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Modeling the Drying Kinetics of Polymer Volatile Systems Using Thermogravimetric Analysis Data

E. G. Viehböck[1,2,*], T. Ehrmann [2], G. R. Berger-Weber[2],
A. Hammer[2], M. Kirchmayr[3],C. Paulik[1,4]
[1] Competence Center CHASE GmbH, Linz, Austria
[2] Institute of Polymer Processing and Digital Transformation, Johannes Kepler University Linz, Linz, Austria
[3]EREMA Engineering Recycling Maschinen und Anlagen Ges.m.b.H., Ansfelden, Austria
[4] Institute of Chemical Technology of Organic Materials, Johannes Kepler University Linz, Linz, Austria

Abstract

Thermogravimetric analysis (TGA) is a well-established technique for investigating the drying kinetics of moist polymers by monitoring mass loss under controlled temperature conditions. In this study, lumped parameter models originally developed for food drying, such as the modified Page and Verma models, were applied to polymer drying processes with good agreement. These empirical models are capable of capturing drying procedures with Fickian as well as with anomalous non-Fickian diffusion behavior, observed at different temperature regimes. We used a model system based on polyamide 6 (PA6) with water as its volatile component. Its drying kinetics were characterized experimentally and served as the foundation for developing and validating predictive drying models. The temperature dependence of the drying process was effectively captured through Arrhenius-type behavior and fitted using nonlinear regression techniques, enabling the development of predictive models with adjusted R^2 values consistently exceeding 0.99. Such models allow to interpolate the drying behavior across various process conditions and to optimize the drying procedures for mitigating polymer degradation while drying to the desired moisture content. Furthermore, the predictive capability of these models paves the way for designing industrial drying processes with reduced need on extensive experiments. In conclusion, looking at the similarities in moisture transport mechanisms between food and polymer systems offers a robust framework for understanding and controlling volatile removal in polymer processing.

Keywords: thermogravimetrical analysis, polymer drying, drying kinetics, modeling, sorption, desorption, volatile removal, polymer processing

1. Introduction

Efficient moisture removal from hygroscopic polymers is essential for stable melt processing and high product quality. Polyamide 6 (PA6) readily absorbs ambient water, which—if not fully removed—can cause hydrolytic degradation, foaming, and ultimately reduced product performance. Conventional drying protocols based on fixed hold-times are often energy-intensive and poorly adaptable to different grades or processing conditions.
Isothermal thermogravimetric analysis (TGA) combined with kinetic modeling offers a predictive alternative. By characterizing drying behavior under controlled thermal conditions, optimized drying schedules can be derived. Among various modeling approaches, the Verma model—with parameters adapted for temperature dependence—offers a balance between physical interpretability and computational efficiency [1].
In this study, PA6 specimens with uniform water content were dried isothermally at various temperatures. After data processing, the Verma model was fitted to each drying curve and generalized across the temperature range using simple temperature-dependent functions. This framework enables accurate prediction of moisture content as a function of time and temperature, offering a scalable tool for energy-efficient industrial PA6 drying.

2. Experimental Methodology

2.1 Sample Preparation

Polyamide 6 (PA6) granules (Ultramid B3S, BASF) were first vacuum-dried at 80 °C for 4 hours to ensure a residual moisture content below 0.1 wt-%. Disc-shaped specimens were then produced by a hot press at 230 °C, applying a load of 10 metric tons for 2 minutes. The resulting specimens had a diameter of 2.2 mm and a thickness of 1.21 mm.

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Subsequent water uptake was induced by immersing the specimens in distilled water at 23 ± 1 °C until an equilibrium state was reached, which was confirmed through periodic gravimetric measurements using an analytical balance. Fickian diffusion behavior was verified using the halftime method, indicating an average saturation time of approximately 15 hours at room temperature [2]. To ensure consistent saturation, all specimens were immersed for a longer duration. The final equilibrium moisture content was determined to be 10.21 ± 0.14 wt% (n = 15). This relatively high uptake is attributed to the reduced crystallinity of the hot-pressed samples (28.7%) compared to the raw granules (45.7%), as determined by differential scanning calorimetry (DSC). The lower crystallinity increases the amorphous fraction, thereby facilitating water uptake [3].

2.2 Isothermal TGA Measurements

Isothermal drying experiments were conducted using a PerkinElmer EGA 4000 top-loading thermobalance (Waltham, MA, USA), which allows for high-resolution mass change measurements under controlled temperature conditions. Each saturated specimen was placed into the microbalance pan at ambient temperature. The system was then heated at a controlled ramp rate of 20 K/min to the target isothermal temperature. The drying process was monitored until the mass loss plateaued, indicating that an equilibrium had been reached.

2.3 Data Processing

2.3.1 Determination of the equilibrium mass m_{eq}

A top-loading microbalance was used in this study, which reduces typical systematic errors associated with other TGA configurations, such as those caused by sample movement or furnace design. Nevertheless, blank measurements were performed to further eliminate measurement artifacts, particularly during the heating phase. Since TGA requires the specimen to be introduced at room temperature followed by a ramp-up to the target isothermal level (20 K/min in this case), buoyancy effects and changes in gas density can artificially increase the measured mass during this transition. To correct for these effects, blank measurements were subtracted from the sample measurements during the ramping phase.

2.3.2 Normalization of the drying curves

To facilitate comparison between drying curves at different temperatures, normalization was applied using the concept of the moisture ratio (MR), which is commonly found in the literature [4, 5, 6]. The MR is defined as:

$$MR(t) = \frac{m(t) - m_{eq}}{m_0 - m_{eq}}, \tag{1}$$

where $m(t)$ is the mass at a given time t, m_0 is the initial saturated mass, and m_{eq} is the final equilibrium mass after complete drying. This dimensionless ratio enables the drying kinetics to be compared independently of absolute water content.

3. Model Development

To capture the isothermal drying kinetics of PA6, we adopted a food drying model proposed by Verma et al.[1]. This form distinguishes a fast and a slow moisture-removal mechanism and defines the moisture ratio $MR(t)$ as follows:

$$MR(t) = A\exp(-k_0 t) + (1 - A)\exp(-k_1 t). \tag{2}$$

Here A $(0 < A < 1)$ serves as a weighting factor that balances the contributions of the two drying phases, distinguishing between the faster and slower moisture removal mechanisms. The parameters k_0 and k_1 represent the corresponding drying rate constants for each phase.

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Since the objective is to develop a predictive model applicable across a wide temperature range, each parameter of the Verma model was treated as temperature dependent. For this purpose, individual isothermal experiments were conducted at discrete temperature levels, and the corresponding model parameters were independently fitted for each temperature. The resulting temperature-dependent parameter values were then plotted as a function of temperature. To enable interpolation and prediction across the entire temperature range, each parameter was subsequently modelled as a continuous function of temperature using the following expressions:

$$A(T) = s_A T - d_A;$$
$$k_i(T) = \exp(s_i T - d_i) \ (i = 0,1). \tag{3}$$

The parameter $A(T)$ is described as a linear function of temperature, where s_A denotes the slope and d_A the offset, capturing how the weighting between the two drying mechanisms changes with temperature. The drying rate constants k_i are modeled as exponential functions of temperature, with s_i and d_i for $(i = 0,1)$ representing the slope and offset in the logarithmic domain, respectively.

4. Results and Discussion

The Verma model, as adapted in this study, was evaluated across a broad temperature range (50 °C to 120 °C) using isothermal thermogravimetric analysis (TGA) data. For each isothermal measurement, the normalized moisture ratio (MR) was computed and fitted with the two-term exponential Verma model. This allowed the extraction of three key parameters: the weighting factor A and the drying rate constants k_0 and k_1.

Initially, these parameters were independently fitted at each temperature. The resulting temperature dependence of each parameter was then modeled using simple empirical functions. This parameterization enables a continuous prediction of the drying behavior across the investigated temperature range.

A comparison between the model predictions and the experimental drying curves at each isothermal level is illustrated in Figure 1, demonstrating the capability of the model to reproduce the characteristic drying behaviour.

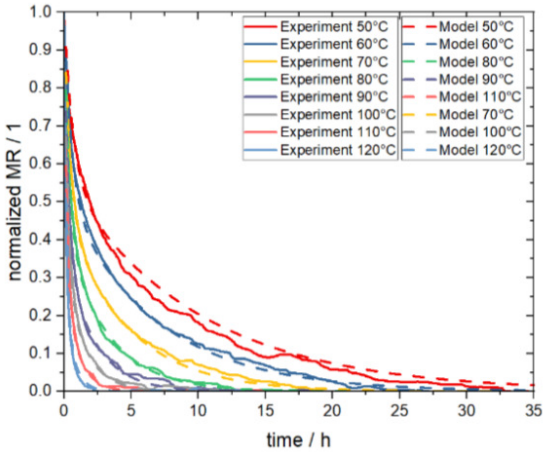

Fig. 1: Comparison between experimentally measured drying data and Verma modelled data.

The corresponding temperature dependence of the fitted parameters is summarized in Figure 2, highlighting the systematic trends used to generalize the model across temperatures.

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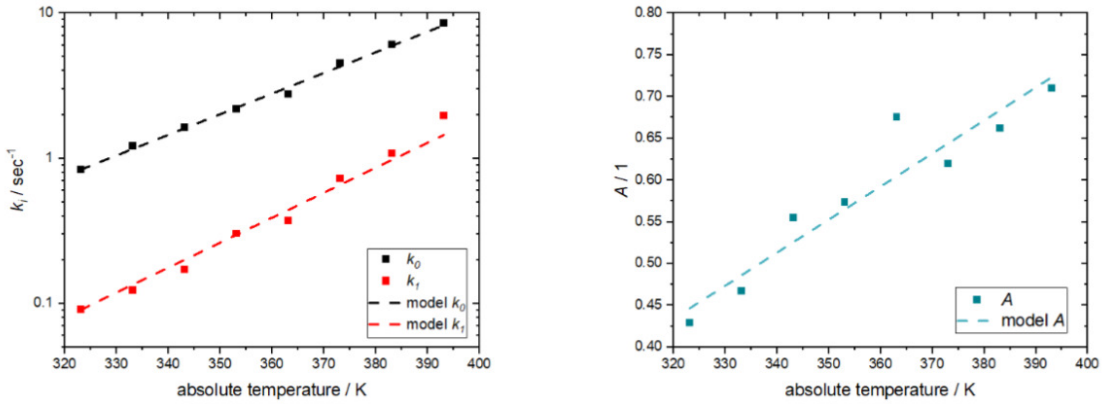

Fig. 2: Temperature-dependent drying kinetics parameters: drying rate constants k_0 and k_1 (left) and weighting factor A (right).

The quality of the model fit was assessed using the coefficient of determination R^2. Across all temperature levels, the model achieved R^2 values greater than 0.99, indicating excellent agreement between the predicted and experimental drying curves. These results confirm that the Verma model, when extended with temperature-dependent parameters, provides a robust framework for capturing the drying kinetics of PA6 under isothermal conditions.

5. Conclusion and Outlook

By describing the drying behavior with only six global parameters, this approach offers a practical and scalable method for predictive modeling in industrial drying simulations. Further work may extend the approach to non-isothermal or multi-stage drying processes or may be extended to account for the influence of varying crystallinity levels, as literature suggests that volatile absorption predominantly occurs in the amorphous regions of semicrystalline polymers.

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