A Discussion on Different Techniques to Enhance the Mechanical and Thermal Properties of Biodegradable Plastics

Abstract

The mechanical properties of biodegradable plastics often fall short compared to traditional plastics, presenting significant challenges in balancing biodegradability with performance. While traditional plastics like polyethylene (PE) and polyethylene terephthalate (PET) offer superior mechanical and thermal properties, many biodegradable alternatives struggle to match these attributes. For instance, poly(lactic acid) (PLA) exhibits favorable economic and thermal properties but is limited by its slow degradation in natural environments. Conversely, polyhydroxybutyrate (PHB) offers excellent biodegradability but has poor mechanical performance. The inherent structural characteristics of biodegradable plastics, such as polymer crystallinity and molecular composition, influence their mechanical and thermal properties. High crystallinity can enhance mechanical strength but often reduces biodegradability by impeding microbial access. Similarly, variations in molecular structure, including the presence of bulky groups or ester linkages, affect both the material's durability and its degradation rate. Efforts to improve biodegradable plastics include the use of chemical additives, natural fiber composites, and copolymerization techniques. Copolymer blends, such as PLA-PHB, offer a promising approach to reconcile the trade-off between biodegradability and mechanical performance. Future research should focus on optimizing these techniques and integrating biomaterials to enhance both the environmental benefits and functional properties of biodegradable plastics. This exploration underscores the ongoing challenge of balancing environmental sustainability with the need for high-performance materials in the development of biodegradable plastics.

1. Introduction: Chronic Problems with Traditional Plastics

Plastics, first developed in England in the 1850s, have been widely utilized for their advantageous physical properties such as flexibility, durability, and low production costs. However, over recent decades, plastics have emerged as a global crisis due to their detrimental impact on environmental health. Petroleum-based plastics like polyethylene (PE) and polyethylene terephthalate (PET) do not degrade naturally, resulting in vast amounts of persistent plastic waste worldwide. These materials pose challenges not only in natural environments—such as soils, freshwater, and marine ecosystems—but also in industrial composting facilities. The issues stem from the inherent structure of plastic polymers, rather than whether they are biobased, or petroleum based. Despite efforts to develop biobased alternatives such as bio-PET or bio-PE, many remain non-biodegradable due to their structural characteristics. Regardless of their origin, whether biobased or petroleum-based, polymers typically polymerize by linking radicalized monomers into long, high-molecular-weight chains known as linear polymers. This structure poses challenges to their degradation rates, influencing their persistence in the environment.

2. An Overview of Decomposition Process of Biodegradable Plastics

Biodegradable plastics are designed to mitigate the persistent issues of traditional plastics. These materials must adhere to stringent standards: they must be biobased polymers and capable of degrading easily in natural environments. However, the effectiveness of biodegradation varies significantly among different polymers. Some degrade well in soil conditions but struggle in marine environments, while others require specific industrial treatments prior to biodegradation. This variability underscores the challenges in achieving widespread biodegradability across different environmental conditions, which is crucial for their practical utility and environmental impact.

2.1. Processes of Abiotic Degradation

The biodegradation of plastics is classified into biological degradation and nonbiological degradation.[1] Abiotic degradation is primarily an industrial process to break down long polymer chains into segments of oligomer chains prior to biotic degradation in the natural environment. In fact, abiotic biodegradation is analogous to decomposition of traditional plastics, but there is subtle difference between two techniques. The primary aim of abiotic biodegradation is to enhance the biodegradability under the natural environment. In consideration of rates of biodegradation under natural environments, oligomer chains, or dimers and monomer, are more favorable than long polymer chains, which is quite obvious looking at the basic principles of kinetics and polymer properties. Abiotic biodegradations incorporate different techniques such as photochemical effects, photothermal effects, hydrolysis, electrocatalytic conversion, etc.

2.1.1. Photochemical Decomposition The photochemical decomposition is often referred as photolysis, induced by ultraviolet (UV) irradiation.[2] In general, absorption of UV rays radicalizes the polymer chain, which results in scission of the polymer chain as well as oxidation of each oligomerized chain; therefore, the photodegradation of polymers covers both pure photodegradation and photooxidative degradation. The general steps of photooxidation, in fact, are very similar to radical halogenation; it starts with chain initiation where hydroperoxide reacts with polymer chain under UV lights, generating free radicals, followed by chain propagation and chain termination. Application of photochemical decomposition to traditional plastics (e.g., polypropylene (PP), polyethylene (PE), polyethylene terephthalate (PET), etc.) results in formation of aliphatic ketones, esters, aldehydes, and aromatic ketones. Similarly, photooxidation of biodegradable plastics, most of which are polyether, also result in oxygenated species, increasing the hydrophilicity of the fragments; in fact, many photooxidation techniques involves catalyst (photocatalysis), which produces desirable products. For instance, the photocatalysis of PLA is provoked by ZnO and the UV screening effect of the ZnO nanoparticles to produce acetic anhydride.[3]

2.1.2. Photothermal Decomposition The photothermal decomposition refers to complete depolymerization of polymer chains into monomers merely by thermal treatment. The depolymerization is primarily related to the ceiling temperature (). At ceiling temperature, the rates of both polymerization and depolymerization become equal.[4] If temperature is higher than , the depolymerization becomes more favorable and vice versa if temperature is lower than . Such photothermal decomposition involving depolymerization at extremely high temperature is referred as chemical recycling by pyrolysis. In fact, the ceiling temperatures of many plastics are typically above 300 ºC, which makes thermal depolymerization itself very undesirable due to high energy requirement; however, depolymerization is possible even at lower temperature than the ceiling temperature as the equilibrium is dependent on many different factors such as presence of light or presence of impurity polymers with lower . For example, addition of light responsive carbon quantum dots (CQDs) allows polymers to depolymerize even at low temperature by generating local temperature gradient.[4]

2.1.3. Electrochemical Decomposition

2.2. Processes of Biotic Degradation

On the other hands, biotic degradation is induced by microbial enzymes, which results in the production of subproducts such as and under aerobic or anaerobic conditions.[5] The major steps of biotic degradation are (1) surface colonization: microorganisms bind to the surface of the polymer; (2) biodeterioration: excreted enzymes initially attack the amorphous regions of plastics to form cracks increasing the surface area; (3) depolymerization: extracellular enzymes hydrolyze chemical bonds to break down the polymers into oligomers, dimers, and monomers; (4) assimilation: depolymerized molecules are transported into the cell via protein transporters; (5) mineralization: smaller molecules are processed via intracellular metabolism.[1] The combination of these parameters determines the biodegradability of plastics. Rate of biochemical reactions between polymer chains and microbial enzymes are dependent on properties of polymer (e.g., crystallinity, molecular weight, high-order structure)[1]; focused discussion of structural properties is discussed later in 3. Structural Characteristics and Mechanical/Thermal Properties of Biodegradable Plastics. The type of microbial interaction and rate of biochemical reaction dramatically vary depending on different environmental conditions: soil, marine environment, anaerobic digestion, industrial composting, landfill, etc.

2.3. Practicability and Biodegradability of Plastics

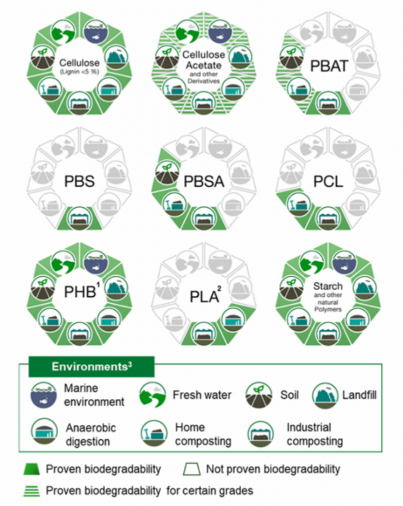


Figure 1: Degradability of biodegradable plastics in different

In fact, not all biodegradable plastics are applicable considering the various parameters such as mechanical and thermal properties, adaptivity to different environments as shown in **Figure 1**, production cost, etc. The section 2.3 discusses only few biodegradable plastics in consideration of practicability and range of biodegradability in different environments. **Table 1** specifically list out degradability of each plastic in different environmental conditions.

2.3.1 Polylactic Acid (PLA) PLA is produced from polymerization of lactic acid with isomeric forms—D-lactic acid and L-lactic acid. In fact, polymerization of racemic mixture of lactic acid (D,L-lactic acid) reinforces the thermal property of PLA, which will be specifically discussed later. There are different chemical synthesis methods for production of lactic acid such as (1) hydrolysis of lactonitrile () from reaction between hydrogen cyanide (HCN) and acetaldehyde () (2) hydrolysis of acrylonitrile and (3) use of propanoic acid.[6] Currently, about 90% of the lactic acid worldwide is obtained via microbial fermentation of first-generation biomass sugars.[6] Agricultural products are converted into D,L-lactic acid by the action of lactic acid bacteria (LAB), notably *Lactobacillus helveticus*, specifically microbial fermentation of carbohydrates. Lactide, the cyclic dimer of lactic acid, with stereoisomers—(L,L)-lactide, (D,D)-lactide, and meso-lactide—are the most essential component of production of PLA, in fact. The production of lactide is achieved through polycondensation of lactic acid and backbiting (transesterification reaction) with catalyst such as solid catalyst (aluminum oxide), azeotropic solvents (e.g., toluene, xylenes), etc. In fact, practicability of PLA is quite notable due to its economic viability, biodegradability, and favorable mechanical or thermal properties, making it one of the most viable options out of many biodegradable plastics; PLA occupies 29.4% of total production of biodegradable plastics in 2021, approximately 1.5 million tons.[1] The steps of biodegradation of PLA are: (1) PLA-degrading microorganisms excrete extracellular depolymerase of PLA, attacking ester links and decomposing the polymer into oligomers, dimers, and monomers; (2) the lower molecular weight oligomer chains enter in microbial membranes, and microbial intracellular enzymes decompose them.[7] However, biodegradability of PLA is quite limited compared to other biobased plastics such as PHB. PLA-degrading microorganisms in natural environments are significantly less than other biodegradable plastics; in other words, it has to be degraded under controlled environmental conditions as it is limited to certain types of microorganism in certain types of environmental conditions. Notably, actinomycetes, filamentous bacteria, effectively degrade PLA at different soil conditions (e.g., pH, temperature, etc.), utilizing protease; bacterial and fungal degradations are possible but rarely reported.[7] Moreover, PLA is fundamentally less susceptible to microbial interactions, and the degradation rate is quite slow compared to other biodegradable polymers; specifically, the additive, lysine diisocyanate, significantly enhance the thermal property of PLA but slows the rate of degradation at the same time. To counteract these issues, the blending process can significantly enhance the biodegradability of PLA or any other plastics with debatable biodegradability. From discussion of PLA, the quintessential challenge of biodegradable plastics becomes quite obvious: difficulty in balancing between biodegradability and mechanical/thermal property.

3. Structural Characteristics and Mechanical/Thermal Properties of Biodegradable Plastics

3.1 Relationship between Polymer Structure and Mechanical/Thermal Properties

3.1.1. Crystallinity There are different parameter and techniques to adjust degree of crystallinity of polymers. The unique state of crystallization of each polymer is determined by chain configuration and rate of cooling during solidification, which is further enhanced by certain techniques, analogous to annealing of metals. To be specific, the tensile strength separates crystalline blocks from the lamellar and stretch the polymer chains, consequently orienting the polymer chains in the direction of tensile axis. Then, the polymer is re-crystallized at temperature below the melting temperature () and above the glass transition temperature (). Crystallinity is a critical factor in determining the mechanical and thermal properties of plastics. Increasing the degree of crystallization stabilizes the rate of specific volume change of polymers beyond their glass transition temperature, as illustrated in **Figure 2**. However, optimal crystallinity varies depending on the application. While enhancing mechanical and thermal properties through increased crystallization is effective, it is often chosen to tailor the functionality of specific plastics rather than solely improve their properties. In practical terms,

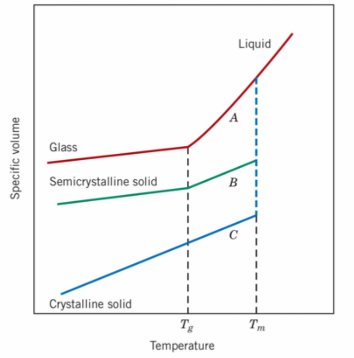


Figure 2: Effects of degree of crystallization on specific volume

this adjustment allows plastics to meet industrial and commercial requirements. For instance, manufacturers of plastic cups often prefer materials with low crystallinity. This preference is evident in the physical properties of many plastic cups, such as high flexibility and transparency. Another chronic issue with crystallization of plastic polymers emerges in consideration of degradability of the plastics. To be specific, chain orientation, regional degree of crystallization, or stretchiness of crystalline and amorphous regions affects diffusion rates of reacting species such as extracellular enzymes, solvents, and oxygen.[1] Consequently, modification of crystallinity significantly hinders both microbial and industrial depolymerization process of polymers, thus, decreases biodegradability of the plastics, which excludes it from consideration. In other words, it is more optimal to make other adjustments while maintaining the crystallinity of

3.1.2. Molecular Structures Another consideration is molecular structure, in other words, structure of monomer units. Such structural properties enhance mechanical durability of polymers and decrease their susceptibility to thermal deformation as well. To be specific, the most considerable parameters is intermolecular force between monomer units, which is adjustable through many different structural properties. For example, presence of bulky groups and aromatic rings strengthen the intermolecular force majorly by adding electron density to the monomer unit. Specifically in consideration of biodegradable plastics, addition of ketone, ether, or ester groups is the most optimal solution as those functional groups induce stronger intermolecular force between each polarizing the monomer units. Even slight differenc molecular structure creates noticeable differences ir thermal properties. For example, consider the struct PHB as shown in **Figure 3**. The monomer units of l both contain ester linkage, which is necessary to ma rigidity as well as susceptibility to hydrolysis. Also, methyl groups in the backbone increases the steric l which reduces chain mobility, thus, contributes to better mechanical and thermal properties: higher stiffness, elastic modulus, brittleness, glass transition temperature, etc. Especially for PHA, the additional alkyl groups attached to the backbone are essential in enhancing these properties. On the other hand, the additional hydroxyalkyl chain () between the hydroxyl and carboxyl groups add flexibility to the polymer chain, which improve the toughness and impact resistance but worsen other properties such as stiffness, elastic modulus, and glass transition temperature; in other words, it has counteracting effects of additional alkyl groups attached to the backbone. Therefore, PHB exhibits relatively poor mechanical and thermal properties as shown in **Table 1**:

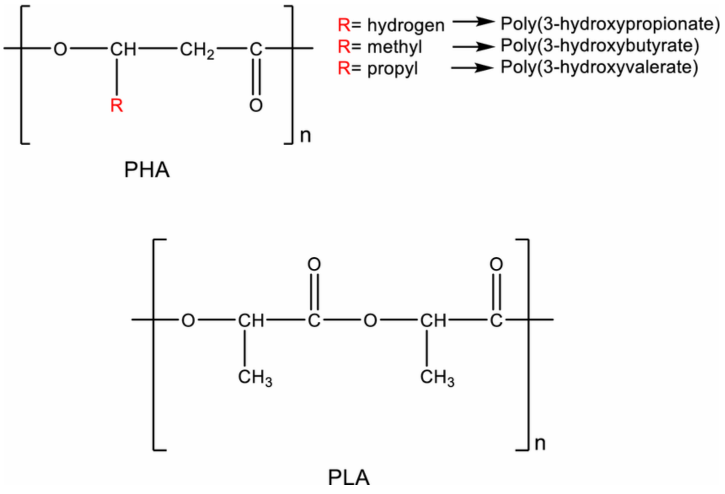
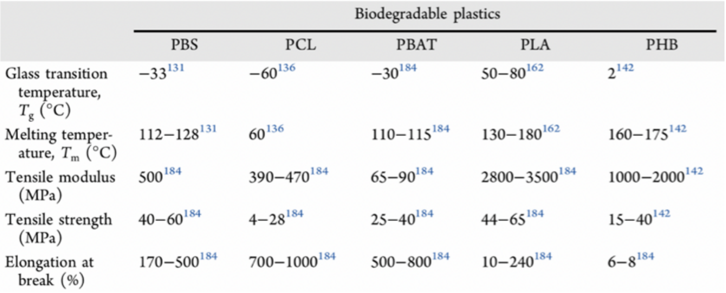


Figure 3: Structures of monomer units of polylactic acid (PLA) and polyhydroxybutyrate (PHB)



	Biodegradable plastics				
	PBS	PCL	PBAT	PLA	PHB
Glass transition temperature, T_g (°C)	−33[131]	−60[136]	−30[184]	50−80[162]	2[142]
Melting temperature, T_m (°C)	112−128[131]	60[136]	110−115[184]	130−180[162]	160−175[142]
Tensile modulus (MPa)	500[184]	390−470[184]	65−90[184]	2800−3500[184]	1000−2000[142]
Tensile strength (MPa)	40−60[184]	4−28[184]	25−40[184]	44−65[184]	15−40[142]
Elongation at break (%)	170−500[184]	700−1000[184]	500−800[184]	10−240[184]	6−8[184]

Table 1: Mechanical and Thermal Properties of Biodegradable Plastics

looking at thermal properties, PHB and PLA have similar melting temperature while PHB has much lower glass transition temperature than PLA does.

3.2 Analysis of Mechanical Properties and Thermal Properties of Biodegradable Plastics

According to the analysis above, each biodegradable plastics display very different mechanical and thermal properties depending on parameters, most notably structural properties. Therefore, each plastic, in fact, require different type of adjustment. For instance, PLA has favorable mechanical and thermal properties but doubtful biodegradability. On the other hand, PHB has favorable biodegradability but poor mechanical and thermal properties. The balance between two parameters can be achieved through different techniques. One of the notable techniques is copolymerization, which will be discussed in detail in the next section. The copolymer is constituted of PLA and PHB.

4. Unlocking the Constraints of Mechanical and Thermal Properties

4.1. Overview of Chemical Additives in Plastics

Reviewing the mechanical and thermal properties of biodegradable plastics in the previous section, it is quite important to enhance these properties in order to expand range of plastics even further. In fact, different types of properties are chosen depending on the specific usage of plastics; however, the most desirable mechanical and thermal properties are the followings in general: stiffness, brittleness, high glass transition temperature, and high melting temperature if applicable. Chemical additives are very general solutions to rectify such issues in general regardless of biodegradability of the plastics. The common chemical additives are stabilizers, flame retardants, plasticizers, etc. all of which have different functions. For instance, plasticizers are majorly used for enhancing the flexibility and elasticity of plastics by expanding the volume between each polymer chain, which is opposed to the general desirable properties of the plastics as mentioned above; plasticizers are very useful under specific circumstances, requiring flexibility and ductility of the plastics, but stiffness and brittleness are more preferred in general but especially for biodegradable plastics. Suitability of additives strictly depends on type of biodegradable plastics as well as effects of additives on degradability of plastics.

4.1.1. Overview of Enhancing Mechanical and Thermal Properties of PLA As noted in Table 1, PLA has relatively low glass transition temperature (~55 ºC without any modification and 50-80 ºC through viable modifications) to that of petroleum plastics. As mentioned in Section 2.3.1, 1:1 racemic mixture of D,L-lactic acid enhance up to 65-72 ºC.[8] In general, Generally, increase of glass transition temperature is achieved by introducing conformational restriction around single bonds by structural rigidity or steric encumbrance. In fact, the addition of alkyl groups rather decreases the glass transition temperature; however, the addition of cyclic aliphatic or aryl groups is more effective in increasing the structural rigidity. Significant distinction between cyclic aliphatic and alkyl groups is that alkyl groups rather add free volume to the polymer, which consequently decreases the glass transition temperature. However, cyclic aliphatic group do not add substantial free volume but rather establishes conformational rigidity, which increases the glass transition temperature. Not all R groups attached to the backbone of PLA are effective in enhancing thermal properties of PLA necessarily. shows the effects of different substituent groups.

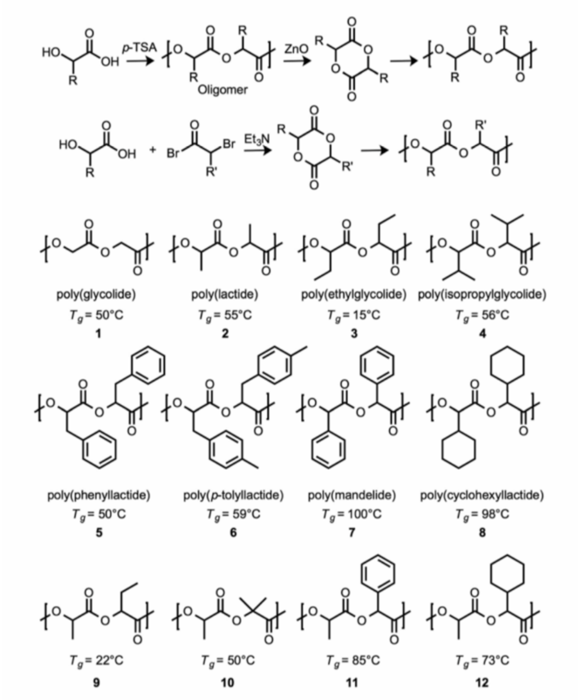


Figure 4: Effects of substituent groups on glass transition temperature of PLA

4.2. Different Techniques

4.2.2: Natural Fiber Reinforced Plastic Composites Formation of composites is one of the viable ways to reinforce the strength of plastics. Nowadays, there are lots of potential candidates for additives: epoxy resins, phenolic resin, silicon, glass fiber, carbon fiber, etc. Among these options, many studies focus on composites of natural fibers and biobased plastics in consideration of biodegradability. The main constituent of natural fibers is cellulose whose elementary unit is anhydro d-glucose containing three hydroxyl groups; therefore, the hydrogen bonds within and between macromolecules strengthen the structure of composites when added to plastics.[9] The strength of cellulose is highly affected by different factors such as chemical structures—majorly anisotropy of microfibrils—as well as crystallinity and degree of polymerization, which is analogous to plastics. One of the examples is hemp fabric/poly(hydroxybutyrate) (PHB) composite which has comparable strength to structural lumber and engineered wood products, with stiffness comparable to most engineered wood product.[10] Along with enhanced mechanical properties, it displays a decent level of biodegradability. According to the assessment—done by measuring the amount of carbon mineralized from these materials during incubation and by examination of the materials by scanning electron micrography (SEM)—PHA-based plastic composite biodegraded at a rate similar to the positive control (cellulose).[11]

4.2. Copolymer Technique Considering all the necessary parameters—biodegradability, mechanical and thermal properties, and practicability—PLA is a quite practical bioplastic;

especially, its favorable mechanical and thermal properties compared to other biodegradable plastics. As mentioned earlier, the only concern with PLA plastics is its biodegradability, which in fact, can potentially be enhanced through many different techniques but essentially copolymer technique. One of the considerable candidates is PLA-PHB complex. In fact, PHB crystals acts as nucleating agent in PLA, which significantly enhance the mechanical properties of PLA while maintaining biodegradability.[12] PLA-PHB blend successfully reinforce the flaws of both PLA and PHB.

4.2. Potential Future Research

The current research on copolymer technique is focused on adding biomaterials such as starch to enhance the biodegradability of the plastics even further. The possible future research may be focused on viable candidates for biomaterials as mentioned above while considering an effective method to maintain the favorable mechanical and thermal properties.

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