

· 综 述 ·

## 微生物降解塑料的研究进展

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**摘 要:** 塑料广泛应用于人类的生活中, 其中约 80% 的塑料垃圾被填埋, 最终成为陆地和海洋垃圾。由于管理与处置不善, 这些废弃物造成了巨大的环境污染, 目前回收再利用是较好的处置方式, 但对某些塑料废弃物并没有妥善的处置方式。生物降解作为环境友好的处置方式, 具有巨大的应用潜力。本文对聚对苯二甲酸乙二醇酯、聚乙烯、聚氯乙烯、聚丙烯、聚苯乙烯和聚氨酯这 6 种常用塑料的降解微生物及生物降解机制进行了总结, 对目前微生物降解塑料存在的问题进行了分析, 并提出了促进微生物降解塑料应用的途径, 为生物降解塑料菌株和降解酶的开发应用、降解机制研究提供理论参考。

**关键词:** 聚对苯二甲酸乙二醇酯, 聚乙烯, 聚氯乙烯, 聚丙烯, 聚苯乙烯, 聚氨酯, 酶, 降解机制

## Advances in microbial degradation of plastics

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**Abstract:** Plastics are widely used in daily life. Due to poor management and disposal, about 80% of plastic wastes were buried in landfills and eventually became land and ocean waste, causing serious environmental pollution. Recycling plastics is a desirable approach, but not applicable for most of the plastic waste. Microbial degradation offers an environmentally friendly way to degrade the plastic wastes, and this review summarizes the potential microbes, enzymes, and the underpinning mechanisms for degrading six most commonly used plastics including polyethylene terephthalate, polyethylene, polyvinyl chloride, polypropylene, polystyrene and polyurethane. The challenges and future perspectives on microbial degradation of plastics were proposed.

**Keywords:** polyethylene terephthalate, polyethylene, polyvinyl chloride, polypropylene, polystyrene, polyurethane, enzyme, degradation mechanism

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聚合物是以化学单体(如乙烯、丙烯等)为原料,通过加聚或缩聚反应聚合而成的高分子化合物(Polymer)<sup>[1]</sup>,塑料主要由合成聚合物及填料、增塑剂、稳定剂、润滑剂、色料等添加剂组成。塑料主要生产原材料包括化石(原油和天然气)、可再生材料(如甘蔗、淀粉和植物油等)和矿物盐<sup>[2]</sup>。

塑料以其防水、廉价、便捷等特点,广泛应用于建筑、机械、农业、食品包装等领域,涉及人类生活的方方面面。2018年全球塑料产量接近3.6亿t,其中我国塑料产量占世界的30%<sup>[3]</sup>。自1964年以来,塑料使用量升高了20倍,如果不加以控制,预计在2035年将年再扩大一倍<sup>[4]</sup>。但塑料的降解是一个极缓慢的过程,聚合物的高分子量、强C-C单键和强疏水表面都导致其难以被酶作用,塑料的晶体和无定型两种状态也加大了降解难度<sup>[5]</sup>。

塑料使用量巨大,难以降解,并且大部分废弃物没有被合理处置,日益累积,给环境造成了巨大的压力。来自陆地的大多数塑料制品被洋流裹挟漂浮至海洋,一部分塑料(如聚乙烯、聚丙烯和扩展聚苯乙烯)漂浮在海面,还有一些塑料(如聚苯乙烯、聚氯乙烯和聚对苯二甲酸乙二醇酯)则逐渐下沉直至海底<sup>[6]</sup>。在物理、光化学和生物因素的共同作用下,塑料可能会被降解为微塑料(Microplastic)或者纳米塑料(Nanoplastic),并随之进入海洋食物链中<sup>[6]</sup>,对人类的健康造成潜在的威胁。

塑料在降解的过程中,除产生各自的单体外,还会释放出一些功能性添加剂,包括抗菌剂、生物稳定剂、抗氧化剂、抗静电剂、外部和内部润滑剂、填料、填充剂、阻燃剂、香料、热稳定剂和光稳定剂、冲击改性剂、颜料和增塑剂<sup>[7]</sup>。这些功能性添加剂会对生物产生负面影响,例如增塑剂能够作为氧化应激诱导剂,使人体细胞以及鱼细胞产生氧化应激,活性氧(Reactive oxygen species, ROS)的含量升高,对细胞造成损害<sup>[8]</sup>。双酚A既可以用作聚碳酸酯的合成材料,也可以

用作抗氧化剂和增塑剂<sup>[9]</sup>,是一种重要的内分泌干扰物,威胁胎儿和儿童的健康<sup>[10]</sup>。

当前对塑料废弃物的处理方式主要有3种:填埋、焚烧或回收处理<sup>[11]</sup>。全球范围内,79%的塑料垃圾通过填埋或成为海洋和陆地垃圾进入了环境,12%被焚烧,仅9%被回收利用<sup>[4]</sup>。生物降解作为环境友好的降解方式,可以通过生物酶或微生物降解塑料废弃物,甚至回收塑料,因此得到了广泛关注。

根据欧洲对不同塑料类型的需求量(图1),目前塑料使用量最大的主要包括聚对苯二甲酸乙二醇酯(Polyethylene glycol terephthalate, PET)、聚乙烯(Polyethylene, PE)、聚氯乙烯(Polyvinyl chloride, PVC)、聚丙烯(Polypropylene, PP)、聚苯乙烯(Polystyrene, PS)和聚氨酯(Polyurethane, PUR)等6种(表1)。其中,聚乙烯又分为线性低密度聚乙烯(Linear low density polyethylene, LLPE)、低密度聚乙烯(Low density polyethylene, LDPE)、中密度聚乙烯(Medium density polyethylene, MDPE)以及高密度聚乙烯(High density polyethylene, HDPE)。本文主要介绍降解这6种塑料的微生物及降解机制,并探讨了塑料生物降解的发展方向。

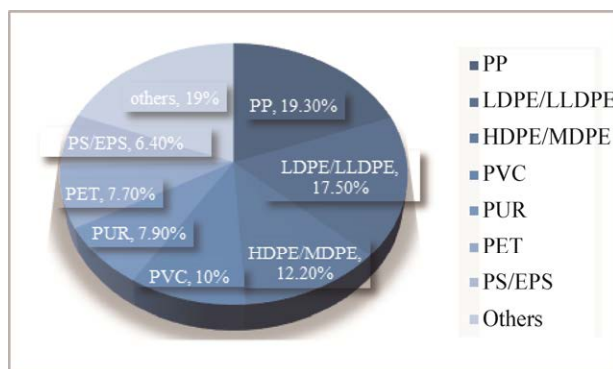


图1 2018年欧洲对不同种塑料的需求量<sup>[12]</sup>

Fig. 1 Demand for different types of plastics in Europe in 2018<sup>[12]</sup>.

表 1 常用 6 种塑料的合成及应用

Table 1 Synthesis and application of six most commonly used plastics

| Plastics type  | Abbreviations | Symbol | Addition polymerization   | Application  |
|--|---------------|--------|---|--|
| Polyethylene terephthalate                               | PET           |        | $\text{HO}-\text{CH}_2-\text{CH}_2-\text{OH} + \text{R-O-C}_6\text{H}_4\text{-O-C}_6\text{H}_4\text{-O-R} \rightarrow \text{R}-\left[\text{O}-\text{CH}_2-\text{CH}_2-\text{O-C}_6\text{H}_4\text{-O-C}_6\text{H}_4\text{-O}\right]_n\text{-OH} + (n-1)\text{R-OH}$ | Mineral water bottles and carbonated beverage bottles for warm or frozen drinks<br><br>Film products, daily necessities (toys, milk bottles, shampoo bottles, water pipes, household utensils) and industrial hollow containers, pipes, calendering tapes and ligatures for packaging, ropes, fishing nets and weaving use fiber, wire and cable, etc. |
| High density polyethylene, 0.941~0.960 g/cm <sup>3</sup> | HDPE          |        | $n \text{ } \text{CH}_2=\text{CH}-\text{CH}_2-\text{CH}_2 \rightarrow \left[ \text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2 \right]_n$   |  |
| Polyvinyl chloride                                       | PVC           |        | $n \text{ } \text{CH}_2=\text{CH}-\text{Cl} \rightarrow \left[ \text{CH}_2-\text{CH}-\text{Cl} \right]_n$   | Raincoats, building materials, plastic films, plastic boxes, etc.  |
| Low density polyethylene, 0.91~0.93 g/cm <sup>3</sup>    | LDPE          |        | $n \text{ } \text{CH}_2=\text{CH}-\text{CH}_2-\text{CH}_2 \rightarrow \left[ \text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2 \right]_n$   | Agricultural film, industrial packaging film, pharmaceutical and food packaging film, machinery parts, daily necessities, building materials, wire and cable insulation, coating and synthetic paper, such as reusable bags, trays and containers, agricultural film, food packaging film, etc.  |
| Polypropylene PP   | PP            |        | $n \text{ } \text{CH}_2=\text{CH}-\text{CH}_3 \rightarrow \left[ \text{CH}_2-\text{CH}-\text{CH}_3 \right]_n$   | Food packaging, candy and snack packaging, hinged lids, microwave containers, pipes, auto parts, bank notes  |
| Polystyrene PS   | PS            |        | $n \text{ } \text{CH}_2=\text{CH}-\text{C}_6\text{H}_5 \rightarrow \left[ \text{CH}_2-\text{CH}-\text{C}_6\text{H}_5 \right]_n$   | Bowls of instant noodle boxes, fast food boxes, building insulation, electrical and electronic equipment, refrigerator liners, glasses frames, etc.  |
| Polyurethane PUR   | PUR           | —      | $n \text{ R}-\text{N}=\text{C}=\text{O} + n \text{ ROH} \rightarrow \left[ \text{R}-\text{NH}-\text{C}(=\text{O})-\text{O}-\text{R} \right]_n$  | Light industry, chemicals, electronics, textiles, medical, construction, building materials, automobiles, national defense, aerospace, aviation, etc.  |

## 1 降解塑料的微生物

生物降解 (Biodegradation) 指通过微生物作用将底物分解转化<sup>[13]</sup>。由需氧微生物完全转化为二氧化碳、水、矿物质和生物质, 或者在厌氧性生物作用转化为二氧化碳、甲烷和腐殖质, 不会留下任何潜在有害物质<sup>[14]</sup>。生物降解主要分为 4 个步骤: 1) 生物退化 (Bio-deterioration): 微生物群落以及非生物因素共同作用将高分子聚合物截成片段; 2) 解聚作用 (Depolymerization): 微生物

分泌酶和自由基, 将聚合物转变为低聚物、二聚体或单体; 3) 同化作用 (Assimilation): 解聚的分子被微生物表面的受体识别从而穿过质膜进入微生物胞内; 4) 矿化作用 (Mineralization): 解聚后的分子在微生物胞内代谢氧化为 CO<sub>2</sub>、N<sub>2</sub>、CH<sub>4</sub> 和 H<sub>2</sub>O 等小分子化合物<sup>[15]</sup>。

塑料降解主要由微生物完成, 一些昆虫幼虫进食塑料也是其肠道微生物在发挥作用<sup>[16]</sup>。降解塑料的真菌主要是丝状真菌, 其菌丝结构有利于

分泌胞外酶并作用于塑料。另外,真菌具有多种策略来降解不同的化合物,包括功能强大的酶系统、强吸附能力和生成生物表面活性剂<sup>[17]</sup>。真菌的疏水蛋白在生物原位修复过程中有重要作用,其双层结构能在疏水/亲水界面形成两亲性膜 (Amphipathic

film),作为生物表面活性剂提高了底物的接触面积,从而大大提高降解效率<sup>[17]</sup>。而细菌缺少类似的结构,所以一般认为真菌的降解能力普遍高于细菌。本文对已报道的降解塑料的真菌和细菌种类及其降解效率进行了归纳总结 (表 2 和表 3)。

表 2 降解塑料的真菌

Table 2 The reported plastics-degrading fungi

| Plastic type | Strain name   | Degradation efficiency (weight loss)                   | Incubation time | Strain source                                  | References |
|--------------|---|--|-----------------|--|------------|
| PE (HDPE)    | <i>Aspergillus flavus</i> PEDX3   | 3.9025%±1.18%  | 28 days         | <i>Galleria mellonella</i> intestinal contents | [18]       |
|              | <i>Penicillium oxalicum</i> NS4 (KU559906)                              | 24.18%   | 30 days         | Plastic garbage dump near Mohanpur campus      | [19]       |
|              |   | 43.73%   | 60 days         |  |            |
|              |   | 55.34%   | 90 days         |  |            |
|              | <i>Penicillium chrysogenum</i> NS10 (KU559907)                          | 17.06%   | 30 days         | Plastic garbage dump near Mohanpur campus      | [19]       |
|              |   | 48.00%   | 60 days         |  |            |
| PVC          |   | 58.598%  | 90 days         |  |            |
|              | <i>Chaetomium globosum</i> (ATCC 16021)                                 | Spores and hyphae begin to absorb PVC                  | 28 days         | Standard strains purchased                     | [20]       |
|              | <i>Mucor rouxii</i>   | (PVC modified with glycerin and urea) began to degrade | 30 days         | Polymer recycling site                         | [21]       |
|              | <i>Phanerochaete chrysosporium</i>                                      | 11%  | 28 days         | Plastic garbage dump                           | [20]       |
| PE (LDPE)    | <i>Aspergillus oryzae</i> strain A5,1 (MG779508)                        | 36.4%±5.53%  | 16 weeks        | Dandola landfill soil                          | [15]       |
|              | <i>Zalerion maritimum</i>   | 56.7%±2.9%   | 14 days         | —  | [22]       |
|              | <i>Rhizopus oryzae</i> NS5  | 8.4%±3%  | 1 month         | Lab isolate                                    | [23]       |
|              |   |  |                 | Accession No. KT160362                         |            |
|              | <i>Penicillium oxalicum</i> NS4 (KU559906)                              | 16.72%   | 30 days         | Plastic garbage dump near Mohanpur campus      | [24]       |
|              |   | 26.70%   | 60 days         |  |            |
|              |   | 36.60%   | 90 days         |  |            |
|              | <i>Penicillium chrysogenum</i> NS10 (KU559907)                          | 19.32%   | 30 days         | Plastic garbage dump near Mohanpur campus      | [25]       |
|              |   | 33.33%   | 60 days         |  |            |
|              |   | 34.35%   | 90 days         |  |            |
| PP           | <i>Phanerochaete chrysosporium</i>                                      | 5.8% (iPP/PLA/nCaCO <sub>3</sub> Nanocomposite)        | 28 days         | Soils from campus of India                     | [26]       |
|              | <i>Aspergillus niger</i> and <i>Paecilomyces variotii</i> co-incubation | 0.62% (PP)   | 30 days         | —  | [27]       |
|              |   | 2.32% (PP/PET/thermoplastic starch blend)              | 30 days         |  |            |
|              | <i>Phanerochaete chrysosporium</i> NCIM 1170 (F1)                       | 9.42% (UV pretreatment)                                | 1 year          | Plastic dump                                   | [27]       |
|              |   | 18.8% (UV pretreatment)                                | 1 year          |  |            |
|              | <i>Engyodontium album</i> MTP091 (F2)                                   |  |                 |  |            |
|              | <i>Lasiodiplodia theobromae</i>   | 1.2%   | 90 days         | Plant endophytes                               | [28]       |
|              |   |  |                 | <i>Psychotria flavida</i>                      |            |
| PUR          | <i>Aspergillus tubingensis</i>  | 90%  | 2 months        | Dumping area in Islamabad, Pakistan            | [29]       |
|              | <i>Chaetomium globosum</i>  | 15%–16%  | 130 days        | —  | [30]       |

表 3 降解塑料的细菌

Table 3 The reported plastics-degrading bacteria

| Plastic type | Strain name  | Degradation efficiency (weight loss)   | Incubation time | Strain source  | References |
|--------------|--|--|-----------------|--|------------|
| PE           | <i>Streptomyces</i> spp. ( <i>S. iakyrus</i> , <i>S. aveblanens</i> , <i>S. warraensis</i> , <i>S. humidus</i> , <i>S. parvullus</i> , <i>S. aburaviensis</i> , <i>S. nigellus</i> , <i>S. misioensis</i> )  | 28.5% (tension change)   | 4 weeks         | Nile Delta   | [31]       |
|              | <i>Alcanivorax borkumensis</i>   | 3.5%±0.34%   | 80 days         | Sea water samples of northern Corsica (Calvi Bay in the Mediterranean sea) | [32]       |
|              | <i>Kocuria palustris</i> M16   | 1%±0.033%  | 30 days         | —  | [33]       |
|              | <i>Pseudomonas</i> sp. MMP1, <i>Acinetobacter</i> sp. MGP1, <i>Bacillus</i> sp. MMP10, <i>Bacillus</i> sp. MGP1 (mixed flora)  | 3.75%  | 6 weeks         | Junkyard in Northern Ibadan  | [34]       |
|              | <i>Bacillus</i> sp.  | 14.7%  | 60 days         | Abandoned landfill in Incheon, South Korea                                 | [35]       |
|              | <i>Paenibacillus</i> sp. (mixed flora)   | —  | —               | —  | —          |
|              | <i>Brevibacillus</i> sp. and <i>Aneurinibacillus</i> sp. (mixed flora)   | LDPE: 58.21%±2%<br>HDPE: 46.6%±3%  | 140 days        | Abandoned garbage dump in Karnataka, India                                 | [36]       |
|              | <i>Bacillus cereus</i> strain A5, a (MG645264)   | 35.72%±4.01%   | 16 weeks        | Dandora junkyard   | [15]       |
|              | <i>Brevibacillus borstelensis</i> strain B2,2 (MG645267)   | 20.28%±2.30%   | 16 weeks        | Dandora junkyard   | [15]       |
|              | <i>Pseudomonas citronellolis</i>   | 18.58%±0.01%   | 30 days         | —  | [16]       |
|              | <i>Erysipelothrix</i> sp. (KX156777), Uncultured CFB group bacterium (FJ024711), <i>Bacteroides bacterium</i> CF (CP006772), <i>Psychromonas</i> sp. (NR116830), <i>Cupriavidus</i> sp. (MG948149), <i>Pleomorphochaeta</i> sp. (NR134177), <i>Sporobacter</i> sp. (KT183425), <i>Clostridium</i> sp. a-nd (FN397991), <i>Dethiosulfovibrio</i> sp. (NR029034), <i>Acetobacterium</i> sp. (NR074548), <i>Cohaesibacter</i> sp. (KT324976), <i>Desulfovibrio</i> sp. (KU892724), <i>Fusibacter</i> sp. (KJ420408) (mixed flora) | 11.7%±0.6%   | 7 months        | Marine   | [37]       |
|              | <i>Bacillus</i> sp. AIIW2  | 0.26%  | 90 days         | Marine   | [38]       |
| PP           | <i>Stenotrophomonas panacihumi</i> PA3-2   | 20.3%±1.39% (molecular weight 10 300)<br>16.6%±1.70% (molecular weight 19 700) | 90 days         | Solid waste open-air dump in South Korea                                   | [39]       |
|              | <i>Bacillus</i> sp. strain 27  | 4.0%   | 40 days         | Sediment samples of Matang mangrove in Peninsular Malaysia                 | [40]       |
|              | <i>Rhodococcus</i> sp. strain 36   | 6.4%   | —               | —  | —          |
|              | Co-culture of <i>Bacillus</i> and <i>Pseudomonas</i>   | 1.95%±0.18%  | 12 months       | —  | [41]       |
|              | <i>Brevibacillus</i> spp. and <i>Aneurinibacillus</i> sp. (mixed flora)  | 56.3%±2% (PP band)<br>44.2%±3% (PP board)                                      | 140 days        | Sewage treatment plant and waste disposal landfill                         | [35]       |
|              | <i>Pseudomonas azotoformans</i> , <i>P. stutzeri</i> , <i>Bacillus subtilis</i> , <i>B. flexus</i>   | 2.5%   | 12 months       | Plastic waste dump soil  | [42]       |
|              | <i>Enterobacter</i> sp., <i>Citrobacter sedlakii</i> , <i>Alcaligenes</i> sp., <i>Brevundimonas diminuta</i>   | 12.4%  | 30 days         | Landfill   | [43]       |
|              | <i>Pseudomonas</i> sp., <i>Bacillus</i> sp.  | 23%  | 30 days         | Soil samples in plastic waste landfill area                                | [44]       |
| PS           | <i>Pseudomonas aeruginosa</i> , <i>Bacillus subtilis</i> , <i>Staphylococcus aureus</i> , <i>Streptococcus pyogenes</i>  | <i>Bacillus subtilis</i> has the highest degradation efficiency                | —               | Soil samples   | [45]       |
|              | <i>Acinetobacter</i> sp.   | 12.14%   | 60 days         | <i>Tribolium castaneum</i> gut of larva                                    | [46]       |
|              | <i>Serratia marcescens</i> , <i>Klebsiella oxytoca</i> , <i>Pseudomonas aeruginosa</i>   | —  | —               | <i>Tribolium castaneum</i> gut of larva                                    | [47]       |
|              | <i>Exiguobacterium</i> sp. strain YT2  | 7.4%±0.4%  | 28 days         | Mealworms that feed on plastic   | [48]       |
|              | <i>Pseudomonas aeruginosa</i> strain DSM 50071   | —  | —               | <i>Zophobas atratus</i> gut  | [49]       |
|              | <i>Bacillus subtilis</i> MZA-75, <i>Pseudomonas aeruginosa</i> MZA85   | Co-cultivation has higher degradation effect                                   | 30 days         | —  | [50]       |
|              | <i>Bacillus amyloliquefaciens</i>  | 30%–44%  | 1 month         | —  | [51]       |

### 1.1 降解 PET 的微生物

聚对苯二甲酸乙二醇酯 (PET) 由对苯二甲酸和乙二醇聚合形成, 分为结晶型和无定形型<sup>[52]</sup>, 由于构成结晶型 PET 的酯键位置被其他成分包围, 降解酶难以接触到, 因此不易降解, 常用于生产一次性饮料瓶、衣服、包装等耐用性强的产品<sup>[53]</sup>。由于 PET 降解速率极低, 大多数研究只证明了其可以降解, 但受时间限制未显示出显著变化。Yoshida 等在富含 PET 的沉积物、土壤、废水和活性污泥中筛选出一株能利用 PET 为碳源的细菌大坂堺菌 *Ideonella sakaiensis*, 它可将 PET 作为碳源和能源, 且其降解效率显著高于其他种群, 6 周基本完全降解晶体化程度 1.9% 的 PET。当在含有 PET 的培养基中生长时, *I. sakaiensis* 能够分泌出两种酶分别降解 PET 和 PET 降解过程的中间产物<sup>[52]</sup>, 其中, 降解 PET 的酶在开发 PET 生物降解和回收工艺以及环境塑料垃圾的生物修复方法方面具有巨大的潜力。PET 属于聚酯型聚合物, 其降解速率主要取决于聚酯链的流动性, 而聚酯链的流动性则与玻璃转化温度成反比, 即当玻璃转化温度升高时, 聚酯链的流动性则降低<sup>[54]</sup>。PET 的玻璃转化温度在 75 °C 左右<sup>[52]</sup>, PET 在 75 °C 以上处于易于降解的高弹态, 而在 75 °C 以下处于不易降解的玻璃态。但目前发现的 PET 降解酶的最适温度一般低于 75 °C, 因此提高 PET

降解酶的作用温度对于提高 PET 的降解效率至关重要。Then 等将二硫键引入 PET 降解酶的  $\text{Ca}^{2+}$  结合位点, 使其变成了高效的、不需要  $\text{Ca}^{2+}$  的热稳定性聚酯酶, 且将其最适反应温度从 69.8 °C 提高到 94.7 °C, 远超过玻璃转化温度, 大大提高了降解速率<sup>[55]</sup>。Müller 等首次发现由褐色嗜热单孢菌 *Thermobifida fusca* 介导的酶反应能在 55 °C 下降解 PET, 21 d 使 PET 膜重量减少了 50%<sup>[56]</sup>。

PET 降解酶包括角质酶、脂酶和酯酶等 (表 4)。Austi 等将 PET 降解酶两个活性位点的残基突变为角质酶中的保守氨基酸, 使其结构与角质酶更加相似, 显著提高了降解 PET 的能力<sup>[53]</sup>。Kawai 等从绿色糖单胞菌 *Saccharomonospor viridis* AHK190 中分离得到了与角质酶相似的另一种酶 Cut190, 经改造后能够高效降解 PET, 并且具有降解其他几类聚酯的能力<sup>[57]</sup>。另外, 对 PET 降解酶的工厂化探索加快了 PET 降解酶的实践。Moog 等将来自 *I. sakaiensis* 的 PETase 酶组装到光合微藻三角褐指藻 *Phaeodactylum tricornutum* 中, 建立了能够分泌 PETase 的微生物工厂, 为 PET 的生物降解工厂化提供了可能<sup>[58]</sup>。Su 等将来自褐色嗜热单孢菌 *Thermobifida fusca* 的角质酶在大肠杆菌中表达后, 不需要信号肽的介导即可通过膜通透性的增强使角质酶释放到培养基中, 并在后续的研究当中实现了酶的高效释放<sup>[59]</sup>。

表 4 降解 PET 的微生物及酶

Table 4 The reported PET degrading microorganisms and enzymes

| Strain name  | Enzyme                           | Reaction temperature (°C) | Incubation time | Degradation efficiency (weight loss) | References |
|--|----------------------------------|---------------------------|-----------------|--------------------------------------|------------|
| <i>Pseudomonas aestusnigri</i> VGXO14 <sup>T</sup> | PE-H (polyester fiber hydrolase) | 30                        | —               | —                                    | [60]       |
| <i>Thermobifida fusca</i> DSM43793                 | Hydrolase                        | 55                        | 3 weeks         | 49.7%±1.0%                           | [56]       |
| <i>Fusarium solani</i> f. sp. pisi DSM 62420       | Cutinase                         | —                         | —               | —                                    | [61]       |
| <i>Saccharomonospora viridis</i>                   | Cutinase (Cut190)                | 63                        | 3 days          | 27%                                  | [57]       |
| <i>Ideonella sakaiensis</i>                        | ISPETase                         | 30                        | 24 hours        | 1%                                   | [62]       |
| <i>Thermobifida fusca</i>                          | TfCut2                           | 70                        | 120 hours       | 97.0%±3.0%                           | [63]       |

## 1.2 降解 PE 的微生物

聚乙烯 (PE) 由乙烯聚合形成, 聚乙烯分为高密度聚乙烯和低密度聚乙烯, 其中高密度聚乙烯主要应用于常见白色药瓶、清洁用品和洗护用品的容器, 低密度聚乙烯主要用于常见的保鲜膜和塑料膜。在降解聚乙烯的真菌中, 以曲霉属 *Aspergillus*、青霉属 *Penicillium* 和根霉属 *Rhizopus* 为主<sup>[21]</sup>。目前所分离得到的大部分真菌主要针对低密度聚乙烯, 1 个月能够使低密度聚乙烯重量减少 10%。Paço 等发现了一株强降解菌株沿海涛旋孢菌 *Zalerion maritimum*, 在 14 d 内就可以使低密度聚乙烯的重量减少 56.7%<sup>[21]</sup>, 其高降解率与 PE 颗粒大小有关。以平均 2–4 mm 的 PE 颗粒为原料, 直接跳过了生物降解过程当中的第一步——生物退化, 因此显著提高了降解效率<sup>[21]</sup>。

## 1.3 降解 PVC 的微生物

聚氯乙烯 (PVC) 是由氯乙烯聚合而成的, 主要应用于雨衣、建材、塑料膜和塑料盒。由于 PVC 在生产过程中添加了大量的氯和添加剂 (如重金属或邻苯二甲酸盐)<sup>[64]</sup>, 当 PVC 填埋或焚烧时会产生氯化氢或氯化二噁英等环境污染物。PVC 本身极难降解, 微生物无法在 PVC 培养基上生长, 需要添加其他化合物。例如铜绿假单胞菌 *Pseudomonas aeruginosa* 和无色杆菌 *Achromobacter* sp. 不能在只有 PVC 存在的条件下生长, 在添加了环氧化紫苏阿籽油以后, 这两种微生物才开始降解基质<sup>[65]</sup>。Singh 和 Pant 提出了一种新型的绿色混合技术, 利用甘油和尿素通过生物降解法和化学改性法将 PVC 改性为 C-PVC, 且毛霉菌 *Mucor rouxii* 对 C-PVC 的生物降解高于 PVC<sup>[20]</sup>。

除单一菌株外, 还可以利用复合微生物菌群对 PVC 进行降解。Giacomucci 等利用厌氧条件下富集的海洋微生物群落处理塑化 PVC 薄膜, 发现 3 个微生物群落 7 个月后可在塑料表面形成致密的生物膜, 聚合物重量降低 11.7%, 且热稳定性和平均分子量显著下降, 表明复合微生物菌群

具有降解聚合物链的能力<sup>[37]</sup>。

## 1.4 降解 PP 的微生物

聚丙烯 (PP) 是由丙烯聚合而成的聚合物, 多用于制造水桶、垃圾桶、篮子和微波炉用食物容器等。其主环是只有碳原子组成的烃结构<sup>[66]</sup>, 因此难以被直接降解。PP 的降解通常由光降解或者化学降解通过分解碳链降低其分子量及疏水性, 继而开始 PP 的生物降解过程<sup>[67]</sup>。且纯 PP 的降解率低于 PP 与其他物质的混合物, 这与混合物中 PP 降解微生物获得的能量比在纯 PP 中更广泛有关。Shimpi 等利用黑曲霉 *Aspergillus niger* 和宛氏拟青霉 *Paecilomyces variotii* 组成的混合菌株对纯 PP 和 PP/PET/热塑性淀粉共混物的降解进行了研究, 30 d 后纯 PP 的降解率仅为 0.62%, 而混合物的降解率可达 2.32%<sup>[24]</sup>。

## 1.5 降解 PUR 的微生物

聚氨酯 (PUR) 由液态异氰酸酯和液态聚酯或者二醇聚酯缩聚而成, 在家具领域、建筑领域、制鞋行业和交通运输行业具有广泛的应用。聚氨酯分为两类: 聚醚型聚氨酯和聚酯型聚氨酯, 目前的研究多针对聚酯型聚氨酯。已有很多聚氨酯降解相关细菌和真菌的文献报道, 但是对于降解聚氨酯的微生物菌群的报道较少。Vargas-Suárez 等研究了 3 个富集微生物群落对聚酯型聚氨酯的降解, 发现了 2 个无法在以 PUR 为唯一碳源的培养基中生长的菌株, 说明微生物群落降解聚合物的优势, 为今后构建复合微生物群落来降解聚氨酯类的聚合物奠定了基础<sup>[68]</sup>。Zafar 等通过模拟堆肥的过程分离得到了降解 PUR 的真菌群落, 并对其降解效果进行了鉴定<sup>[69]</sup>, 优化后堆肥工艺具有生物降解聚氨酯废弃物的巨大潜力。

目前已有关于 PUR 降解的生物反应器的设计研究, Gautam 等利用假丝酵母玫瑰脂肪酶 (*Candida rugosa* lipase, EC 3.1.1.3) 对固体聚氨酯的降解, 建立了表征固体聚氨酯降解动力学的数学模型<sup>[70]</sup>, 这些信息将有助于开发生物反应器的



实际应用,以使用脂肪酶处理聚氨酯废物。

## 1.6 降解 PS 的微生物

聚苯乙烯 (PS) 由苯乙烯聚合而成,主要应用于碗装泡面盒、发泡快餐盒。高抗冲性聚苯乙烯 (High impact polystyrene, HIPS) 是常用的 PS 之一,是由弹性体改性 PS 制成的热塑性材料<sup>[71]</sup>。Sekhar 等从垃圾填埋厂中分离得到了 4 种能够降解 HIPS 的细菌: 肠杆菌 *Enterobacter* sp.、赛氏柠檬酸杆菌 *Citrobacter sedlakii*、产碱菌 *Alcaligenes* sp. 和缺陷短波单胞菌 *Brevundimonas diminuta*, 30 d 内可使 HIPS 的质量下降 12.4%<sup>[43]</sup>。Mohan 等从垃圾填埋区域分离得到具有降解 HIPS 的能力的 1 株芽孢杆菌 *Bacillus* sp. 和 1 株假单胞菌 *Pseudomonas* sp., 其中芽孢杆菌处理 30 d 后 HIPS 膜的重量减少了 23%<sup>[44]</sup>。

另外,有研究表明一些昆虫的幼虫能够进食并降解 PS,例如超级蠕虫 *Zophobas atratus* 的幼虫能够食用、降解和矿化 PS<sup>[72]</sup>。超级蠕虫可以在 28 d 内仅以聚苯乙烯泡沫作为唯一饮食,平均聚苯乙烯泡沫塑料的消耗量为 0.58 mg/d,是粉虫的 4 倍<sup>[72]</sup>。Urbanek 等对不同类型的 PS 进行了粉虫 *Tenebrio molitor* 养殖研究,以跟踪肠道微生物群落多样性的变化。结果表明 PS 降解菌主要分布在  $\gamma$ -变形菌 Gammaproteobacteria、芽孢杆菌 Bacilli、梭菌 Clostridia、酸杆菌 Acidobacteria、放线菌 Actinobacteria、 $\alpha$ -变形菌 Alphaproteobacteria 和黄杆菌 Flavobacteria 等纲,优势属是肠杆菌 *Enterobacter*、乳球菌 *Lactococcus* 和肠球菌 *Enterococcus*<sup>[47]</sup>。

目前发现的能够降解塑料的微生物种类有限,筛选得到的降解 PE 的微生物种类相对较多,且降解效率比其他类型塑料的降解效率略高,但是距离应用仍然有一段距离。而目前分离到的降解 PP 的微生物通常无法单独降解塑料,需要添加一些有机物才能降解。而有关 PET 微生物降解的研究进展较为迅速,在 Yoshida 等分离得到一株高效降解菌后,有关降解酶改造的研究就开始进

行,因此较其他类型的塑料相关的成果更多。能够降解 PS 的不仅有微生物,还有一些昆虫的幼虫可以自然取食塑料,这就使塑料的生物降解不仅仅局限在微生物当中,有助于塑料污染早日解决。

## 2 降解机理

### 2.1 PET 微生物降解机制

PET 降解机制为表面亲水化,PET 水解酶将聚合物表面的聚合链末端或环状结构作为靶点进行酶解,由此提高了聚合物的亲水性,从而提高了后续酶解效率<sup>[73]</sup>。Han 等解析了来自 *I. sakaiensis* 的 PET 酶结构,并通过结构分析、基因突变及活性测定等方法,提出 PET 酶的底物结合模式及催化过程的关键特征。PET 酶是典型的丝氨酸水解酶,拥有保守的  $\alpha/\beta$  水解酶折叠和由丝氨酸、组氨酸及精氨酸残基组成的催化三联体,分子内有 2 个二硫键,可加强酶的热稳定性和与 PET 结合的特异性。当 PET 未接近底物结合部位时,催化中心附近的氨基酸位点 W156 在晶体结构中可呈现不同构象,底物 PET 进入结合位点,羰基被置于活性位点并被水解,水解后产生苯甲酸等产物<sup>[74]</sup>。

PET 的代谢途径:酶作用于酯键后将 PET 降解为对苯二甲酸 (Terephthalic acid, TPA) 和乙二醇 (Ethylene glycol, EG),并生成了不完全水解产物单 (2-羟乙基) 对苯二甲酸酯 (Mono (2-hydroxyethyl) terephthalate, MHET) 和双 (2-羟乙基) 对苯二甲酸酯 (Bis (2-hydroxyethyl) terephthalate, BHET)<sup>[75]</sup>。MHET 可以在 MHETase 作用下继续水解成为 TPA 和 EG<sup>[52]</sup>。之后 TPA 和 EG 可进入胞内,经过一系列转变成为原儿茶酸以后,进入三羧酸循环 (Tricarboxylic acid cycle, TCA cycle),从而与微生物新陈代谢联系起来<sup>[75]</sup>。

### 2.2 PE 微生物降解机制

PE 的生物降解主要分为两个步骤:首先氧化



聚乙烯, 将极性基团引入到碳氢骨架中, 增强微生物对聚乙烯表面的附着, 然后降解氧化的 PE<sup>[76]</sup>。PE 的代谢过程中涉及氧化、脱氢和 C-C 键断裂的几个步骤, 最终进入到 TCA 循环。小的脂肪族碳氢化合物 (大约 20 个碳原子) 可以直接运输到细菌细胞中, 然后开始降解<sup>[77]</sup>。

### 2.3 PS 微生物降解的机制

Tischler 等通过乙烯侧链氧合, 建立了苯乙烯代谢途径 (图 2)。苯乙烯首先在苯乙烯单氧酶的作用下生成氧化苯乙烯, 然后经氧化苯乙烯异构酶作用生成苯乙醛, 再经苯乙醛脱氢酶的作用生成乙酸苯酯, 最后经乙酸苯酯的多个降解酶作用生成三羧酸循环中间产物苯乙酸, 从而进入微生物新陈代谢。这种侧链氧合途径是苯乙烯需氧降

解最常见的途径, 如多种变形杆菌属、假单胞菌属和黄杆菌属均采用此途径<sup>[78]</sup>。

### 2.4 PUR 微生物降解机理

降解 PUR 的酶多是脂酶、酯酶和蛋白酶, 图 3 显示了其可能的作用位点。Cregut 等对 PUR 降解机制进行了简单描述。根据定位 PUR 降解酶可分为膜结合型和分泌型。膜结合型接触并粘附在 PUR 表面, 由此水解氨基甲酸酯键, 释放 PUR 片段或单体。而对不溶性的 PUR, 则释放大量的分泌酶到环境中, 与底物结合从而降解 PUR。由于分泌酶与底物的结合效率并不高, 可通过研磨 PUR 增加接触面积, 提高酶与 PUR 的结合效率, 促进降解<sup>[79]</sup>。Do Canto VP 等利用同源建模技术, 首次确定了聚氨酯降解酶的三维结构。其理论模

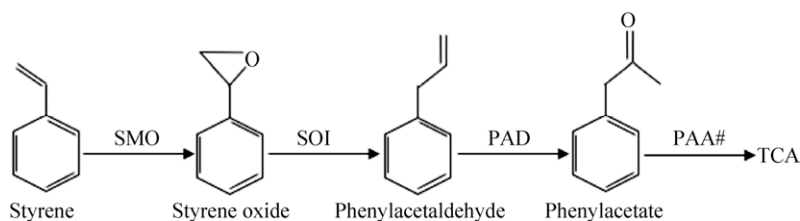


图 2 PS 的代谢途径<sup>[78]</sup>

Fig. 2 PS metabolic pathway<sup>[78]</sup>. The involved enzymes comprise styrene monooxygenase (SMO), styrene oxide isomerase (SOI), phenylacetaldehyde dehydrogenase (PAD), and multiple enzymes of phenylacetate degradation (PAA#) leading to intermediates of the tricarboxylic acid cycle (TCA).

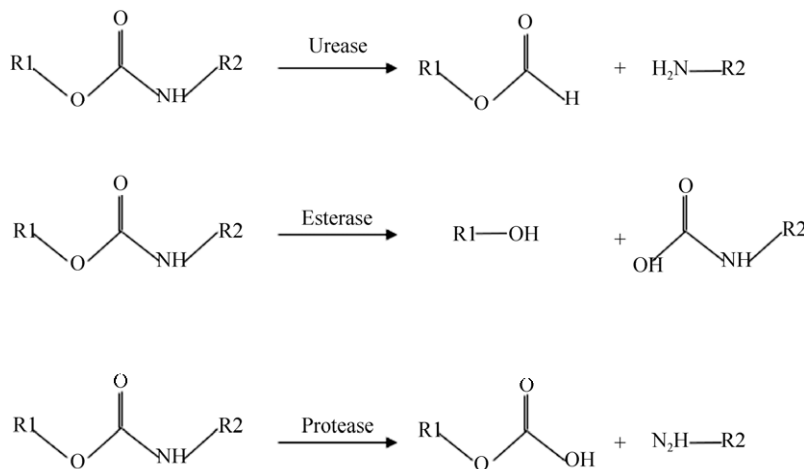


图 3 降解 PUR 的酶的可能作用位点<sup>[79]</sup>

Fig. 3 Possible sites of PUR degradation enzymes<sup>[79]</sup>.

型显示出良好的立体化学性质,并通过分子动力学模拟观察其结构稳定性。分子对接结果表明,聚氨酯单体与模拟酶有良好的相互作用<sup>[80]</sup>。

人们对微生物降解塑料机理的研究还很欠缺,常用的6种塑料类型中,PVC和PP的降解机理仍然不明确,聚醚型聚氨酯的降解机理的研究更是少之又少,而目前已知的降解机理也只是对降解过程有了初步的了解,对于限速酶、酶作用的机制等问题仍然有待探索,这也是制约微生物塑料降解发展的关键问题。

### 3 总结与展望

当前关于微生物塑料降解的研究正在稳步进行,但是仍然存在很多问题:1)发现的具有降解塑料能力的菌株资源有限,并且针对不同类型的塑料,研究进展差距较大。降解PET的酶的改造已经有了多种尝试,已经进入工厂化探索阶段,但是能够降解PVC和PS的微生物非常有限,仍然停滞在筛选阶段。2)降解效率不高,无法投入到生产应用中。目前筛选到的具有降解塑料能力的菌株的降解效率有限,而且多为实验室条件下的研究,需要更多的研究来探明在自然环境中的降解情况。Satti等认为除了筛选出具有降解塑料潜能的微生物种群,还应该发展塑料降解微生物的降解模拟系统,最终应用于自然环境<sup>[81]</sup>。3)对酶的改造有限。如前所述,对降解PET的酶的改造主要有两方面,一是提高其催化效率,二是增加酶的分泌量。但是降解其他类型塑料的酶的改造尚未有所进展,距离生产实践还有很长的一段路。4)降解机理不明确。当前对降解机理的研究较少,已了解到的机理也只是对降解过程有了初步了解,对于限速酶、酶的作用原理等问题仍然有待探索。5)检测方法有限。对微生物降解塑料的研究多利用底物重量的变化来评价塑料降解程度,采用傅里叶变换红外光谱仪(Fourier transform infrared spectrometer, FTIR)来检测化学键的变化,扫描隧道显微镜(Scanning

tunneling microscope, STM)或者原子力显微镜(Atomic force microscopy, AFM)来检测塑料表面结构的变化,但是未考虑聚合物内部化学添加剂对于塑料重量变化以及表面结构的影响,如增塑剂、阻燃剂、抗氧化剂、热稳定剂、固化剂、紫外光稳定剂、润滑剂、杀菌剂、色素等<sup>[82]</sup>,而这些影响又是不可忽略的,因此需要选择或开发更先进的手段对塑料的降解结果进行更全面、更细致的鉴定。

针对微生物降解塑料存在的问题,可以从以下几个方面开展研究:1)降解塑料微生物的发现与挖掘。黄粉虫降解塑料<sup>[83]</sup>给我们两个启示,即可以从特殊环境中发现新的降解塑料微生物资源,同时黄粉虫提示我们塑料降解需要合适的载体。2)高效筛选体系。利用生物信息学手段结合新型的筛选方法,大量筛选具有高效降解能力的菌株。如Cregut等基于目前已发现的塑料降解微生物的相关基因,利用隐马尔科夫模型建立了一种搜索算法,对500多种可能具有PET降解能力的微生物进行了筛选,确认了4种新的PET水解酶<sup>[84]</sup>,创建了一种高效的筛选方法。另外,通过宏基因组和下一代测序技术相结合等方法<sup>[79]</sup>,甚至可以从宏基因组中筛选相关塑料降解基因检测不可培养目标微生物或菌群。3)塑料降解菌群(Syncom)筛选与构建。从我们对秸秆降解微生物菌群的研究<sup>[85]</sup>发现,很多生物学过程是通过微生物菌群共同作用,通过筛选能够降解塑料的菌群,同时结合合成生物学的方法,构建高效降解塑料的生物体系。4)微生物降解塑料机理。塑料作为稳定的高分子材料,降解过程较为复杂,通过降解过程的酶学、化学及能量代谢等研究,确定关键酶及其机制,通过对降解关键酶的基因改造提高其活性和产量,从而提高塑料降解效率,加快微生物降解塑料走向实践。5)探究微生物降解塑料加工技术。在塑料制品加工过程中技术改良,既保证使用过程中的持久性,又使其在用后易于降解。例如Brunner等提出可以在塑料生产过程中加入

具有高效降解塑料能力的真菌孢子或相应的酶,塑料废弃之后与湖水或海水接触的过程中,即可触发孢子的生长或使酶开始发挥作用,从而降解塑料,既满足了使用的需求,又不致使塑料在环境中持久性堆积<sup>[86]</sup>。6) 微塑料的微生物降解。近年来很多研究都证明了微塑料对自然环境的严重危害<sup>[87-89]</sup>,而目前对微塑料降解的研究还处在起始阶段,探究微塑料的微生物降解,对于研制功能性的微塑料降解制剂、解决微塑料污染问题具有重大的意义。

由于塑料污染量持续上升,在研究如何高效降解塑料的同时,也应当关注减少塑料的使用量或提升塑料使用循环效率的方法,保持塑料使用和降解的平衡。生物可降解塑料具有生物可降解性、生物兼容性、可持续性,并且其降解产物无毒或低毒,对环境友好。例如聚羟基脂肪酸酯(Polyhydroxyalkanoates, PHA) 是很多细菌细胞生成的一种胞内聚酯,具有类似于合成塑料的物化特性,并且具有生物可降解性、生物相容性、气体阻隔性等优良特性<sup>[90]</sup>。真菌是自然界中广泛存在的一类生物,可在培养基上产生单条管状菌丝,并聚集组成条形纤维状的菌丝体。美国 Bayer 和 McIntyre 利用真菌栽培制备菌丝体基塑料(俗称“蘑菇塑料”),并迅速创立了 Ecovative Design LLC 公司投入产业化生产和应用<sup>[91]</sup>。为了提高塑料循环使用的效率,目前有许多环保公司专注于环保再生材料产品的设计、开发与创意推广,例如将塑料回收并重新加工成为日用品,或者减少塑料的使用并创造替代它的材料。

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