies to:

$$\frac{\partial X}{\partial t} = \frac{\partial}{\partial \xi}\left[D_\xi\frac{\partial X}{\partial \xi}\right] \tag{26}$$

This equation has the same form as Fick's second law for a non-shrinking system, although the shrinkage is taken into account in the modified diffusion coefficient.

2.4. Diffusion coefficient of water

The water diffusion coefficient, D in maltodextrin and PVP were expressed by the following basic equation as a function of the water content, X (kg H_2O/kg solid):

$$D_{30\,^\circ\mathrm{C}} = \exp\left(-\frac{a+bX}{1+cX}\right) \tag{27}$$

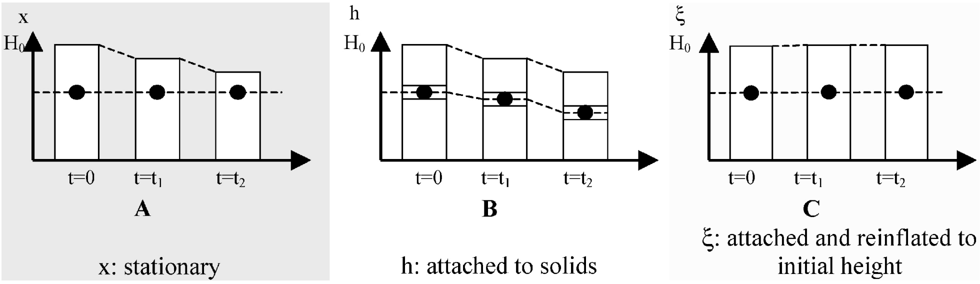

Fig. 2. Coordinate systems in a shrinking film.

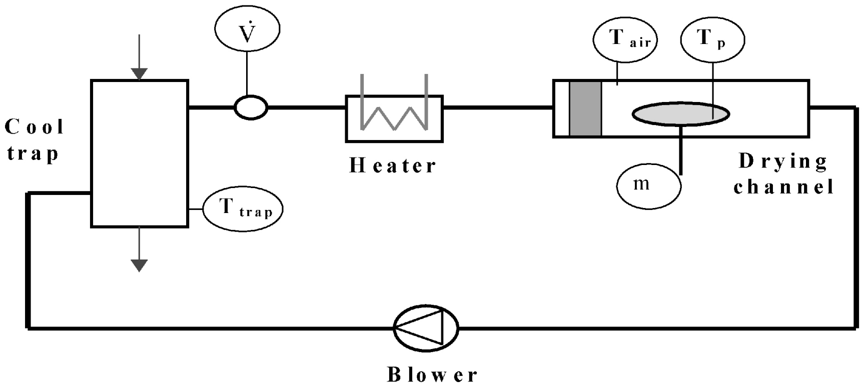

Fig. 3. Flowsheet.

and an Arrhenius type temperature dependency [16,18] with the activation energy, E_a (kJ/mol):

$$D = D_{30\,^{\circ}\mathrm{C}} \exp\left(-\frac{E_a}{R}\left(\frac{1}{T} - \frac{1}{T_{30\,^{\circ}\mathrm{C}}}\right)\right) \tag{28}$$

$$E_a = \frac{d + 190X}{1 + 10X} \tag{29}$$

Following the viscosity approach [7,12], the Williams–Landel–Ferry (WLF) equation may be used to express the behavior of the diffusion coefficient with the temperature difference to the glass transition temperature ($T - T_g$) in the range above T_g.

$$\log_{10}\left(\frac{D}{D(T_g)}\right) = \frac{C_1(T - T_g)}{C_2 + (T - T_g)} \tag{30}$$

The behavior of the diffusion coefficient can be described with only three parameters by using the WLF Eq. (30).

3. Experimental

The setup for the drying experiments of the thin film is shown schematically in Fig. 3. The airflow is adjusted with a blower, humidified in a cool trap and later heated to obtain the desired air conditions. Passing the flow through several meshes ensures a homogeneous airflow in the drying channel. This is confirmed by CFD calculations and experimental measurements. Two independent techniques were used to determine the external heat transfer coefficient: isothermal water evaporation experiments and heat transfer experiments. These were carried out at different air temperatures, air humidities and air velocities. The results were expressed in terms of a Reynolds–Nusselt correlation. The mass loss and temperature were recorded continuously for the following conditions: temperature from 30 to 70 °C, air humidity from 4 to 22%, airflow from 0.5 to 1.0 m/s, initial solid content from 25 to 50% and initial layer height from 0.6 to 2.0 mm.

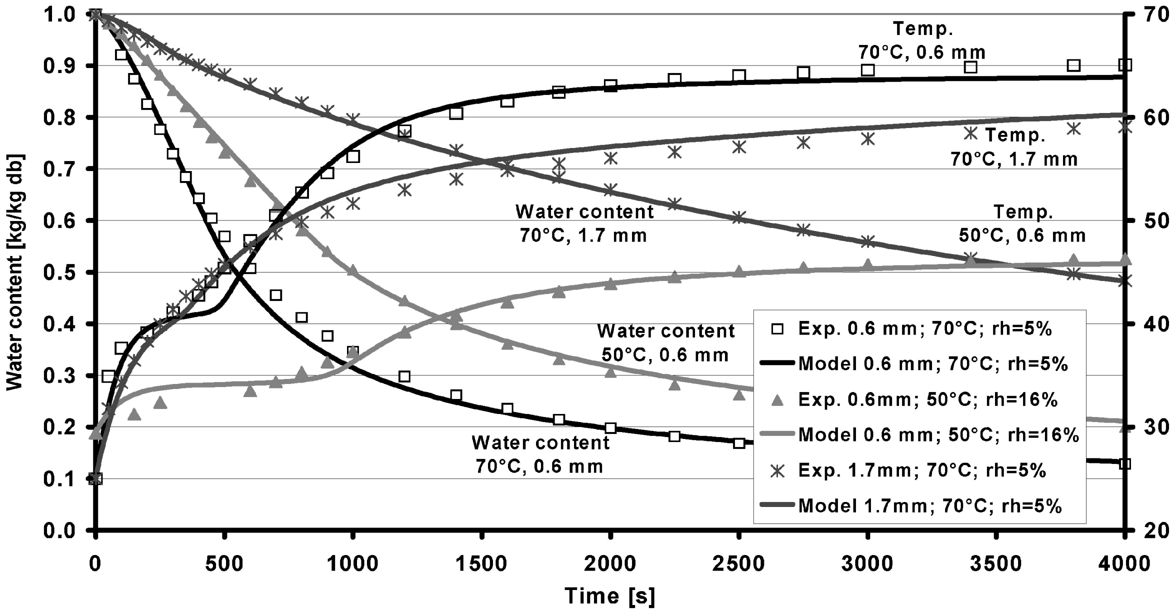

Fig. 4. Comparison model and experiments for the drying kinetics of maltodextrin with a TFD.

Maltodextrin with a dextrose equivalent (DE) of 33 was dissolved in the water. In the PVP experiments, a PVP (averaged MW = 10,000) water solution at an initial solid concentration of 45% was used. In order to avoid the internal convection in the film, 0.1% agar–agar was optionally added to the solutions.

4. Results and discussion

The drying kinetics predicted by the model and experiments are compared for maltodextrin and PVP solutions. Fig. 4 shows the water content and temperature profile of maltodextrin as a function of air temperature (50 and 70 °C) and film thickness (0.6 and 1.7 mm), which are the most sensitive parameters. They show excellent agreements in both temperature and water content, for all conditions. However, the drying kinetics without added agar–agar (not displayed) showed a much faster drying than the ones with agar–agar, especially for thick layers. This difference is explained by the internal convection, which is more important in a thick layer, but can be avoided by addition of gellifying agent.

The resulting diffusion coefficients follow Eqs. (27)–(29) and are obtained by fitting all water content and temperature profiles of 11 different kinetics. They are illustrated in Fig. 5 and compared to the literature values [3,4,8,13,17]. The calculated diffusion coefficients show a good agreement with the data found in literature near 30 °C. They decrease sharply in the region of the glass transition. The comparison of the drying kinetics for PVP resulting from the model and the experiments are displayed in Fig. 6. They show an excellent agreement for both the 0.7 and 2.0 mm film. The

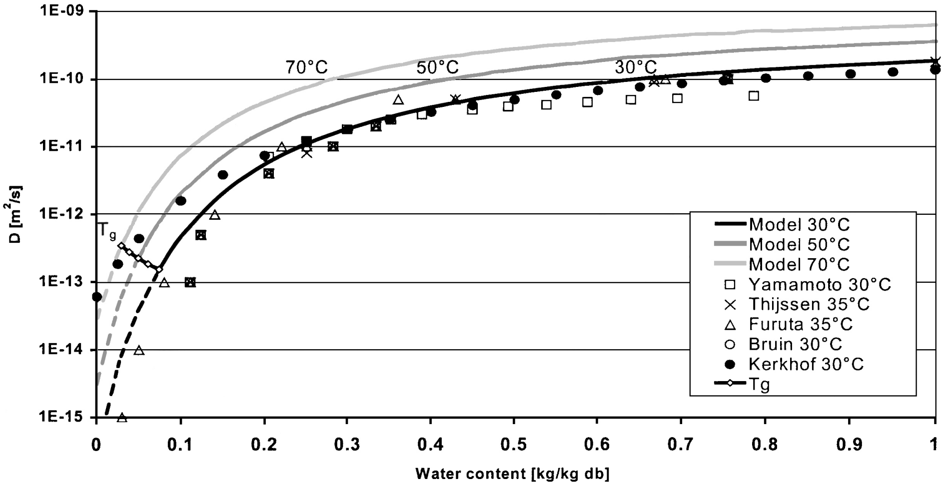

Fig. 5. Diffusion coefficients for maltodextrin.

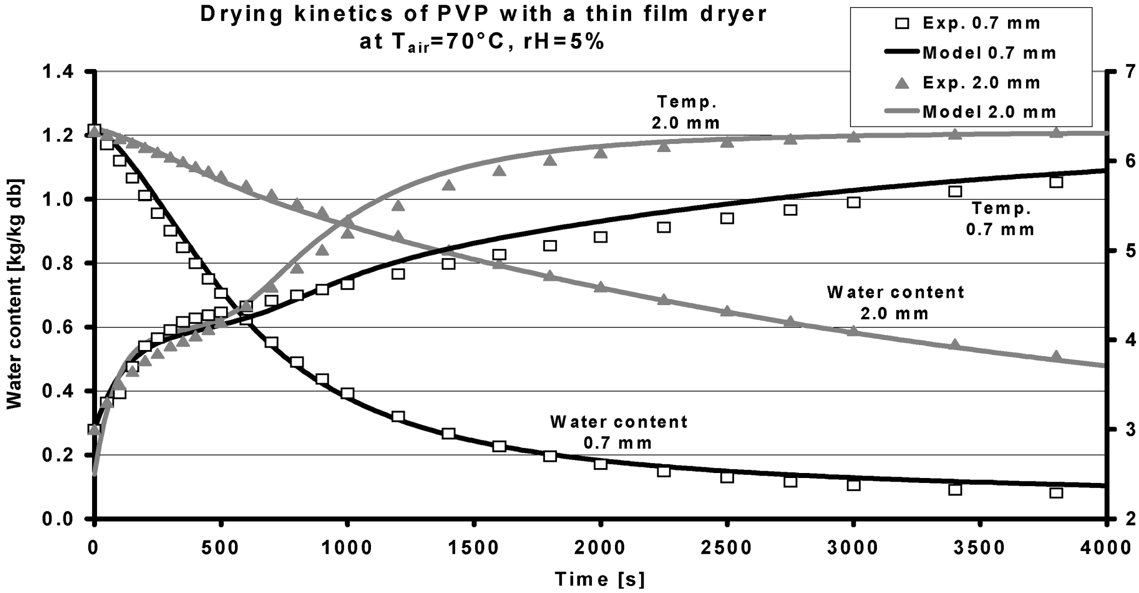

Fig. 6. Comparison model and experiments for the drying kinetics of PVP.

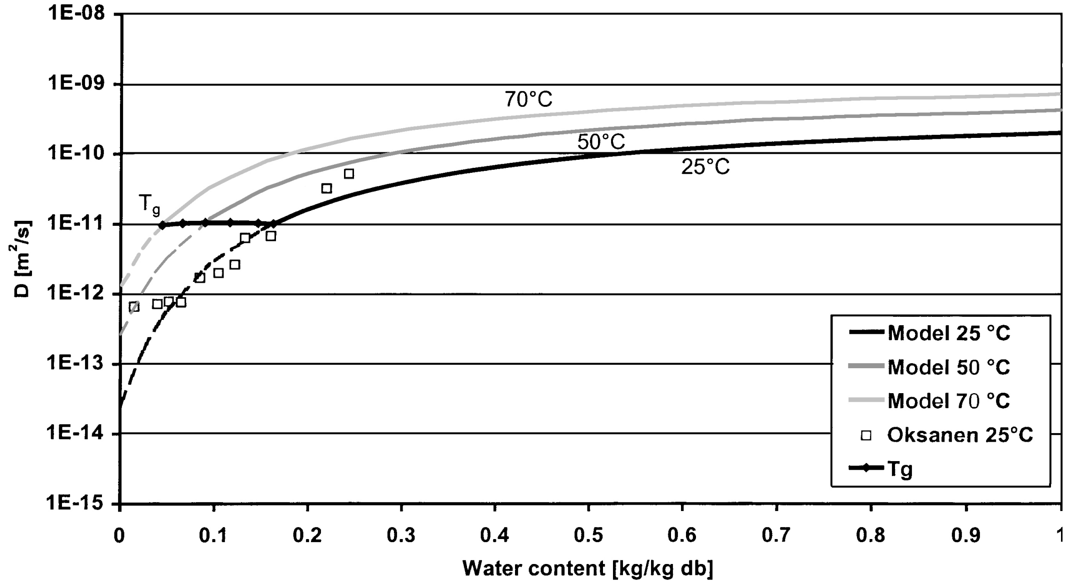

Fig. 7. Diffusion coefficient for PVP.

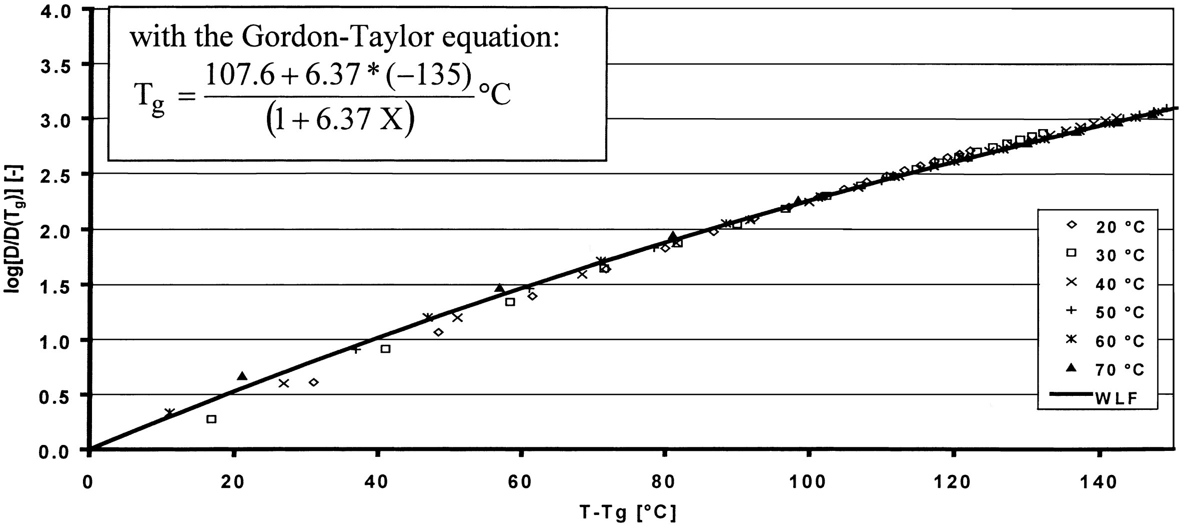

Fig. 8. WLF equation for the diffusion coefficients for maltodextrin.

influence of agar–agar (not displayed) was negligible in the case of PVP.

The resulting diffusion coefficients for PVP are plotted in Fig. 7. They show a good agreement with the data from [9] at 25 °C. The parameters (Eqs. (27) and (29)) for the diffusion coefficients for the maltodextrin and PVP are given in Table 1.

Applying the WLF Eq. (30) to the obtained diffusion coefficients allows to express the diffusion coefficient as a function of the glass transition temperature, which depends on the moisture content (Gordon–Taylor equation). The excellent fit (three parameters: $D(T_g)$, C_1, C_2) for the maltodextrin is shown in Fig. 8.

Table 1
Parameter for the diffusion coefficients for maltodextrin and PVP

Parameter	Maltodextrin (DE 33)	PVP (k15)
a	35.8	30.8
b	215	195
c	10.2	9.2
d	100	75

5. Conclusion

A thin film dryer (TFD) has been used to validate the modeling of a shrinking system. It is a powerful, but simple method to determine reliable water diffusion coefficients of viscous products.

The calculated diffusion coefficients are based on the fit of the model and the experiments for several conditions at the same time. The obtained diffusion behavior for maltodextrin and PVP showed a good agreement with literature. In case of maltodextrin, agar–agar had to be added to avoid internal convection. However, the addition of agar was not required in the PVP solution, which may be related to the higher viscosity of the PVP solution compared to the maltodextrin solution. A higher viscosity will naturally suppress the internal convection.

The diffusion coefficients were well described by the WLF equation, which relates them to the difference between the actual temperature and the glass transition temperature, T_g (water content dependent).

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