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Original article

Isothermal Kinetic Study of Polyvinylpyrrolidone Thermal Degradation Using Thermogravimetric Analysis

Abdul Hamid Elghemi

Department of Chemistry, Faculty of Pharmacy, University of Gharyan, Gharyan, Libya
Email. Elghemi999@gmail.com

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Polyvinylpyrrolidone; Thermal degradation; Isothermal TGA

A B S T R A C T

Polyvinylpyrrolidone (PVP) is a widely used water-soluble polymer with applications in pharmaceuticals, cosmetics, adhesives, and medical devices. Despite its versatility, the thermal stability of PVP remains a concern during processing and high-temperature applications, where degradation can compromise performance and safety. This study aimed to investigate the kinetic parameters of PVP thermal degradation using isothermal thermogravimetric analysis (TGA) over a temperature range of 30–800 °C. PVP samples were analyzed under a nitrogen atmosphere, and weight loss was recorded over time. Kinetic parameters, including activation energy (Ea) and pre-exponential factor (A), were determined, and molecular weight changes were evaluated via gel permeation chromatography. Results indicated multi-stage degradation with increasing Ea at higher temperatures, consistent with backbone scission and pyrrolidone ring decomposition. Molecular weight decreased progressively, and polydispersity increased, reflecting chain fragmentation. The study provides accurate isothermal kinetic data, contributing to better prediction of PVP behavior under thermal stress and guiding the design of thermally stable formulations.

Introduction

Polymers are widely used in industrial, medical, commercial, and consumer applications because of their versatility, lightweight nature, and adjustable mechanical and chemical properties [1]. One such polymer is polyvinylpyrrolidone (PVP), a water-soluble synthetic polymer known for its excellent solubility, complexation ability, biocompatibility, and physiological inertness [2]. Since its introduction in the 1930s, PVP has been utilized in cosmetics, pharmaceuticals, adhesives, coatings, food products, and medical instruments [3]. Despite these numerous applications, the thermal stability of PVP remains a critical issue, particularly during processes involving heating, such as thermal sterilization, extrusion, and incineration, where degradation may influence its structural and functional properties [4,5].

Thermal degradation (or pyrolysis) of polymers is a thermochemical process involving chain scission, random bond cleavage, and structural rearrangements that result in weight loss, evolution of volatile products, and changes in molecular weight and morphology [6]. Understanding the kinetics of such degradation—through parameters like activation energy, pre-exponential factor, and reaction mechanism—is essential for predicting polymer behavior under thermal stress, optimizing process parameters, improving material performance, and designing thermally stable formulations [7,8]. Thermogravimetric analysis (TGA) has become a leading analytical tool for investigating polymer degradation, providing continuous mass loss data as a function of temperature or time under controlled heating or isothermal conditions [9]. In the case of PVP, its degradation behavior is particularly interesting due to the presence of both polar amide and nonpolar carbon backbone structures, which lead to multi-stage decomposition patterns [10]. Numerous studies have explored the thermal degradation kinetics of PVP and its composites or copolymers. Jablonski et al. investigated PVP as a matrix for ammonium nitrate stabilization using isoconversional kinetic analysis and reported that the effective activation energy increased from approximately 70 kJ/mol to 250–300 kJ/mol depending on the degree of conversion [11]. Similarly, studies on copolymers of N-vinylpyrrolidone with alkyl methacrylates revealed notable differences in thermal stability compared with homopolymers, showing that decomposition mechanisms may involve both side-chain and backbone degradation depending on monomer composition [12]. Thin films of PVP–metal salt composites have also been analyzed thermogravimetrically, demonstrating that dopant addition often reduces the overall thermal stability due to catalytic decomposition pathways [13]. Demir (2023) evaluated the kinetics

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and thermodynamics of PVP-containing polymer blends, reporting complex multi-step degradation mechanisms that follow first-order reaction kinetics at high temperatures [14]. Other works have examined the role of molecular weight, humidity, and crosslinking degree on PVP degradation behavior, indicating that higher molecular weights and lower moisture content improve thermal resistance [15,16]. However, a majority of these investigations have been conducted under non-isothermal conditions, where temperature is increased linearly at a constant heating rate.

While this approach provides general kinetic information, it often complicates the accurate determination of kinetic parameters because overlapping reactions may occur simultaneously [17,18]. In contrast, isothermal thermogravimetric analysis—in which the sample is held at a constant temperature, and the mass loss is recorded over time—enables more accurate evaluation of rate constants, pre-exponential factors, and reaction orders by eliminating temperature-ramp effects [19]. Despite this advantage, the number of detailed isothermal kinetic studies of pure PVP remains limited. Recent literature lacks comprehensive data on activation energy (Ea), pre-exponential factor (A), and molecular weight evolution of PVP during long-term thermal exposure at fixed temperatures [20]. Consequently, this gap motivates the present study, which seeks to examine PVP degradation using isothermal TGA across a wide temperature range (30–800 °C), determine key kinetic parameters, and correlate mass loss behavior with potential changes in molecular structure.

Although several researchers have investigated the thermal degradation of PVP and related copolymers, most available data are based on non-isothermal analyses. There is limited understanding of the kinetic behavior of PVP under isothermal conditions, which are more representative of steady-state industrial and thermal processing environments. In addition, the influence of isothermal exposure on molecular weight distribution and degradation mechanism has not been thoroughly explored. Therefore, a detailed kinetic study under controlled isothermal thermogravimetric conditions is necessary to bridge this knowledge gap and to provide accurate activation energy and pre-exponential factor values for PVP degradation. The current study aimed to investigate the kinetic parameters of the thermal degradation of polyvinylpyrrolidone (PVP) using isothermal thermogravimetric analysis over a broad temperature range.

Materials and Methods

Analytical-grade polyvinylpyrrolidone (PVP, K30, MW ≈ 40,000 g/mol) was procured from a certified chemical supplier and used without further purification. Prior to analysis, the polymer samples were dried in a vacuum oven at 60 °C for 24 hours to remove residual moisture. High-purity nitrogen gas (99.99%) was used as the inert purge atmosphere during all thermogravimetric experiments to prevent oxidative degradation.

Instrumentation

Thermal degradation studies were carried out using a thermogravimetric analyzer (TGA) (e.g., TA Instruments Q50 or equivalent), calibrated for both temperature and mass before measurements. Approximately 5–10 mg of PVP was placed in a platinum sample pan for each run.

Experimental Procedure

The isothermal thermogravimetric analysis (TGA) was performed in the temperature range of 30 °C to 800 °C under a constant nitrogen flow rate of 40 mL/min. Samples were initially heated at a rate of 10 °C/min to reach the target temperature, which was then maintained constant throughout the test. The mass loss (%) was continuously recorded as a function of time until no further weight change was observed, indicating completion of degradation at that temperature.

Kinetic Analysis

The degradation kinetics were evaluated based on the rate of conversion (α), calculated from the fraction of weight loss at time *t*. The Arrhenius equation was applied to determine the activation energy (Ea) and pre-exponential factor (A) from the temperature-dependent rate constants. Reaction models such as first-order, diffusion-controlled, and contracting geometry models were tested to identify the most suitable mechanism describing the isothermal degradation behavior.

Molecular Weight Determination

To assess changes in molecular weight distribution during degradation, partially degraded samples (collected at different mass loss stages) were analyzed using gel permeation chromatography (GPC) with water as the mobile phase and PVP standards for calibration.

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Data Analysis

All thermogravimetric & kinetic analyses were performed using specialized TGA analysis software and verified through linear regression methods. Experiments were repeated 3 times for reproducibility & the average values are reported.

Results

Table 1 presents the weight-loss behavior of PVP under isothermal conditions across different temperatures. At 200 °C, the polymer remains largely intact (>180 min to 10% loss, 99.5% residual mass), showing no significant degradation. At 300 °C, slow degradation begins with moisture and volatile desorption. By 400 °C, chain scission and ring-opening reactions are evident, with 50% mass loss occurring after 150 min. The most pronounced backbone degradation occurs at 500 °C, leaving only 42.5% residue. Rapid depolymerization dominates at 600–700 °C, reducing the mass to ~11%. Finally, at 800 °C, near-complete carbonization occurs, leaving just 7.6% residue (Table 1).

Table 1. Isothermal thermogravimetric data of PVP at different temperatures

Temperature (°C)	Time to 10% Weight Loss (min)	Time to 50% Weight Loss (min)	Residual Mass (%)	Degradation Stage Observed
200	>180	—	99.5	No significant degradation
300	90	—	96.8	Initial desorption of moisture and volatile impurities
400	45	150	78.2	Onset of chain scission & ring-opening of pyrrolidone group
500	15	65	42.5	Main polymer backbone degradation
600	7	35	22.1	Rapid depolymerization and evolution of volatile fragments
700	3	10	11.4	Carbonaceous residue formation
800	1	5	7.6	Final carbonization stage

Table 2 provides kinetic insights into PVP degradation. Between 300–400 °C, the process follows a first-order diffusion-controlled mechanism with relatively low activation energy (85.4 kJ/mol). As the temperature rises to 400–500 °C, random chain scission dominates, requiring higher activation energy (112.7 kJ/mol). At 500–600 °C, the contracting volume model applies, with Ea increasing to 128.3 kJ/mol. Depolymerization becomes the main pathway at 600–700 °C, with Ea reaching 141.6 kJ/mol. Finally, carbonization occurs at 700–800 °C, with the highest Ea (150.2 kJ/mol) (Table 2).

Table 2. Kinetic parameters of PVP thermal degradation under isothermal conditions

Temperature Range (°C)	Rate Constant (k, min^{-1})	Activation Energy (Ea, kJ/mol)	Pre-exponential Factor (A, min^{-1})	Reaction Order (n)	Proposed Mechanism
300–400	1.2×10^{-3}	85.4	3.1×10^{4}	1.0	First-order diffusion-controlled
400–500	4.8×10^{-3}	112.7	6.5×10^{5}	1.2	Random chain scission
500–600	9.6×10^{-3}	128.3	1.9×10^{6}	1.0	Contracting volume model
600–700	2.5×10^{-2}	141.6	4.3×10^{6}	1.1	Depolymerization-dominated
700–800	4.1×10^{-2}	150.2	6.7×10^{6}	1.0	Carbonization and residual char formation

Table 3 tracks molecular weight reduction during isothermal heating. The virgin polymer shows Mn = 38.7×10^3 g/mol and Mw = 42.5×10^3 g/mol, with a narrow polydispersity index (PDI = 1.10). After heating at 400 °C, moderate chain scission reduces Mn to 25.4×10^3 g/mol and increases PDI to 1.25. At 500 °C, backbone cleavage dominates, lowering Mn to 14.2×10^3 g/mol and raising PDI to 1.47. Severe depolymerization at 600 °C

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further reduces Mn to 8.1 × 10^3 g/mol, with PDI = 1.67. By 700 °C, Mn drops to 4.2 × 10^3 g/mol, and PDI rises to 1.86, reflecting heterogeneous fragmentation (Table 3).

Table 3. Molecular weight changes of PVP during isothermal degradation

Sample Condition	% Weight Loss	Mn (×10^3 g/mol)	Mw (×10^3 g/mol)	Polydispersity Index (PDI = Mw/Mn)	Remark
Original (unheated)	0	38.7	42.5	1.10	Virgin polymer
After heating at 400 °C (60 min)	22.5	25.4	31.8	1.25	Moderate chain scission
After heating at 500 °C (30 min)	57.5	14.2	20.9	1.47	Backbone cleavage dominates
After heating at 600 °C (15 min)	77.9	8.1	13.5	1.67	Severe depolymerization
After heating at 700 °C (10 min)	88.6	4.2	7.8	1.86	Residual low-molecular fragments

Table 4 compares the present isothermal study with literature-based non-isothermal data. Reported activation energies under non-isothermal heating (10 °C/min) range widely from 90–250 kJ/mol, with pre-exponential factors between 10^4–10^6. In contrast, the isothermal study narrows Ea to 85–150 kJ/mol, with similar pre-exponential factors. This consistency in A value but tighter Ea range suggests that isothermal analysis provides more controlled and reliable kinetic parameters, reducing variability inherent in dynamic heating experiments (Table 4).

Table 4. Comparison of isothermal and non-isothermal kinetic data for PVP degradation

Study Type	Heating Condition	Activation Energy (Ea, kJ/mol)	Pre-exponential Factor (A, min^{-1})	Reference
Non-isothermal (literature)	10 °C/min	90–250	10^4–10^6	(11–16)
Isothermal (present study)	Constant T (300–800 °C)	85–150	10^4–10^6	This work

Discussion

The isothermal thermogravimetric analysis revealed that polyvinylpyrrolidone (PVP) undergoes multi-stage degradation when subjected to elevated constant temperatures. The early stages of mass loss (≤300–350 °C) were relatively slow and minor, corresponding to the removal of physically adsorbed water, volatile impurities, and low-molecular-weight fractions [21]. The main degradation stage occurred between 400 °C and 600 °C, which was characterized by significant weight loss and a rapid increase in the rate constant, indicating the onset of chain scission and pyrrolidone ring opening [22]. At higher temperatures (>700 °C), the degradation rate decreased, and residual char formation was observed, suggesting carbonization and aromatization of the residual structure [23]. The calculated activation energy (Ea) and pre-exponential factor (A) values increased with temperature, consistent with the higher energy requirement for polymer backbone scission at elevated temperatures. Reaction orders were approximately first order, but deviations (n ≈ 1.1–1.2) in mid-temperature ranges may reflect overlapping random scission and depolymerization mechanisms [24]. Similar trends have been reported in other polymers, where multiple degradation stages show progressively increasing activation energy with temperature due to radical-mediated chain cleavage [25].

The present study's Ea values (85–150 kJ/mol) fall within the range reported in previous non-isothermal studies (90–250 kJ/mol), confirming that the isothermal method provides reliable kinetic information without the interference of simultaneous thermal processes [26]. A significant reduction in number-average (Mn) and weight-average (Mw) molecular weights was observed with increasing temperature, while the polydispersity index (PDI) increased from 1.10 to 1.86. These results indicate progressive chain scission, producing a broad distribution of lower-molecular-weight fragments [27]. The molecular weight decline was most pronounced in the 400–600 °C range, consistent with the main thermal degradation stage observed in TGA. Similar behavior has been reported in polymer blends where elevated temperature induces random bond cleavage, leading to higher PDI and fragmentation [28]. The thermal degradation mechanism of PVP under isothermal conditions

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appears to proceed via three primary pathways: (a) random chain scission in the polymer backbone, (b) depolymerization (unzipping) producing monomeric fragments, and (c) pyrrolidone ring opening followed by volatile release [29].

At lower temperatures, chain scission dominates, whereas depolymerization becomes more significant at higher temperatures. The observed increase in activation energy at higher temperature stages supports this mechanism, as bond rearrangement and radical stabilization become rate-limiting [30]. The presence of polar amide groups and a non-polar carbon backbone may contribute to the multi-step decomposition, as previously observed in TGA and differential scanning calorimetry studies on PVP and its composites [31]. Additionally, metal ions or dopants can catalyze decomposition, reducing the overall thermal stability, although this study focused on pure PVP [32]. Compared to previous non-isothermal studies, the isothermal TGA approach provides clearer separation of degradation stages and more accurate determination of kinetic parameters. The current data align with results obtained by Demir (2023), who reported multi-step degradation with first-order kinetics in PVP blends [33].

Similarly, recent work on PVP thin films showed major weight loss between 400–500 °C, corresponding to polymer backbone cleavage [34]. The advantage of isothermal analysis lies in the elimination of temperature ramp effects, allowing better modeling of real-time degradation kinetics relevant to industrial and sterilization conditions. Thus, this study contributes to closing the existing gap in kinetic data for PVP degradation under constant temperature exposure. These findings are significant for predicting PVP stability during processing operations such as extrusion, sterilization, and drying. The kinetic parameters obtained can guide optimization of manufacturing and storage conditions, as well as the design of PVP-based composites with improved thermal resistance [(35].

Conclusion

The thermal degradation kinetics of polyvinylpyrrolidone (PVP), analyzed through isothermal thermogravimetric analysis, revealed that the process follows a single-step decomposition with activation energy values consistent with polymer degradation mechanisms. The results confirm that thermal stability decreases with increasing temperature, supporting the applicability of the Arrhenius model. The kinetic parameters obtained align well with literature data, validating the reliability of the experimental approach. This study provides essential insight into the degradation pathway of PVP, enhancing its potential optimization in pharmaceutical and polymer engineering applications.

Recommendations

Further studies should focus on non-isothermal kinetic modeling to complement the current findings and provide a broader thermal stability profile. It is recommended to evaluate the influence of molecular weight and additives on PVP degradation behavior. Incorporating complementary techniques such as FTIR and DSC can elucidate the structural and thermal transitions during pyrolysis. Computational modeling could also refine the prediction of kinetic parameters. Lastly, future research should explore the implications of these thermal behaviors for PVP's role in controlled drug delivery and biocompatible materials.

Conflict of interest. Nil

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