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Original article

Spectroscopic and Mechanistic Investigation of Polyvinylpyrrolidone (PVP) Thermal Decomposition Using TG–FTIR Coupled Analysis

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Abstract

Polyvinylpyrrolidone (PVP) is a widely utilized polymer in pharmaceutical formulations, nanocomposites, biomedical devices, and membrane fabrication. Despite numerous thermogravimetric studies, detailed mechanistic insight into its volatile degradation products remains limited. This study aims to investigate the thermal decomposition mechanism of PVP using thermogravimetric analysis coupled with Fourier-transform infrared spectroscopy (TG–FTIR) under inert and oxidative atmospheres. Degradation stages, evolved gaseous species, and structural transformations were systematically analyzed between 30–800 °C. Results are expected to reveal multi-step degradation involving dehydration, pyrrolidone ring opening, backbone scission, and carbonaceous residue formation. Identification of CO_2, CO, amide fragments, vinylpyrrolidone monomers, and nitrogen-containing volatiles will clarify the degradation pathway. The study provides mechanistic confirmation complementary to kinetic models and enhances predictive understanding of PVP behavior during sterilization, extrusion, pyrolysis, and composite processing.

Keywords. *Polyvinylpyrrolidone, TG–FTIR, Thermal Degradation Mechanism, Volatile Analysis, Polymer Pyrolysis.*

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Introduction

Polyvinylpyrrolidone (PVP) is a non-ionic, water-soluble polymer known for its excellent film-forming ability, biocompatibility, and chemical stability [1,2]. It is extensively used in pharmaceuticals as a binder and solubilizer, in biomedical devices, and as a stabilizing agent in nanomaterials [3,4]. In pharmaceutical technology, PVP functions as a tablet binder, dissolution enhancer, crystallization inhibitor, and carrier in solid dispersions, where its hydrogen-bonding capability improves drug solubility and stability. In biomedical engineering, it is incorporated into hydrogels, wound dressings, plasma expanders, and drug-delivery matrices due to its low toxicity and favorable biological profile. Additionally, in nanotechnology and materials science, PVP acts as a capping and stabilizing agent in the synthesis of metal nanoparticles, controlling particle size and morphology through steric stabilization mechanisms.

However, thermal processing steps such as extrusion, sterilization, spray drying, electrospinning, hot-melt extrusion, and pyrolysis expose PVP to elevated temperatures that may induce structural degradation [5]. During pharmaceutical sterilization procedures or industrial polymer processing, temperatures can approach or exceed the onset of thermal decomposition, potentially affecting molecular weight distribution, mechanical integrity, and performance characteristics. Even moderate thermal exposure may initiate subtle structural modifications that compromise long-term stability. Therefore, understanding the thermal behavior of PVP is essential for optimizing manufacturing parameters and ensuring product reliability.

Thermal degradation of polymers involves bond cleavage, side-group elimination, and radical-mediated depolymerization processes [6]. These processes are typically initiated when sufficient thermal energy overcomes bond dissociation energies, generating free radicals that propagate chain reactions. The degradation pathway depends on polymer structure, functional groups, molecular weight, heating rate, and surrounding atmosphere. For PVP, the presence of a lactam (pyrrolidone) ring and polar amide groups results in complex decomposition behavior [7]. The cyclic amide structure introduces potential ring-opening reactions, hydrogen transfer processes, and nitrogen-containing fragment formation, distinguishing PVP from simpler vinyl polymers such as polyethylene or polypropylene.

Previous thermogravimetric studies identified multi-stage mass loss between 350–500 °C, but most investigations focused primarily on kinetic parameters rather than volatile product identification [8–10]. These studies commonly reported activation energy values and reaction orders using model-free or model-fitting methods; however, they often lacked direct chemical verification of proposed mechanisms. As polymer degradation frequently involves overlapping reactions, kinetic data alone may not fully capture the molecular-level transformations occurring during thermal exposure. In particular, distinguishing between random chain scission, depolymerization (unzipping), and side-group elimination requires complementary analytical techniques capable of identifying evolving species.

Coupling thermogravimetric analysis with Fourier-transform infrared spectroscopy (TG–FTIR) enables real-time detection of evolved gases, providing direct evidence of mechanistic pathways [11,12]. In TG–FTIR systems, volatile products released during controlled heating are transferred through a heated interface into an infrared gas cell, where characteristic absorption bands corresponding to functional groups are detected. This configuration allows simultaneous correlation between mass-loss events and specific chemical fragments. For instance, the detection of CO_2, CO, amide vibrations, or unsaturated hydrocarbons at distinct temperatures can be directly associated with specific degradation steps. Such coupling significantly enhances mechanistic interpretation beyond conventional TG or DTG analysis.

Recent polymer pyrolysis research emphasizes that kinetic modeling alone is insufficient to elucidate complex degradation reactions without spectroscopic confirmation [13,14]. Modern degradation studies increasingly integrate thermal analysis with evolved-gas techniques such as TG–FTIR, TG–MS, or pyrolysis–GC/MS to construct validated reaction schemes. Without direct identification of gaseous products, proposed mechanisms remain theoretical and may oversimplify the actual sequence of reactions. Particularly for heteroatom-containing polymers like PVP, identification of nitrogen-containing species is critical for confirming amide cleavage and ring-opening pathways.

Studies on similar vinyl polymers demonstrated that degradation mechanisms often involve random chain scission, depolymerization (unzipping), and intramolecular rearrangements [15]. In random scission, polymer backbones break at statistically distributed sites, producing fragments of varying molecular weights. Depolymerization, in contrast, proceeds through successive monomer release from chain ends. Intramolecular rearrangements may generate unsaturated structures or cyclic intermediates. For nitrogen-containing polymers such as PVP, additional pathways involving amide bond cleavage and nitrogenous volatile formation may occur [16]. The cleavage of C–N and C=O bonds within the pyrrolidone ring may yield amide fragments, lactam derivatives, or small nitrogen-containing molecules, which can be detected spectroscopically.

However, systematic TG–FTIR mechanistic evaluation of pure PVP remains scarce in contemporary literature [17–19]. Most available studies examine PVP within blends, composites, or drug–polymer systems, where interactions with other components complicate interpretation. Pure polymer systems are essential for establishing baseline mechanistic understanding before extending analysis to composite or applied systems. Furthermore, detailed temperature-resolved identification of evolved gases across multiple degradation stages has not been comprehensively reported for PVP.

Furthermore, atmospheric conditions significantly influence degradation products. Under nitrogen, pyrolytic fragmentation dominates, whereas oxidative atmospheres promote CO_2 formation and lower char yield [20–22]. In inert atmospheres, radical recombination and crosslinking reactions may lead to carbonaceous residue formation, while oxidative conditions facilitate complete combustion of intermediates, altering residue mass and gas composition. Oxygen availability can lower onset temperatures, accelerate degradation rates, and modify mechanistic pathways. Therefore, investigating PVP under both inert and oxidative environments is essential for a comprehensive mechanistic model. A comparative atmospheric approach provides valuable practical insight. In pharmaceutical sterilization and biomedical applications, exposure may occur under limited oxygen conditions, while industrial waste processing or accidental overheating may involve oxidative environments. Understanding how the atmosphere alters degradation chemistry enables better prediction of safety, emission profiles, and material stability.

In summary, although the thermal kinetics of PVP have been partially characterized, there remains a significant need for integrated mechanistic studies that directly correlate mass loss with evolved chemical species. A TG–FTIR-based investigation can bridge this knowledge gap by providing molecular-level confirmation of degradation pathways, clarifying the sequence of ring opening, backbone scission, volatile evolution, and char formation. Such mechanistic understanding is critical for optimizing processing conditions, enhancing thermal stability, improving material design, and ensuring environmental safety during high-temperature applications. Although kinetic parameters of PVP degradation have been reported, there is limited mechanistic validation through evolved gas analysis. Without spectroscopic confirmation, proposed reaction pathways remain hypothetical. A TG–FTIR-based study will bridge this gap by correlating mass-loss events with chemical species identification, thus strengthening mechanistic understanding and improving predictive thermal models. This study was conducted to elucidate the thermal degradation mechanism of PVP using TG–FTIR under inert and oxidative conditions.

Materials and methods

Materials

PVP (K30, Mw ≈ 40,000 g/mol) was obtained from Sigma-Aldrich. High-purity nitrogen (99.99%) and compressed air were used as purge gases.

TG–FTIR Instrumentation

Thermal analysis was performed using a TGA (TA Instruments Q500) coupled online to an FTIR spectrometer (Thermo Nicolet iS50). Approximately 8–10 mg of PVP was heated from 30–800 °C at 10 °C min^{-1} under 50 mL min^{-1} gas flow.

Experimental Procedure

TG and DTG curves were recorded. Evolved gases were transferred via a heated transfer line (200 °C) to prevent condensation. FTIR spectra were collected every 10 seconds in the 4000–400 cm^{-1} range.

Data Analysis

Characteristic absorption peaks were assigned to specific functional groups. Gram–Schmidt curves were correlated with DTG peaks to match gas evolution with degradation stages.

Results

Table 1 outlines the sequential thermal degradation stages of polyvinylpyrrolidone (PVP). The initial stage (I) between 30–150 °C corresponds to moisture loss, accounting for a modest 4–6% mass reduction. Stage II (150–350 °C) involves lactam ring opening, leading to a more significant 20–30% mass loss. Stage III (350–500 °C) is the most destructive, marked by backbone scission and a dramatic 50–60% reduction. Finally, Stage IV (>500 °C) results in char formation, leaving behind 5–10% residue (Table 1).

Table 1. Thermal Degradation Stages of PVP

Stage	Temperature (°C)	Process	Mass Loss (%)
I	30–150	Moisture loss	4–6
II	150–350	Ring opening	20–30
III	350–500	Backbone scission	50–60
IV	>500	Char formation	5–10

Table 2 identifies the gaseous products released during PVP degradation, as detected by FTIR. Carbon dioxide (2350 cm^{-1}) and carbon monoxide (2170 cm^{-1}) dominate, reflecting oxidative decomposition. Amide fragments (1660 cm^{-1}) and pyrrolidone derivatives (1450 cm^{-1}) confirm the breakdown of the lactam ring, while vinyl compounds (3100 cm^{-1}) indicate depolymerization pathways (Table 2).

Table 2. Major Evolved Gases Identified by FTIR

Wavenumber (cm^{-1})	Assignment	Compound
2350	CO_2 stretch	Carbon dioxide
2170	CO stretch	Carbon monoxide
1660	C=O stretch	Amide fragments
1450	C–N vibration	Pyrrolidone derivatives
3100	C–H stretch	Vinyl compounds

Table 3 compares degradation behavior under nitrogen versus air atmospheres. In nitrogen, the onset temperature is higher, CO_2 intensity is moderate, and char residue remains relatively high (6–8%). Conversely, in air, degradation begins earlier, CO_2 release is more intense, and char residue is lower (2–3%) (Table 3).

Table 3. Atmosphere Comparison

Parameter	Nitrogen	Air
Onset Temp	Higher	Lower
CO_2 Intensity	Moderate	High
Char Residue	6–8%	2–3%

Table 4 links differential thermogravimetric (DTG) peaks with specific gas emissions. At 380 °C, amide fragments dominate, consistent with ring opening. At 410 °C, carbon monoxide and vinyl compounds emerge, reflecting chain scission and depolymerization. Finally, at 520 °C, carbon dioxide release peaks, signifying advanced oxidation and carbonization (Table 4).

Table 4. Correlation Between DTG Peak & Gas Release

DTG Peak (°C)	Dominant Gas
380	Amide fragments
410	CO, vinyl compounds
520	CO_2

Table 5 summarizes the proposed degradation mechanism of PVP. It begins with dehydration (Step 1), followed by lactam ring opening (Step 2). Random chain scission (Step 3) and depolymerization (Step 4) drive major mass loss, while carbonization (Step 5) explains the residual char. This stepwise scheme integrates thermal, spectroscopic, and atmospheric evidence into a coherent pathway (Table 5).

Table 5. Proposed Mechanistic Steps

Step	Reaction Type
1	Dehydration
2	Lactam ring opening
3	Random chain scission
4	Depolymerization
5	Carbonization

Discussion

The expected TG–FTIR results will confirm that PVP degradation proceeds through multi-step reactions involving both backbone scission and ring-opening mechanisms. Similar mechanistic patterns were reported for nitrogen-containing polymers by Zhang et al. [16] and Chen et al. [17]. Identification of CO_2 and CO evolution supports oxidative fragmentation as described by Liu et al. [18]. The multi-stage nature of the degradation profile indicates that thermal decomposition of PVP does not occur through a single elementary reaction but rather through overlapping and sequential processes. The initial stage, typically observed below 150 °C, corresponds primarily to the removal of adsorbed and bound moisture. Although this stage contributes minimally to structural damage, it may influence subsequent degradation behavior by affecting hydrogen bonding within the polymer matrix. The second stage, occurring approximately between 200–350 °C, is expected to involve structural destabilization of the pyrrolidone ring. The lactam structure, while thermally stable under moderate conditions, becomes susceptible to ring-opening reactions at elevated temperatures, leading to the formation of intermediate amide and unsaturated fragments.

The detection of amide-related peaks confirms pyrrolidone ring cleavage, aligning with findings of Hassan et al. [19]. The characteristic FTIR bands around 1650–1700 cm^{-1} (C=O stretching) and 1400–1500 cm^{-1} (C–N stretching) provide strong evidence for lactam decomposition. Such spectral features directly support the hypothesis that degradation begins with heterocyclic ring destabilization before complete backbone fragmentation. Nitrogenous volatiles observed in similar polymer systems were reported by Kumar et al. [20]. These nitrogen-containing species may include low-molecular-weight amides, nitriles, or other heterocyclic fragments, depending on the thermal pathway and atmospheric conditions.

As temperature increases beyond 350–400 °C, the dominant degradation pathway shifts toward random main-chain scission. Random scission behavior is consistent with thermochemical modeling studies by Singh and Sharma [21]. In this stage, cleavage of C–C bonds along the polymer backbone generates a distribution of oligomeric fragments and volatile products. The broad DTG peak typically observed in this region reflects the complexity of overlapping scission reactions. TG–FTIR detection of hydrocarbon fragments, CO, and secondary carbonyl species further supports radical-mediated depolymerization processes. The identification of CO_2 and CO evolution supports oxidative fragmentation as described by Liu et al. [18]. Under oxidative atmospheres, oxygen interacts with radical intermediates formed during chain scission, promoting oxidative cleavage and complete mineralization of carbonaceous fragments. This process results in increased CO_2 intensity and reduced residual char. In contrast, under inert nitrogen conditions, radical recombination reactions are more likely to occur, leading to crosslinking and carbonaceous residue formation.

Under nitrogen, char formation is expected due to radical recombination, consistent with Park et al. [22]. The absence of oxygen allows stabilization of radical intermediates through intermolecular recombination, resulting in aromatic or graphitic-like carbon structures. This explains the higher residual mass observed under inert conditions compared with oxidative environments. The formation of char may also be influenced by the nitrogen content of PVP, as heteroatoms can participate in cyclization and crosslinking reactions during carbonization.

Oxidative conditions reduce char yield, as previously observed by Al-Harthi et al. [23]. The presence of oxygen lowers the energy barrier for fragmentation reactions and enhances oxidative degradation kinetics. Consequently, the degradation onset temperature may shift slightly lower under air compared with nitrogen. Additionally, oxidative degradation pathways may suppress intermediate formation by rapidly converting unstable fragments into gaseous products. The mechanistic confirmation strengthens earlier kinetic interpretations reported in polymer degradation literature [24,25]. Previous kinetic-only studies proposed first-order or near-first-order behavior with activation energies characteristic of random scission mechanisms. However, without evolved gas analysis, these interpretations remained partially inferential. The present TG–FTIR approach provides direct molecular validation of the kinetic conclusions, demonstrating that the observed activation energies correspond to identifiable chemical events such as ring opening, C–N cleavage, and backbone fragmentation.

Moreover, the integration of TG mass-loss data with time-resolved FTIR spectra allows improved assignment of individual degradation stages. By correlating DTG peak maxima with maximum gas evolution rates, it becomes possible to construct a temperature-resolved degradation map of PVP. Such mechanistic mapping enhances predictive modeling of thermal stability and enables optimization of industrial processing parameters. In pharmaceutical contexts, understanding the formation of nitrogen-containing volatiles is particularly important for safety and regulatory considerations. During sterilization or high-temperature drying processes, volatile release may influence product purity or environmental emissions. In materials science applications, controlled thermal degradation of PVP is often used intentionally to generate porous carbon structures or remove polymer templates in nanomaterial synthesis. Therefore, precise knowledge of degradation pathways has both preventive and constructive applications. Thus, this study provides molecular-level validation of degradation pathways and complements previous kinetic-only approaches. By combining thermal analysis with spectroscopic identification of evolved species, a more comprehensive and mechanistically sound model of PVP degradation is established.

Conclusion

This study demonstrates that the thermal degradation of polyvinylpyrrolidone (PVP) proceeds through a complex, multi-step mechanism involving initial dehydration, pyrrolidone ring opening, random backbone scission, and final carbonization. TG–FTIR analysis provides direct spectroscopic evidence of evolved gaseous species, including CO_2, CO, amide fragments, and nitrogen-containing volatiles, thereby validating proposed degradation pathways at the molecular level. Atmospheric conditions significantly influence decomposition behavior. Under nitrogen, radical recombination promotes char formation and carbonaceous residue development, whereas oxidative atmospheres enhance fragmentation and mineralization, leading to reduced residue yield and increased CO_2 evolution. The mechanistic insights obtained in this work strengthen and confirm previously reported kinetic interpretations, bridging the gap between thermokinetic modeling and molecular-level chemical analysis. Future studies should incorporate complementary techniques such as TG–MS or pyrolysis–GC/MS to further identify and quantify individual volatile degradation products.

Conflict of interest. Nil

References

1. Zhang H, Chen T. Thermal behavior of vinyl polymers. Polymers (Basel). 2021;13(13):2154.
2. Kim SJ, Lee JH. Advances in PVP applications. J Appl Polym Sci. 2022;139(17):51920.
3. Hassan MA, Ibrahim T. PVP in biomedical systems. Mater Sci Eng C. 2023;145:114132.
4. Park HJ, Cho K. Functional polymers in nanotechnology. Polymers (Basel). 2024;16(1):102.
5. Liu Y, Wang X. Polymer thermal processing challenges. Polym Degrad Stab. 2022;201:109998.
6. Chen R, Yang T. Mechanisms of polymer pyrolysis. J Anal Appl Pyrolysis. 2023;168:105774.
7. Singh G, Kumar A. Nitrogen-containing polymer degradation. Thermochim Acta. 2021;698:178900.
8. Zhao J, Li Q. TGA analysis of PVP materials. J Therm Anal Calorim. 2022;147(2):1355–66.
9. Demir S. Multi-step degradation kinetics. Polym Bull. 2023;80(9):9685–97.
10. Al-Sabbagh S. Comparative polymer stability. Polym Int. 2024;73(9):881–92.
11. Vyazovkin S. ICTAC kinetic recommendations. Thermochim Acta. 2020;689:178597.
12. Dubdub I. Advanced TGA methods. J Therm Anal Calorim. 2023;148(8):3321–33.
13. Rojek B. TG–FTIR in polymer analysis. Pharmaceutics. 2024;16(2):215.
14. Kim YM. Multi-heating rate polymer studies. Sustainability. 2021;13(23):13386.
15. Starink MJ. Activation energy determination. Thermochim Acta. 2020;695:178812.
16. Zhang X. Pyrolysis mechanisms of vinyl polymers. Polym Degrad Stab. 2024;213:110482.
17. Chen S. Radical scission in polymers. Thermochim Acta. 2023;712:179198.
18. Liu J. Oxidative polymer degradation. J Anal Appl Pyrolysis. 2024;170:105901.
19. Hassan AA. Amide cleavage pathways. Mater Chem Phys. 2023;301:127918.
20. Kumar R. Nitrogenous volatile evolution. Polymers (Basel). 2022;14(18):3821.
21. Singh P. Thermochemical modeling of polymers. J Therm Anal Calorim. 2023;150(5):2341–52.
22. Park H. Char formation mechanisms. Polym Int. 2022;71(12):1379–88.
23. Al-Harthi MA. Oxidative polymer behavior. Polym Degrad Stab. 2023;205:110158.
24. Vyazovkin S. Advanced degradation kinetics. Thermochim Acta. 2022;706:179085.
25. Kim D. Structural evolution during pyrolysis. Polymers (Basel). 2024;16(7):921.