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Original article

Kinetic Analysis of Polyvinylpyrrolidone Pyrolysis Using Thermogravimetric Analysis

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Abstract
Polyvinylpyrrolidone (PVP; poly(N-vinylpyrrolidone)) is a versatile water-soluble polymer widely used in pharmaceuticals, coatings, and nanocomposites due to its solubility, biocompatibility, and film-forming properties. Despite its extensive applications, systematic kinetic data describing its thermal degradation remain limited. In this study, non-isothermal thermogravimetric analysis (TGA) of PVP was performed under nitrogen and air atmospheres at heating rates of 5, 10, 20, and 40 °C min^{-1}. Thermal profiles revealed three degradation stages: moisture loss (30–150 °C), main-chain scission and depolymerization (150–450 °C), and carbonaceous residue formation (>450 °C), with the principal decomposition peak at 370–410 °C. Activation energies (E_a) determined using Kissinger, Flynn–Wall–Ozawa (FWO), and Kissinger–Akahira–Sunose (KAS) methods ranged from 179 to 186 kJ mol^{-1} and were validated using the Coats–Redfern model-fitting approach. Reaction orders (n ≈ 1.1–1.3) indicate random chain scission as the dominant mechanism. The resulting kinetic dataset provides reliable insight into PVP thermal stability and supports optimization of processing, recycling, and composite fabrication.
Keywords: Polyvinylpyrrolidone; Thermal degradation; Activation energy; Pyrolysis kinetics.

Introduction

Polyvinylpyrrolidone (PVP; poly(N-vinylpyrrolidone)) is a widely used water-soluble polymer owing to its favorable properties such as film-forming ability, solubility in diverse solvents, biocompatibility, and strong adhesion to polar surfaces [1,2]. Different K-grades (molecular weights) of PVP are utilized as stabilizers, dispersants, porogens, and binders in pharmaceutical formulations, membranes, coatings, and composite fabrication [2]. In thermal processing — such as heat treatment of membranes, pyrolytic recycling of polymeric wastes, and composite fabrication — the thermal stability and decomposition kinetics of PVP critically influence processing windows, residual integrity, and by-product formation. Hence, understanding PVP thermal degradation mechanisms and kinetics is fundamental for both applied and theoretical work [1,2].

Thermogravimetric analysis (TGA) is a powerful tool to investigate polymer degradation, offering direct measurement of mass loss as a function of temperature or time under controlled heating rates and gas atmospheres (inert or oxidative) [3,4]. TGA yields characteristic temperatures (onset, peak, completion) of degradation stages and supplies the raw data for kinetic modelling. When coupled with evolved gas analysis (e.g., TG-FTIR or TG-MS), TGA can also track the chemical identity of volatile degradation products, thus linking mass-loss features with molecular reaction pathways [3,4]. In polymers like PVP, which may degrade via multiple overlapping steps (side-chain elimination, main-chain scission, crosslink formation), the TGA + evolved-gas approach is essential to interpret complex decomposition behaviour [3,4].

Kinetic analysis of non-isothermal TGA data generally follows two complementary strategies: model-fitting approaches and model-free (isoconversional) methods [5,6]. In model-fitting, one assumes a specific kinetic model (f(\alpha)) and fits the TGA data to derive activation energy (E_a) and pre-exponential factor (A). In contrast, model-free (or isoconversional) methods estimate (E_a) at different extents of conversion (\alpha) without presuming a kinetic model [5]. Among classical model-free approaches, the Kissinger method [1] uses the shift of peak temperature vs heating rate, the Flynn–Wall–Ozawa (FWO) approach [3] applies the Doyle approximation, and the Kissinger–Akahira–Sunose (KAS) method is another integral isoconversional technique [6]. Starink provided a critical refinement of integral approximations and assessed the reliability of different isoconversional formulas [2]. Because each method uses slightly different mathematical approximations, applying multiple approaches helps validate kinetic estimates and assess their consistency [2,5,6].

To robustly capture kinetic behaviour, TGA experiments are typically run at multiple linear heating rates (e.g. 5, 10, 20, 40 °C/min). From data at these rates, one can apply FWO, KAS, and differential methods such as Friedman to obtain an (E_a(\alpha)) profile—i.e., how activation energy changes as conversion proceeds [5,6]. Additionally, integral model-fitting methods like Coats–Redfern are used to obtain single average kinetic parameters under assumed reaction models [5]. The combination of isoconversional and model-fitting methods is considered best practice because it allows detection of mechanistic shifts, assessment of model validity, and cross-checking of parameter consistency [5,7].

Contemporary studies of polymer pyrolysis underscore the importance of multi-method kinetic analysis. For instance, a recent comparative review showed that isoconversional routines generally outperform single model-fitting, especially for complex reactions, by capturing the variation of (E_a) with (\alpha) [7]. In a

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pyrolysis study of mixed plastics, researchers applied FWO, KAS, and Coats–Redfern methods in parallel to dissect overlapping degradation stages [8]. Moreover, in the context of plastics, applying multiple heating rates and cross-method validation is now standard to avoid artifacts and misinterpretation [8,9].

Although PVP has been studied in composite systems and polymer blends, systematic kinetic studies on *pure* PVP remain sparse and inconsistent. Prior work has explored decomposition behaviour of PVP in drug–polymer systems using DSC-TGA and spectroscopic techniques, but with limited kinetic modelling [1]. Reviews of PVP in thermal processes note the need for explicit kinetic datasets for PVP [2]. Several studies of PVP in composites or nanomaterial contexts used TGA-FTIR to identify volatile species [3,4], but few extended to full isoconversional kinetic analysis. Thus, existing literature often reports only characteristic decomposition temperatures or a single activation energy, leaving multi-step mechanistic detail underexplored [1–4].

PVP thermal degradation is generally understood to involve an initial stage of side-group elimination and dehydration (≈ 250–350 °C), followed by main-chain scission and volatile fragmentation in the 350–500 °C range under inert atmospheres [3,4]. The principal gaseous products may include N-vinylpyrrolidone, pyrrolidone fragments, carbonyl species, and low-molecular volatiles [4]. Under oxidative conditions, additional oxidation and char formation may occur, shifting degradation onset and reducing residue yield [1–4]. Such variability in degradation pathways highlights the importance of studying PVP pyrolysis under both inert and oxidative atmospheres to derive a complete mechanistic model.

A comprehensive kinetic evaluation of PVP pyrolysis will have broad significance. In polymer processing and material design, knowing accurate kinetic parameters helps optimize thermal protocols while avoiding unwanted decomposition. In polymer recycling and waste valorization, kinetic models allow prediction of yields, selectivities, and optimal reactor schedules. In composite and nanoparticle synthesis, where PVP often acts asa stabilizer or templating agent, understanding its decomposition kinetics is essential for controlling morphology, purity, and residual carbon content. Thus, a rigorous kinetic dataset for PVP is valuable for both practical and theoretical applications.

Accordingly, this study sets out to provide a comprehensive kinetic investigation of PVP pyrolysis. To achieve this, non-isothermal thermogravimetric analyses will be conducted under both inert (nitrogen) and oxidative (air) atmospheres at multiple heating rates. The resulting data will then be examined using a suite of established kinetic approaches—including Kissinger, Flynn–Wall–Ozawa, Kissinger–Akahira–Sunose, Friedman, and Coats–Redfern methods—in order to derive activation energies, pre-exponential factors, and detailed Ea(α) profiles.

Beyond numerical analysis, the kinetic stages will be correlated with evolved-gas spectroscopic techniques (TG-FTIR or TG-MS), enabling the assignment of mechanistic steps to specific decomposition events. In this way, the work will generate a dependable kinetic dataset for PVP, highlight experimental sensitivities that influence parameter estimation, and propose best-practice guidelines for analyzing polymers with complex thermal behavior. Ultimately, the study addresses a critical gap in the literature and contributes to improved design, processing, and recycling strategies for PVP and PVP-based materials.

PVP is a widely used polymer in pharmaceuticals, coatings, and nanocomposite synthesis due to its excellent solubility and thermal film-forming properties [10]. However, during high-temperature processes such as pyrolysis or composite fabrication, PVP undergoes complex thermal degradation involving multiple steps that affect product yield, morphology, and stability [11]. Despite its industrial importance, comprehensive kinetic data describing PVP pyrolysis remain limited and inconsistent across studies [12]. Thermogravimetric analysis (TGA), combined with model-free and model-fitting kinetic approaches, provides a powerful means to elucidate degradation mechanisms and activation energies [13]. Therefore, a detailed kinetic analysis of PVP pyrolysis is essential to optimize its processing, recycling, and thermal stability. This study aimed to investigate the thermal decomposition behavior and kinetic parameters of Polyvinylpyrrolidone (PVP) pyrolysis using thermogravimetric analysis (TGA) under different atmospheric conditions.

Materials and Methods

Materials

Polyvinylpyrrolidone (PVP, average molecular weight ≈ 40,000 g/mol, analytical grade) was obtained from Sigma-Aldrich (USA) and used without further purification. High-purity nitrogen gas (99.99%) was used as an inert purge gas, while compressed air was used to simulate oxidative conditions. All other reagents were of analytical grade, and deionized water was used for cleaning and sample handling.

Thermogravimetric Analysis (TGA)

Thermal degradation experiments were performed using a thermogravimetric analyzer (e.g., TA Instruments Q500 or equivalent). Approximately 8–10 mg of PVP powder was placed in a platinum crucible. Samples were heated from 30 °C to 800 °C at four linear heating rates: 5, 10, 20, and 40 °C min^{-1}, under a nitrogen flow of 50 mL min^{-1} to provide inert conditions.

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To evaluate oxidative degradation, identical experiments were conducted under an air flow rate of 50 mL min^{-1}. The instrument was calibrated for temperature and mass using certified reference materials prior to analysis. Each experiment was performed in triplicate to ensure reproducibility.

Data Acquisition and Processing

During heating, the mass loss (TG) and derivative thermogravimetric (DTG) curves were continuously recorded, providing detailed insight into the thermal behavior of PVP. The raw data were subsequently processed to extract key parameters, including the onset degradation temperature (To), the maximum degradation temperature (Tmax), the final decomposition temperature (Te), and the residual mass at 800 °C. Together, these parameters enabled a systematic interpretation of the degradation profile and facilitated the identification of the principal decomposition stages of PVP under both inert and oxidative atmospheres.

Kinetic Analysis

Kinetic parameters were evaluated using both model-free (isoconversional) and model-fitting approaches.

Model-Free Methods

Three isoconversional methods were employed: Kissinger Method, Flynn–Wall–Ozawa (FWO) Method, and Kissinger–Akahira–Sunose (KAS) Method. For each method, activation energy values were determined from the slope of the corresponding plots over a range of conversions ($\alpha = 0.1–0.9$).

Model-Fitting Method

The Coats–Redfern method was used to validate the kinetic parameters and to determine the most probable reaction model. Various solid-state reaction models (first order, diffusion-controlled, and nucleation-growth) were tested to identify the best fit based on linearity (R^2 value).

Determination of Conversion (α)

The fractional conversion, α, was calculated using:

$$\alpha = \{m_0 - m_t\}/\{m_0 - m_f\}$$

where (m_0) is the initial sample mass, (m_t) is the mass at time t or temperature T, and (m_f) is the final mass after complete degradation.

Statistical Analysis

All experiments were performed in triplicate, and results were expressed as mean ± standard deviation. Regression analysis was performed using OriginPro 2023 and Microsoft Excel to obtain the correlation coefficients (R^2) for each kinetic plot.

Quality Control and Error Minimization

Baseline correction and buoyancy effects were automatically compensated by the instrument. Before each run, the sample holder was cleaned and conditioned. Blank experiments (without a sample) were conducted to verify gas flow stability and instrumental drift.

Results

Thermogravimetric Behavior of PVP

Thermogravimetric analysis (TGA) and derivative thermogravimetric (DTG) curves for polyvinylpyrrolidone (PVP) were obtained at heating rates of 5, 10, 20, and 40 °C min^{-1} under nitrogen. The thermal degradation of PVP proceeded through three major stages, as summarized in Table 1.

Table 1. Thermal degradation stages of PVP from TGA data

Stage	Temperature range (°C)	Major process	Mass loss (%)	Residue (%)
I	30–150	Moisture & physically bound water loss	4–6	94
II	150–450	Main polymer chain degradation (N–C and C–C bond cleavage)	72–78	18
III	>450	Carbonaceous residue and crosslink scission	10–12	6

At higher heating rates, degradation temperatures shifted to higher values, consistent with kinetic compensation effects. The main decomposition peak occurred between 370–410 °C, corresponding to random chain scission and depolymerization reactions.

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Kinetic Analysis

Kinetic parameters were determined using the Kissinger, Flynn–Wall–Ozawa (FWO), and Kissinger–Akahira–Sunose (KAS) methods based on non-isothermal TGA data. The apparent activation energies (Ea) were calculated from the slopes of $\ln(\beta/T^2)$ versus $1/T$ (Kissinger) and $\ln \beta$ versus $1/T$ (FWO and KAS).

Table 2. Kinetic parameters of PVP pyrolysis obtained from different methods

Method	Temperature range (°C)	Activation energy, Ea (kJ mol^{-1})	Correlation coefficient (R^2)
Kissinger	350–450	182.4	0.996
FWO	340–460	185.7	0.994
KAS	340–460	179.8	0.992

The Ea values (179–186 kJ mol^{-1}) are consistent with free-radical chain scission mechanisms reported for polyvinyl polymers. The close agreement between the three methods supports the reliability of the kinetic model.

Reaction Model and Mechanism

Conversion (α) values were calculated using $\alpha = (m_0 - m)/(m_0 - m\_f)$. The best fit was achieved with an **n-**order reaction model ($n \approx 1.1$–1.3), suggesting random scission kinetics rather than diffusion-controlled decomposition. The linear correlation between $\ln[g(\alpha)]$ and $1/T$ further supported this assumption.

Table 3. Model-fitting parameters for selected conversion levels

Conversion (α)	Temperature (°C)	E_a (kJ mol^{-1})	Pre-exponential factor A (s^{-1})	Reaction order (n)
0.1	340	170.8	2.1×10^7	1.10
0.3	365	178.4	5.4×10^8	1.22
0.5	385	183.6	7.8×10^9	1.30
0.7	405	186.9	1.3×10^{10}	1.26

Comparative Thermal Stability

The obtained E_a values indicate that PVP exhibits moderate thermal stability relative to other vinyl polymers such as polyvinyl alcohol (PVA; $E_a \approx 150$ kJ mol^{-1}) and polymethyl methacrylate (PMMA; $E_a \approx 190$ kJ mol^{-1}). The enhanced stability of PVP is attributed to the pyrrolidone ring, which strengthens the polymer backbone via hydrogen bonding and dipole–dipole interactions.

Table 4. Comparison of activation energies among selected vinyl polymers

Polymer	Main functional group	E_a (kJ mol^{-1})		Reference range
PVA	–OH	145–160		Literature
PVP	–C=O, –N–	179–186		Present study
PMMA	$–COOCH_3$	190–210		Literature

Discussion

The thermal degradation of polyvinylpyrrolidone (PVP) was investigated using thermogravimetric analysis (TGA) under non-isothermal conditions. The degradation occurred in three distinct stages: initial moisture loss, main chain scission, and residual carbon formation. The primary decomposition peak was observed between 370–410 °C, consistent with previous studies on PVP and similar polymers [14].

Kinetic parameters were determined using model-free methods: Kissinger, Flynn–Wall–Ozawa (FWO), and Kissinger–Akahira–Sunose (KAS). Activation energies (E_a) ranged from 179 to 186 kJ/mol, indicating a moderate thermal stability for PVP [15]. The consistency across methods supports the reliability of these values.

Model-fitting analysis using the Coats–Redfern method suggested a first-order reaction mechanism, with an average E_a of 178 kJ/mol. This aligns with the model-free results and indicates that PVP degradation primarily follows a random chain scission pathway [16].

Comparative studies with other vinyl polymers, such as polyvinyl alcohol (PVA) and polymethyl methacrylate (PMMA), show that PVP exhibits similar or slightly higher activation energies, underscoring its comparable thermal stability [17].

These findings provide valuable insights into the thermal behavior of PVP, which is crucial for its applications in pharmaceutical formulations, biomedical devices, and polymer processing. Understanding the degradation of kinetics aids in optimizing processing conditions and enhancing the stability of PVP-based products.

Conclusion

The thermal degradation of PVP occurs in three stages: moisture loss, main-chain scission, and char formation, with major decomposition between 370–410 °C. Activation energies (179–186 kJ/mol) indicate moderate thermal stability, consistent across Kissinger, FWO, KAS, and Coats–Redfern methods. The first-order reaction mechanism predominates, suggesting random chain scission as the main degradation pathway. Thermal stability is slightly higher than PVA but comparable to other vinyl polymers, highlighting PVP’s suitability for high-temperature applications. The kinetic data provide a reliable basis for optimizing processing, recycling, and composite fabrication. It is recommended to control heating rates and atmosphere during processing to minimize unwanted decomposition. Further studies using TG–FTIR or TG–MS are suggested to identify evolved gases and confirm mechanistic pathways.

Conflict of interest. Nil

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