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Computational Insights into the Thermal Stability and Degradation Pathways of Poly(butylene adipate-co-terephthalate)

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Abstract

The thermal decomposition pathways, bond dissociation free energies, and product distributions of biodegradable poly(butylene adipate-co-terephthalate) (PBAT) copolymer under inert atmosphere have been investigated using density functional theory (DFT). Calculations at the B3LYP/6-311++G(d,p) level identified the most stable molecular geometries, and decomposition processes were thoroughly analyzed. Based on vibrational frequency analyses and bond dissociation energy calculations, three primary decomposition pathways (ptw1, ptw2, and ptw3) were characterized, and their Gibbs free energy changes were computed. The results indicated that pathway ptw1 (61.41 kcal/mol) has the lowest energy barrier and is the most thermodynamically favorable route for decomposition. Additionally, low molecular weight aliphatic compounds, CO_2, adipate, and terephthalate derivatives were determined as the primary decomposition products. These findings provide significant insights into the thermal stability of PBAT and the environmental impacts of its decomposition products, contributing to the development of sustainable polymer applications.

Keywords: Degradation products, DFT, Poly(butylene adipate-co-terephthalate), Thermal degradation mechanism

1. Introduction

Recently, the production of petroleum-based plastics has increased rapidly due to their low cost, versatility, and wide availability, making them indispensable in modern industry [1]. However, this growth has also created severe waste management challenges, leading to environmental pollution and negative ecological impacts [2]. In response, sustainable and biodegradable polymers have attracted growing attention as promising alternatives to conventional plastics [3]. Such materials can be derived from both bio-based sources (e.g., polylactic acid (PLA), polyhydroxyalkanoates (PHA), and starch-based polymers) and fossil resources (e.g., polycaprolactone (PCL) and poly(butylene adipate-co-terephthalate) (PBAT)) [4–6]. Due to their improved biodegradability compared to traditional plastics, these polymers have the potential to reduce environmental persistence and mitigate waste accumulation [7].

Poly(butylene adipate-co-terephthalate) (PBAT) is a synthetic aliphatic–aromatic copolyester valued for its flexibility, mechanical strength, and biodegradability [8]. Its properties vary depending on the ratio of adipate (aliphatic) and terephthalate (aromatic) segments, which makes it suitable for applications such as compostable packaging, agricultural films, and biomedical devices [9–12]. PBAT is further regarded as an environmentally friendly material due to its susceptibility to microbial degradation and relatively high thermal stability [13–15]. Polymer degradation is a complex, multi-step process that typically begins with bond cleavage, followed by molecular rearrangements leading to smaller fragments [16–18]. Thermal degradation is of particular importance, as exposure to high temperatures can generate volatile compounds and residues with potential risks to human health and the environment. For instance, while polyolefins release hydrocarbons upon degradation, PVC produces chlorine-based hazardous by-products. Experimental techniques such as thermogravimetric analysis (TGA) and gas chromatography–mass spectrometry (GC–MS) are widely used to identify these products. Recent pyrolysis–GC/MS studies on PBAT have reported a variety of degradation compounds including tetrahydrofuran, cyclopentanone, benzoic acid, 3-butenyl 4-hydroxybutyl adipate, and but-3-enyl hydrogen terephthalate [19]. Other studies have confirmed the presence of benzoic,

adipic, and terephthalic acids as well as volatile species such as 1,3-butadiene, benzene, diphenyl, and benzophenone [20,21].

Complementary to experimental studies, quantum chemical methods such as density functional theory (DFT) provide powerful tools for investigating degradation mechanisms at the molecular level. DFT can predict reaction pathways, energy barriers, and transition states with high accuracy, thereby offering valuable insights into processes that are experimentally challenging to capture [22–26]. For example, Didovets and Brela applied DFT to examine the effects of solvent and temperature on the degradation thermodynamics of nylon 6 and polyhydroxybutyrate (PHB) [16]. Similarly, DFT-based studies have clarified catalytic degradation pathways of polystyrene, highlighting the role of acidic and basic catalysts on activation energies and product distributions [27]. Martínez and co-workers further explored the potential toxicity of PBAT and its degradation products through quantum chemical calculations of electron transfer capacity [28]. Despite these contributions, detailed theoretical studies directly addressing PBAT degradation pathways, energy barriers, and product formation remain scarce.

In this study, density functional theory (DFT) methods were employed to investigate the thermal degradation mechanism of PBAT under inert atmospheric conditions. The work aims to identify possible intermediate and final products, providing a theoretical framework that complements experimental findings and supports the development of new evaluation and management strategies for PBAT degradation products.

2. Computational methodology

Computational chemistry methods were employed to elucidate the initial bond-breaking events that trigger the thermal degradation mechanism and identify the degradation products of biodegradable poly(butylene adipate-co-terephthalate) (PBAT) copolymer under an inert (N_2) atmosphere. To do this efficiently, a simplified "model oligomer" was created instead of simulating the entire complex polymer chain. A representative PBAT copolymer model was constructed by combining one monomer unit (n = 1) from the poly(butylene adipate) (PBA) segment with one monomer unit (m = 1) from the poly(butylene terephthalate) (PBT) segment. This common and reliable approach is justified because bond cleavage is a local phenomenon, primarily influenced by the immediate atoms surrounding the bond, not by distant parts of the chain. This method effectively balances computational feasibility with chemical accuracy, allowing for a precise mapping of the bond energies to determine which ones are most likely to break first, a technique proven to align with experimental results for similar polymers [29,30]. The conformational analysis of this model was initially performed using the SPARTAN 14 [31] computational chemistry program at the semi-empirical PM6 level. Subsequently, all conformers within a 5 kcal/mol energy window relative to the lowest-energy PM6 conformer were re-optimized using the DFT-B3LYP [32,33] method to determine the most stable geometry and its corresponding electronic structure. To further investigate the thermal degradation mechanism and resultant degradation products, potential bond cleavage pathways were predicted through vibrational frequency analysis of the most stable copolymer structure. The optimized geometries and electronic properties of the molecular and radical species involved in each step of the proposed degradation pathways were then computed at the DFT-B3LYP/6-311++G(d,p) level. Additionally, Gibbs free energies were calculated individually for all steps of the proposed mechanisms at the DFT-B3LYP/6-311++G(d,p) level. All thermodynamic calculations were performed using the Gaussian 16 [34] program at 298 K and 1 atm. In the figures illustrating the degradation steps, the numbers shown on the arrows denote the indices of the atoms between which bond cleavage occurs.

3. Results and Discussion

Figure 1 presents the most stable conformer of the poly(butylene adipate-co-terephthalate) (PBAT) copolymer, which was determined by optimizing all conformers identified using the semi-empirical PM6 method in the SPARTAN 14 program, at the B3LYP/6-311G++(d,p) level. The depicted structure clearly illustrates the interactions between the aliphatic segments (butylene and adipate) and the aromatic segment (terephthalate), as well as the positioning of the ester bonds. Literature reports indicate that the ratio and conformational arrangement of these aromatic and aliphatic segments are crucial in defining the thermal and mechanical properties of PBAT [35,36]. In particular, the bond lengths and angles of the carbonyl (C=O) groups play a critical role in predicting the initial steps of the thermal degradation mechanism. Consequently, the detailed electronic structure information obtained at the B3LYP level provides a solid foundation for elucidating the thermal degradation pathways, the formation of harmful intermediates, and the overall molecular stability of PBAT.

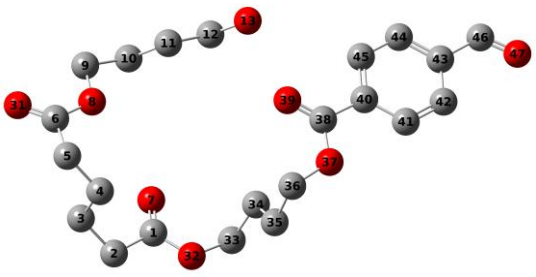

Figure 1. The most stable geometry of the PBAT copolymer, obtained at the B3LYP/6-311G++(d,p) level. Hydrogen atoms have been omitted for clarity, while red and gray colors represent oxygen and carbon atoms, respectively.

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To elucidate the thermal degradation mechanism of the PBAT copolymer under an inert atmosphere, potential bond cleavage pathways during degradation were determined by analyzing the harmonic vibrational frequencies of the model copolymer calculated at the DFT-B3LYP/6-311++G(d,p) level. Harmonic vibrational frequencies provide critical insights into the dynamic properties of molecular structures and the nature of interatomic bonds. In particular, the stretching mode frequencies serve as key parameters that reflect the strength of a bond between two atoms. These frequencies are typically interpreted within the framework of Hooke's law, expressed as $\omega = \sqrt{(k/\mu)}$, where ω is the vibrational frequency, k is the bond force constant, and μ is the reduced mass of the bonded atoms. High stretching frequencies indicate a high bond force constant, suggesting that the bond is more robust and resistant to degradation. Consequently, the vibrational data obtained at the DFT-B3LYP/6-311++G(d,p) level enable predictions about which bonds in the PBAT copolymer are most susceptible to cleavage during thermal degradation. This detailed harmonic frequency analysis facilitates an in-depth modeling and interpretation of the degradation mechanism [37]. As illustrated in Figure 2, three distinct degradation pathways (ptw1, ptw2, and ptw3) were evaluated, and potential radical intermediates were identified for each route. The initial degradation step is initiated by the cleavage of the weakest bonds in the PBAT chain. Specifically, the bond between the ester carbonyl carbon and oxygen (ROC–OR′) exhibits partial double-bond character due to resonance effects, which render the carbonyl carbon more electron deficient and, hence, increase the bond energy. In contrast, the alkyl–oxygen bond (ROCO–R′) in the aliphatic portion, being further removed from the carbonyl group and lacking resonance stabilization, displays a typical single-bond character with a more freely distributed electron density and lower bond energy. Therefore, the initial degradation step proceeds via the cleavage of the alkyl–oxygen (ROCO–R′) bond in the aliphatic segment of the ester linkage. Thermodynamic feasibility for the three identified pathways was assessed by calculating the free energy changes (ΔG), which were found to be 61.41-63.11 and 72.32 kcal/mol for the ptw1, ptw2, and ptw3 pathways, respectively. These results indicate that the ptw1 pathway has the lowest energy barrier, suggesting it to be thermodynamically the most favorable process. The Boltzmann distribution, which describes the probability of molecules occupying different energy levels, can be used to express the likelihood that a molecule will overcome a specific energy barrier (such as the activation energy for bond cleavage) via the expression $\exp(-\Delta G/(RT))$, where ΔG is the free energy change for bond cleavage, R is the universal gas constant, and T is the absolute temperature [38]. Given that the ptw1 pathway exhibits the lowest ΔG (61.41 kcal/mol), a greater proportion of molecules is expected to surmount this barrier and react. Although the ptw2 pathway has a slightly higher energy barrier (63.11 kcal/mol), increasing the temperature elevates the average kinetic energy of the molecules, thereby enhancing the probability of this pathway occurring. Conversely, the high ΔG of the ptw3 pathway (72.32 kcal/mol) results in a markedly lower fraction of molecules being able to overcome this barrier—even at elevated temperatures—rendering the ptw3 pathway negligible. However, in contrast to thermodynamic preference, the temperature dependence of the degradation kinetics can be described by the Arrhenius equation, $k = A \exp(-E_a/RT)$. This relation indicates that the rate constant increases exponentially with temperature. At elevated temperatures, in addition to the pathway with the lower activation free energy (ptw1), higher-barrier routes such as ptw2 can also become kinetically accessible. This behavior provides a theoretical basis for the experimentally observed, temperature-dependent shifts in product distributions. Overall, our findings indicate that polymer degradation is governed by both thermodynamics and kinetics, and that these two factors compete with one another at high temperatures. Moreover, an evaluation of the radical intermediates formed along each degradation pathway revealed that oxygen-containing groups, due to their high electronegativity, significantly contribute to radical stabilization, a finding that is further corroborated during the second degradation step.

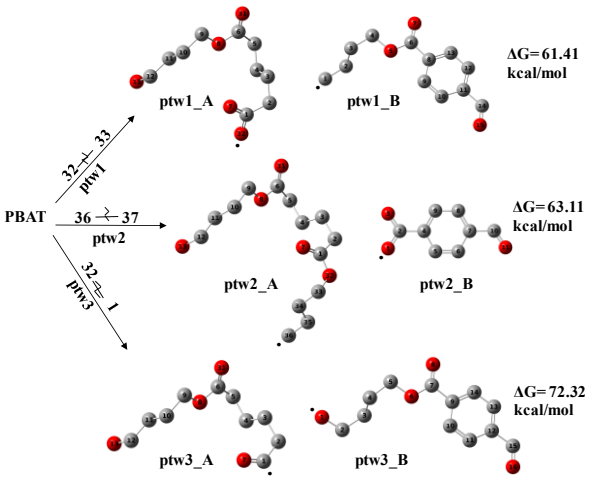

Figure 2. The most stable geometries of the initial thermal degradation mechanism steps of the PBAT copolymer and its resulting products, as obtained at the B3LYP/6-311G++(d,p) level. For clarity, hydrogen atoms have been omitted, while red and gray colors denote oxygen and carbon atoms, respectively.

The second degradation step aims to further elucidate the thermal degradation process of the PBAT copolymer by examining the transformation of intermediate radicals—formed in the initial cleavage—into lower molecular weight species through intrachain rearrangements and additional bond breakages (Figure 3). Computational results reveal that during this stage, the cleavage of ester

groups and the stabilization mechanisms of radicals in the aliphatic segments become more pronounced. Specifically, factors influencing the stability of the degradation products closely correlate with the weakening of carbonyl (C=O) and ester (C–O) bonds. The calculated Gibbs free energy values indicate that the energy requirements for these second-step reactions are lower than those for the initial degradation steps, suggesting that the radicals produced early on may propagate more rapidly along the polymer chain and thereby accelerate the overall degradation process. Furthermore, the stability of the generated radical species is significantly enhanced by the electron-withdrawing effects of oxygen-containing functional groups, which play a decisive role in determining the selectivity of the degradation mechanism. As depicted in Figure 3, the second degradation pathways exhibit distinct behaviors in the aliphatic and aromatic segments: degradation of the aliphatic regions yields volatile, low molecular weight compounds, whereas the aromatic segments tend to produce more stable intermediates. This divergence is a critical factor in the thermodynamic control of the degradation mechanism, directly affecting the product distribution in an inert atmosphere. In particular, the analysis of gas-phase products generated via high-temperature radical reactions offers vital details about both the degradation kinetics and the environmental impact of PBAT. A detailed investigation of the ptw1 pathway during the second degradation step shows that the formation of radical intermediates leads to the generation of CO_2, small aliphatic fragments, and aromatic ring compounds. As the degradation progresses, increasingly stable and volatile products emerge, suggesting an enhanced transition of products into the gas phase in the later stages of thermal degradation. Conversely, in the ptw2 pathway, the dissociation of an aliphatic chain segment results in the formation of two ethylene molecules and an aliphatic radical, with a calculated free energy change (ΔG = +14.62 kcal/mol) indicating that this process is thermodynamically less favorable. In the case of the aromatic segment, the formation of CO_2 and a benzaldehyde radical is observed, with a ΔG value of –11.77 kcal/mol, suggesting that this pathway favors the release of volatile compounds such as CO_2 into the gas phase. Moreover, as noted earlier, carbon-centered radicals generated in this stage are kinetically unstable due to their relatively low electronegativity compared to oxygen and tend to rapidly rearrange into more stable molecules (with a ΔG of +17.89 kcal/mol for the ptw1_B pathway). In contrast, the strong electronegative effect of oxygen stabilizes oxygen-centered radicals by balancing the electron distribution, thereby favoring the formation of more stable intermediates. These findings collectively demonstrate that oxygen-containing structures play a pivotal role in radical stabilization during the degradation process, critically influencing the final product distribution. Overall, the results elucidate the thermodynamic favorability of various degradation pathways in the thermal decomposition of the PBAT copolymer and highlight the significant impact of volatile product formation on the mechanism's progression.

In the third decomposition stage, the pathways through which intermediate radicals and stable molecules formed in the preceding steps rearrange into final decomposition products have been examined in detail, and the theoretical results obtained are illustrated in Figure 4. As shown in Figure 4(a), during the third step of the ptw1 decomposition pathway, previously formed intermediate radical species (ptw1_A_01 and ptw1_B_01) undergo extensive fragmentation under increasing thermal effects. It has been determined that the formation of methyl pentanoate and propanol radicals is thermodynamically unfavorable (ΔG = +99.53 kcal/mol). Additionally, lower molecular weight structures such as benzene derivatives and carbon dioxide (CO_2) were calculated to form in this step. The third decomposition stage of the ptw2 pathway, depicted in Figure 4(b), yields different products. The intermediate radical formed in the previous step of this pathway (ptw2_A_01) leads to the formation of molecules such as adipic acid and butanol radical, which is also thermodynamically unfavorable (ΔG = +61.03 kcal/mol). Finally, the third decomposition stage of the ptw3 pathway, shown in Figure 4(c), indicates the formation of more complex fragmentation products resulting from radical reactions. This pathway exhibits significantly higher bond dissociation free energies compared to the other two pathways, suggesting, as expected, that the ptw3 pathway is less probable and can only occur at higher temperatures. Products formed via this pathway include aromatic radicals, carbon dioxide, and butanol radicals. The results obtained are largely consistent with literature studies concerning the pyrolytic decomposition mechanism of PBAT. According to the literature, the fundamental structural units of PBAT, namely butylene adipate and butylene terephthalate, decompose through alpha cleavage of ester bonds and hydrogen transfer, followed by decarboxylation resulting in CO_2 release during thermal degradation. Additionally, previous studies observing adipic acid derivatives and radical decomposition products support the products identified in the present study. In particular, the presence of methyl pentanoate and propanol radicals can be considered potential intermediates in the PBAT decomposition mechanism and aligns well with previously reported esterified and hydroxylated derivatives [19,39].

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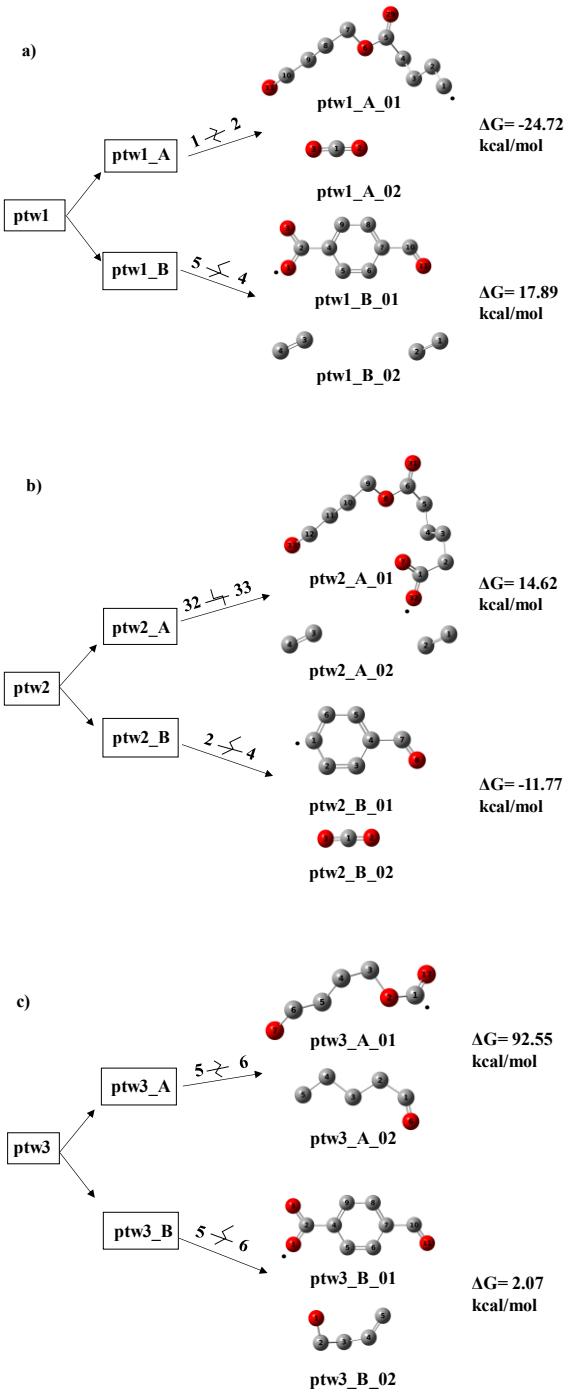

Figure 3. The second thermal degradation mechanism steps of the PBAT copolymer along with the most stable geometries of the resulting products, as obtained at the B3LYP/6-311G++(d,p) level. For clarity, hydrogen atoms have been omitted, and red and gray colors represent oxygen and carbon atoms, respectively.

Considering these findings, molecular reorganization particularly around ester and carbonyl groups not only accelerates bond cleavage in aliphatic chains but also enhances resonance stabilization effects in aromatic segments, thus determining the thermodynamic stability of the final products. Furthermore, the formation of radical species in later stages of PBAT degradation reduces the thermal stability of the polymeric chain, consequently increasing the rate of thermal degradation. During this transformation process, the formation of volatile compounds and persistent aromatic residues plays a critical role in maintaining the thermodynamic and kinetic balance of the reaction.

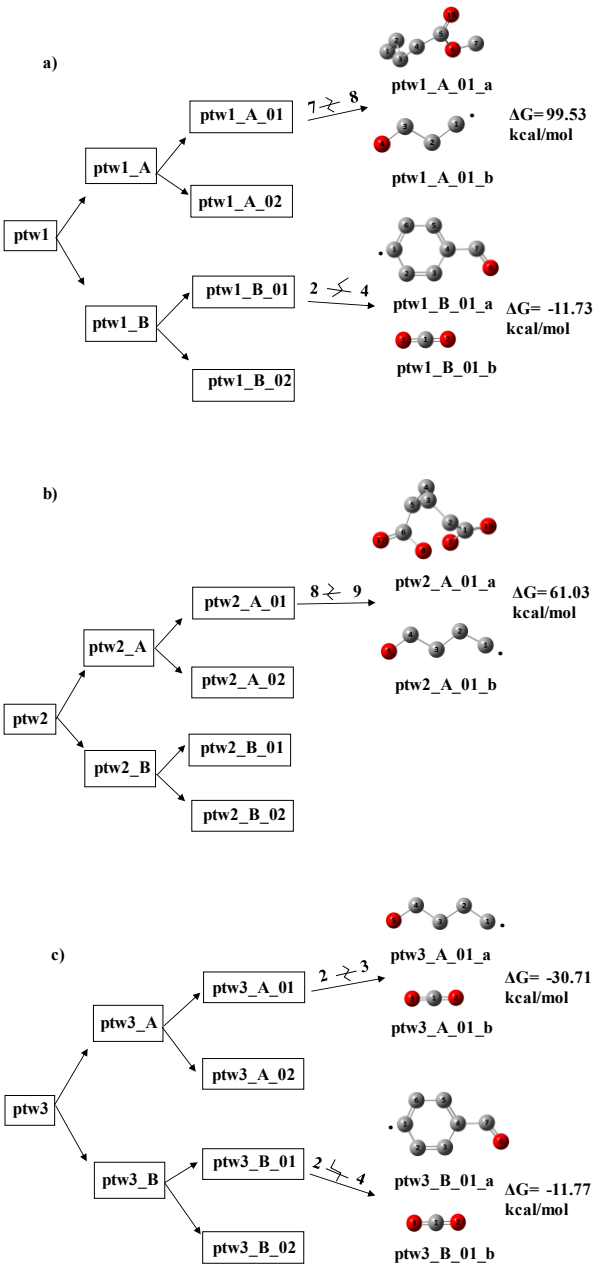

Figure 4. The third thermal degradation mechanism steps of PBAT copolymer along with the most stable geometries of the resulting products, as obtained at the B3LYP/6-311G++(d,p) level. For clarity, hydrogen atoms have been omitted, and red and gray colors represent oxygen and carbon atoms, respectively.

Table 1. Degradation products of PBAT: comparison between this study and literature

Degradation product	In this study	Literature data
CO_2	**CO_2** (main product of all pathways)	**CO_2** evolution [40]
Aliphatic compounds	**Ethylene**, butanol, methyl pentanoate, propanol radical	**Ethylene**, 1,4-Butanediol, short-chain alcohols [28,41]
Adipic acid derivatives	**Adipic acid,** and its ester derivatives	**Adipic acid**, 3-butenyl4-hydroxybutyl adipate [19,20]
Terephthalate derivatives	**Butenyl terephthalate** isomers, **terephthalic acid**	dimethyl terephthalate, **di(3-butenyl) terephthalate, terephthalic acid** [19,28,39,41]
Aromatic compounds	**Benzoic acid**, benzaldehyde radical	Tetrahydrofuran, cyclopentanone, **benzoic acid** [19,28,41]
Radical intermediates	Oxygen-centered and carbon-centered radicals	Not directly reported

To further strengthen the discussion, the degradation products identified in this study were systematically compared with those reported in the literature, as summarized in Table 1. The comparison clearly demonstrates that our theoretical predictions are in good agreement with experimentally observed pyrolysis and degradation products of PBAT. For example, CO_2 was consistently found as a major product across all pathways in both this study and experimental reports. Similarly, aliphatic compounds such as ethylene and butanol identified in our calculations correspond well with experimentally detected species, including ethylene, 1,4-butanediol, and other short-chain alcohols. Adipic acid and its ester derivatives, as well as terephthalate-related compounds, were also found in both the present work and prior studies, supporting the validity of the proposed pathways. In addition, aromatic compounds (benzoic acid, benzaldehyde radicals) and radical intermediates predicted by our calculations align closely with experimental findings of benzoic acid and other aromatic by-products. Taken together, this side-by-side comparison highlights that the computationally derived degradation pathways not only reproduce experimentally reported products but also provide molecular-level insights into radical intermediates that are challenging to detect experimentally. This consistency reinforces the reliability of our mechanistic interpretations and underscores the complementary role of DFT in elucidating the thermal decomposition behavior of PBAT.

4. Conclusion

The present study provides computational insights into the thermal degradation mechanism of PBAT, highlighting three primary decomposition pathways. Among these, ptw1 was identified as the most favorable due to its lowest Gibbs free energy barrier. Radical intermediates formed in the early stages were shown to propagate degradation through lower-energy processes, with oxygen-containing groups playing a critical role in stabilizing these species and shaping the overall product distribution. The release of low molecular weight aliphatic fragments, CO_2, adipate, and terephthalate derivatives aligns well with previously reported experimental findings.

Beyond confirming degradation routes, these results carry broader implications for the rational design of PBAT and related biodegradable polyesters. By understanding the thermodynamically preferred pathways, structural modifications—such as altering the ratio of aliphatic and aromatic segments or introducing stabilizing side groups—may be considered to enhance thermal stability while minimizing the release of environmentally concerning by-products such as CO_2. Furthermore, the identification of key radical intermediates opens opportunities for targeted experimental studies, for example, through pyrolysis–GC/MS or in situ spectroscopic monitoring, to validate the predicted intermediates and products.

Overall, this work establishes a theoretical framework that can guide both experimental investigations and material design strategies aimed at developing safer and more durable PBAT-based materials. Future studies combining computational and experimental approaches will be essential to optimize the balance between biodegradability, thermal stability, and environmental impact in next-generation sustainable polymers.

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Author's Contributions

Sıla Gümüştaş: Drafted the manuscript, performed the calculations, analyzed the results, and prepared the figures.

Kardelen Şener: Contributed to the writing of the introduction section and performed some of the calculations.

Armağan Kınal: Supervised the calculations, contributed to result interpretation, and assisted in manuscript preparation.

Ethics

There are no ethical issues after the publication of this manuscript.

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