

Comparison on Modelling of Drying Kinetics of Granular Polymers PA6 by Diffusion Models and Normalization Method

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Abstract :

In this work, the drying behaviour of single granular PA6, hanging in the flow direction of hot air in a drying chamber, was investigated. In the experiments, the air was passed through the chamber at constant very low velocity in the drying chamber of about 0.01 m/s but in a variety of temperatures (60, 70 and 80 °C). In order to obtain drying data, the changes in the mass of the polymer were measured by magnetic suspension balance. The variations of moisture content and drying rates with time were used to test two diffusion models (i.e. Arrhenius and Vrentas Duda) and normalization model (developed by van Meel) given in the literature. A one-dimensional model for diffusion inside isothermal and spherical single particle was used. The simulation was performed by solving the diffusion equation by pdepe command editor in Matlab and fitting the value of D simultaneously. The fitting procedure was conducted by minimizing the sum square of error (SSE) between mean particle moisture obtained from measurement and simulation. The measured drying rates do not indicate the first constant drying rate period and then the critical moisture content for any of the investigated temperatures of drying. By Arrhenius model, it founded the diffusion coefficient of moisture migration is $6.15 \times 10^{-12} \text{ m}^2/\text{s}$ for 60°C, and by linear regression from three different temperatures drying data result the activation energy 54.3 kJ/mole. However, the Arrhenius model given not a good agreement. Furthermore, the normalization of drying curves does not work well due to each temperature has a different normalized drying curve. Finally, the Vrentas-Duda model was found the best for explaining the drying behaviour of PA6. By using this model, the phenomenon of drying tail or plateau diffusion can be properly described.

Keywords: Diffusion, Drying, Modelling, Normalization, Polymer

1. Introduction

In the production of polymers, drying is one of the major recovery operations employed to obtain a final saleable product from a reaction process [1]. Since it consumes large amounts of energy, the drying process deserves attention towards both energy savings and improvement of the quality of dried polymer. Furthermore, a study of drying kinetics could be helpful in the selection of adequate drying systems. In this work, the study focuses on drying of granular of PA6 where water is the moisture in the wet polymer particles. The moisture content, X, in PA6 is an extremely important variable affecting both processing and end use properties, due to the fact that nylon 6 is a very hygroscopic polymer. For example, at 50% RH and 23°C (= normal condition) nylon can absorb moisture to about 3% [2]. Therefore, drying process is needed to decrease the moisture content below 0.1% for product quality. The big problems in drying of nylon are low temperature limits (70-80°C) and the oxidative deterioration and discoloration at low moisture content. Usually, nylon is dried in vacuum or in recirculating dehumidified air (dew point lower than -18 °C). For these conditions, the drying time ranges from 10 to 24 hours [2].

Many investigations have been conducted by applying Fick's law diffusion equation for modelling of drying kinetics, such as in drying of starch [3], drying of onion [4], and drying of yellow pea starch [5]. Several investigation have been conducted in order to determine diffusion kinetics and sorption equilibrium of water on PA. The Flory-Huggins model gives a good agreement with sorption isotherm for water in PA-66 and PA-610 [6]. The water in nylon 6 is immobile at low water content, and considerably mobile at higher water contents [7]. The mechanism of water sorption in nylon is firmly bounded water, loosely bound water, and sites for capillary condensed water [8]. The diffusion of water in nylon depends on temperature and moisture content [8]. However, those investigations have not yet considered the drying tail phenomenon during terminal drying of nylon 6.

Therefore, in this work the drying kinetics of single particle of PA6 will be measured and modelled by two different diffusion model (i.e. Arrhenius model and Vrentas-Duda model) and normalization method.

2. Material and Methods

2.1 Experimental Methods

A magnetic suspension balance (MSB) produced by Rubotherm (Bochum, Germany) has been used for determination of drying kinetics and sorption equilibrium. Dry nitrogen from the flask has been used to determine the dry sample mass with temperature 80°C. Single particle measurements are performed in drying process. The material properties are 2.9 mm of particle diameter and 1150 kg/m³ of solid density.

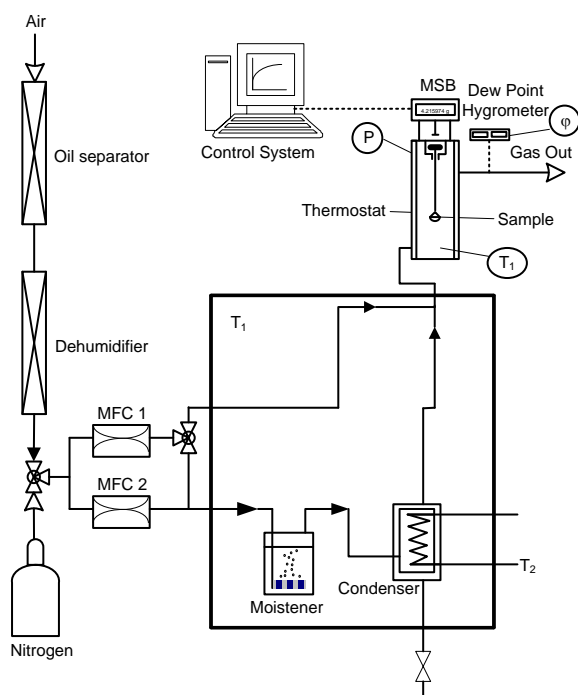


Fig. 1. Schematic representation of experimental setup for the MSB gravimetric method

The data recorded and stored in soft copy (computer) and used used to calculate:

- the moisture content at each time, which is derived from weight of sample

$$X(t) = \frac{M(t) - M_{dry}}{M_{dry}}$$

- the drying rate

$$\dot{m}(t) = \frac{M(t) - M(t+1)}{t(t+1) - t(t)} \frac{\rho_p d_p}{6M_{dry}}$$

where $M(t)$ and $M(t+1)$ are weight of sample at time t and weight of sample at time $t+1$, respectively.

2.2 Modeling

Diffusion Model

A one-dimensional model for diffusion inside isothermal and spherical single particle has been used according to the relationship:

$$\frac{\partial X}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 D \frac{\partial X}{\partial r} \right) \quad (1)$$

where D , r , and t are the diffusion coefficient, the radial coordinate, and time, respectively.

The boundary and initial conditions can be expressed as

$$t = 0, \quad 0 \leq r \leq R, \quad X = X_0, \quad (2)$$

$$t > 0, \quad r = 0, \quad \frac{\partial X}{\partial r} = 0, \quad (3)$$

$$t > 0; \quad r = R, \quad -\rho_p D \frac{\partial X}{\partial r} = \rho_g \beta_g (Y_{eq} - Y); \quad (4)$$

Here, β_g , Y_{eq} , and Y are the gas-side mass transfer coefficient, the moisture content of gas in equilibrium with moisture content of the solid, and the moisture content of inlet gas, respectively. Y_{eq} is calculated from the sorption isotherm curve of products. The sorption equilibrium curves have been measured but the results are not depicted in this article. The initial moisture content in the simulations is set equal to X_{cr} , where for PA6 it is equal to 0.13, the value actual in the experimental work.

The simulation is performed by solving the diffusion equation by pdepe command editor in Matlab and fitting the value of D simultaneously. The fitting procedure is conducted by minimizing the sum square of error (SSE) between mean particle moisture obtained from measurement and simulation:

$$SSE = \sum_{i=1}^n (X_{\text{exp}} - X_{\text{sim, mean}})^2 \quad (5)$$

The mean value of moisture content (simulation) is defined as

$$X_{\text{mean}} = \frac{1}{V} \int_V X \, dV, \quad (6)$$

where V is the computational domain volume inside of a single particle in radial direction.

For the diffusion coefficient is predicted by both Arrhenius diffusion model and Vrentas-Duda diffusion model. The respective Arrhenius diffusion coefficient can be expressed as [9]:

$$D = A \exp\left(-\frac{\tilde{E}}{\tilde{R}T}\right), \quad (7)$$

where A is a pre-exponential rate factor, \tilde{E} is the activation energy, and \tilde{R} is the gas constant.

To determine the value of constants A and \tilde{E} in eq. (7), the experiments have been carried out at three different values of drying temperature. Then, the linear regression is performed by transforming eq. (7) to

$$\ln D = \ln A - \frac{\tilde{E}}{\tilde{R}} \frac{1}{T}. \quad (8)$$

According to the Vrentas and Duda diffusion model [9], the solvent self-diffusion coefficient, D_1 , is given by

$$D_1 = D_0 \exp\left(-\frac{\tilde{E}}{\tilde{R}T}\right) \exp\left(\frac{-(\omega_1 \hat{V}_1^* + \xi \omega_2 \hat{V}_2^*)}{\omega_1 \left(\frac{K_{11}}{\gamma}\right) (K_{21} - T_{g1} + T) + \omega_2 \left(\frac{K_{12}}{\gamma}\right) (K_{22} - T_{g2} + T)}\right), \quad (9)$$

and the binary mutual diffusion coefficient, D, is expressed by

$$D = D_1 (1 - \phi_1)^2 (1 - 2\chi\phi_1), \quad (10)$$

with subscripts 1 and 2 referring to the solvent and polymer, respectively.

Here, D_0 is a pre-exponential factor, \tilde{E} is the critical energy that a molecule must possess to overcome the attractive forces holding it to its neighbours, γ is an overlap factor, \hat{V}_i^* is the specific hole free-volume of component i required for a diffusion jump, ω_i is the weight fraction of component i, T_g is glass transition temperature, and ξ is the ratio of the molar volume of the jumping unit of the solvent to that of the polymer. K_{11} and K_{21} are free-volume parameters for the solvent, while K_{12} and K_{22} are those for the polymer; ϕ_1 is the solvent volume fraction, and χ is the polymer-solvent interaction parameter.

Although there are 13 parameters in eqs (9) and (10) grouping some of them together means that only 10 parameters ultimately need to be evaluated: K_{11}/γ , $K_{21}-T_{g1}$, K_{12}/γ , $K_{22}-T_{g2}$, \hat{V}_1^* , \hat{V}_2^* , χ , D_0 , \tilde{E} , and ξ . These parameters can be estimated from thermodynamic data [10], except of D_0 and ξ that are estimated from experimental data by fitting. The fitting procedure is performed by minimizing the sum square of error (SSE) between mean particle moisture obtained from measurement and simulation (see eq. (5)). The activation energy is set equal to zero ($\tilde{E} = 0$) assuming negligible energy effects [9].

Normalization Method

Normalization is a common method in order to describe measured drying curves by reduction to just one normalized (or characteristic) drying curve for the considered product, developed by van Meel, 1958. The normalized drying rate \dot{v} is defined as the quotient of the actual drying rate \dot{m} , and the drying rate of the first drying period \dot{m}_1

$$\dot{v} = \frac{\dot{m}}{\dot{m}_1}, \quad (11)$$

and the normalized moisture content (of the solid), η , is represented by

$$\eta = \frac{X - X_{eq}}{X_{cr} - X_{eq}}, \quad (12)$$

where X_{eq} is the equilibrium moisture content. Both \dot{v} and η take values between 0 and 1.

The first drying rate period can be calculated by

$$\dot{m}_1 = \beta_g \rho_g (Y_{eq}(T_p, X) - Y). \quad (13)$$

3. Result and Discussion

3.1. Measured drying curve

Figure 2 (left diagram) shows the measured moisture content versus time of different single particles of PA6 for a variation of temperature. At the beginning, the moisture content decreases quickly until a value of 0.06 has been attained. Then, after the moisture content has reached a value of 0.02, the decrease of moisture content becomes very slow. This last period is called third drying period or tail of drying. Therefore, in industrial practice, the drying process of PA6 is performed at the maximum temperature of 80°C and for a long time of 24 hours until the residual moisture content achieves 0.001 for product quality [2].

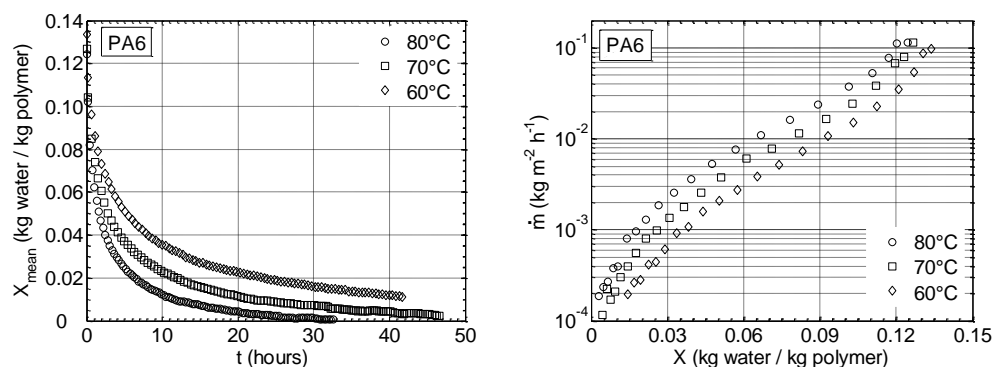


Figure. 2. The influence of temperature on measured moisture content (left diagram) and drying rate (right diagram) in single particle drying of PA6 [$\dot{M}_g = 6$ mg/s, $Y = 0.5$ g/kg, $P = 1$ bar]

Figure 2 (right diagram) shows the measured drying rates versus moisture content corresponding to the data from Fig 2. (left diagram). The drying rates do not indicate the first constant drying rate period and then the critical moisture content for any of the investigated temperatures of drying. This means that the drying rate is never controlled by gas-side mass transfer. The initial drying rates are by an order of magnitude smaller than the theoretical first period drying rates for the given process conditions ($Sh = 2$, $Y = 0.5$ g/kg). For instance, the drying rate measured at initial moisture content and a temperature of 60°C is 0.10 kg/m²/h while the theoretical drying rate in the first drying period (using eq. (13)) is 1.31 kg/m²/h. Therefore, it can be concluded that drying kinetics of PA6 is mainly controlled by internal diffusion of moisture inside the particle. This conclusion is in a agreement with the findings of many authors. Finally, the drying rate decreases tremendously close to zero at the end of the drying process. This is caused by the fact that diffusion coefficient decreases extremely when the moisture content is close to zero since the water vapour in PA6 is comparatively immobile at low water content, but quite mobile at higher water contents. The value of the diffusion coefficient will be discussed thoroughly in the section on the application of the diffusion model, while the mobility of water molecules at different water contents will be discussed in the section about sorption equilibrium.

3.2. Arrhenius Diffusion Model

Figure 3 shows that the comparison between measured data and calculation using the Arrhenius diffusion model of moisture content (left diagram) and drying rate (right diagram) does not give a good agreement at the end of drying of PA6. This is caused by the fact that the diffusion coefficient of the Arrhenius model depends only on temperature. Then, in the prediction the decrease of drying rate depends only on the difference of moisture content between core and surface of the particle. The drying process is faster in prediction than in measurement. It can be seen that at moisture contents lower than 0.06, the predicted moisture content is lower than the measured moisture content, and the predicted drying rate is higher than the measured one. Then, Fig 4 shows that the temperature influence is captured correctly by an Arrhenius plot of effective diffusion coefficients. As a result of linear regression, the pre-exponential factor, A , and the activation energy, \tilde{E} , which are summarized in Table 1.

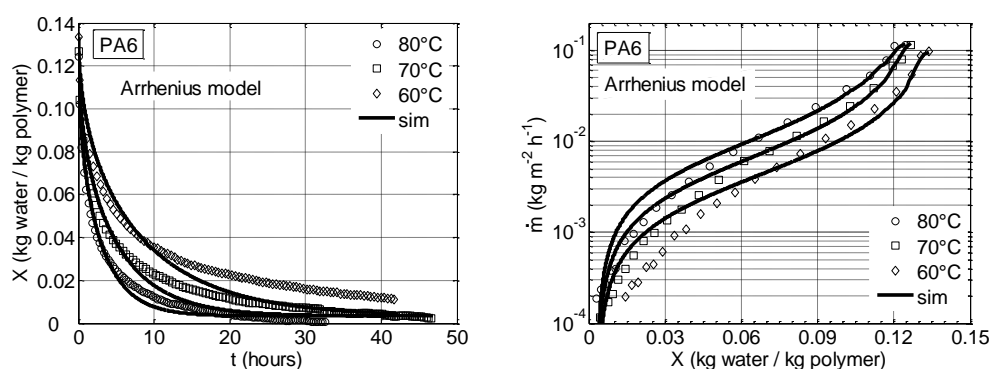


Figure 3. Comparison between measurement and calculation using Arrhenius diffusion model for moisture content (left diagram) and drying rate (right diagram) of single particles of PA6

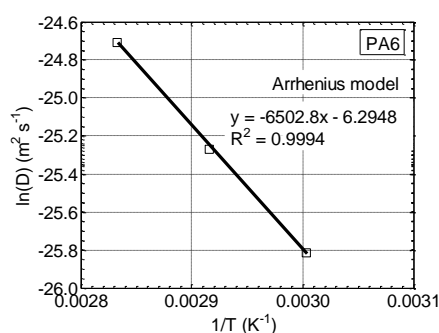


Figure 4. Plot of diffusion coefficients

Table 1. Constants in Arrhenius model for PA6

T (°C)	D (m ² /s)	SSE	A (m ² /s)	\tilde{E} (kJ/mol)
80	1.86E-11	4.93E-02		
70	1.06E-11	6.46E-02	1.85E-03	54.3
60	6.15E-12	3.51E-01		

3.3. Vrentas-Duda Diffusion Model

Figure 5 shows a good agreement between measured and simulated data for both the moisture content (left diagram) and the drying rate (right diagram) when using the Vrentas-Duda diffusion model. By using this model, the phenomenon of drying tail or plateau diffusion can be properly described. This phenomenon is caused by diffusion coefficient falling tremendously close to zero when moisture content decreases (see Fig. 5, right diagram), since the water in nylon 6 is comparatively immobile at low water contents, but rather mobile at higher water contents [7]. Furthermore, Fig. 6 (left diagram) shows that the profile of moisture content over the radius is steep during the whole drying process. The moisture content in the centre of the particle is still high even after a long time of drying, while the moisture content at the surface of the particle is almost zero. This is caused by the fact that the diffusion coefficient close to the surface of particle is much lower than close to the centre of the particle (see Fig. 6, right diagram). The fitted values of D_0 and ξ , are $4.02\text{E-}08 \text{ m}^2/\text{s}$ and 0.498 , respectively.

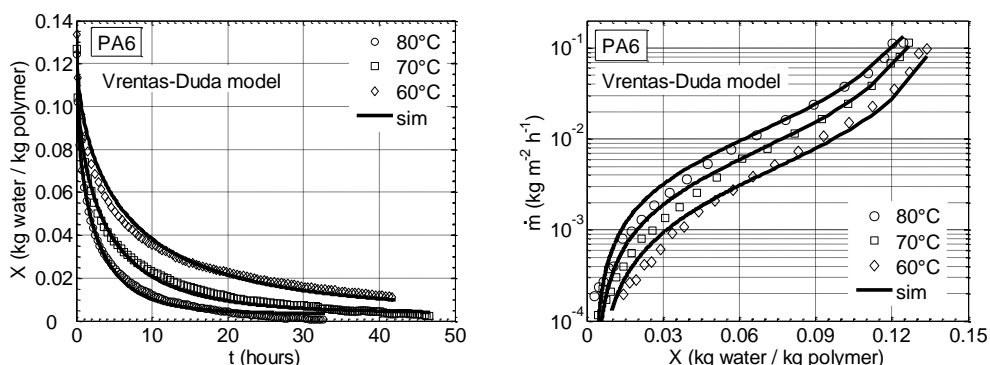


Figure. 5 Comparison between measurement and calculation of moisture content (left diagram) and drying rate (right diagram) during single particle drying of PA6 using Vrentas-Duda diffusion model.

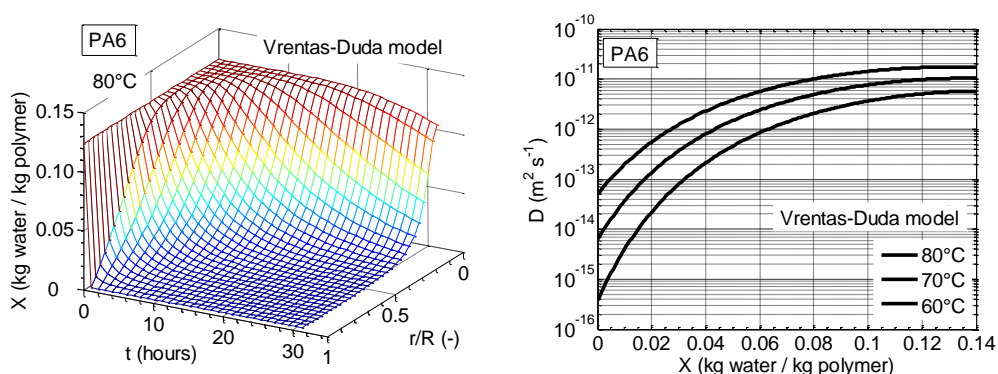


Figure. 6 Simulation results using Vrentas-Duda model for single particle drying of PA6; profile of moisture content (left diagram), and dependence of diffusion coefficients on temperature and moisture content (right diagram)

3.4. Normalization Method

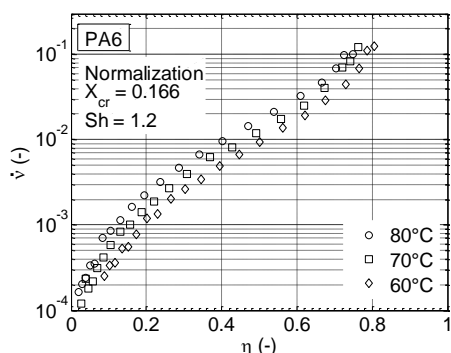


Figure 7. Normalization drying curve of PA6

Figure 7 shows that the normalization of drying curves of PA6 does not work well. Each temperature has a different normalized drying curve. The normalization for PA6 is conducted by means of theoretical first period constant drying rates calculated with a Sherwood number adjusted to 1.2. The critical moisture content, X_{cr} , is obtained by means of extrapolation of measured drying curves to the theoretical value of first period drying rate. This gives $X_{cr} = 0.166$ after averaging the values of X_{cr} obtained by extrapolation for all three investigated temperatures. Even if the calculated first period drying rate is decreased by reducing the Sherwood number to 0.3 (minimal Sherwood number for cylindrical object), the normalization of the drying curves for PA6 still does not work well.

4. Conclusion

Both Arrhenius model and Normalization method given not a good agreement to predict drying kinetics of PA6. Finally, the Vrentas-Duda model was found the best for explaining the drying behaviour of PA6. By using this model, the phenomenon of drying tail or plateau diffusion can be properly described.

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