

· 综 述 ·

生物可降解塑料在不同环境条件下的降解研究进展

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金琰, 蔡凡凡, 王立功, 宋超, 金文雄, 孙俊芳, 刘广青, 陈畅. 生物可降解塑料在不同环境条件下的降解研究进展. 生物工程学报, 2022, 38(5): 1784-1808.

JIN Y, CAI FF, WANG LG, SONG C, JIN WX, SUN JF, LIU GQ, CHEN C. Advance in the degradation of biodegradable plastics in different environments. Chin J Biotech, 2022, 38(5): 1784-1808.

摘 要: 当前社会塑料制品的使用需求持续增加, 塑料垃圾处理压力不断增大, 减缓塑料污染成为当务之急, 生物可降解塑料因可在一定生物活性环境下较快降解而备受关注, 具有广阔的应用前景。生物可降解塑料降解条件复杂, 影响因素众多, 对不同生物可降解塑料降解规律, 降解微生物和功能酶的透彻掌握, 是实现其全面利用和高效资源化处置的基础和前提。文章系统梳理了常见生物可降解塑料的种类、性能、优缺点和主要用途, 全面综述了生物可降解塑料的降解机理、降解微生物和功能酶, 以及生物可降解塑料在不同环境条件下的降解周期和程度, 以期为生物可降解塑料的微生物降解研究提供借鉴, 为生物可降解塑料废弃物的高效处理处置和彻底降解提供科学参考。

关键词: 生物可降解塑料; 降解机制; 微生物; 解聚酶; 需氧; 厌氧

Advance in the degradation of biodegradable plastics in different environments

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Abstract: With the continuously increasing demands of plastic products in the current society, the challenge of disposing plastic waste is constantly increasing, leading to the urgent need of mitigating

Received: September 21, 2021; **Accepted:** November 9, 2021; **Published online:** November 23, 2021

Supported by: National Key Research and Development Program of China (2018YFD0800103)

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基金项目: 国家重点研发计划 (2018YFD0800103)

plastic pollution. As a consequence, much attention has been paid to biodegradable plastics due to their degradability in a bio-active environment under certain conditions. Biodegradable plastics herald vast development potentials and considerable market prospects. The degradation of numerous types of biodegradable plastics will be affected by many factors. A thorough understanding of degradation mechanisms as well as functional microbial strains and enzymes is the key to comprehensive utilization and efficient treatment and disposal of biodegradable plastics. The article summarized the types, properties, advantages and disadvantages, and main applications of common biodegradable plastics. The degradation mechanisms, functional microbial strains and enzymes, as well as the degradation degree and duration under different environmental conditions, were also summarized. This review may help better understand the degradation of biodegradable plastics wastes.

Keywords: biodegradable plastics; degradation mechanism; microbes; depolymerase; aerobic; anaerobic

塑料是三大有机合成材料之一，在各个领域应用广泛，用量与日俱增，目前，超过 60% 的塑料在使用后被填埋或随意丢弃^[1]。以聚乙烯 (polyethylene, PE) 和聚丙烯 (polypropylene, PP) 为主要的传统塑料在自然环境中难以分解，对生态环境构成严重威胁。为遏制传统塑料引发的一系列环境污染问题，国家发展改革委和生态环境部于 2021 年 9 月印发了“十四五”塑料污染治理行动方案的通知，提出了严格的塑料污染限期整治目标，这将推动我国生物可降解塑料进入快速发展期。

生物可降解塑料因含有易发生反应的化学键，能够在一定生物活性环境下，如好氧堆肥、水体、厌氧或土壤环境，通过微生物的作用，降解转化为二氧化碳 (CO₂)、甲烷 (CH₄) 等代谢产物。随着国家塑料污染治理工作逐步落实，生物可降解塑料替代传统塑料成为必然趋势。但生物可降解塑料种类繁多，性能各异，降解条件复杂，在不适合的处理处置条件下可能难以有效降解，进而导致环境污染，制约生物可降解塑料的开发应用。本文针对常见生物可降解塑料的性能、降解机理、降解功能微生物和功能酶以及在不同自然和受控条件下的降解情

况进行系统综述。对生物可降解塑料降解机理和降解程度的系统归纳，将为生物可降解塑料废弃物的高效处理处置和彻底降解提供科学参考，对生物可降解塑料制品的全面推广具有重要意义。

1 生物可降解塑料的种类和性能

生物可降解塑料可由天然高分子化合物加工而成，也可由微生物代谢或化学手段合成。天然高分子类生物可降解塑料以热塑性淀粉 (thermoplastic starch, TPS) 为主，微生物代谢合成类生物可降解塑料主要是聚羟基烷酸酯 (polyhydroxyalkanoate, PHA)，化学合成类生物可降解塑料包括聚乳酸 (poly(lactic acid), PLA)、聚丁二酸丁二酯 (poly(butylene succinate), PBS)、聚丁二酸-己二酸丁二酯 (poly(butylene succinate-co-butylene adipate), PBSA)、聚对苯二甲酸-己二酸丁二酯 (poly(butylene adipate-co-terephthalate), PBAT)、聚己内酯 (poly(ϵ -caprolactone), PCL)、聚碳酸亚丙酯 (poly(propylene carbonate), PPC)、聚乙烯醇 (poly(vinyl alcohol), PVA) 等。以下对常见生物可降解塑料的中文名称、英文名称、英文缩写、

聚合物的结构式和主要用途进行总结比较, 详见表 1。

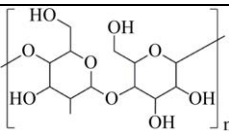
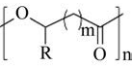
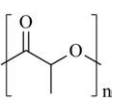
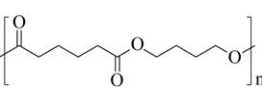
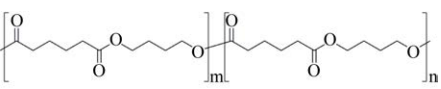
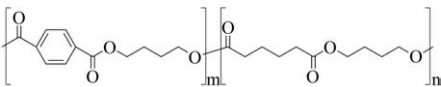
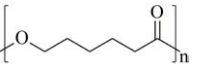
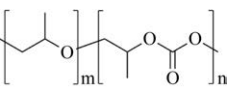

1.1 热塑性淀粉 (TPS)

淀粉是应用最早的生物可降解塑料基材之一, 淀粉分子间具有较强的氢键相互作用力, 受热条件下流动性差, 玻璃化转化温度与分解温度接近, 加工成型困难。通过在淀粉中加入增塑剂, 使增塑剂和淀粉之间的氢键代替淀粉

分子间和分子内的氢键, 可提高淀粉分子的活动能力, 降低淀粉的玻璃化转化温度, 从而实现淀粉的热塑成型^[4]。TPS 原料来源广泛, 生产加工技术相对成熟, 降解性能优良, 与其他生物可降解塑料共混可提升共混塑料的分解能力。但 TPS 力学性能、热稳定性以及耐水性不足, 难以单独使用。TPS 商品化程度高, 价格在 1 万元/t 左右。

表 1 常见的生物可降解塑料汇总

Table 1 Summary of common biodegradable plastics

Type	Abbreviations	Structural formulas	Application ^[2-3]
Thermoplastic starch	TPS		Packaging, shopping bags, garbage bags, mulch films, disposable tableware and disposable medical products
Polyhydroxyalkanoate	PHA		Tissue engineering, medical implant, controlled drug delivery system, packaging, mulch films and disposable medical products
Poly(lactic acid)	PLA		Packaging, shopping bags, garbage bags, mulch films, disposable tableware, disposable medical products, building materials and textiles
Poly(butylene succinate)	PBS		Packaging, shopping bags, garbage bags, pesticide and fertilizer sustained-release materials, mulch films and disposable tableware
Poly(butylene succinate-co-butylene adipate)	PBSA		Packaging, shopping bags, garbage bags and mulch films
Poly(butylene adipate-co-terephthalate)	PBAT		Packaging, shopping bags, garbage bags, mulch films and disposable tableware
Poly(ε-caprolactone)	PCL		Medical implant, controlled drug delivery system, absorbable surgical sutures and cryogenic packaging
Poly(propylene carbonate)	PPC		Cryogenic packaging, mulch films, foam materials, controlled drug delivery system and high barrier materials
Poly(vinyl alcohol)	PVA		Soluble packaging and high barrier materials and medical implant

1.2 聚羟基烷酸酯 (PHA)

聚羟基烷酸酯 (PHA) 是由微生物在碳源充足, 氮、磷、微量元素等缺乏时, 将多余碳源储存起来而合成的脂肪族聚酯。其结构式如表 1 所示, m 可以是 1-4, 短链 PHA 的 R 基团为 -H、-CH₃、-C₂H₅, 包括聚羟基丁酸酯 (poly(3-hydroxybutyrate), PHB)、聚羟基戊酸酯 (poly(3-hydroxyvalerate), PHV) 等; 中长链 PHA 的 R 基团为 -C₃H₇ 到 -C₁₃H₂₇, 包括聚羟基己酸酯 (polyhydroxyhexanoate, PHH)、聚羟基辛酸酯 (polyhydroxyoctanoate, PHO) 等。此外, 将不同 PHA 单体按一定比例共聚可获得共聚酯。如聚 3-羟基丁酸戊酸酯 (poly(3-hydroxybutyrate-co-3-hydroxyvalerate), PHBV) 和聚 3-羟基丁酸 4-羟基丁酸酯 (poly(3-hydroxybutyrate-co-4-hydroxybutyrate), P34HB)。PHA 的物理性质与其分子构成和单体结构密切相关, 短链 PHA 结晶度较高, 表现出良好的刚性; 中长链 PHA 结晶度低, 表现出良好的弹性^[5]。但 PHA 的热降解温度和熔融温度相近, 加工窗口窄, 加工成型较为困难^[6]。PHA 商品化程度一般, 根据纯度的不同, 价格有较大差异, 介于 3-15 万元/t。

1.3 聚乳酸 (PLA)

聚乳酸 (PLA) 是由乳酸为原料制备的脂肪族聚酯。可通过微生物以玉米、小麦秸秆等为原料发酵制得乳酸后再缩合加工而成。乳酸有右旋 (D-lactic acid, D-LA) 和左旋 (L-lactic acid, L-LA) 2 种旋光异构体, 因此其均聚物有 3 种, 其中半结晶的聚 L-乳酸 (poly(L-lactic acid), PLLA) 和聚 D-乳酸 (poly(D-lactic acid), PDLA) 分子链推拉时不易发生移动, 表现出较强的刚性; 无定形的聚 D-L-乳酸 (poly(D, L-lactic acid), PDLLA) 分子链推拉时易发生移动, 表现出较强的柔性^[7]。PLA 具有较好的水

汽阻隔性和透明性, 在制备硬质生物可降解塑料制品方面具有较大潜力, 但质脆, 抗冲击性较差, 难以满足软包装领域的应用要求, 在低于熔融温度下加工会使相对分子质量大幅下降, 加工成型难度大^[8]。PLA 商品化程度高, 价格区间在 3-4 万元/t。

1.4 二元酸二元醇共聚酯 (PBS、PBSA、PBAT 等)

二元酸二元醇共聚酯包括聚丁二酸丁二酯 (PBS)、聚丁二酸-己二酸丁二酯 (PBSA)、聚对苯二甲酸-己二酸丁二酯 (PBAT) 等, 其中 PBS 和 PBSA 属于脂肪族聚酯, PBAT 含有苯环结构, 属于脂肪族芳香族共聚酯。

PBS 由丁二酸和 1,4-丁二醇为主要原料制备。丁二酸和丁二醇可通过纤维素、淀粉、葡萄糖、果糖、乳糖等为原料发酵制得, 也可通过石油资源加工获得。PBS 可通过与传统塑料相似的挤出、吹塑、压模等方法进行加工, 原料来源广泛, 耐热性能较好, 但质脆, 较强的疏水性导致降解速率较慢^[9]。PBSA 由丁二酸、1,4-丁二醇和己二酸为主要原料制备。PBSA 共聚物中己二酸的含量会影响其热性能和力学性能。相较于 PBS, PBSA 的降解性能和柔韧性有所改善^[10], 但脆性较大, 抗冲击性较差。PBAT 由对苯二甲酸、1,4-丁二醇和己二酸为主要原料制备。其中脂肪族链段赋予 PBAT 良好的柔韧性和生物降解性, 芳香族链段则用于提高 PBAT 的力学性能和加工性能。PBAT 熔点和力学性能与低密度聚乙烯 (low-density polyethylene, LDPE) 相似, 加工温度范围广, 可采用传统设备和方法进行加工, 但柔韧性过高, 刚性挺度不足, 对氧气和水汽的阻隔性能差, 降解速率慢, 较难通过一些严格的降解标准^[11]。二元酸二元醇共聚酯商品化程度较高, 目前价格在 3 万元/t 左右。

1.5 聚己内酯 (PCL)

聚己内酯 (PCL) 是由 ϵ -己内酯通过催化剂催化开环聚合制备的脂肪族聚酯。其结构中的重复单元含有运动性强的 C-C 键和 C-O 键, 此结构赋予 PCL 较好的柔韧性和生物降解性。PCL 熔点低, 在室温下呈橡胶态, 易热塑成型^[12], 但刚性不足, 60 °C 左右的低熔点限制了其高温条件下的应用。商品化程度一般, 目前价格在 5–7 万元/t。

1.6 聚碳酸亚丙酯 (PPC)

聚碳酸亚丙酯 (PPC) 是由 CO₂ 和环氧丙烷 (propylene oxide, PO) 通过催化剂催化开环聚合制备的聚碳酸酯。PPC 不易燃, 具有较好的柔韧性、水汽阻隔性、生物降解性和生物相容性。但 PPC 是无定形聚合物, 分子间作用力小, 拉伸强度低, 力学性能差; 主链上存在大量酯基, 易水解、热解断链, 热分解温度低, 加工性能差^[13]; 存在末端羟基, 热稳定性差, 在较高温度下容易发生解拉链式降解; 30–40 °C 玻璃化转化温度限制了其在高温条件下的应用^[13]。PPC 商品化程度一般, 价格在 5–8 万元/t。

1.7 聚乙烯醇 (PVA)

聚乙烯醇 (PVA) 是由醋酸乙烯合成聚醋酸乙烯后通过醇解制备的高分子聚合物, 其物理化学性能很大程度上取决于醇解度。根据醇解度的不同可分为完全醇解型、部分醇解型和低醇解型。醇解度 87%–88% 的部分醇解型 PVA 具有最好的水溶性, 而醇解度更高或更低的 PVA 水溶性均变差。PVA 具有韧性、透明性、气体阻隔性和抗静电性, 但易受潮, 吸湿后气体阻隔性降低, 加工性能变差^[14]。PVA 商品化程度一般, 目前市场价格在 1.2–2.5 万元/t。

综上所述, 生物可降解塑料种类繁多, 性能各异, 通过不同生物可降解塑料的共混改性可使共混塑料获得优良的加工性能和机械性能, 满足塑料的应用要求。此外, 较高的价格是制约生物可降解塑料广泛应用的瓶颈, 降低其生产成本应是今后的研究重点。

2 生物可降解塑料的降解机理

生物可降解塑料发生降解的本质是聚合物中化学键的断裂, 通过在聚合物分子链中引入弱性化学键或易发生反应的化学键可使聚合物更易发生降解。分子链的开裂方式分为 4 种: 分子链解聚型、分子链无规断裂型、分子链弱键分离型、分子链侧链或小分子脱出型^[15]。一般来讲, 聚合物通过水解作用进行解聚, 产生低聚物和单体的过程是生物可降解塑料降解的限速步骤。微生物水解是细菌、真菌和藻类等天然微生物利用现有的酶, 催化聚合物链发生断链, 最终产生低聚物和单体的过程。但对于 PLA、聚对苯二甲酸乙二醇酯、聚羧酸盐等聚合物而言, 非生物水解的作用至关重要^[16]。生物可降解塑料的水解通过表面侵蚀或整体侵蚀进行, 整体侵蚀在聚合物表面和内部均匀发生, 首先通过水在聚合物无定形区域的扩散引发水解反应, 低聚物缓慢扩散到聚合物表面后逐渐溢出。表面侵蚀则从聚合物表面开始, 聚合物体积减小 (图 1), 表面侵蚀的速率远高于整体侵蚀^[17]。当水解速度超过水扩散到主体中的速度, 或当催化剂 (例如, 酶) 不能穿透主体聚合物时, 会发生表面侵蚀, 表面侵蚀是疏水和半结晶聚合物以及水解速率较快的聚合物发生降解的主要机制。当水的扩散速度超过水解反应速度时, 会发生整体侵蚀^[16–18]。

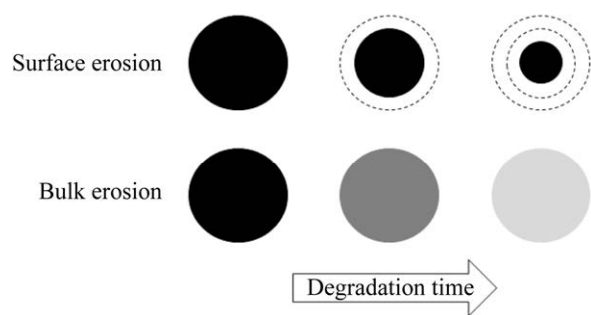


图1 生物可降解塑料的表面侵蚀和整体侵蚀^[17]
Figure 1 Surface and bulk erosion of biodegradable plastics^[17].

生物可降解塑料的降解很大程度上取决于聚合物的成分和结构。聚合物结构越接近天然聚合物越易降解,因此淀粉基、纤维素基等天然高分子类和 PHA 等微生物代谢合成类生物可降解塑料较易降解。只有线性链结构的脂肪族聚酯比包含苯环的芳香族聚酯易降解^[3],芳香单元较难被微生物破坏。紧密堆积的结晶区域阻碍了酶的攻击,因此聚合物无定形区域比结晶区域易分解^[19]。高柔韧性的聚合物链更贴合酶的活性部位,因此具有较低熔融温度的聚合物由于其聚合物链较高的柔性而更容易被生物降解^[19]。直链比含有支链和交联的聚合物易降解,因为酶较难渗透到复杂的网格结构中。亲水性强的聚合物更易降解,因为酶更易接近水溶性底物。聚合物表面越粗糙,微生物越易附着。以下根据生物可降解塑料降解过程中的不同断键机理展开具体介绍。

2.1 含糖苷键生物可降解塑料的降解

包括淀粉基、纤维素基材料在内的多糖基生物可降解塑料,均通过糖苷键的断裂进行解聚,生成低聚物和单体后被微生物利用。糖苷键的水解酶多样,包括淀粉酶、纤维素酶、壳聚糖酶等,微生物酶对多糖糖苷键的降解效率通常较高。

TPS 是目前常见的生物可降解塑料,其主要成分——淀粉,具有强吸湿性,水分子渗透到其结构中,使水解较易发生。淀粉分子有 2 个官能团在降解过程中起重要作用:易发生取代反应的-OH 基团和易发生断链的 C-O-C 键^[16]。TPS 的降解速率取决于易降解的淀粉,微生物分解淀粉后,破坏 TPS 结构的完整性,增加微生物与剩余组分的接触面积,从而提升酶对剩余组分的可及性^[20]。在好氧条件下,淀粉通过根霉、曲霉以及枯草芽孢杆菌等产生的糊精酶、麦芽糖苷酶和葡糖苷酶先后转化为糊精、麦芽糖和葡萄糖;在厌氧条件下,淀粉在水解菌群产生的水解酶的作用下先后转化为麦芽糖和葡萄糖,葡萄糖透过细胞膜进入细胞,被完全转化。

2.2 含酯键生物可降解塑料的降解

以 PHA、PLA、PBS、PBSA 和 PCL 为主的脂肪族聚酯和以 PBAT 为主的脂肪族芳香族共聚酯中存在不稳定的酯键,容易受到酶的攻击发生水解裂解和解聚,从而生成低聚物和单体,单体通过细胞膜进入细胞,经过 β -氧化,最终在有氧条件下产生 CO_2 和 H_2O ,在厌氧条件下产生 CH_4 。脂肪族聚酯和脂肪族芳香族共聚酯的水解解聚如图 2、图 3 所示^[21]。

聚酯酯键的水解酶包括脂肪酶、酯酶、蛋白酶、角质酶和 PHA 解聚酶等,它们具有不同的底物偏好和界面活性,催化酯键断裂形成醇和羧酸,例如,蛋白酶倾向降解 α -酯键,PHB 解聚酶倾向于降解 β -酯键,脂肪酶则倾向于降解 γ - ω 酯键^[17,22]。酶对生物可降解塑料的水解

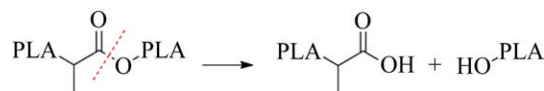


图2 脂肪族聚酯的解聚机制^[21]

Figure 2 Depolymerization of aliphatic polyesters^[21].

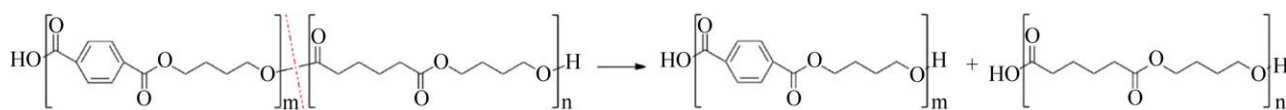


图3 脂肪族芳香族共聚酯的解聚机制^[21]

Figure 3 Depolymerization of aliphatic-aromatic co-polyesters^[21].

主要分为2步：酶吸附于聚合物的活性位点；由疏水结构域结合位点和催化位点诱导键的酶促水解断裂，将不同大小的低聚物释放到周围介质中^[23]。在这些水解酶中，脂肪酶不溶于水，倾向于水解长链和油水界面的底物，Tokiwa等^[24]报道称脂肪酶可水解含有较多亚甲基的聚酯酯键，如PCL、PBS、PBSA和聚丁二酸乙二酯(poly(ethylene succinate), PES)，但难降解具有高熔点(T_m)的旋光性聚合物，如PHB和PHV。此外，对沿碳主链有较多侧链的聚合物活性较低^[25]。酯酶溶于水，优先水解短链脂肪酸，对水溶性底物更活跃。角质酶来自 α/β 水解酶超家族酶，是丝氨酸酯酶，同时具备脂肪酶和酯酶的部分特性^[3]，具有广泛的底物特异性。相对于酯酶，角质酶可水解脂质；与脂肪酶相比，角质酶不受界面相互作用的影响，可更有效地水解疏水性底物^[3]。蛋白酶也被称为肽酶，在广泛的pH和温度范围内表现出稳定性和活性，蛋白酶对PLA的降解至关重要。Reeve等^[26]报道称来自林伯氏白色念珠菌(*Tritirachium album* Limber)的蛋白酶K不能裂解PLA的D-立体异构体，因此认为蛋白酶K识别PLA的L-乳酸单位。PHA解聚酶通常由较低分子量的多肽组成，其催化中心类似于脂肪酶催化中心，但它们的活性位点在空间排列上有差异^[25]。目前已知的PHA解聚酶没有脂肪酶活性，若底物为具备 ω -羟基酸(ω -hydroxyacids)的聚合物，如聚4-羟基丁酸酯(poly(4-hydroxybutyrate), P4HB)和聚6-羟基己酸酯(PCL)，一些脂肪酶具备PHA解

聚酶活性^[27]。

不同的水解酶对不同生物可降解塑料起作用。PHA的水解酶主要是PHA解聚酶，水解产物因PHA类型而异，PHB水解生成3-羟基丁酸，PHBV水解产生3-羟基丁酸和3-羟基戊酸，P34HB水解生成3-羟基丁酸和4-羟基丁酸。PHA解聚酶对短链PHA的解聚作用显著，中长链PHA的侧链结构较多，影响解聚酶与酯键的结合^[17]。

除蛋白酶外，脂肪酶、酯酶和角质酶也对PLA的降解起作用，使其水解为不同链长的乳酸低聚物($n=2-13$)和单体^[3,28]。PLA的水解通过酯键的随机断裂发生，断链优先发生在非结晶区域。PLA断链后，羧基端基起催化作用，以自催化和自维持的方式影响PLA的水解(图4)^[18]。自催化效应使PLA在分子结构内部发生整体侵蚀的速率快于在其表面发生的表面侵蚀的速率。分子内部水解产生的低聚物缓慢向聚合物边界游离并溢出，聚合物中心的低聚物仍被包裹，从而限制了同化速率^[18]。PLA的水解速率受温度和pH值的影响，通过高温水解($>55\text{ }^\circ\text{C}$)降低分子量后，生物降解可更快地进行^[29]。此外，酸性和碱性条件也可促进PLA的水解，在碱性条件下，PLA通过酯键的无规断裂水解生成丙交酯后再转化为乳酸；在酸性条件下，PLA通过链段酯键断裂直接水解为乳酸^[17]。

PBS和PBSA在脂肪酶、酯酶、角质酶的催化作用下发生水解，PBS水解为1,4-丁二醇(1,4-butanediol, B)、丁二酸(succinic acid, S)、

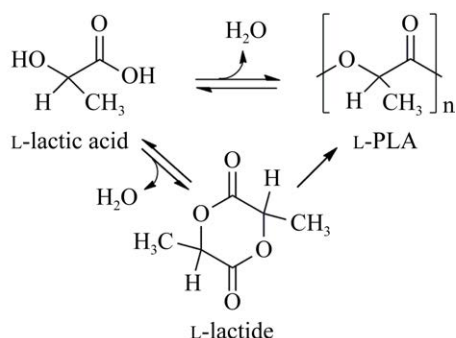


图 4 PLA 的内部自催化降解^[18]

Figure 4 Self-catalyzed degradation of polylactic acid^[18].

SB、SBS、BSB 和 SBSB 为主的水溶性单体和低聚物^[30]。PBSA 生成 B、S 和己二酸 (adipic acid, A) 3 种单体以及 3 种单体以酯键相互连接而成的低聚物。PBSA 中己二酸单元比 1,4-丁二醇单元降解快, 而丁二酸单元更难降解^[31], 己二酸的加入降低了 PBSA 的结晶度, 无定形区域松散结构的增多, 使其更易被生物降解^[19]。PBAT 在酯酶、角质酶的催化下发生水解, 水解产物除 B、A、和对苯二甲酸 (terephthalic acid, T) 3 种单体外, 还含有 BA、BT、ABA、BTB、TBT、ABT 等低聚物, PBAT 的降解首先发生在 BA 连段, BT 链段较难降解^[32], 相对于 PBS, PBAT 中对苯二甲酸的添加, 降低了酶对其中酯键的可及性, 使 PBAT 的降解速率下降^[33]。在酶解过程中, 含 3 个以上酯键的低聚物与酶的亲和力强, 降解速度快, 因此水解产物主要为含 1-3 个酯键的单体和低聚物^[30]。

PCL 可在脂肪酶、酯酶、蛋白酶、角质酶、几丁质酶等的催化下发生水解^[3]。其水解

产物主要是 6-羟基己酸的单体、二聚体、三聚体和四聚体的混合物^[34]。此外, PCL 较高的结晶度和较强的疏水性, 使其水解较困难, 相对于结晶区域, PCL 无定形区域可更有效地降解^[35]。

2.3 含碳酸酯键生物可降解塑料的降解

聚碳酸酯的降解主要以碳酸酯键断裂的方式进行, 聚碳酸酯比聚酯更耐酸水解, 易发生碱水解, 但在碱性条件下, 聚碳酸酯的降解速率比聚酯慢。造成这种现象的一个原因可能是这两种聚合物中碳原子和氧原子的电负性差异。聚碳酸酯中的羰基碳原子比相应聚酯中的羰基碳原子更亲电, 聚碳酸酯中的羰基碳原子在碱性条件下更易受到氢氧根离子的攻击, 导致聚碳酸酯在水解产生羧基后, 进一步被催化裂解为羟基并释放 CO_2 ^[33]。以 PPC 为代表的聚碳酸酯的解聚见图 5。

由环氧化合物和 CO_2 制备的聚碳酸酯, 例如聚碳酸亚乙酯 (poly(ethylene carbonate), PEC) 和聚碳酸亚乙酯-丙酯共聚酯 (poly(ethylene-co-propylene carbonate), PEPC), 在根霉脂肪酶的催化作用下可发生降解生成简单的二元醇^[36]。Suyama 等^[37]采用水解聚酯的酶, 研究其对聚碳酸四亚甲基酯 (poly(tetramethylene carbonate), PTC) 的水解作用, 研究结果表明, 水解 PTC 的酶包括: 柱状假丝酵母 (*Candida cylindracea*) 合成的胆固醇酯酶、假单胞菌 (*Pseudomonas* sp.) 合成的脂蛋白脂肪酶以及由染色粘性菌 (*Chromobacterium viscosum*) 和少根根霉 (*Rhizopus arrhizus*) 合成的脂肪酶。

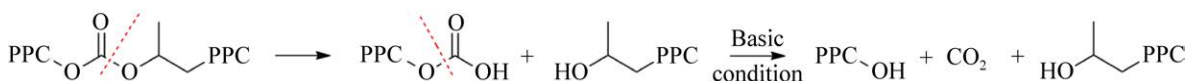


图 5 脂肪族聚碳酸酯的解聚机制

Figure 5 Depolymerization of aliphatic polycarbonates.

2.4 含多羟基生物可降解塑料的降解

PVA 链结构中含有多个羟基, 微生物降解发生在 PVA 相邻的 2 个羟基处, 其降解途径主要有两种^[38], 一种是通过次生醇氧化酶 (secondary alcohol oxidases, SAO) 氧化 PVA, 使 PVA 的 2 个相邻羟基形成 β -二酮结构, 然后在 β -二酮水解酶 (β -diketone hydrolase, BDH) 的水解作用下, β -二酮的不稳定 C-C 键发生断裂。当 β -二酮两侧的碳链长度不同时, 水解裂解发生在碳链长度较短的一侧, 从而在较长段和较短段分别生成甲基酮和羧酸, 水解产生的低聚物和单体进入细胞通过 β -氧化三羧酸循环进行代谢。图 6 总结了由 SAO 和 BDH 两种酶参与的 PVA 代谢。另一种途径是通过氧化 PVA 的 1 个羟基, 形成 β -羟基酮后, 通过醛缩酶反应在 β -羟基酮处断裂 C-C 键, 生成甲基酮和醛, 其中吡咯喹啉醌 (pyrroloquinoline quinone, PQQ) 依赖性的 PVA 脱氢酶 (PVA dehydrogenase, PVA-DH) 及其载脂酶 (apoenzyme) 分别参与羟基氧化和醛缩酶型裂解, 粪产碱杆菌 (*Alcaligenes faecalis*) KK314 被报道通过这种途径降解 PVA^[39]。此外产生 apoPVA-DH 的鞘氨醇盒菌 (*Sphingopyxis* sp.) 113P3 (曾用名: 假单胞菌 *Pseudomonas* sp. 113P3、鞘氨醇单胞菌 *Sphingomonas* sp. 113P3) 对 PVA 的代谢途径相对特殊, 水解过程不形成 β -二酮和 β -羟基酮, 这种菌株存在一种不同于 BDH 的周质氧化 PVA 水解酶 (oxiPVA hydrolase, OPH), 这种酶对单酮和二酮没有活性^[40]。PVA-DH 属于胞内酶, PVA 必须进入细胞周质后才能通过第二种途径进行降解, 细胞外的 SAO 可能有助于 PVA 解聚到合适大小, 使其被周质间隙吸收^[40]。

目前, 多数生物可降解塑料属于聚酯, 其生物降解主要通过酯键的水解断裂发生, 影响酯键断裂的因素众多, 需要对生物可降解塑料

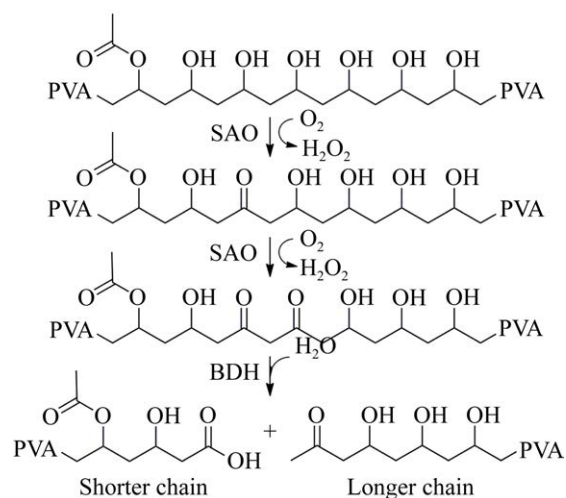


图 6 聚乙烯醇的解聚机制^[38]

Figure 6 Depolymerization of polyvinyl alcohol^[38].

降解机理进行系统研究, 完全掌握生物可降解塑料的降解规律及特点, 为实现生物可降解塑料的快速完全降解奠定基础。

3 生物可降解塑料的降解微生物

降解生物可降解塑料的菌株包括中温细菌、高温细菌和真菌, 存在于堆肥、淡水、海洋、厌氧和土壤等多种自然环境中, 分泌不同的酶, 具有不同的最适作用条件和对生物可降解塑料的降解效率。功能微生物和功能酶的高效利用对加速生物可降解塑料的降解具有重要意义。表 2 总结了生物可降解塑料的降解微生物和功能酶。

3.1 PHA 的降解微生物

降解 PHA 的菌种多样, 已在多种环境中被分离出来。约 90% 能够降解淀粉的微生物具有降解短链 PHA 的能力, 但不能降解大分子量和复杂的中长链 PHA^[5]。Tseng 等^[66]对大约 341 株嗜热放线菌在 50 °C 条件下进行筛选, 其中有 31 株可同时分解 PHB、PCL 和 PES, 这些菌株属于小双孢菌属 (*Microbispora*) (25.8%)、马杜拉

表 2 生物可降解塑料的降解微生物和功能酶

Table 2 Strains and enzymes with the potential to degrade biodegradable plastics

Enzymes	Strains	Properties	Source	Types of plastic degraded	References	
Lipase	<i>Acidovorax delafieldii</i> BS-3	Gram-negative bacterium; 30 °C ^a	Soil	PBS, PBSA	[41]	
	<i>Aspergillus niger</i> MTCC 2594	Fungus; pH 7.0, 37 °C	–	PLA, PCL	[42]	
	<i>Burkholderia cepacia</i> PBSA-1	Gram-negative bacterium; 37 °C ^a	Activated sludge	PBSA	[43]	
	<i>Burkholderia</i> sp.	Gram-negative bacterium; pH 8.0, 30 °C ^a	–	PCL	[44]	
	<i>Lactobacillus plantarum</i> MTCC 4461, <i>Lactobacillus brevis</i> MTCC 4460, and their co-culture	Gram-positive bacterium; pH 8.1, 37 °C ^a	–	PCL	[35]	
	<i>Paenibacillus amylolyticus</i> TB-13	Gram-positive bacterium; pH 10.0, 50 °C	Soil	PDLLA, PBS, PBSA, PCL; not degrade PHBV	[45]	
	<i>Pseudomonas aeruginosa</i> PBSA-2	Aerobic, Gram-negative bacterium; 37 °C ^a	Cultivating soil	PBSA	[43]	
	<i>Pseudomonas</i> sp.	Aerobic, Gram-negative bacterium; pH 7.0, 35 °C ^a	–	PTC	[37]	
	<i>Pseudomonas</i> sp. DS04-T	Aerobic, Gram-negative bacterium; pH 8.0, 50 °C	Activated sludge	PLLA	[46]	
	<i>Rhizopus arrhizus</i>	Fungus; pH 7.0, 30 °C ^a	–	PLLA, PCL	[47]	
	<i>Rhizopus arrhizus</i>	Fungus; pH 5.6, 37 °C ^a	–	PEC, PEPC	[36]	
	<i>Rhizopus oryzae</i>	Fungus; pH 8.0, 30 °C ^a	–	PCL	[44]	
	<i>Sphingobacterium</i> sp. S2	Gram-negative bacterium; pH 6.0, 40 °C	Compost	PLA	[48]	
	<i>Streptomyces</i> sp. SCM_MKPN-8	Gram-positive bacterium; pH 7.0, 30 °C ^a	Agricultural soil	PLA, PBS	[49]	
	Esterase	<i>Alcanivorax borkumensis</i> ABO2449	Aerobic, Gram-negative bacterium; pH 9.5–10, 30–37 °C	Seawater and marine sediments	PDLLA, PCL, PHBV, PBSA, PES; not degrade PHB, PBS, PDLA, PLLA	[28]
		<i>Bacillus sinithii</i> PL 21	Gram-positive bacterium; pH 5.5, 60 °C	Compost	PLLA	[50]
		<i>Brevundimonas</i> sp. MRL-AN ₁	Aerobic, Gram-negative bacterium; pH 6.0–8.0, 30–37 °C	Soil	PCL, PES, PLA, PHB, PHBV	[51]
		<i>Candida cylindracea</i>	Gram-positive bacterium; pH 7.0, 35 °C ^a	–	PTC	[37]
<i>Leptothrix</i> sp. TB-71		Aerobic, Gram-negative bacterium; 30 °C ^a	Soil and freshwater	PBSA, PCL, PES; not degrade PLA, PBS, PHBV	[52]	
<i>Ralstonia</i> sp. MRL-TL		Aerobic, Gram-negative bacterium; pH 7.0, 50 °C	Hot spring	PCL, PES, PLLA, PHB, PHBV	[53]	
<i>Rhodospseudomonas palustris</i> RPA1511		Gram-negative bacterium; pH 9.5–10, 55–60 °C	–	PDLLA, PCL, PBSA; not degrade PHB, PHBV, PBS, PES, PDLA, PLLA	[28]	
<i>Roseateles depolymerans</i> TB-87		Aerobic, Gram-negative bacterium; pH 9.0, 30 °C	Freshwater	PBS, PBSA, PCL, PBST; not degrade PLA	[32]	
	<i>Thermobifida alba</i> AHK119	Gram-positive bacterium; pH 6.0, 45–55 °C	Compost	PBSA, PBAT, PCL	[54]	

(待续)

(续表 2)

Enzymes	Strains	Properties	Source	Types of plastic degraded	References
Cutinase	<i>Aspergillus oryzae</i> RIB40	Fungus; pH 9.0, 35–55 °C		PBS, PBSA	[55]
	<i>Clostridium</i> sp.	Anaerobic, Gram-positive bacterium; pH 7.0, 35 °C ^a	Anaerobic sewage sludge	PCL	[56]
	<i>Cryptococcus</i> sp. S-2	Yeast; pH 8.0, 30 °C ^a	Air	PLA, PBS, PCL, PHB	[44]
	<i>Fusarium moniliforme</i>	Fungus; pH 9.0–10.0; 22 °C ^b	–	PCL	[34]
	<i>Fusarium solani</i> wild-type strains 77-2-3 and ATCC 38136	Fungus; pH 9.0–10.0, 22 °C ^b	–	PCL	[34]
	<i>Thermobifida fusca</i> DSM 43793	Gram-positive bacterium; pH 6.0–7.0, 65–70 °C		PBAT, PCL; not degrade PHB	[57]
Protease	<i>Actinomadura keratinolytica</i> T16-1	Gram-positive bacterium; pH 10.0, 70 °C	Forest soil	PLLA, PDLLA	[58-59]
	<i>Amycolatopsis</i> sp. SCM_MK2-4	Gram-positive bacterium; pH 7.0, 30 °C ^a	Agricultural soil	PLA, PCL	[49]
	<i>Amycolatopsis</i> sp. SCM_MK3-3	Gram-positive bacterium; pH 7.0, 30 °C ^a	Agricultural soil	PLA	[49]
	<i>Laceyella sacchari</i> LP175	Aerobic, Gram-positive bacterium; pH 9.0, 60 °C	Forest soil	PLLA	[60]
	<i>Streptomyces</i> sp. SCM_MKPN-9	Gram-positive bacterium; pH 7.0, 30 °C ^a	Agricultural soil	PLA, PBS	[49]
	<i>Tritirachium album</i> Limber	Fungus; pH 8.0, 30 °C ^a	–	PLLA, PDLLA	[44]
PHA depolymerases	<i>Aspergillus fumigatus</i> 76T-3	Fungus; pH 6.4, 55 °C	Soil of hot springs	PHB, PES, PBS	[61]
	<i>Bacillus</i> sp. IBP-VN2;	Natural seawater; pH 7.0–7.5, 27–30 °C ^a	Tropical coastal waters	PHB, PHBV	[62]
	<i>Enterobacter</i> sp. IBP-VN				
	<i>Enterobacter</i> sp. IBP-VN1;				
	<i>Enterobacter</i> sp. IBP-VN4;				
	<i>Enterobacter</i> sp. IBP-VN5;				
	<i>Gracilibacillus</i> sp. IBP-VN3				
	<i>Clostridium botulinum</i>	Anaerobic, Gram-positive bacterium; pH 6.8, 37 °C ^b	Anaerobic sewage sludge	PHB, PHBV	[56]
	<i>Pseudomonas fluorescens</i> GK13	Aerobic, Gram-negative bacterium; pH 9.5, 40 °C	Activated sludge	PHO	[63]
	<i>Pseudomonas lemoignei</i> LMG 2207	Aerobic, Gram-negative bacterium; pH 8.0, 37 °C ^b	Soil, compost	PHB, PHV	[64]
<i>Streptomyces</i> sp. AF-111	Aerobic, Gram-positive bacterium; pH 7.0–8.0, 35–55 °C	Sewage sludge treatment plant	PHBV	[65]	
SAO and BDH	<i>Pseudomonas</i> sp.	Aerobic, Gram-negative bacterium; pH 7.0, 30 °C ^a	–	PVA	[38]
PVA-DH	<i>Alcaligenes faecalis</i> KK314	Gram-negative bacterium; pH 7.5, 30 °C ^a	River water	PVA	[39]
	<i>Sphingopyxis</i> sp. 113P3	Gram-negative bacterium; pH 7.2, 37 °C	Activated sludge	PVA	[40]

a: the experimental conditions for the activity of the enzyme; b: pH and temperature are optimum condition and experimental condition for the activity of the enzyme, respectively. The others are the optimal conditions for the activity of the enzyme.

放线菌属 (*Actinomadura*) (12.9%)、高温放线菌属 (*Thermoactinomyces*) (9.7%)、链霉菌属 (*Streptomyces*) (48.4%) 和糖单孢菌属 (*Saccharomonospora*) (3.22%)。与好氧降解相比, PHB 和 PHBV 的厌氧降解更快。Abou-Zeid 等^[56]鉴定出 2 株降解 PHB 和 PHBV 的菌株, 它们与肉毒杆菌 *Clostridium botulinum* 的 16S rRNA 表现出 94.9% 的序列同源性。当以分离的单一菌株作为接种物时, 37 °C 条件下经 75 h 降解, PHB 粉在不控制 pH 时, pH 会由 7.0 下降至 4.8, 而降解率停留在 75%; 若控制 pH 维持在 6.8 左右, 约 90% 的 PHB 粉在 50 h 内被降解。此结果说明, 若以单一菌株作为接种物, 系统的稳定性较难维持。此外, 真菌也可降解 PHA, 包括子囊菌门 Ascomycota、接合菌亚门 Zygomycotina、担子菌纲 Basidiomycetes 和半知菌纲 Deuteromycetes^[5]。Kim 等^[67]通过在 28、37 和 60 °C 条件下开展实验, 分离来自农场土壤和活性污泥的多株 PHB 降解真菌, 其中烟曲霉 (*Aspergillus fumigatus*) LAR 9 分布最广, 在 3 个温度下均可降解 PHB; 筒青霉 (*Penicillium simplicissimum*) LAR 13 对 PHB 的降解率最高, 27 °C 条件下经 28 d 降解后, 降解率达到 64.5%。

3.2 PLA 的降解微生物

PLA 降解微生物大多来自芽胞杆菌科 (Bacillaceae)、小单孢菌科 (Micromonosporaceae)、假诺卡氏科 (Pseudonocardiaceae)、链孢囊菌科 (Streptosporangiaceae)、高温放线菌科 (Thermoactinomycetaceae) 和高温单孢菌科 (Thermomonosporaceae)^[68]。Satti 等^[68]从堆肥中分离出了 4 株 PLA 水解菌 (金黄杆菌 (*Chryseobacterium* sp.) S1、鞘氨醇杆菌 (*Sphingobacterium* sp.) S2、铜绿假单胞菌 (*Pseudomonas aeruginosa*) S3 和 S4), 它们在中温条件下对 PLA 具有较高的降解率。此研究证

明了在 30 °C 左右的中温条件下, 微生物对 PLA 的解聚作用。其中 *Sphingobacterium* sp. S2 表现出脂肪酶活性, 此酶的最高比活性达 260 U/mg^[48], 在土壤中额外投加此菌株后, 显示出对 PLA 膜矿化率的显著增加^[69]。Hajjighasemi 等^[28]报道了来自泊库岛食烷菌 (*Alcanivorax borkumensis*) ABO2449 和沼泽红假单胞菌 (*Rhodopseudomonas palustris*) RPA1511 菌株的 PDLA 降解活性酯酶。在 35 °C 条件的 36 h 内, RPA1511 的活性酯酶对 PDLA 的降解率达到 40%, 而 ABO2449 对 PDLA 的降解率高达 90%。Hanphakphoom 等^[60]从来自森林土壤的嗜热放线菌高温放线糖莱斯菌 (*Laceyella sacchari*) LP175 中证明了 PLA 降解蛋白酶对 PLLA 降解的促进作用, 此酶的比活性高达 328 U/mg。此外, 真菌被证明具有分解 PLA 的能力。来自隐球菌 (*Cryptococcus* sp.) S2 的纯化角质酶可有效降解 PLA 和其他聚酯, 如 PBS 和 PCL。在 30 °C 条件下, 此酶分别在 60、5 和 30 h 内将 PLA、PBS 和 PCL 降解完全, 但在该条件下, PHB 仅部分降解^[44]。

3.3 二元酸二元醇共聚酯的降解微生物

对于二元酸二元醇共聚酯系列 (PBS、PBSA、PBAT 等), 不含芳香单元的 PBS 和 PBSA 的降解性能明显优于含芳香单元的共聚酯。Hayase 等^[31]从土壤中分离的短小芽胞杆菌 (*Bacillus pumilus*) 1-A 菌株, 在 30 °C 条件下 14 d 内对 PBS 的降解率达到 90%, 对 PBSA 的降解率高达 100%, 而对 PBAT 的降解率不高 (4.8%)。Lee 等^[43]从活性污泥中分离出 2 株 PBSA 降解菌, 洋葱伯克霍尔德菌 (*Burkholderia cepacia*) PBSA-1 和 *Pseudomonas aeruginosa* PBSA-2。在 37 °C 条件下, 2 株菌株均通过产生脂肪酶使 PBSA 在 40 d 后达到 78% 的降解率。Nakajima-Kambe 等^[52]报道了来自纤毛菌 (*Leptothrix* sp.) TB-71 菌株的 PBSA 降解酯酶。在 30 °C 条件下,

3 d内该菌株对 PBSA 的降解率介于 96%–100% 之间,对 PES 的降解率达到 100%,5 d 内对 PCL 的降解率达到 43%。此外,通过琼脂平板的透明圈和液体培养基的澄清现象, Maeda 等^[55]证实了真菌米曲霉 (*Aspergillus oryzae*) RIB40 在 30 °C 条件下,5 d 内对 PBS 和 PBSA 的显著降解。从此真菌中分离纯化的角质酶对 PBS、PBSA 和 PLA 的比活性分别为 0.42 U/mg、11 U/mg 和 0.067 U/mg。此酶以醇和羧酸作为识别位点,对底物的亲和性取决于碳链长度。

对于脂肪族芳香族共聚酯, Shah 等^[32]从淡水中分离出 1 株脂肪族芳香族共聚酯分解菌, *Roseateles depolymerans* TB-87, 其产生的酯酶, 对 PBA、PBSA、聚对苯二甲酸-丁二酸丁二酯 (poly(butylene succinate-co-terephthalate), PBST) 和 PCL 等均具有分解作用。Kleeberg 等^[70]从高温堆肥中分离出 20 多株脂肪族芳香族共聚酯降解菌株,嗜热放线菌发挥了突出作用,似乎主导最初的降解步骤,其中菌株褐色热单孢菌 (*Thermomonospora fusca*) K13g 和 K7a-3 对共聚酯的降解率比普通堆肥微生物高 20 倍。Kleeberg 等^[57]从褐色嗜热裂孢菌 (*Thermobifida fusca*) DSM 43793 (曾用名: *Thermomonospora fusca* DSM 43793) 中纯化出具有高度脂肪族芳香族共聚酯水解活性的嗜热水解酶,该酶在 pH 6.0–7.0, 温度 65–70 °C 时活性最高,酶的特性介于酯酶和脂肪酶之间,可能是一种角质酶。Witt 等^[71]利用上述菌株 *Thermomonospora fusca* DSM 43793 在 55 °C 条件下开展降解实验, PBAT 在 22 d 内的降解率高达 99.9%。此外,真菌也参与 PBAT 的降解。Trinh 等^[72]在中温条件下 (30 °C) 评估了 29 种细菌和真菌对 PBAT 的降解效果,这些菌株大多分离自土壤。降解 21 d 后,2 株细菌 (枯草芽孢杆菌 (*Bacillus subtilis*) ATCC 6051 和 ATCC 21332) 和 3 株真菌 (黑曲

霉 (*Aspergillus niger*) ATCC 16888、淡紫拟青霉 (*Paecilomyces lilacinus*) ATCC 200182 和嗜松青霉 (*Penicillium pinophilum*) ATCC 9644) 使共聚酯膜出现视觉变化。

3.4 PCL 的降解微生物

PCL 降解菌在自然界中存在较多, Khan 等^[35]报道称短乳杆菌 (*Lactobacillus brevis*) MTCC4460、植物乳杆菌 (*Lactobacillus plantarum*) MTCC4461 和它们的混合菌群可通过产生脂肪酶降解 PCL。37 °C 条件培养 10 d, PCL 膜的质量损失分别在 MTCC4461 的脂肪酶浓度为 5 mg/mL 以及 MTCC4460 和 MTCC4461 混合菌群的脂肪酶浓度为 10 mg/mL 时达到最高,为 60% 和 50%。从温泉水中分离的嗜热劳尔氏菌 (*Ralstonia* sp.) MRL-TL^[53] 和从土壤中分离的短波单胞菌 (*Brevundimonas* sp.) MRL-AN₁^[51] 可能通过生产 PCL 降解酯酶作用于 PCL。*Ralstonia* sp. MRL-TL 菌株在 50 °C 条件下,10 d 内降解了超过 60% 的 PCL 膜; *Brevundimonas* sp. MRL-AN₁ 菌株在 37 °C 条件下,10 d 内降解了超过 80% 的 PCL 膜。Abou-Zeid 等^[56]从厌氧污泥中分离了 2 株中温 PCL 降解菌,它们与 *Clostridium botulinum* 的 16S rRNA 表现出 91.7% 的序列同源性,可能是梭菌属新种,其分泌的 PCL 降解酶可能是角质酶,但降解速率不高,在 37 °C 条件下,最大降解速率仅 0.14 mg/周。Chua 等^[73]从土壤中分离了嗜热菌株热紫链霉菌 (*Streptomyces thermoviolaceus* subsp. *thermoviolaceus*) 76T-2, 并从培养基上清液中纯化出 2 种 PCL 解聚酶,其中 1 种具有几丁质酶活性。在 40–50 °C 温度范围内, PCL 可在 6 h 内被纯化的 76T-2 菌株完全降解。真菌在 PCL 的降解中显示出重要作用。真菌菌株粉红螺旋聚孢霉 (*Clonostachys rosea*) 16G^[74] 和草酸青霉 (*Penicillium oxalicum*) DSYD05 及其突变株

DSYD05-1^[75]均表现出对 PCL 的分解潜力。在 28 °C 条件下, *Clonostachys rosea* 16G 菌株对 PCL 膜的降解率在 30 d 内达到 52.91%, 对淀粉基购物袋的降解率在 16 d 内达到 100%。而 *Penicillium oxalicum* DSYD05-1 的解聚酶具有广泛的底物特异性, 除 PCL 外, 还可降解 PHB 和 PBS, 但不能降解 PLA, 在 28 °C 条件下, 该菌株在 9 d 内对 PCL 薄膜降解完全, 降解过程分为 3 个阶段, 在第 1 阶段, 薄膜质量缓慢下降; 第 2 阶段, 薄膜的降解速度迅速增加, 薄膜快速失重可能与 PCL 无定形区域的快速降解有关; 在最后一个阶段, 质量下降放缓, 可能是由于剩余的结晶区降解较慢。

3.5 PVA 的降解微生物

降解 PVA 的菌种大多是假单胞菌属 (*Pseudomonas*) 或鞘氨醇单胞菌属 (*Sphingomonas*), 还包括其他一些革兰氏阴性细菌 (*Alcaligenes faecalis* 和 γ -变形菌门 γ -proteobacteria)、革兰氏阳性细菌 (巨大芽孢杆菌 (*Bacillus megaterium*)、解淀粉类芽孢杆菌 (*Paenibacillus amylolyticus*)、微杆菌 (*Microbacterium barkeri*) 和委内瑞拉链霉菌 (*Streptomyces venezuelae*) 和真菌 (分解木质素的白腐菌和褐腐菌、青霉菌)^[38]。根据代谢过程中的主要水解酶, 产生 SAO 的菌种包括 *Pseudomonas* sp. O-3、泡囊假单胞菌 (*Pseudomonas vesicularis*) PD、*Pseudomonas* sp. VM15C 和 *Sphingopyxis* sp. PVA3; 产生 PVA-DH 的菌种有 *Pseudomonas* sp. VM15C、*Sphingopyxis* sp. 113P3 和 *Alcaligenes faecalis* KK314^[38]。

目前分离出部分具备高效降解生物可降解塑料的功能微生物和功能酶, 但在产品生产和废弃物处理处置过程中, 实际应用的案例较少, 应重视对降解功能微生物和功能酶的开发应用, 通过生物强化等手段, 提高生物可降解塑料的分解速率和程度, 减轻环境压力。

4 生物可降解塑料在不同环境条件下的降解

生物可降解塑料的降解与微生物的种类和数量以及温度、湿度、氧含量、pH 值、降解持续时间、紫外辐射等环境因素有关^[2,76-77]。在一定温度范围内, 酶活性会随温度的升高而增强, 合适的湿度和 pH 是微生物生存的关键, 含氧量决定了微生物的种类。例如, PBAT 仅可在好氧条件下达到较高的降解率^[78], 而 PLA 在较高的温度下进行非生物水解降低分子量后进而开始生物降解^[77,79]。生物可降解塑料种类繁多, 降解环境多变, 降解条件复杂, 影响因素众多, 系统归纳总结生物可降解塑料在好氧堆肥、淡水、海水、厌氧和土壤环境中的降解周期和程度对其使用后的处理处置具有重要意义。

4.1 生物可降解塑料在好氧堆肥条件下的降解

生物可降解塑料的好氧堆肥分为家庭堆肥和工业堆肥, 分别采用 (28±2) °C 和 (58±2) °C。相对于家庭堆肥, 工业堆肥条件下微生物对生物可降解塑料的分解更加有效, 有利于提高其降解速率和程度。为了使微生物保持良好的生物活性, 需要为其生长繁殖提供适宜的条件, 如湿度 (50%–60%)、氧气浓度 (超过 5%) 和碳氮比 (20 : 1–40 : 1)。在低温好氧堆肥条件下 TPS 和 PCL 可在 3 个月内完成分解, 而 PLA、PBS 较难降解。升高温度有利于提高生物可降解塑料的分解速率, 高温条件下的降解性能: PHB>PCL>PLA>PBSA>PBS>PBAT。表 3 详细总结了生物可降解塑料在好氧堆肥条件下的降解情况。

4.2 生物可降解塑料在淡水和海水条件下的降解

在水体环境中, 因微生物的种类和数量、营养物质、温度、溶解氧量等存在较大差异,

生物可降解塑料的降解情况会有所不同, 评估生物可降解塑料在水体环境的降解情况相对复杂, 需要充分考虑上述影响因素。目前在水体条件下开展的生物可降解塑料的降解研究通常采用两种条件, 接种外源微生物和控制温度的受控条件以及不接种外源微生物和不控制温度的自然条件, 两种不同条件下生物可降解塑料的降解情况有明显差异, 相对于受控条件, 生物可降解塑料在缺乏营养物质和微生物的自然条件下降解速率通常较慢。在淡水条件下, TPS、PHA 和 PVA 可较快实现分解, PBS、PBSA

和 PPC 分解情况次之, PLA 较难分解。在海水条件下, TPS 和 PHA 可较快完成分解, PCL 和 PBS 次之, PLA 和 PBAT 较难分解。表 4 和表 5 详细总结了生物可降解塑料在淡水和海水条件下的降解情况。

4.3 生物可降解塑料在厌氧条件下的降解

在厌氧降解过程中, 生物可降解塑料主要通过胞外酶的作用使长链聚合物转化为低聚物和单体, 随后, 低聚物和单体进入细胞, 被胞内酶进一步分解。具有苯环的脂肪芳香族共聚酯在此条件下难以实现完全分解, 通过进一步

表 3 生物可降解塑料在好氧堆肥条件下的降解研究

Table 3 Degradation of biodegradable plastics in compost

Type	Shape	Conditions	Biodegradation period (d)	Biodegradation indicator	Biodegradability (%)	References
TPS	Film	28 °C, home composting	90	CO ₂ produced	90	[77]
PHA						
	Film (PHB)	58 °C, industrial composting	45	CO ₂ produced	100 ^a	[77]
	Film (PHB)	58 °C	110	CO ₂ produced	79.9	[80]
	Film (PHB)	55 °C, 70% humidity	28	CO ₂ produced	80	[81]
	Film (PHO)	28 °C, home composting	365	CO ₂ produced	22	[77]
	Film (PHO)	58 °C, industrial composting	124	CO ₂ produced	100 ^a	[77]
PLA	Film	28 °C, home composting	365	CO ₂ produced	<20	[77]
	Film	58 °C, industrial composting	75	CO ₂ produced	100 ^a	[77]
	Film	58 °C	8	Weight loss	100	[82]
	Film	55 °C, 70% humidity	28	CO ₂ produced	70	[81]
	Film	58 °C, 60% humidity	30	Weight loss	60	[83]
	Sheet	58 °C	120	CO ₂ produced	85.8	[84]
PBS	Film	28 °C, home composting	365	CO ₂ produced	<20	[77]
	Film	58 °C, industrial composting	207	CO ₂ produced	92 ^a	[77]
	Film	58 °C, 50%–55% humidity	90	CO ₂ produced	60.7	[85]
	Powder	58–65 °C, 50%–55% humidity	160	CO ₂ produced	90	[86]
PBSA	Film	58 °C, 50%–55% humidity	90	CO ₂ produced	92.1	[85]
PBAT	Film	58 °C, industrial composting	90	CO ₂ produced	50–60	[78]
	Sheet	58 °C	120	CO ₂ produced	23.7	[84]
PCL	Film	28 °C, home composting	88	CO ₂ produced	91	[77]
	Film	58 °C, industrial composting	45	CO ₂ produced	100 ^a	[77]

a: biodegradability is expressed based on the comparison with cellulose.

表 4 生物可降解塑料在淡水条件下的降解研究

Table 4 Degradation of biodegradable plastics in freshwater

Type	Shape	Conditions	Biodegradation period	Biodegradation indicator	Biodegradability	References
TPS	Film	21 °C	28 d	CO ₂ produced	94% ^a	[77]
PHA	Film (PHB)	21 °C	56 d	CO ₂ produced	90% ^a	[77]
	Film (PHB)	25 °C	365 d	Weight loss	8.5%	[87]
	Film (PHO)	21 °C	56 d	CO ₂ produced	51% ^a	[77]
PLA	Film	21 °C	56 d	CO ₂ produced	Not significant	[77]
	Film	25 °C	365 d	Weight loss	<2%	[87]
	Film	28 °C	21 d	Weight loss	4.5%	[88]
PBS	Film	21 °C	56 d	CO ₂ produced	3% ^a	[77]
	Film	25 °C	80 d	O ₂ consumed	31%	[89]
	Film	Before modification, inoculated with soil suspension	50 d	Weight loss	11%	[90]
	Film	After modification, inoculated with soil suspension	50 d	Weight loss	8%	[90]
PBSA	Film	Before modification, inoculated with soil suspension	50 d	Weight loss	16%	[90]
	Film	After modification, inoculated with soil suspension	50 d	Weight loss	9%	[90]
PCL	Film	30 °C	28 d	Weight loss	7.6%	[91]
	Film	21 °C	56 d	CO ₂ produced	52% ^a	[77]
	Film	25 °C	365 d	Weight loss	<2%	[87]
PPC	Film	28 °C	21 d	Weight loss	9.5%	[88]
PVA	Wastewater containing PVA	20–25 °C, biological aerated filter	24 h (HRT ^b)	PVA removal	64.4%	[92]
	Wastewater containing PVA	20–25 °C, biocontact oxidation reactor	30 h (HRT)	PVA removal	74.5%–81.3%	[92]
	Wastewater containing PVA	25 °C, aerobic membrane bioreactor	9 h (HRT)	PVA removal	100%	[92]

a: biodegradability is expressed based on the comparison with cellulose; b: hydraulic retention time (HRT).

的好氧处理或将消化物施用于土壤，可实现最终的生物分解。厌氧消化产生的 CH₄ 可被集中收集，作为清洁能源高效利用，且沼液残渣可作为有机肥料用于农业生产，相对于好氧降解有更多优势。在中温厌氧消化条件下，TPS 和短链 PHA 可在较短的时间内完成降解，降解性

能：PHB>TPS>PHBV>PVA，PLA、PCL、PBS 和 PBAT 较难分解；高温厌氧条件对生物可降解塑料的降解更加有效，PLA 和 PCL 的降解速率加快，而 PBS 和 PBAT 依旧较难降解，降解速率：PHB>TPS>PLA>PCL。表 6 详细总结了生物可降解塑料在厌氧条件下的降解情况。

表 5 生物可降解塑料在海水条件下的降解研究

Table 5 Degradation of biodegradable plastics in seawater

Type	Shape	Conditions	Biodegradation period (d)	Biodegradation indicator	Biodegradability	References
TPS	Film	30 °C	28	CO ₂ produced	92% ^a	[77]
PHA	Film (PHB)	30 °C	43	CO ₂ produced	89% ^a	[77]
	Film (PHB)	25 °C	14	BOD removal	80%	[93]
	Film (PHB)	21 °C, static incubation	49	Weight loss	99%	[94]
	Film (PHB)	12–22 °C, dynamic incubation	90	Weight loss	30%	[94]
	Film (PHBV)	21 °C, static incubation	49	Weight loss	99%	[94]
	Film (PHBV)	12–22 °C, dynamic incubation	90	Weight loss	30%	[94]
	Film (PHO)	30 °C	56	CO ₂ produced	38% ^a	[77]
	PLA	Film	30 °C	56	CO ₂ produced	7% ^a
Film		25 °C	365	Weight loss	<2%	[87]
Sheet		Natural seawater	364	Weight loss	Not significant	[95]
PBS	Film	30 °C	56	CO ₂ produced	21% ^a	[77]
	Sheet	Natural seawater	364	Weight loss	<2%	[95]
PBAT	Sheet	Natural seawater	364	Weight loss	<2%	[95]
PCL	Film	25 °C	365	Weight loss	<2%	[87]
	Film	30 °C	56	CO ₂ produced	80% ^a	[77]
	Film	25 °C	70	Weight loss	25%	[96]
	Sheet	Natural seawater	364	Weight loss	32%	[95]

a: biodegradability is expressed based on the comparison with cellulose.

表 6 生物可降解塑料在厌氧条件下的降解研究

Table 6 Degradation of biodegradable plastics under anaerobic conditions

Type	Shape	Conditions	Biodegradation period (d)	Biodegradation indicator	Biodegradability	References
TPS	Film	35 °C, aqueous anaerobic	56	Biogas produced	99% ^a	[77]
	Film	52 °C, high-solids anaerobic	127	Biogas produced	73%	[77]
PHA	Film (PHB)	35 °C, aqueous anaerobic	56	Biogas produced	100% ^a	[77]
	Film (PHB)	37 °C	70	Weight loss	23%	[56]
	Film (PHB)	37 °C, incubated sludge	9	Weight loss, biogas produced	100%, 100% ^c	[56]
	Powder (PHB)	35 °C, untreated	40	Biogas produced	67%	[97]
	Powder (PHB)	35 °C, alkaline-thermal pretreated	40	Biogas produced	91%	[97]
	Powder (PHB)	37 °C	9	Biogas produced	90%	[98]
	Film (PHB)	52 °C, high-solids anaerobic	127	Biogas produced	83%	[77]
	Powder (PHB)	55 °C	14	Biogas produced	90%	[99]
	Film (PHBV)	37 °C	70	Weight loss	22.5%	[56]
Film (PHBV)	37 °C, incubated sludge	42	Weight loss, biogas produced	60%, 29% ^c	[56]	

(待续)

(续表 6)

Type	Shape	Conditions	Biodegradation period (d)	Biodegradation indicator	Biodegradability	References
PLA	Film (PHO)	35 °C, aqueous anaerobic	56	Biogas produced	6.5% ^a	[77]
	Film (PHO)	52 °C, high-solids anaerobic	127	Biogas produced	5%	[77]
	Film	35 °C, aqueous anaerobic	56	Biogas produced	Not significant	[77]
	Film	35 °C	39	Biogas produced	8.6%	[100]
	Film	35 °C	28	Biogas produced	Not significant	[91]
	Powder	37 °C	277	Biogas produced	29%–49%	[98]
	Film	52 °C, high-solids anaerobic	80	Biogas produced	80%	[77]
	Powder	55 °C	75	Biogas produced	75%	[99]
	Powder	55 °C	60	Biogas produced	90%	[79]
	PBS	Film	35 °C, aqueous anaerobic	56	Biogas produced	Not significant
Film		35 °C	100	Biogas produced	2%	[89]
Film		52 °C, high-solids anaerobic	127	Biogas produced	12%	[77]
Film		Natural anaerobic landfill	90	Weight loss	Not significant	[89]
PBAT	Film	35 °C	39	Biogas produced	5.9%	[100]
	Film	37 °C	126	Biogas produced	2.2%	[101]
	Film	55 °C	126	Biogas produced	8.3%	[101]
PCL	Film	35 °C, aqueous anaerobic	56	Biogas produced	2.5% ^a	[77]
	Film	35 °C	28	Weight loss	Not significant	[91]
	Film	37 °C, methane sludge	70	Weight loss	7.6%	[56]
	Film	37 °C, sewage sludge	42	Weight loss, biogas produced	30%, 16% ^c	[56]
	Powder	37 °C	277	Biogas produced	3%–22%	[99]
	Film	52 °C, high-solids anaerobic	127	Biogas produced	85%	[77]
	Powder	55 °C	50	Biogas produced	80%	[99]
PVA	PVA-14 000 ^b	27 °C, river sediment	125	TOC ^d removal	60%	[102]
	PVA-2 000 ^b	27 °C, river sediment	125	TOC removal	85%	[102]
	PVA-14 000 ^b	27 °C, anaerobically treated activated sludge	175	TOC removal	60%	[102]
	PVA-2 000 ^b	27 °C, anaerobically treated activated sludge	175	TOC removal	35%	[102]
	Wastewater containing PVA	32–34 °C, anaerobic baffle reactor	2 (HRT)	PVA removal	80%	[92]

a: biodegradability is expressed based on the comparison with cellulose; b: 14 000 and 2 000 represent the number-average molecular weight of PVA; c: biodegradability is expressed as weight loss and produced biogas, respectively; d: total organic carbon (TOC).

4.4 生物可降解塑料在土壤条件下的降解

生物可降解塑料可被土壤中的多种微生物分解,如芽孢杆菌属、假单胞菌属、链球菌属和葡萄球菌属^[2],其降解情况受土壤条件的影响,如土壤中的微生物种类和数量、土壤含水率和土壤酸碱度。此外,当大量生物可降解塑料投加到土壤中时,生物分解过程会消耗土壤中的氧气,产生代谢产物,对土壤环境造成干扰。TPS、短链 PHA、PCL 和 PPC 可在土壤条件下较快分解,降解性能: PHB>TPS>PCL>PPC, PLA、PBS 和 PBAT 分解较慢。表 7 详细总结了生物

可降解塑料在土壤条件下的降解情况。

综上所述,生物可降解塑料降解条件复杂,影响因素众多,在不同环境条件下的分解情况存在较大差异。此外,由于实验条件、环境、操作和接种物等的不同,生物可降解塑料的降解情况在文献报道中也存在一定差别,难以对它们进行明确的比较衡量。综合看来,除 TPS 和 PHB 外,生物可降解塑料在自然和受控条件下分解速率依旧较慢,较难实现彻底分解,随意丢弃到自然环境将引发环境积累问题,生物可降解塑料的处理处置问题可能制约行业发展。未来需要

表 7 生物可降解塑料在土壤条件下的降解研究
Table 7 Degradation of biodegradable plastics in soil

Type	Shape	Conditions	Biodegradation period (d)	Biodegradation indicator	Biodegradability	References
TPS	Film	25 °C	136	CO ₂ produced	95.5% ^a	[77]
PHA	Film (PHB)	25 °C	136	CO ₂ produced	100% ^a	[77]
	Film (PHB)	Natural soil	180	Weight loss	64.3%	[103]
	Film (PHB)	Natural soil, 15 cm depth	365	Weight loss	98%, 46% ^b	[104]
	Pellet (PHB)	Natural soil, 15 cm depth	365	Weight loss	55%, 28% ^b	[104]
	Film (PHBV)	Natural soil, 15 cm depth	365	Weight loss	61%, 14% ^b	[104]
	Pellet (PHBV)	Natural soil, 15 cm depth	365	Weight loss	35%, 8% ^b	[104]
	Film (PHO)	25 °C	136	CO ₂ produced	6% ^a	[77]
	PLA	Film	25 °C	136	CO ₂ produced	Not significant
Sheet		30% humidity	98	Weight loss	10%	[105]
Powder		25 °C, 60% humidity	28	Total soil carbon removal	13.8%	[106]
Powder		25 °C, 60% humidity	28	Weight loss	Not significant	[106]
PBS	Film	25 °C	136	CO ₂ produced	Not significant	[77]
	Film	25 °C, 60% humidity	28	Weight loss	1.2%	[106]
	Powder	25 °C, 60% humidity	28	Total soil carbon removal	16.8%	[106]
PBAT	Film	27 °C	365	CO ₂ produced	20%–30%	[78]
PCL	Film	25 °C	136	CO ₂ produced	92% ^a	[77]
	Film	28 °C, 60% humidity, soil and landfill leachate	60	Weight loss	89.7%	[107]
	Film	28 °C, 60% humidity, soil	60	Weight loss	22%	[107]
PPC	Film	Natural soil, 15 cm depth	150	Weight loss	39.7%	[108]

a: biodegradability is expressed based on the comparison with cellulose; b: biodegradability in two tropical soils with different weather conditions and microbial communities.

重视生物可降解塑料的降解研究,采用生物强化、预处理等措施突破其降解慢的瓶颈,为实现生物可降解塑料的快速彻底降解寻找出路。

5 讨论与展望

中国作为塑料生产和消费第一大国,塑料废弃物处理压力巨大,以PE、PP为代表的传统塑料在自然条件下极难分解,对生态环境构成严重威胁。研发、制备和应用生物可降解塑料是促进生态、经济与社会可持续发展的必然要求,具有广阔的发展潜力和市场空间。然而,目前对于生物可降解塑料的研究大多集中在改善其机械性能和加工性能方面,而关注降解的系统研究或详细综述较少。

迄今为止,研究人员已筛选出一些高效降解生物可降解塑料的功能微生物并纯化出功能酶,评估了生物可降解塑料在不同环境条件下的降解性能,但对于生物可降解塑料的研究仍存在以下问题:(1)多数生物可降解塑料降解速率缓慢,难以满足目前资源化处理技术(好氧堆肥、厌氧消化)对降解周期的要求,制约行业发展,生物可降解塑料的降解速率和程度亟待提高。(2)虽然目前筛选出了多株生物可降解塑料降解功能菌并纯化了功能酶,但大多停留在实验室开发阶段,使用功能微生物和功能酶对降解过程进行生物强化的案例较少。(3)针对生物可降解塑料在自然和受控条件下的降解研究文献不多,所用方法和条件各异,造成报道的结果差别较大,对生物可降解塑料的科学应用不利。此外,共混改性的生物可降解塑料以及其内部的化学添加剂,如增容剂、扩链剂、增塑剂、阻燃剂、杀菌剂、色素等对降解的影响也有待深入研究。(4)标准规范亟待完善。目前有关部门大多仅采用好氧堆肥标准作为决定生物可降解塑料能否上市的仲裁标准,因此生

物可降解塑料在其他环境条件下的降解性能难以有效保障,无法合理制定废弃物的处理处置策略。(5)生物可降解塑料价格相对昂贵,机械性能不高。生物可降解塑料的价格普遍高于传统PE塑料,如何在保证较高生物可降解性能的前提下,降低生产成本、提升机械性能,需要深入研究,不同材质的生物可降解塑料产品需要进一步研究和开发。

针对上述问题,可从以下几个方面开展研究:(1)针对生物可降解塑料降解缓慢的问题,一方面可从产品入手,在生产过程中添加功能酶或真菌孢子,当生物可降解塑料废弃后,酶或真菌在合适的湿度、温度、含氧量等条件下发挥作用;另一方面针对废弃生物可降解塑料的处理处置过程,通过投加适合该环境条件的功能微生物或复合菌系进行生物强化,有利于实现高效彻底降解。(2)重视生物可降解塑料的降解研究,在同一工作条件下开展系统实验,对不同生物可降解塑料的降解性能进行科学评价和全面比较,完全掌握生物可降解塑料的降解规律及特点,明确添加剂对其降解的影响,合理运用添加剂。(3)对于生物可降解塑料产品,上市前应参照标准充分评估其在不同环境下的降解性能,并明确标注降解的环境条件,为其废弃后的处理处置提供建议和指导,减少环境积累,有关部门应参照国家标准严格把控产品质量,规范市场准入。(4)深入研究生物可降解塑料的改性方法和加工技术,提升生物可降解塑料的机械性能;研发原料生产新方法,提高技术和制造成熟度,降低生物可降解塑料生产成本。对生物可降解塑料的降解机理和降解程度的系统掌握,将为生物可降解塑料废弃物的高效处理处置和彻底降解提供科学指导,推动生物可降解塑料制品全面而广泛的应用。

REFERENCES

- [1] Geyer R, Jambeck JR, Law KL. Production, use, and fate of all plastics ever made. *Sci Adv*, 2017, 3(7): e1700782.
- [2] Folino A, Karageorgiou A, Calabrò PS, et al. Biodegradation of wasted bioplastics in natural and industrial environments: a review. *Sustainability*, 2020, 12(15): 6030.
- [3] Satti SM, Shah AA. Polyester-based biodegradable plastics: an approach towards sustainable development. *Lett Appl Microbiol*, 2020, 70(6): 413-430.
- [4] 严海彪, 胡慧, 金科. 淀粉基塑料制备与降解性能的现状与进展. *塑料*, 2020, 49(5): 96-101.
Yan HB, Hu H, Jin K. Progress in preparation and degradation of starch-based plastics. *Plastics*, 2020, 49(5): 96-101 (in Chinese).
- [5] Meereboer KW, Misra M, Mohanty AK. Review of recent advances in the biodegradability of polyhydroxyalkanoate (PHA) bioplastics and their composites. *Green Chem*, 2020, 22(17): 5519-5558.
- [6] Turco R, Santagata G, Corrado I, et al. *In vivo* and *post-synthesis* strategies to enhance the properties of PHB-based materials: a review. *Front Bioeng Biotechnol*, 2020, 8: 619266.
- [7] Hobbs SR, Parameswaran P, Astmann B, et al. Anaerobic codigestion of food waste and polylactic acid: effect of pretreatment on methane yield and solid reduction. *Adv Mater Sci Eng*, 2019, 2019: 4715904.
- [8] Nofar M, Sacligil D, Carreau PJ, et al. Poly(lactic acid) blends: processing, properties and applications. *Int J Biol Macromol*, 2019, 125: 307-360.
- [9] Xu J, Guo BH. Poly(butylene succinate) and its copolymers: research, development and industrialization. *Biotechnol J*, 2010, 5(11): 1149-1163.
- [10] Puchalski M, Szparaga G, Biela T, et al. Molecular and supramolecular changes in polybutylene succinate (PBS) and polybutylene succinate adipate (PBSA) copolymer during degradation in various environmental conditions. *Polymers*, 2018, 10(3): 251.
- [11] 张婷, 张彩丽, 宋鑫宇, 等. PBAT 薄膜的制备及应用研究进展. *中国塑料*, 2021, 35(7): 115-125.
Zhang T, Zhang CL, Song XY, et al. Research progress in preparation and applications of PBAT films. *China Plast*, 2021, 35(7): 115-125 (in Chinese).
- [12] Mahmoud Salehi AO, Heidari Keshel S, Sefat F, et al. Use of polycaprolactone in corneal tissue engineering: a review. *Mater Today Commun*, 2021, 27: 102402.
- [13] 刘小文, 潘莉莎, 徐鼎, 等. 聚碳酸亚丙酯共混改性研究进展. *化工进展*, 2010, 29(5): 901-908, 975.
Liu XW, Pan LS, Xu N, et al. Advances in blending of poly(propylene carbonate). *Chem Ind Eng Prog*, 2010, 29(5): 901-908, 975 (in Chinese).
- [14] Aslam M, Kalyar MA, Raza ZA. Polyvinyl alcohol: a review of research status and use of polyvinyl alcohol based nanocomposites. *Polym Eng Sci*, 2018, 58(12): 2119-2132.
- [15] 张敬勋. 聚碳酸亚丙酯在膜制品中的应用研究[D]. 青岛: 青岛科技大学, 2017.
Zhang JX. Application research of poly(propylene carbonate) for film products[D]. Qingdao: Qingdao University of Science & Technology, 2017 (in Chinese).
- [16] Kasirajan S, Ngouajio M. Polyethylene and biodegradable mulches for agricultural applications: a review. *Agron Sustain Dev*, 2012, 32(2): 501-529.
- [17] Haider TP, Völker C, Kramm J, et al. Plastics of the future? The impact of biodegradable polymers on the environment and on society. *Angew Chem Int Ed Engl*, 2019, 58(1): 50-62.
- [18] Elsayy MA, Kim KH, Park JW, et al. Hydrolytic degradation of polylactic acid (PLA) and its composites. *Renew Sustain Energy Rev*, 2017, 79: 1346-1352.
- [19] Díaz A, Katsarava R, Puiggali J. Synthesis, properties and applications of biodegradable polymers derived from diols and dicarboxylic acids: from polyesters to poly(ester amide)s. *Int J Mol Sci*, 2014, 15(5): 7064-7123.
- [20] Shah AA, Hasan F, Hameed A, et al. Biological degradation of plastics: a comprehensive review. *Biotechnol Adv*, 2008, 26(3): 246-265.
- [21] Al-Itry R, Lamnawar K, Maazouz A. Improvement of thermal stability, rheological and mechanical properties of PLA, PBAT and their blends by reactive extrusion with functionalized epoxy. *Polym Degrad Stab*, 2012, 97(10): 1898-1914.
- [22] Ghosh SK, Pal S, Ray S. Study of microbes having potentiality for biodegradation of plastics. *Environ Sci Pollut Res*, 2013, 20(7): 4339-4355.
- [23] Numata K, Abe H, Doi Y. Enzymatic processes for biodegradation of poly(hydroxyalkanoate)s crystals. *Can J Chem*, 2008, 86(6): 471-483.
- [24] Tokiwa Y, Calabia BP. Review Degradation of microbial polyesters. *Biotechnol Lett*, 2004, 26(15): 1181-1189.

- [25] Kumar A, Gross RA, Jendrossek D. Poly(3-hydroxybutyrate)-depolymerase from *Pseudomonas lemoignei*: catalysis of esterifications in organic media. *J Org Chem*, 2000, 65(23): 7800-7806.
- [26] Reeve MS, McCarthy SP, Downey MJ, et al. Polylactide stereochemistry: effect on enzymic degradability. *Macromolecules*, 1994, 27(3): 825-831.
- [27] Jaeger KE, Steinbüchel A, Jendrossek D. Substrate specificities of bacterial polyhydroxyalkanoate depolymerases and lipases: bacterial lipases hydrolyze poly(*omega*-hydroxyalkanoates). *Appl Environ Microbiol*, 1995, 61(8): 3113-3118.
- [28] Hajighasemi M, Nocek BP, Tchigvintsev A, et al. Biochemical and structural insights into enzymatic depolymerization of polylactic acid and other polyesters by microbial carboxylesterases. *Biomacromolecules*, 2016, 17(6): 2027-2039.
- [29] Hamad K, Kaseem M, Yang HW, et al. Properties and medical applications of polylactic acid: a review. *Express Polym Lett*, 2015, 9(5): 435-455.
- [30] Kitakuni E, Yoshikawa K, Nakano K, et al. Biodegradation of poly(tetramethylene succinate-co-tetramethylene adipate) and poly(tetramethylene succinate) through water-soluble products. *Environ Toxicol Chem*, 2001, 20(5): 941-946.
- [31] Hayase N, Yano H, Kudoh E, et al. Isolation and characterization of poly(butylene succinate-co-butylene adipate)-degrading microorganism. *J Biosci Bioeng*, 2004, 97(2): 131-133.
- [32] Shah AA, Eguchi T, Mayumi D, et al. Purification and properties of novel aliphatic-aromatic co-polyesters degrading enzymes from newly isolated *Roseateles depolymerans* strain TB-87. *Polym Degrad Stab*, 2013, 98(2): 609-618.
- [33] Artham T, Doble M. Biodegradation of aliphatic and aromatic polycarbonates. *Macromol Biosci*, 2008, 8(1): 14-24.
- [34] Murphy CA, Cameron JA, Huang SJ, et al. *Fusarium* polycaprolactone depolymerase is cutinase. *Appl Environ Microbiol*, 1996, 62(2): 456-460.
- [35] Khan I, Ray Dutta J, Ganesan R. *Lactobacillus* sps. lipase mediated poly(ϵ -caprolactone) degradation. *Int J Biol Macromol*, 2017, 95: 126-131.
- [36] Zhou M, Takayanagi M, Yoshida Y, et al. Enzyme-catalyzed degradation of aliphatic polycarbonates prepared from epoxides and carbon dioxide. *Polym Bull*, 1999, 42(4): 419-424.
- [37] Suyama T, Tokiwa Y. Enzymatic degradation of an aliphatic polycarbonate, poly(tetramethylene carbonate). *Enzym Microb Technol*, 1997, 20(2): 122-126.
- [38] Kawai F, Hu XP. Biochemistry of microbial polyvinyl alcohol degradation. *Appl Microbiol Biotechnol*, 2009, 84(2): 227-237.
- [39] Matsumura S, Tomizawa N, Toki A, et al. Novel poly(vinyl alcohol)-degrading enzyme and the degradation mechanism. *Macromolecules*, 1999, 32(23): 7753-7761.
- [40] Klomklang W, Tani A, Kimbara K, et al. Biochemical and molecular characterization of a periplasmic hydrolase for oxidized polyvinyl alcohol from *Sphingomonas* sp. strain 113P3. *Microbiology (Reading)*, 2005, 151(pt 4): 1255-1262.
- [41] Uchida H, Shigeno-Akutsu Y, Nomura N, et al. Cloning and sequence analysis of poly(tetramethylene succinate) depolymerase from *Acidovorax delafieldii* strain BS-3. *J Biosci Bioeng*, 2002, 93(2): 245-247.
- [42] Nakajima-Kambe T, Edwinoliver NG, Maeda H, et al. Purification, cloning and expression of an *Aspergillus niger* lipase for degradation of poly(lactic acid) and poly(ϵ -caprolactone). *Polym Degrad Stab*, 2012, 97(2): 139-144.
- [43] Lee SH, Kim MN. Isolation of bacteria degrading poly(butylene succinate-co-butylene adipate) and their *lip A* gene. *Int Biodeterior Biodegrad*, 2010, 64(3): 184-190.
- [44] Masaki K, Kamini NR, Ikeda H, et al. Cutinase-like enzyme from the yeast *Cryptococcus* sp. strain S-2 hydrolyzes polylactic acid and other biodegradable plastics. *Appl Environ Microbiol*, 2005, 71(11): 7548-7550.
- [45] Akutsu-Shigeno Y, Teeraphatpornchai T, Teamtisong K, et al. Cloning and sequencing of a poly(DL-lactic acid) depolymerase gene from *Paenibacillus amylolyticus* strain TB-13 and its functional expression in *Escherichia coli*. *Appl Environ Microbiol*, 2003, 69(5): 2498-2504.
- [46] Wang ZY, Wang Y, Guo ZQ, et al. Purification and characterization of poly(L-lactic acid) depolymerase from *Pseudomonas* sp. strain DS04-T. *Polym Eng Sci*, 2011, 51(3): 454-459.
- [47] Tsuji H, Kidokoro Y, Mochizuki M. Enzymatic degradation of biodegradable polyester composites of poly(L-lactic acid) and poly(ϵ -caprolactone). *Macromol Mater Eng*, 2006, 291(10): 1245-1254.
- [48] Satti SM, Abbasi AM, Marsh TL, et al. Statistical optimization of lipase production from

- Sphingobacterium* sp. strain S2 and evaluation of enzymatic depolymerization of poly(lactic acid) at mesophilic temperature. *Polym Degrad Stab*, 2019, 160: 1-13.
- [49] Penkhruw W, Khanongnuch C, Masaki K, et al. Isolation and screening of biopolymer-degrading microorganisms from northern Thailand. *World J Microbiol Biotechnol*, 2015, 31(9): 1431-1442.
- [50] Sakai K, Kawano H, Iwami A, et al. Isolation of a thermophilic poly-L-lactide degrading bacterium from compost and its enzymatic characterization. *J Biosci Bioeng*, 2001, 92(3): 298-300.
- [51] Nawaz A, Hasan F, Shah AA. Degradation of poly(ϵ -caprolactone) (PCL) by a newly isolated *Brevundimonas* sp. strain MRL-AN₁ from soil. *FEMS Microbiol Lett*, 2015, 362(1): 1-7.
- [52] Nakajima-Kambe T, Toyoshima K, Saito C, et al. Rapid monomerization of poly(butylene succinate)-co-(butylene adipate) by *Leptothrix* sp.. *J Biosci Bioeng*, 2009, 108(6): 513-516.
- [53] Shah AA, Nawaz A, Kanwal L, et al. Degradation of poly(ϵ -caprolactone) by a thermophilic bacterium *Ralstonia* sp. strain MRL-TL isolated from hot spring. *Int Biodeterior Biodegrad*, 2015, 98: 35-42.
- [54] Hu XP, Thumarat U, Zhang X, et al. Diversity of polyester-degrading bacteria in compost and molecular analysis of a thermoactive esterase from *Thermobifida alba* AHK119. *Appl Microbiol Biotechnol*, 2010, 87(2): 771-779.
- [55] Maeda H, Yamagata Y, Abe K, et al. Purification and characterization of a biodegradable plastic-degrading enzyme from *Aspergillus oryzae*. *Appl Microbiol Biotechnol*, 2005, 67(6): 778-788.
- [56] Abou-Zeid DM, Müller RJ, Deckwer WD. Degradation of natural and synthetic polyesters under anaerobic conditions. *J Biotechnol*, 2001, 86(2): 113-126.
- [57] Kleeberg I, Welzel K, VandenHeuvel J, et al. Characterization of a new extracellular hydrolase from *Thermobifida fusca* degrading aliphatic-aromatic copolyesters. *Biomacromolecules*, 2005, 6(1): 262-270.
- [58] Sukkhum S, Tokuyama S, Tamura T, et al. A novel poly(L-lactide) degrading actinomycetes isolated from Thai forest soil, phylogenic relationship and the enzyme characterization. *J Gen Appl Microbiol*, 2009, 55(6): 459-467.
- [59] Panyachanakul T, Kitpreechavanich V, Tokuyama S, et al. Poly(DL-lactide)-degrading enzyme production by immobilized *Actinomadura keratinilytica* strain T16-1 in a 5-L fermenter under various fermentation processes. *Electron J Biotechnol*, 2017, 30: 71-76.
- [60] Hanphakphoom S, Maneewong N, Sukkhum S, et al. Characterization of poly(L-lactide)-degrading enzyme produced by thermophilic filamentous bacteria *Laceyella sacchari* LP175. *J Gen Appl Microbiol*, 2014, 60(1): 13-22.
- [61] Jung HW, Yang MK, Su RC. Purification, characterization, and gene cloning of an *Aspergillus fumigatus* polyhydroxybutyrate depolymerase used for degradation of polyhydroxybutyrate, polyethylene succinate, and polybutylene succinate. *Polym Degrad Stab*, 2018, 154: 186-194.
- [62] Volova TG, Boyandin AN, Vasiliev AD, et al. Biodegradation of polyhydroxyalkanoates (PHAs) in tropical coastal waters and identification of PHA-degrading bacteria. *Polym Degrad Stab*, 2010, 95(12): 2350-2359.
- [63] Schirmer A, Jendrossek D, Schlegel HG. Degradation of poly(3-hydroxyoctanoic acid)[P(3HO)] by bacteria: purification and properties of a P(3HO) depolymerase from *Pseudomonas fluorescens* GK13. *Appl Environ Microbiol*, 1993, 59(4): 1220-1227.
- [64] Mergaert J, Schirmer A, Hauben L, et al. Isolation and identification of poly(3-hydroxyvalerate)-degrading strains of *Pseudomonas lemoignei*. *Int J Syst Bacteriol*, 1996, 46(3): 769-773.
- [65] Akbar S, Hasan F, Nadhman A, et al. Production and purification of poly(3-hydroxybutyrate-co-3-hydroxyvalerate) degrading enzyme from *Streptomyces* sp. AF-111. *J Polym Environ*, 2013, 21(4): 1109-1116.
- [66] Tseng M, Hoang KC, Yang MK, et al. Polyester-degrading thermophilic actinomycetes isolated from different environment in Taiwan. *Biodegradation*, 2007, 18(5): 579-583.
- [67] Kim MN, Lee AR, Yoon JS, et al. Biodegradation of poly(3-hydroxybutyrate), Sky-Green[®] and Mater-Bi[®] by fungi isolated from soils. *Eur Polym J*, 2000, 36(8): 1677-1685.
- [68] Satti SM, Shah AA, Auras R, et al. Isolation and characterization of bacteria capable of degrading poly(lactic acid) at ambient temperature. *Polym Degrad Stab*, 2017, 144: 392-400.
- [69] Satti SM, Shah AA, Marsh TL, et al. Biodegradation of poly(lactic acid) in soil microcosms at ambient temperature: evaluation of natural attenuation, bio-augmentation and bio-stimulation. *J Polym*

- Environ, 2018, 26(9): 3848-3857.
- [70] Kleeberg I, Hetz C, Kroppenstedt RM, et al. Biodegradation of aliphatic-aromatic copolyesters by *Thermomonospora fusca* and other thermophilic compost isolates. Appl Environ Microbiol, 1998, 64(5): 1731-1735.
- [71] Witt U, Einig T, Yamamoto M, et al. Biodegradation of aliphatic-aromatic copolyesters: evaluation of the final biodegradability and ecotoxicological impact of degradation intermediates. Chemosphere, 2001, 44(2): 289-299.
- [72] Tan FT, Cooper DG, Marić M, et al. Biodegradation of a synthetic co-polyester by aerobic mesophilic microorganisms. Polym Degrad Stab, 2008, 93(8): 1479-1485.
- [73] Chua TK, Tseng M, Yang MK. Degradation of poly(ϵ -caprolactone) by thermophilic *Streptomyces thermoviolaceus* subsp. *thermoviolaceus* 76T-2. AMB Express, 2013, 3(1): 8.
- [74] Urbanek AK, Rymowicz W, Strzelecki MC, et al. Isolation and characterization of Arctic microorganisms decomposing bioplastics. AMB Express, 2017, 7(1): 148.
- [75] Li F, Yu D, Lin XM, et al. Biodegradation of poly(ϵ -caprolactone) (PCL) by a new *Penicillium oxalicum* strain DSYD05-1. World J Microbiol Biotechnol, 2012, 28(10): 2929-2935.
- [76] Bátor V, Åkesson D, Zamani A, et al. Anaerobic degradation of bioplastics: a review. Waste Manag, 2018, 80: 406-413.
- [77] Narancic T, Verstichel S, Reddy Chaganti S, et al. Biodegradable plastic blends create new possibilities for end-of-life management of plastics but they are not a panacea for plastic pollution. Environ Sci Technol, 2018, 52(18): 10441-10452.
- [78] Anunciado MB, Hayes DG, Astner AF, et al. Effect of environmental weathering on biodegradation of biodegradable plastic mulch films under ambient soil and composting conditions. J Polym Environ, 2021, 29(9): 2916-2931.
- [79] Yagi H, Ninomiya F, Funabashi M, et al. Anaerobic biodegradation tests of poly(lactic acid) under mesophilic and thermophilic conditions using a new evaluation system for methane fermentation in anaerobic sludge. Int J Mol Sci, 2009, 10(9): 3824-3835.
- [80] Weng YX, Wang XL, Wang YZ. Biodegradation behavior of PHAs with different chemical structures under controlled composting conditions. Polym Test, 2011, 30(4): 372-380.
- [81] Tabasi RY, Ajjji A. Selective degradation of biodegradable blends in simulated laboratory composting. Polym Degrad Stab, 2015, 120: 435-442.
- [82] Arrieta MP, López J, Rayón E, et al. Disintegrability under composting conditions of plasticized PLA-PHB blends. Polym Degrad Stab, 2014, 108: 307-318.
- [83] Mihai M, Legros N, Alemdar A. Formulation-properties versatility of wood fiber biocomposites based on polylactide and polylactide/thermoplastic starch blends. Polym Eng Sci, 2014, 54(6): 1325-1340.
- [84] Intaraksa P, Rudeekit Y, Siriyota P, et al. The ultimate biodegradation of the starch based biodegradable plastics. Adv Mater Res, 2012, 506: 327-330.
- [85] 赵剑豪, 王晓青, 曾军, 等. 聚丁二酸丁二醇酯及聚丁二酸/己二酸-丁二醇酯在微生物作用下的降解行为. 高分子材料科学与工程, 2006, 22(2): 137-140.
- Zhao JH, Wang XQ, Zeng J, et al. Studies on biodegradation behavior of poly(butylene succinate) and poly(butylene succinate-co-butylene adipate) by microorganisms. Polym Mater Sci Eng, 2006, 22(2): 137-140 (in Chinese).
- [86] Anstey A, Muniyasamy S, Reddy MM, et al. Processability and biodegradability evaluation of composites from poly(butylene succinate) (PBS) bioplastic and biofuel co-products from Ontario. J Polym Environ, 2014, 22(2): 209-218.
- [87] Bagheri AR, Laforsch C, Greiner A, et al. Fate of so-called biodegradable polymers in seawater and freshwater. Glob Challenges, 2017, 1(4): 1700048.
- [88] 王淑芳, 陶剑, 郭天瑛, 等. 脂肪族聚碳酸酯(PPC)与聚乳酸(PLA)共混型生物降解材料的热学性能、力学性能和生物降解性研究. 离子交换与吸附, 2007, 23(1): 1-9.
- Wang SF, Tao J, Guo TY, et al. Thermal characteristics, mechanical properties and biodegradability of polycarbonates/poly(lactic acid) (PPC/PLA) blends. Ion Exch Adsorpt, 2007, 23(1): 1-9 (in Chinese).
- [89] Cho HS, Moon HS, Kim M, et al. Biodegradability and biodegradation rate of poly(caprolactone)-starch blend and poly(butylene succinate) biodegradable polymer under aerobic and anaerobic environment. Waste Manag, 2011, 31(3): 475-480.
- [90] 王磊. PBS 及其共聚物的丁二酰氯扩链及降解研究[D]. 西安: 陕西科技大学, 2012.
- Wang L. Study on degradation and chain extender of

- PBS and PBS-based polyester[D]. Xi'an: Shaanxi University of Science & Technology, 2012 (in Chinese).
- [91] Massardier-Nageotte V, Pestre C, Cruard-Pradet T, et al. Aerobic and anaerobic biodegradability of polymer films and physico-chemical characterization. *Polym Degrad Stab*, 2006, 91(3): 620-627.
- [92] 李功松, 陈小光, 汪彩华. 含 PVA 废水处理工艺探讨. *工业水处理*, 2019, 39(10): 20-25, 31.
Li GS, Chen XG, Wang CH. Discussion on treatment process of wastewater containing PVA. *Ind Water Treat*, 2019, 39(10): 20-25, 31 (in Chinese).
- [93] Tachibana K, Urano Y, Numata K. Biodegradability of nylon 4 film in a marine environment. *Polym Degrad Stab*, 2013, 98(9): 1847-1851.
- [94] Thellen C, Coyne M, Froio D, et al. A processing, characterization and marine biodegradation study of melt-extruded polyhydroxyalkanoate (PHA) films. *J Polym Environ*, 2008, 16(1): 1-11.
- [95] 王格侠, 黄丹, 张维, 等. 典型生物降解聚酯在海水中的降解性能. *功能高分子学报*, 2020, 33(5): 492-499.
Wang GX, Huang D, Zhang W, et al. Degradation performance of typical biodegradable polyesters in seawater. *J Funct Polym*, 2020, 33(5): 492-499 (in Chinese).
- [96] Tsuji H, Suzuyoshi K. Environmental degradation of biodegradable polyesters 1. Poly(ϵ -caprolactone), poly[(R)-3-hydroxybutyrate], and poly(L-lactide) films in controlled static seawater. *Polym Degrad Stab*, 2002, 75(2): 347-355.
- [97] Benn N, Zitomer D. Pretreatment and anaerobic co-digestion of selected PHB and PLA bioplastics. *Front Environ Sci*, 2018, 5: 93.
- [98] Yagi H, Ninomiya F, Funabashi M, et al. Mesophilic anaerobic biodegradation test and analysis of eubacteria and archaea involved in anaerobic biodegradation of four specified biodegradable polyesters. *Polym Degrad Stab*, 2014, 110: 278-283.
- [99] Yagi H, Ninomiya F, Funabashi M, et al. Thermophilic anaerobic biodegradation test and analysis of eubacteria involved in anaerobic biodegradation of four specified biodegradable polyesters. *Polym Degrad Stab*, 2013, 98(6): 1182-1187.
- [100] Ren YN, Hu J, Yang MR, et al. Biodegradation behavior of poly(lactic acid) (PLA), poly(butylene adipate-co-terephthalate) (PBAT), and their blends under digested sludge conditions. *J Polym Environ*, 2019, 27(12): 2784-2792.
- [101] Svoboda P, Dvorackova M, Svobodova D. Influence of biodegradation on crystallization of poly(butylene adipate-co-terephthalate). *Polym Adv Technol*, 2019, 30(3): 552-562.
- [102] Matsumura S, Kurita H, Shimokobe H. Anaerobic biodegradability of polyvinyl alcohol. *Biotechnol Lett*, 1993, 15(7): 749-754.
- [103] Jain R, Tiwari A. Biosynthesis of planet friendly bioplastics using renewable carbon source. *J Environ Health Sci Eng*, 2015, 13: 11.
- [104] Boyandin AN, Prudnikova SV, Karpov VA, et al. Microbial degradation of polyhydroxyalkanoates in tropical soils. *Int Biodeterior Biodegrad*, 2013, 83: 77-84.
- [105] Wu CS. Preparation, characterization, and biodegradability of renewable resource-based composites from recycled polylactide bioplastic and sisal fibers. *J Appl Polym Sci*, 2012, 123(1): 347-355.
- [106] Adhikari D, Mukai M, Kubota K, et al. Degradation of bioplastics in soil and their degradation effects on environmental microorganisms. *J Agric Chem Environ*, 2016, 5(1): 23-34.
- [107] de Campos A, Marconato JC, Martins-Franchetti SM. The influence of soil and landfill leachate microorganisms in the degradation of PVC/PCL films cast from DMF. *Polimeros*, 2012, 22(3): 220-227.
- [108] 杨晓庭, 吴景贵, 李建明, 等. 半干旱地区土壤中 PPC 地膜与普通地膜的降解特征研究. *环境科学与技术*, 2020, 43(11): 45-53.
Yang XT, Wu JG, Li JM, et al. Study on degradation characteristics of PPC plastic film and ordinary plastic film in semi-arid soil. *Environ Sci Technol*, 2020, 43(11): 45-53 (in Chinese).

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