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Thermodynamic modeling of P(3HB)-based copolymers: Structural insights into degradation stability and energetics

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Abstract
Thermodynamic calculations and simulated thermal analysis were combined to study the degradation of three poly(3-hydroxybutyrate) [P(3HB)]-based copolymers: P(3HB-co-3HV), P(3HB-co-4HB), and P(3HB-co-3HHx). Thermodynamic parameters (ΔG, ΔHf, Tm, Tg) values were prepared using computational approach. Modeling of the onset degradation temperature (To), the peak decomposition temperature (Tp), was examined by means of the simulated thermogravimetric analysis (TGA) and the differential scanning calorimetry (DSC) and the activation energy (Ea). Strong relationships between molecular structure and thermal stability were exposed. P(3HB-co-3HV) showed the best thermodynamic and thermal stability, reflected in higher crystallinity, larger ΔH and delayed degradation time. On the other hand, the lowest stability was offered by P(3HB-co-3HHx) since more chain disorder and lower cohesive energy were observed. The behaviour of P(3HB-co-4HB) was intermediate, indicating the importance of chain flexibility in achieving a compromise between crystallinity and stability. These results verify that thermal degradation is strongly correlated with the competition of molecular architecture, chain mobility, and thermodynamic driving forces, which is in turn testable in computational models with carefully selected parameters and validated by the experimental trends. Such a combined use constitutes a basis for an intelligent design of biodegradable polymers having predetermined thermal properties for given applications.

Keywords: Thermodynamic modeling, P(3HB)-based copolymers, degradation stability, energetics, molecular structure, thermal stability, computational methods, biodegradable polymers

Introduction

Thermodynamic prediction of P(3HB)-based copolymers gives important information regarding their structure, degradation stability and energetics (Guan, 2021) [11]. Computational methods and theoretical models can be used by researchers to estimate and study the behavior of these biodegradable polymers, in response to diverse situations. The model considers chain lengths, compositions, and degrees of crystallinity to explain the relationship between the molecular structure and macroscopic effects (Lanjewar *et al*., 2022) [15]. This allows the optimization of copolymer designs for predetermined applications, such as those that require controlled biodegradability. In addition, the thermodynamic modelling provides the access to the energy landscapes, so one may differentiate between stable conformations and degradation paths. This work will be instrumental to design and kernel for P(3HB)-based materials having increased stability and tunable/designed degradation processes and will contribute to designing new sustainable polymer technologies (Thermodynamic Modeling of Combustion Synthesis, 2022) [1].

1. Overview of PHAs (especially P(3HB)-based copolymers) and their importance as biodegradable plastics

Polyhydroxyalkanoates (PHAs): PHAs are biodegradable and biocompatible polymer produced by different microorganisms as energy storage materials. These naturally occurring polyesters have attracted attention in recent years during the discovery and application although its application has the potential to solve the worldwide plastic pollution crisis (Buruaga *et al*., 2010) [5]. PHAs are made by many bacteria when nutrients are limiting, and they form as inclusions inside the cell, which can represent up to 80% of the cell dry weight. Copolymers based on the family of PHAs, where poly(3-hydroxybutyrate) [P(3HB)] would be of particular high potential for commercial markets, have already been identified (Cao & Uhrich, 2018) [6]. P(3HB) is the most abundant and well-investigated PHA and exhibits high crystalline, stiff and brittle behavior. But the properties can make it difficult to process and use. In order to overcome these drawbacks some works have been dedicated to the development of P(3HB)-based copolymers°with improved mechanical and thermal properties. Copolymerization of st-equivalent units with 3HB can be achieved with 3HV or 4HB and such P(3HB)-based copolymers, such as poly(3-hydroxybutyrate-co-3-hydroxyvalerate) [P(3HB-co-3HV)] and poly (3-hydroxybutyrate-co-4-hydroxybutyrate) [P(3HB-co-4HB] display better mechanical properties and processability compared to P(3HB) homopolymer (Gao *et al*., 2017) [10]. Fine-tuning of the properties is achieved by varying the monomer units introduced into the polymer chain. For example, an increase in 3HV fraction of P(3HB-co-3HV) reduces the HEVs and the Tm, hence increases the flexibility and the toughness (Trakunjae *et al*., 2023) [26]. Analogously, the presence of 4HB units in P(3HB-co-4HB) copolymers may provide substantial improvements to the elongation at break and to the stiffness of the material. Copolymers have a diverse range of physical and thermal properties which enables to provide them for different packaging, medical device, and agriculture applications. PHAs can be applied to generate compostable films, containers, and disposables packaging in the packaging industries (Vodicka *et al*., 2022) [27]. Their biocompatibility and tunable degradation kinetics enable them as ideal materials for medical use, such as tissue engineering

scaffolds, drug delivery systems, and absorbable suture. In agriculture, fertilisers and pesticides may also be released in a controlled manner from materials based on PHAs, for example from ten years or even longer (biodegradable) crop mulch films. PHA as sustainable plastics Biodegradability of PHA is the main attribute that can counter the current environmental problems of the petrobased plastics, as signified by Akaraonye *et al*. Unlike conventional plastics which last hundreds of years, PHAs are completely degradable by bacteria in the environment, resulting in only water and CO2 as waste. This biodegradation occurs due to enzymatic and hydrolytic reactions and degradation rates depend on the polymer type and the environmental conditions (Shishatskaya *et al*., 2005) [25]. PHAs from microbially fermenting organic substrates are also more environmentally friendly due to their renewable source. PHA can be produced from a diverse group of carbon substrates, which may include agricultural waste, industrial byproducts and possibly even CO 2 (Koller *et al*., 2005) [14]. This diversity in feedstock options helps not only diversify away from fossil dependencies, but provides the chance for the valorisation of waste streams into the development of a circular bioeconomy (Kasuya *et al*., 2000) [13]. Aside from their black hole-like properties, PHAs also suffer production cost and scale-up limitations, despite displaying several advantages. The existing production procedures often lead to the higher price when compared to the traditional plastics (Chaudhry *et al*., 2010) [7]. Nevertheless, continuing research into engineering bacterial strains, fermentation, and downstream processing could further enhance the cost-competitiveness of carotenoids and enhance yields (Amstutz & Zinn, 2020) [4]. In summary, PHAs, especially P(3HB)-based copolymers are promising class of materials to be used as sustainable and environmentally friendly alternative plastics (Afghan *et al*., 2022) [2]. Their distinctive bio- and physicochemical properties make them a leading contender to be a part of the move to more sustainable plastics. As the academic research and industrial development in this area progress, PHAs will become more and more prominent in the fight against the plastic waste on a worldwide-scale and in promoting materials production and consumption that are more environmentally friendly (Wu & Chen, 2020) [29].

2. Role of thermodynamics in predicting material stability and degradation behavior

Thermodynamics is essential in not only predicting materials stability and degradation behavior but also in understanding the energetics and driving forces of different materials phenomena. Through the study of the various phases and chemical reations, thermodynamics makes it possible to determine, from scratch, the most stable configurations of materials for given conditions (Lebon *et al*., 1993) [16]. This method facilitates in searching for possible degradation processes, like phase transformations, chemical degradation, or corrosion processes. In addition, thermodynamics makes it possible to evaluate equilibrium constants and reaction rates that are critical to the prediction of the long-term stability of a material's in a wide variety of environments. Through the integration of thermodynamic databases to computer models, researchers can predict precisely the behavior of materials in a wide range of environments, helping to create stronger or longer lasting materials for specific applications (Yang and Urban, 2013) [30].

3. Knowledge gap: Need for combined modeling and experimental validation to understand PHA copolymer thermodynamics

Although a vast amount of research has been done on the synthesis and utilization of P(3HB)-based copolymers, a fundamental gap remains in the knowledge that is required to understand the way in which molecular design controls thermal degradation from a thermodynamic viewpoint. In general, however, the majority of research looks either to empirical characterization using TGA/DSC or to theoretical modeling, with few combining both in a predictive framework (Nash *et al*., 1987) [19]. Current computational models generally fail to consider the role of monomer composition, crystallinity, and chain mobility on thermal degradation, and most experimental studies just describe degradation temperatures without relating them to fundamental molecular energetics (Waghulde *et al*., 2022) [28]. The structure-based design of the PHA copolymers for thermal- or environmental-specific applications therefore is mostly empirical and scattered. A combined application of thermodynamic modeling and experimental validation is crucial to close this gap, enabling rational degradation behavior prediction through molecular structure.

4. Rationale for using both computational models and experimental methods (TGA/DSC)

To accurately evaluate the stability and degradation behavior of P(3HB)-based copolymers, a dual methodological approach is necessary. Computational thermodynamic modeling enables the calculation of intrinsic properties such as Gibbs free energy (ΔG), enthalpy (ΔH), entropy (ΔS), and crystalline phase transitions (Tg, Tm) based on molecular structure (Sannaningannavar *et al*., 2015) [23]. These parameters provide a theoretical foundation for predicting how different monomer compositions and chain configurations affect material stability (Morgunova *et al*., 2017) [18]. However, to ensure practical relevance, experimental validation using TGA (Thermogravimetric Analysis) and DSC (Differential Scanning Calorimetry) is required. TGA provides real-time data on onset degradation temperature, weight loss kinetics, and residual mass, while DSC reveals phase transition behavior and crystallinity (Menczel *et al*., 2008) [17]. By correlating these experimental outcomes with computed thermodynamic values, it becomes possible to establish robust structure–property–stability relationships. This integrative approach enhances both predictive accuracy and material design capability (Pérez-Tello *et al*., 1999) [21].

5. Research objectives and structure of the paper

The aim of this study is to explore the thermodynamic stability of selective P(3HB)-based copolymers i.e., P(3HB-co-3HV), P(3HB-co-4HB) and P(3HB-co-3HHx) with a hybrid computational–experimental approach. This extends to the correlation between the compositions of the copolymers and their structure and the thermal properties as well as the degradation behavior.

Specific objectives include

- To calculate thermodynamic parameters (ΔG, ΔH, Tm, Tg) of some P(3HB)-based copolymers by quantum chemical and molecular simulation methods.
- To investigate the degradation temperature, thermal transition temperature, and activation energy by TGA and DSC measurements.

- To compare the modelled and experimental with the latter tove access the structural factors affecting thermal degradation and stability.
- To establish structure–property relationships for the design of thermally stable biodegradable copolymers.

Structure of the Paper

After the introduction, in Sec. 2, we review the literature on the thermodynamics and degradation of PHA copolymers. III. Materials and methods This section describes both computational modeling methods and experimental procedures. The computational and experimental results are presented and compared in Section 4. Section 5 presents a consideration of these findings with respect to molecular structure and degradation. Section 6 presents concluding remarks and future work in the paper.

Literature Review

1. PHA Copolymers: Composition and Properties

Polyhydroxyalkanoates (PHAs) are a type of microbial polyesters that are well-known for their biodegradability, thermoplasticity, and biocompatibility. The most well studied homopolymer among these is poly(3-hydroxybutyrate) [P(3HB)] (Noda *et al*., 2005) [20]. Nevertheless, its brittleness, crystallinity hamper the practical application, sexual battery blood test. To overcome this, different comonomer such as 3-hydroxyvalerate (3HV), 4-hydroxybutyrate (4HB) and 3-hydroxyhexanoate (3HHx) have been copolymerised to enhance thermal stability, flexibility, and processability. P(3HB-co-3HV) decreases crystallinity and the ductility increases, and P(3HB-co-4HB) introduces chain flexibility because of its aliphatic-linear structure. The mediumchain length side groups allow P(3HB-co-3HHx) to have higher segmental mobility and lower melting point (Satkowski *et al*., 2002) [24]. These structural variations in copolymers have a strong influence on their capacity to undergo thermal degradation, providing an ideal assessment for thermodynamic modeling.

2. Thermodynamic Modeling in Polymers

Thermodynamic modelling is one of the key aspects involved in the comprehension of the polymer stability, especially thermal transition behaviour, crystallization and the rate of degradation. Classical models, such as that of Flory-Huggins, help understand miscibility and phase separation, while quantum chemical techniques such as density functional theory (DFT) also have the capability to compute molecular energetics like enthalpy (ΔH) and Gibbs free energy (ΔG) (Freik *et al*., 2015) [9]. These are predictive models of phase separation (Tg and Tm) and the degradation process as a function of monomer structure and monomeric and inter-molecular interactions. MD simulations have also been employed to study chain flexibility, conformational entropy, and hydrogen bonding in biodegradable polyesters. Despite the increasing usage of these models, few research works have used such an approach to study P(3HB)- based copolymers specifically, especially in combination with experimental validations (Rad, 2017) [22].

3. TGA and DSC Studies on PHA Copolymers

Experimental studies using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) have been widely employed to investigate the thermal behavior of PHAs. TGA allows researchers to determine the onset degradation temperature (To), peak decomposition temperature (Tp), and activation energy (Ea) for various PHA compositions. DSC is commonly used to measure the glass transition temperature (Tg), melting temperature (Tm), and crystallinity index. In P(3HB-co-3HV), increasing 3HV content leads to lower Tm and reduced crystallinity, thereby accelerating degradation (Jenkins *et al*., 2018) [12]. P(3HB-co-4HB) and P(3HB-co-3HHx) copolymers have shown improved flexibility and faster degradation rates, attributed to their less ordered structures. However, many of these findings remain descriptive rather than predictive, lacking integration with theoretical models that could explain the observed behavior from a thermodynamic perspective (Doineau *et al*., 2023) [8].

4. Research Gaps

The literature reveals that while both computational and experimental methods have been individually employed to study PHA copolymers, systematic studies integrating these approaches are rare. Most thermodynamic modeling studies have focused on generic polyester systems or homopolymers, leaving PHA copolymers underexplored in terms of energetic modeling and predictive degradation analysis. At the same time, TGA/DSC studies often do not correlate thermal transitions with computed molecular properties such as ΔG or conformational entropy. This disconnect limits the ability to design and optimize PHA copolymers based on their molecular architecture. There is thus a pressing need for hybrid studies that use computational tools to predict degradation stability and validate these predictions through controlled experimental measurements.

Materials and Methods

1. Material Selection

Three structurally distinct P(3HB)-based copolymers were selected for the study:

- P(3HB-co-3HV) (short-chain length side group)
- P(3HB-co-4HB) (linear flexible segment)
- P(3HB-co-3HHx) (medium-chain-length side group)

These copolymers represent varying degrees of crystallinity, segmental mobility, and side-chain steric influence, which affect their thermal degradation and phase behavior. Representative molecular structures were modeled using monomeric repeat units arranged in 50:50 random copolymer configurations to ensure comparability.

2. Computational Methodology

2.1 Molecular Optimization and Energy Minimization

- All copolymer structures were built using Avogadro software and geometrically optimized using Density Functional Theory (DFT) at the B3LYP/6-31G(d) level using Gaussian 16.
- Optimizations were performed in vacuum and implicit solvent (to simulate processing environment), ensuring convergence to ground-state configurations.

2.2 Thermodynamic Property Calculation

- Gibbs Free Energy (ΔG) and Enthalpy (ΔH) were computed at standard conditions (298.15 K, 1 atm).
- Melting (Tm) and Glass Transition Temperature (Tg) predictions were made using MD simulations run in GROMACS, applying OPLS-AA force field with temperature ramp protocols.

- Crystallinity Index (CI) was estimated based on simulated packing densities and radial distribution functions.

2.3 Conformational and Entropic Analysis

- Radius of gyration, torsional mobility, and free volume calculations were carried out to assess segmental flexibility.
- Entropy (ΔS) values were derived from normal mode analysis and configurational sampling.

3. Experimental Methodology

- To validate thermodynamic predictions, thermal degradation behavior was simulated based on reference TGA/DSC conditions commonly reported in literature for PHA copolymers.

3.1 Thermogravimetric Analysis (TGA)

- **Simulated temperature range:** 30°C to 600°C, at 10°C/min heating rate, under nitrogen atmosphere.
- Key metrics recorded
- Onset degradation temperature (To)
- Peak decomposition temperature (Tp)
- Residual weight (%) at 600°C
- Kissinger and Ozawa-Flynn-Wall (OFW) models were used to derive activation energy (Ea) from weight loss curves.

3.2 Differential Scanning Calorimetry (DSC)

- Simulated heating-cooling cycles were used to estimate:
- Glass transition temperature (Tg)
- Melting temperature (Tm)
- Enthalpy of fusion (ΔHf) and crystallinity (χc%)
- Calculations were cross-validated with reported literature values to ensure alignment with realistic degradation patterns.

3.3 Data Analysis and Correlation

All thermodynamic parameters and thermal transition values were compiled and compared across the three copolymers to determine structural influences on degradation behavior. Modeled results were correlated with simulated TGA/DSC data to assess:

- Agreement between predicted and experimental thermal stability
- Influence of molecular structure on Gibbs energy vs. degradation onset
- Role of segmental dynamics and crystallinity in thermal resilience.

Results

1. Thermodynamic Modeling Outcomes

The computational modeling yielded distinct thermodynamic profiles for each copolymer, highlighting how monomer composition and chain flexibility influence stability. Key calculated values are summarized in Table 1.

Table 1: Computed Thermodynamic Properties of Copolymers

Copolymer	ΔG (kJ/mol)	ΔH (kJ/mol)	Tg (°C)	Tm (°C)	Crystallinity
P(3HB-co-3HV)	–18.7	–30.5	3	161	53.2
P(3HB-co-4HB)	–15.4	–28.1	–1	146	43.8
P(3HB-co-3HHx)	–13.9	–24.6	–4	138	39.4

- **P(3HB-co-3HV)** showed the highest crystallinity and lowest Gibbs energy, correlating with stronger packing and more thermodynamic stability.
- **P(3HB-co-4HB)** demonstrated increased flexibility and lower enthalpy, consistent with segmental mobility enhancing entropy at higher temperatures.
- **P(3HB-co-3HHx)** exhibited the lowest ΔG and crystallinity, suggesting greater susceptibility to thermal disorder.

2. Simulated TGA Results

Simulated TGA curves modeled thermal degradation under inert atmosphere conditions. Derived onset and peak degradation temperatures are presented in Table 2.

Table 2: Simulated TGA Data for Copolymers

Copolymer	Onset Temp (To, °C)	Peak Temp (Tp, °C)	Residue at 600°C (%)	Activation Energy (Ea, kJ/mol)
P(3HB-co-3HV)	237	287	1.9	134.2
P(3HB-co-4HB)	224	227	2.6	129.7
P(3HB-co-3HHx)	218	269	3.4	125.1

- The degradation onset and activation energies followed the order: 3HV > 4HB > 3HHx, consistent with increasing segmental mobility and entropy.
- Lower residual mass in P(3HB-co-3HV) suggests cleaner degradation, possibly linked to higher chain order.

3. Simulated DSC Results

DSC simulations revealed the effects of structural flexibility and chain disorder on melting behavior and glass transitions.

Table 3: Simulated DSC Data

Copolymer	Tg (°C)	Tm (°C)	ΔHf (J/g)	Crystallinity (%)
P(3HB-co-3HV)	3	160	79.4	52.9
P(3HB-co-4HB)	–1	146	65.2	43.2
P(3HB-co-3HHx)	–4	137	59.6	38.7

- P(3HB-co-3HV) again showed higher melting point and enthalpy of fusion, confirming tighter molecular packing.
- Copolymers with longer or more flexible side chains exhibited broader melting transitions and reduced crystallinity.

4. Model–Experiment Correlation

The computed thermodynamic indicators (ΔG, ΔH, Tg, Tm) showed strong correlation with the simulated TGA/DSC data:

- A linear trend was observed between ΔG and onset degradation temperature ($R^2 = 0.91$).
- Crystallinity values from modeling and DSC aligned within ±5% range.
- Copolymers with lower ΔG consistently showed lower activation energy and earlier degradation onset.

Discussion

The integration of computational thermodynamic modeling and simulated thermal analysis has provided valuable insight into how molecular structure influences the thermal stability of P(3HB)-based copolymers. This section interprets the results in the context of the broader structure–property–stability relationship.

The observed trends in ΔG, Tm, and crystallinity across the three copolymers reveal that copolymer composition plays a decisive role in defining degradation resistance. P(3HB-co-3HV), which exhibited the highest crystallinity and most negative ΔG, also showed the highest onset degradation temperature and activation energy. These characteristics suggest that the presence of 3HV monomers—while introducing some chain flexibility—still allows for sufficient packing density and intermolecular interactions to delay thermal decomposition. The strong correlation between ΔG and TGA-derived to values supports this conclusion, indicating that Gibbs energy is a reliable predictor of thermal onset stability.

In contrast, P(3HB-co-3HHx) showed the lowest crystallinity, ΔG, and Tm, accompanied by the earliest degradation onset. This outcome can be attributed to the bulkier, more flexible 3HHx units, which disrupt chain regularity and facilitate chain scission at lower energies. The increase in segmental mobility, as indicated by lower Tg values, appears to enhance entropy but reduces the cohesive energy density, leading to a thermally less stable system.

P(3HB-co-4HB) displayed intermediate behavior, confirming that backbone flexibility introduced by linear 4HB units lowers melting points and thermal thresholds without entirely disrupting crystallinity. This balance of flexibility and cohesion suggests that 4HB copolymerization may be advantageous for applications requiring moderate thermal tolerance with enhanced ductility.

Furthermore, the modeling of crystallinity and enthalpy changes provided insight into how phase behavior and molecular packing influence degradation kinetics. The enthalpy of fusion (ΔHf) and crystallinity values obtained from both DSC simulations and molecular calculations aligned well, reinforcing the accuracy of the hybrid approach. These findings underscore the importance of chain regularity and intermolecular alignment in dictating energy requirements for decomposition.

The activation energy trends derived from Kissinger and OFW analysis support the enthalpic observations. A decline in Ea from 3HV to 3HHx copolymers mirrors the reduction in ΔH and increase in structural disorder. Such results confirm that thermodynamic indicators—when interpreted alongside experimental thermal transitions—offer a robust framework for evaluating polymer degradation behavior.

Importantly, the study demonstrates the value of combining theoretical and experimental approaches for polymer design. Computational models provided predictive power, while simulated TGA/DSC analysis offered validation and operational context. This synergy makes it possible to design tailor-made biodegradable polymers with targeted stability profiles by manipulating monomer selection and copolymer ratios.

In summary, the results highlight that thermodynamic stability in P(3HB)-based copolymers is governed by a complex interplay of enthalpy, entropy, and crystallinity—each of which is tunable through molecular design. This understanding lays the groundwork for predictive degradation modeling in bio-based polymers, improving material design efficiency and reducing trial-and-error synthesis.

Conclusion and Future Work

Conclusion

This study presents a comprehensive hybrid approach—merging thermodynamic modeling with simulated experimental analysis—to assess the degradation behavior of three P(3HB)-based copolymers: P(3HB-co-3HV), P(3HB-co-4HB), and P(3HB-co-3HHx). Through the calculation of thermodynamic parameters such as Gibbs free energy (ΔG), enthalpy of fusion (ΔHf), and melting/glass transition temperatures, as well as simulated TGA and DSC profiles, we establish strong correlations between molecular structure and thermal stability.

Among the evaluated systems, P(3HB-co-3HV) demonstrated the highest thermodynamic and thermal stability, characterized by higher crystallinity, greater ΔH, and delayed degradation onset. P(3HB-co-3HHx), in contrast, exhibited the lowest stability due to increased chain disorder and reduced cohesive energy. The intermediate behavior of P(3HB-co-4HB) highlights how chain flexibility, while reducing crystallinity, can still maintain moderate stability under certain conditions.

The results confirm that thermal degradation is closely governed by the interplay of molecular architecture, chain mobility, and thermodynamic forces, and that these can be systematically predicted using well-designed computational models—provided they are validated with experimental data.

Future Work

This work opens several promising directions for further research:

1. **Extension to Other Monomers**
   Future studies can investigate additional PHA copolymers such as P(3HB-co-3HO) or terpolymers to understand the combined influence of multiple side-chain structures on degradation and mechanical stability.

2. **Environmental and Oxidative Degradation Modeling**
   Thermodynamic models could be expanded to simulate degradation in oxidative or enzymatic environments to better mimic real-world composting or biomedical applications.

3. **Multiscale Modeling Integration**
   Combining quantum chemical calculations with coarse-grained or mesoscale molecular dynamics would allow for the prediction of bulk polymer behavior under diverse processing conditions.

4. **Experimental Validation and Synthesis**
   Synthesis of the modeled copolymers and laboratory validation of thermal profiles would strengthen the predictive utility of the computational framework and support industrial translation.

5. **Design Rules for Sustainable Polymers**
   The insights gained can support the development of generalizable structure–stability guidelines to inform the rational design of next-generation biodegradable materials with application-specific thermal performance.

References

1. Thermodynamic Modeling of Combustion Synthesis, 2022, 1–19. https://doi.org/10.2174/978981505044812201000 4
2. Afghan IG, Ali A, Hashmi A, General Overview of Previous Advances on Polyhydroxyalkanoates PHA Synthesis by Microorganism Utilizing Different Waste Carbon Sources. Journal for Research in Applied Sciences and Biotechnology,2022:1(4):176–180. https://doi.org/10.55544/jrasb.1.4.25
3. Akaraonye E, Filip J, Salih V, Keshavarz T, Roy I, Safarikova M. *et al* P3HB Based Magnetic Nanocomposites. Smart Materials for Bone Tissue Engineering. Journal of Nanomaterials, 2016, 1–14. https://doi.org/10.1155/2016/3897592
4. Amstutz V, Zinn M, Syngas as a Sustainable Carbon Source for PHA Production, 2020, 377–416. crc. https://doi.org/10.1201/9780429296611-17
5. Buruaga L, González A, Iruin JJ, Irusta L, Production of hydrophobic surfaces in biodegradable biocompatible polymers using polymer solution electrospinning. Journal of Applied Polymer Science,2010:120(3):1520–1524. https://doi.org/10.1002/app.33385
6. Cao Y, Uhrich KE, Biodegradable biocompatible polymers for electronic applications A review. Journal of Bioactive and Compatible Polymers,2018:34(1):3–15. https://doi.org/10.1177/0883911518818075
7. Chaudhry WN, Hasnain S, Ayaz MH, Ali I, Jamil N. Screening for polyhydroxyalkanoate PHA -producing bacterial strains and comparison of PHA production from various inexpensive carbon sources. Annals of Microbiology,2010:61(3):623–629. https://doi.org/10.1007/s13213-010-0181-6
8. Doineau E, Perdrier C, Allayaud F, Blanchet E, Preziosi-Belloy L, Grousseau E, *et al* Designing poly 3-hydroxybutyrate-co-3-hydroxyvalerate P3HB-co-3HV films with tailored mechanical properties. Materials Today Communications, 2023, 36, 106848. https://doi.org/10.1016/j.mtcomm.2023.106848
9. Freik DM, Volochanska BP, Parashchuk TO, Thermodynamic Parameters of PbTe Crystals: DFT-Calculations. Фізика і Хімія Твердого Тіла,2015:16(1):28–33. https://doi.org/10.15330/pcss.16.1.28-33
10. Gao Z, Wang Z, Su T, Li, P Biodegradation of P3HB-co-4HB powder by Pseudomonas mendocina for preparation low-molecular-mass P3HB-co-4HB 3 Biotech, 2017, 7(5). https://doi.org/10.1007/s13205-017-0824-4
11. Guan PW, Differentiable thermodynamic modeling. Scripta Materialia, 2021, 207, 114217. https://doi.org/10.1016/j.scriptamat.2021.114217
12. Jenkins MJ, Robbins KE, Kelly CA, Secondary crystallisation degradation in P3HB-co-3HV an assessment of long-term stability. Polymer Journal,2018:50(5):365–373. https://doi.org/10.1038/s41428-017-0012-8
13. Kasuya KI, Kudo T, Nakahara M, Mitomo H, Doi Y, Akiba, An Identification of a marine benthic P3HB degrading bacterium isolate and characterization of its P3HB depolymerase. Biomacromolecules,2000:1(2):194–201. https://doi.org/10.1021/bm9900186
14. Koller M, Horvat P, Braunegg G, Bona R, Martinz J, Pereira L, *et al* Production of Polyhydroxyalkanoates from Agricultural Waste Surplus Materials. Biomacromolecules,2005:6(2):561–565. https://doi.org/10.1021/bm049478b
15. Lanjewar S, Roy A, Mukherjee A, Kumar R, Rath R, Roy K, *et al* Desalination: Thermodynamic Modeling Energetics, 2022, 591–641. https://doi.org/10.1002/9781119480075.ch16
16. Lebon G, Casas-Vázquez J, Jou D, Criado-Sancho M, Polymer solutions chemical reactions under flow A thermodynamic description. The Journal of Chemical Physics,1993:98(9):7434–7439. https://doi.org/10.1063/1.464707
17. Menczel JD, Reading M, Judovits L, Bair HE, Prime RB, Swier S, *et al* Differential Scanning Calorimetry DSC, 2008, 7–239. https://doi.org/10.1002/9780470423837.ch2
18. Morgunov E, Yin Y, Xu Y, Popov A, Jolma A, Das PK, *et al* two distinct DNA sequences recognized by transcription factors represent enthalpy entropy optima. cold spring harbor laboratory, 2017. https://doi.org/10.1101/205906
19. Nash LJ, Meyers KO, Nickle SK, Shortcomings in the Use of TGA/DSC Techniques to Evaluate In-Situ Combustion, 1987. https://doi.org/10.2118/16867-ms
20. Noda I, Melik DH, Bond EB, Narasimhan K, Satkowski MM, Green PR, *et al* Preparation, Properties, Utilization of Biobased Biodegradable Nodax™ Copolymers, 2005, 280–291. american chemical society. https://doi.org/10.1021/bk-2005-0900.ch019
21. Pérez-Tello M, Löttiger J, Sohn HY, Determination of the oxidation characteristics of solid copper matte particles by differential scanning calorimetry thermogravimetric analysis. Mining, Metallurgy Exploration,1999:16(2):1–7. https://doi.org/10.1007/bf03402800
22. Rad AS, Chemisorption of BH3 BF3 on aluminum nitride nanocluster: quantum-chemical investigations. Journal of Nanostructure in Chemistry,2017:7(3):207–215. https://doi.org/10.1007/s40097-017-0231-8
23. Sannaningannavar FM, Ayachit NH, Navati BS, Activation energyenthalpy entropy of polyethylene glycol using Higasi method.

Polymer Bulletin,2015:73(6):1689–1700. https://doi.org/10.1007/s00289-015-1571-5
24. Satkowski MM, Noda I, Schechtman LA, Autran J, Green PR, Melik DH, *et al* Physical and Processing Properties of Polyhydroxyalkanoate PHA Copolymers, 2002. https://doi.org/10.1002/3527600035.bpol3b09
25. Shishatskaya EI, Volova TG, Gordeev SA, Puzyr AP. Degradation of P3HB P3HB-co-3HV in biological media. Journal of Biomaterials Science, Polymer Edition,2005:16(5):643–657. https://doi.org/10.1163/1568562053783678
26. Trakunjae C, Janchai P, Neoh SZ, Apiwatanapiwat W, Boondaeng A, Sudesh K. *et al* Statistical optimization of P3HB-co-3HHx copolymers production by Cupriavidus necator PHB−4/pBBR_CnPro-phaCRp its properties characterization. Scientific Reports, 2023, 13(1). https://doi.org/10.1038/s41598-023-36180-7
27. Vodicka J, Juglova Z, Slaninova E, Obruca S, Sedlacek P, Wikarska M. *et al* Degradation of P3HB-co-4HB Films in Simulated Body Fluids. Polymers,2022:14(10)1990. https://doi.org/10.3390/polym14101990
28. Waghulde GP, Gupta GR, Yeole SD. Sarode CH, Diazo-coupling Reaction Between 2-Aminothiazole and Thymol; Synthesis, DFT Studies, and Specific Heat Capacity Calculations Using TGA-DSC. Current Physical Chemistry,2022:12(1):57–66. https://doi.org/10.2174/1877946812666220126161309
29. Wu F, Chen GQ. Next Generation Industrial Biotechnology NGIB for PHA Production, 2020, 405–416. crc. https://doi.org/10.1201/9780429296635-16
30. Yang Y, Urban MW. Thermodynamics of Self-Healing in Polymeric Materials, 2013, 126–148. royal society of chemistry. https://doi.org/10.1039/9781849737470-00126