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·塑料生物降解资源的发掘·

典龙阳 山东大学微生物技术国家重点实验室(研究院)教授，博士生导师。山东省泰山学者青年专家，山东省海外优秀青年基金获得者，山东大学齐鲁青年学者。研究方向集中在利用合成化学和合成生物学手段，围绕塑料降解、生物质利用、天然产物和药物中间体及高附加值化学品开发等开展相关的基础与应用研究，在 *Chemical Reviews*、*Angewandte Chemie International Edition*、*ACS Catalysis* 等发表多篇研究成果，主持多项省部级研究课题，应邀担任包括科技部重点研发计划等项目评审专家。

苏田源 山东大学微生物技术国家重点实验室(研究院)长聘副研究员、硕士生导师。主要研究方向为塑料废弃物的生物降解及资源化利用，目前主持国家自然基金青年项目、山东省自然基金青年项目，并参与国家重点研发计划项目及国家自然科学基金委员会与欧盟委员会环境生物技术合作研究项目“合成塑料降解转化微生物菌群”。近年来在 *Frontiers in Microbiology*、*iScience*、*Chemosphere*、*Microbial Biotechnology* 等期刊发表学术论文 20 余篇，累计他引 400 余次。

生物降解聚烯烃类塑料研究进展

袁英博，周汶楷，梁泉峰，典龙阳*，苏田源*，祁庆生

山东大学 微生物技术国家重点实验室，山东 青岛 266237

袁英博，周汶楷，梁泉峰，典龙阳，苏田源，祁庆生. 生物降解聚烯烃类塑料研究进展[J]. 生物工程学报，2023，39(5): 1930-1948.
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摘 要：聚烯烃类塑料是一类以 C–C 键为骨架的高分子材料，被广泛应用于日常生活的各个领域。由于具有稳定的化学性质并且难以被环境中的微生物快速降解，聚烯烃塑料废弃物在全球范围内持续积累，造成了严重的环境污染及生态危机。近年来，利用生物方法降解聚烯烃类塑料引起了研究人员的广泛关注。自然界丰富的微生物资源为生物降解聚烯烃类塑料废弃物提供了可能，已

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*Corresponding authors. E-mail: DIAN Longyang, longyang_dian@sdu.edu.cn; SU Tianyuan, sutianyuan@sdu.edu.cn
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经有一些对聚烯烃塑料具有降解能力的微生物被陆续报道。本文总结了聚烯烃类塑料生物降解资源及生物降解机制的研究进展，提出了目前聚烯烃类塑料生物降解过程存在的问题，并对未来的研究方向进行了展望。
关键词：聚烯烃类塑料；生物降解；降解机制；废物处理；环境保护

Advances in biodegradation of polyolefin plastics

YUAN Yingbo, ZHOU Wenkai, LIANG Quanfeng, DIAN Longyang*, SU Tianyuan*, QI Qingsheng

State Key Laboratory of Microbial Technology, Shandong University, Qingdao 266237, Shandong, China

Abstract: Polyolefin plastics are a group of polymers with C−C backbone that have been widely used in various areas of daily life. Due to their stable chemical properties and poor biodegradability, polyolefin plastic waste continues to accumulate worldwide, causing serious environmental pollution and ecological crises. In recent years, biological degradation of polyolefin plastics has attracted considerable attention. The abundant microbial resources in the nature offer the possibility of biodegradation of polyolefin plastic waste, and microorganisms capable of degrading polyolefin have been reported. This review summarizes the research progress on the biodegradation microbial resources and the biodegradation mechanisms of polyolefin plastics, presents the current challenges in the biodegradation of polyolefin plastics, and provides an outlook on future research directions.
Keywords: polyolefin plastics; biodegradation; degradation mechanisms; waste treatment; environmental protection

塑料是一类通过加聚或缩聚反应聚合而成的高分子聚合物[1]，具有生产成本低、化学稳定性好、耐腐蚀、绝缘性强、生物安全性高等优点，被广泛应用于农业、工业、建筑业等多种行业，是人类生活和生产过程中不可或缺的重要基础材料。受 2019 全球新冠疫情的影响，塑料产量激增，尤其是聚烯烃类塑料。据统计，中国 2020 年 1–2 月的口罩产量高达 1.1 亿个，同比增加了 450% [2]。除口罩外，一次性医疗用品以及一次性包装袋的使用在疫情期间大幅增加，由此产生的塑料废弃物在自然环境下难以被快速降解，造成的环境问题及生态危机日益加剧[3]。尤其是每年释放到海洋中的塑料垃圾会让数百万只海洋动物因误食而窒息死亡[4]；同时，塑料微粒还会随着食物链富集，进入人体血液，严重威胁人类健康[5]。据统计，2015 年全球有 79%的塑料垃圾未得到有效处理，按照目前趋势下去，到 2050 年，大约会有 120 亿 t 塑料垃圾被填埋或遗弃环境中[6]。

传统的塑料垃圾处理方法主要包括填埋法和焚烧法，填埋法占用土地、容易造成环境二次污染；焚烧法会排放大量 CO_2 及二噁英等有害气体。传统处理方法耗能大、对生态环境造成严重的二次污染，因此急需开发更加安全绿色的塑料废弃物处置技术。目前从自然界中已经发现一些可以降解塑料废弃物的微生物和

酶，尽管降解速率较低，但这预示着利用生物技术降解塑料废弃物是可行的[7]。利用生物技术降解塑料废弃物具有条件温和、绿色可持续等优点，近年来备受研究者的关注。本文综述了含 C−C 键的聚烯烃类塑料的物理化学特性、从不同环境中分离到的具有生物降解能力的微生物资源及潜在的生物降解机制，特别是针对聚烯烃类塑料难以被直接高效生物降解的难题，提出了结合物理化学处理方法的生物降解方案，以期促进生物技术在聚烯烃类塑料高效降解中的应用。

1 聚烯烃类塑料的分类及结构特点

根据化学结构的差异，塑料聚合物可以分为两大类(图 1)，一类是含有酯键的聚酯类塑料，主要包括聚对苯二甲酸乙二醇酯(polyethylene terephthalate, PET)和聚氨酯(polyurethane, PUR)，另外一类是以 C−C 键为骨架的聚烯烃类塑料，主要包括聚乙烯(polyethylene, PE)、聚苯乙烯(polystyrene, PS)、聚丙烯(polypropylene, PP)和聚氯乙烯(polyvinyl chloride, PVC)。聚烯烃类塑料的使用范围更为广泛，占据了全球塑料制品的 77%[8]。

其中 PE 是全球生产量最高的塑料聚合物，由乙烯聚合而成，分子量从几万到几十万不等，分子式为$(C_2H_4)_n$。PE 无毒无味，手感似蜡，具有极强的化学稳定性及绝缘性，能够耐受大多数有机酸碱腐蚀。根据分子结构及密度，PE 可以分为高密度聚乙烯(high-density polyethylene, HDPE)、低密度聚乙烯(low-density polyethylene, LDPE)及线性低密度聚乙烯(linear low-density polyethylene, LLDPE)。HDPE 相比于 LDPE 和 LLDPE 有较高的耐温、耐油性，此外电绝缘性

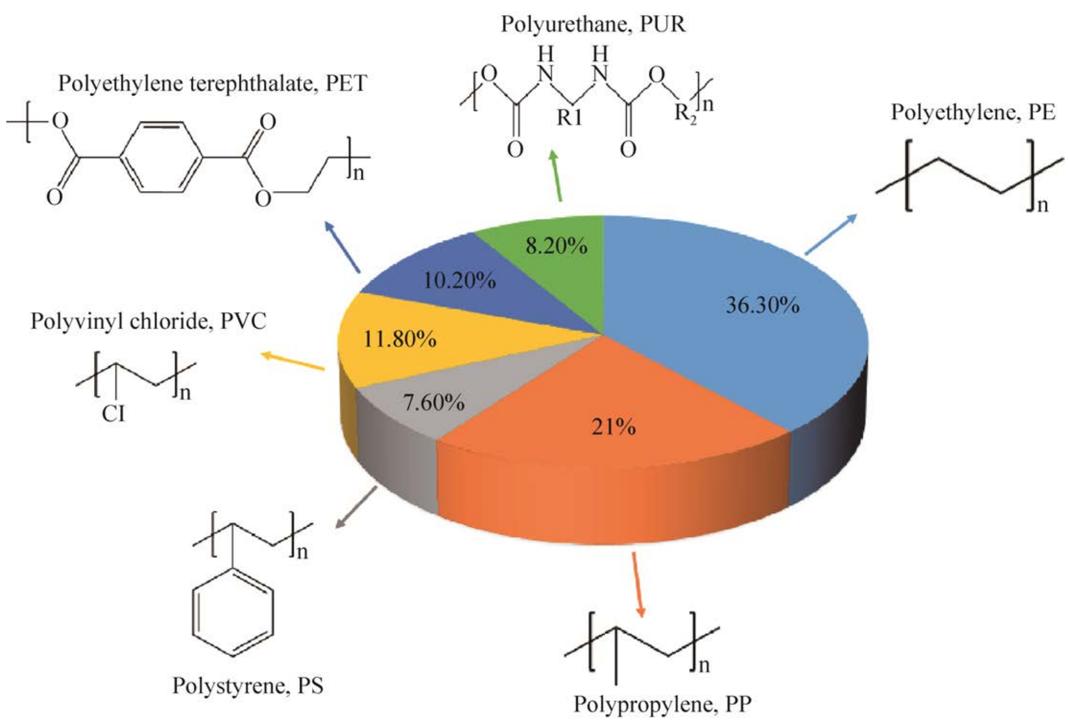

图 1 塑料的分类及市场占比

Figure 1 Classification and market share of plastics.

和抗冲击性好，主要应用于生产薄膜制品、日用品及工业用的各种中空容器、管材等；LDPE 由于其密度较低，材质最软，主要用作地膜、工业包装膜、药品食品包装膜等；LLDPE 是乙烯与少量高级 α-烯烃在催化剂作用下聚合而成的共聚物，外观上与 LDPE 类似，透明性较差，具有低温下抗冲击强度高的优点，主要用于生产管材、电线电缆等。由于高密度和高结晶度，HDPE 比 LDPE 和 LLDPE 更难被生物降解[9]。

产量居全球第二的是 PP,其化学结构与 PE 类似，但不同之处在于 PP 侧链含有甲基 ($-CH_3$)，是一种半结晶性材料，疏水性好，结晶度高，具有优良的力学性能；熔融温度约为 164–170 °C，比 PE 高 40%–50%；PP 可以被浓硫酸和浓硝酸侵蚀，对其他化学试剂较为稳定。鉴于其良好的材料性能，PP 广泛应用于各类商品包装、医疗用品、汽车配件等，被称为“包装塑料”，但 PP 很难被生物降解。另一方面，由于包装产品普遍使用周期较短，每年会产生大量的 PP 废弃物，例如疫情期间，全球每月使用和丢弃的口罩数量高达 1 290 亿个，其中核心材料熔喷布是以 PP 为原材料生产的，居民日常使用的口罩很难按照废弃医疗器械流程处理，遗弃到环境中将造成严重的环境问题。

PVC 是由氯乙烯单体在过氧化物、偶氮化合物等引发剂或在光、热作用下按自由基聚合反应机理聚合而成的聚合物，具有稳定的物理化学性质，广泛应用于雨衣、建材和塑料盒等。由于 PVC 中含有氯和多种添加剂[10] (双酚 A、邻苯二甲酸盐等)，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[11]。

PS 是由苯乙烯单体经自由基加聚反应合成的聚合物，其线性主链的骨架原子连接有苯环。PS 具有透明度高、刚度大、玻璃化温度高等特点，常被用于一次性餐具、儿童玩具等，但 PS 在高温下会产生有毒单体苯乙烯，世界卫生组织已经将 PS 列入 3 类致癌物。发泡 PS 比重低，易于漂浮于水面，是主要的海洋漂流物，海洋生物误食后会对消化系统造成伤害甚至死亡。

聚烯烃类塑料都含有高键能 C−C 键构成的稳定碳链骨架，不同材料的结构差异在于侧链基团，赋予了其不同的材料性能及应用范围。同时，聚烯烃类塑料的结构特点使其普遍难以被生物降解，主要原因是：(1) 聚烯烃类塑料化学结构稳定，主要由高键能的−C−C−和−C−H−共价键构成，缺乏易被氧化和水解的基团[12]；(2) 高分子量长链结构使其无法进入微生物细胞内被胞内酶降解；(3) 高度疏水性及高结晶度使其难以与细胞或酶接触发生生物降解反应[13]。

2 生物降解聚烯烃类塑料的微生物

塑料的生物降解是指在一定的条件下，通过细菌、真菌、甚至是某些昆虫的生理活动使塑料中的化学键断裂，分子量逐步变小，最终被同化吸收并支持细胞生长的过程。虽然聚烯烃类塑料化学结构稳定，难以被一般的微生物降解，但目前已经陆续发现一些微生物具有降解 PE、PP、PS、PVC 等聚烯烃类塑料的能力。

2.1 真菌对聚烯烃类塑料的降解

真菌可以在各种土壤条件下生长，并通过孢子扩散繁殖。一般来说，真菌对塑料等污染物具有较强的降解能力，这主要是由于真菌具有强大的酶系统、吸附能力以及产生天然生物表面活性剂的能力，这些特性使真菌能够利用塑料底物作为碳和电子的来源，为细胞提供物质和能量。近年来，已经发现很多对聚烯烃塑料具有降解作用的真菌(表 1)。

表 1 降解聚烯烃类塑料的真菌

Table 1 Fungal degradation of polyolefin plastics

Plastic type	Fungi	Source	Pretreatment method	Reaction condition	Degradation result	References
PE	*Aspergillus clavatus* JASK1	Landfill soil	Unpretreated LDPE films (bags)	Shaken flasks incubated for 90 days	Weight loss: 35.0%	[14]
	Collectotrichum fructicola	Culture collection of the Institute of Excellence in Fungal Research (CEFR)	LDPE microplastic granules made of LDPE film	90 days at 25 °C	Weight loss: 48.8%	[15]
	Penicillium citrinum	Plastic waste dump yard	Unpretreated LDPE films	90 days at 28 °C	Weight loss: 38.8%	[16]
	Cephalosporium	National Collection of Industrial Microorganism (NCIM)	Nitric acid treated HDPE film	20 days at 28 °C	Weight loss: 7.2%	[17]
	Aspergillus terreus BAYF5	Rhizosphere soil	PE films	60 days at room temperature	Weight loss: 58.5%	[18]
	Trichoderma viride RH03	Landfill soil	LDPE films	45 days at 28 °C	Weight loss: 5.1%	[19]
	Alternaria alternata FB1	Sea	Unpretreated LDPE film	28 days at 28 °C	Molecular weight: decreased 95.0%	[20]
	Aspergillus flavus PEDX3	*Galleria mellonella* gut	Unpretreated LDPE film	28 days at 25 °C	Reduction in the molecular weight	[21]
	Meyerozyma guilliermondii ZJC1	Larvae of *Plodia interpunctella*	Unpretreated PE film	60 days at 30 °C	Weight loss: 13.9%	[22]
	Aspergillus tubingensis VRKPT1 and *A. flavus* VRKPT2	Coastal area of India	Unpretreated HDPE film	12 weeks at 30 °C	Weight loss: 6.0% and 8.5%, respectively	[23]
PVC	*Chaetomium globosum*	André Tosello Culture Collection (ATCC)	Unpretreated PVC film	28 days at 28 °C	Weight loss: 9.0%	[24]
	Phanerochaete chrysosporium PV1	Soil	Unpretreated PVC film	7 weeks at 28 °C	Molecular weight reduction	[25]

大多数降解聚烯烃塑料的真菌是从土壤中分离得到的，尤其是长期存放塑料垃圾的填埋场。例如在垃圾填埋场分离得到的棒曲霉(*Aspergillus clavatus*) JASK1 与未经处理的 LDPE 膜孵育 3 个月后可使 LDPE 的重量损失 35.0%[14]，红外光谱(fourier transform infrared spectrometer, FTIR)检测到新的氧化基团，扫描电镜(scanning electron microscope, SEM)观察到 LDPE 膜明显破损，孵育 4 周后检测到 2.3 g/L 矿化产物 CO_2；同样来自垃圾填埋场的桔青霉(*Penicillium citrinum*)，在相同条件下孵育 3 个月后 LDPE 膜的重量损失达 38.8%[16]。除 PE 外，从土壤中还分离到小部分可以降解 PVC 的真菌，例如黄孢原平革菌(*Phanerochaete* *chrysosporium*) PV1 与 PVC 膜孵育 7 周后，PVC 膜的分子量明显降低[25]，SEM 和 FTIR 也分别观察到 PVC 膜表面破损并产生新的官能团。

海洋中存在大量塑料垃圾及微塑料颗粒，同时具有丰富的微生物资源。2022 年，孙超岷研究员在山东青岛汇泉湾分离得到 1 株降解 PE 的海洋真菌链格孢菌(*Alternaria alternata*) FB1[20]，该菌与 PE 膜孵育 120 d 后会产生明显的生物膜，通过 SEM 观察到 PE 膜表面出现破损，FTIR 检测到新的官能团−OH，气相-质谱(gas chromatograph-mass spectrometer, GC-MS)检测到降解产物二甘醇胺；此外，在印度沿海地区分离到塔宾曲霉(*Aspergillus tubingensis*) VRKPT1 和黄曲霉(*Aspergillus flavus*) VRKPT2 两株真菌，与 HDPE 培养 1 个月后，失重率分别为 6.0%和 8.5%[23]。

近年来，昆虫摄食聚烯烃塑料引起了研究人员的关注，最具代表性的包括鞘翅目(*Tenebrionidae*)的黄粉虫(*Tenebrio molitor*)[26]、黑粉虫(*Tenebrio obscurus*)[27]、大麦虫(*Zophobas morio*)[28]和鳞翅目(*Pyralidae*)的大蜡螟(*Galleria mellonella*)[29]、印度谷螟(*Plodia interpunctella*)[30]等，很可能此类昆虫的肠道微生物对聚烯烃塑料的生物降解发挥了重要作用。2022 年，东北林业大学张国财研究团队在蜡虫的肠道中分离得到了 1 株季也蒙迈耶氏酵母(*Meyerozyma guilliermondii*) ZJC1 (*Mg*ZJC1)和 1 株粘质沙雷氏菌(*Serratia marcescens*) ZJC2 (*Sm*ZJC2)[22]，并对蜡虫体内的 PE 生物降解机制进行了预测(图 2)：首先蜡虫通过咀嚼将塑料变成碎片进入到肠道，在肠道微生物的作用下降解成小分子，菌株 *Mg*ZJC1 可以降解 PE 产生有机酸和醛；菌株 *Sm*ZJC2 可以降解 PE 产生有机酸、盐酸盐和苯酚。作者通过多种手段证明了这 2 株菌能够降解 PE，首先与 *Mg*ZJC1 及 *Sm*ZJC2 孵育 60 d 后 PE 的重量损失分别达到 13.9%和 3.6%；SEM 观察到 PE 膜发生明显破损；FTIR 也显示有新的官能团产生，如−C=O 和−C−O−C 等；利用凝胶渗透色谱(gel permeation chromatography, GPC)确定了 PE 的分子量明显降低[22]。同样在蜡虫肠道中分离到的 *A. flavus* PEDX3 在与 HDPE 培养 28 d 后也有明显的分子量降低，FTIR 显示出现新的−OH，−C=O 和−C−O−C 等含氧基团[21]。

2.2 细菌对聚烯烃类塑料的降解

除真菌外，来自垃圾填埋场、废水、污泥等环境中的细菌也被报道具有聚烯烃塑料的生物降解能力(表 2)。细菌的生长速度较真菌快，遗传操作手段丰富，代谢途径清晰，更加便于聚烯烃塑料生物降解机制的研究。

相比于真菌，降解聚烯烃类塑料的细菌种类更多，降解底物的范围更广，真菌的生物降解研究大多集中在 PE，而细菌对 PE、PP、PS 和 PVC 等不同类型的聚烯烃塑料都有降解作用。土壤中降解聚烯烃类塑料的细菌以芽孢杆菌(*Bacillus* sp.)为主，如土壤中分离得到的 *Bacillus* sp.与高抗冲聚苯乙烯(high-impact polystyrene, HIPS)膜孵育 30 d 后可使 PS 膜失重 23.7%[43]；在红树林土壤中分离到的蜡样芽孢杆菌(*Bacillus cereus*)对经过紫外线照射预处理的 PP 粉末和 PE 粉末均具有降解作用，失重率在 40 d 内分别达到 3.6%和 1.6%，与 *B. cereus* 同时分离得到的 *B. gottheilii* 对经过紫外线照射处理的 PE 粉末也有降解作用，40 d 内失重率达 6.2%[37]，对于 PE 的降解率明显低于上述 HIPS，除了不同菌株间降解能力差异，另外一个重要原因是 HIPS 是 PS 和聚丁二烯的混合物，相比于纯的 PE 更易降解。此外，还有一些芽孢杆菌如 *Bacillus* sp. MYK2[60]、*B. amyloliquefaciens* BSM-1 和 *B. amyloliquefaciens* BSM-2 等也被分离鉴定具有降解不同类型聚烯烃类塑料的

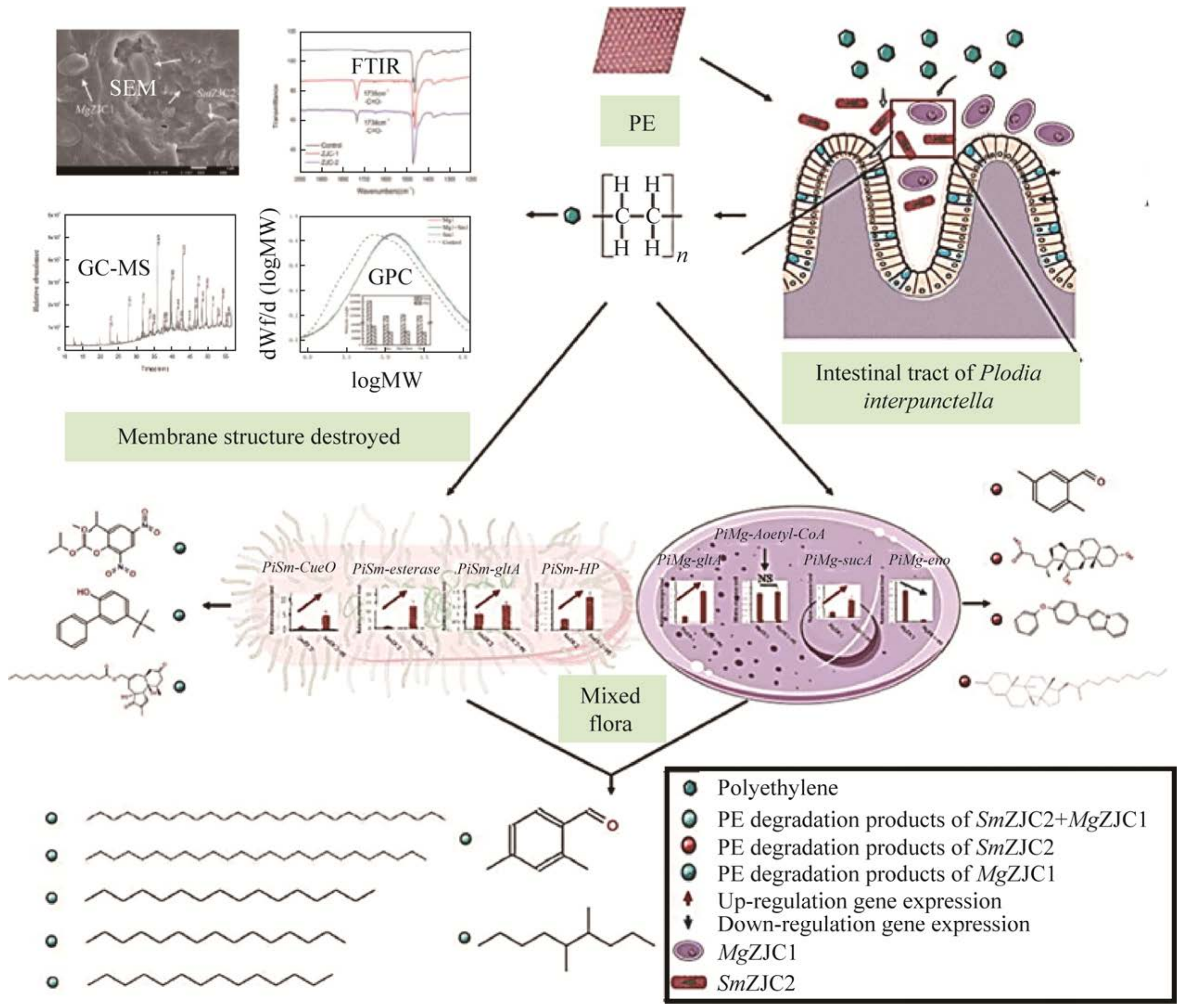

图 2　*Mg*ZJC1 和 *Sm*ZJC2 降解聚乙烯示意图[22]

Figure 2　Scheme of polyethylene degradation by strains *Mg*ZJC1 and *Sm*ZJC2[22].

表 2　降解聚烯烃类塑料的细菌

Table 2　Bacterial degradation of polyolefin plastics

Plastic type	Bacteria	Source	Pretreatment method	Reaction condition	Degradation result	References
PE	*Rhodococcus ruber* C208	PE agricultural waste in soil	Unpretreated LDPE film	8 weeks at 37 °C	Weight loss: 7.5%	[31]
	Rhodococcus sp.	Three forest soils	Preoxidized LDPE film	30 days at 30 °C	Confirmation of adherence	[32]
	Spingobacterium moltivorum IRN19	Plastic dump soil	UV-irradiated LDPE film	4 weeks at 30 °C	Weight loss: 26.8%±3.04%	[33]
	Stentrophomonas sp.	Plastic debris in soil	Unpretreated LDPE film	30 days at 28 °C	Change in chemical properties	[34]
	Stentrophomonas pavanii	Solid waste dump site	Modified LDPE	56 days at 30 °C	Confirmed by FTIR	[35]
	S. marcescens	Soil	LLDPE powder made of LLDPE film	70 days at 30 °C	Weight loss: 36.0%	[36]
	Bacillus gottheilii and *Bacillus cereus*	Soil	UV-pretreated PE powder	40 days at 30 °C	Weight loss: 6.2% and 1.6%, respectively	[37]

(待续)

(续表 2)

Plastic type	Bacteria	Source	Pretreatment method	Reaction condition	Degradation result	References
	Alcanivorax borkumensis	Mediterranean Sea	Unpretreated LDPE film	7 days at 30 °C	Weight loss: 3.5%	[38]
	Pseudomonas aeruginosa PAO1	ATCC	Unpretreated LDPE film	120 days at 37 °C	Weight loss: 20.0%	[39]
	Enterobacter sp. D1	Guts of wax moth *Galleria mellonella*	Unpretreated PE film	31 days at 37 °C	Morphology changes	[40]
	Enterobacter asburiae YT1 and *Bacillus* sp. YP1	Guts of plastic-Eating waxworms	Unpretreated LLDPE film	60 days at 30 °C	Weight losses of 6.1% and 10.7% after incubation with *E. asburiae* YT1 and *Bacillus* sp. YP1, respectively	[41]
	Raoultella ornithinolytica MP-1	Solid waste dump site	Unpretreated PE film	30 days at 28 °C	Weight loss: 4.4%	[42]
PS	*Pseudomonas* sp.	Soil	Unpretreated high-impact PS films	30 days at 30 °C	Weight loss: more than 10.0%	[43]
	Bacillus sp.	Soil	Unpretreated high-impact PS films	30 days at 30 °C	Weight loss: 23.7%	[43]
	Exiguobacterium sp. strain YT2	Guts of the larvae of *Tenebrio molitor Linnaeus*	Unpretreated styrofoam PS films	60 days	Weight loss: 7.4% Mw decrease: 11.0%	[44]
	Exiguobacterium sp. strain YT2	Degraded plastic waste	High-impact PS	30 days at 30 °C	Weight loss: 12.4%	[45]
	R. ruber C208		Unpretreated styrofoam PS films	8 weeks at 28 °C	Weight loss: 0.8%	[46]
PP	*Stenotrophomonas panacihumi* PA3-2	Soil	Unpretreated PP powder	90 days at 37 °C	Mw decreased	[47]
	R. rhodochrous ATCC 29672	ATCC	PP film with pro-oxidant additives	180 days	Changes in ATP levels	[48]
	Bacillus flexus	Plastic dumping site	UV-pretreated PP film	1 year	Weight loss: 2.5%	[49]
	Pseudomonas sp. WZH-4	Guts of insect larvae	Unpretreated PP	30 days at 37 °C	Weight loss: 4.57%	[50]
	Bacillus cereus	Mangrove sediments	UV-pretreated PP granules	40 days at 30 °C	Weight loss: 3.6%	[37]
	Sporosarcina globispora	Mangrove sediments	UV-pretreated PP granules	40 days at 30 °C	Weight loss: 11.0%	[37]
	Bacillus sp.	Municipal compost waste	Unpretreated PP powder	15 days at 37 °C	Weight loss: 10.0%–12.0%	[51]
	Psychrobacillus sp.	Plastic dumping site	Unpretreated PP	60 days at 30 °C	Weight loss: 6.0%	[52]
	Pseudomonas sp.	Plastic dumping site	Unpretreated PP	60 days at 37 °C	Weight loss: 4.6%	[53]
	Staphylococcus sp.	Plastic dumping Site	Unpretreated PP	60 days at 37 °C	Weight loss: 5.0%	[54]
PVC	*P. citronellolis*	Collection of microorganisms and cell cultures	PVC film with 30% additives	30 days at 30 °C	Weight loss: 19.0%	[55]
	Alteromonas sp. BP-4.3	Marine	Unpretreated PVC film	60 days at 30 °C	Weight loss: 1.8%	[56]
	Achromobacter denitrificans Ebl13	Compost	Thermo-oxidative pretreated LDPE film	30 days at 30 °C	Weight loss: 12.3%	[57]
	Klebsiella sp. EMBL-1	Guts of insect larvae	Unpretreated PVC film	90 days at 30 °C	Weight loss: 19.6%	[58-59]

能力[61]。除芽孢杆菌外，来自土壤的鸟氨酸拉乌尔菌(*Raoultella ornithinolytica*) MP-1 在 60 d 内可使 PE 失重达 4.4%，膜表面出现明显破损[42]；假单胞菌(*Pseudomonas* sp.) WZH-4[53]、葡萄球菌(*Staphylococcus* sp.)[54]、冷杆菌(*Psychrobacillus* sp.) LICME-ZWZR-10[52]等可以降解 PP；克雷伯菌(*Klebsiella pneumoniae*)[62]、莴苣不动杆菌(*Acinetobacter dijkshoorniae*)[63]可以降解 PE；戈登氏菌(*Gordonia* sp.)能降解 PS，降解率为 2.7%−7.7%[64]。最近，本课题组在山东东营石油污染的土壤中筛选到 1 株鸟氨酸拉乌尔菌(*Raoultella* sp.) DY2415，该菌对 PS 和紫外线照射处理过的 PE (UVPE)都具有明显的降解作用，60 d 内可以使 UVPE 失重达 8.0%，通过 FTIR 观察到新的官能团如−OH、−C=O 等，SEM 显示塑料膜表面有大量细菌附着并产生明显裂缝。

海洋也是聚烯烃塑料降解细菌的重要来源。2018 年，研究者在海洋沉积物中分离得到了红球菌(*Rhodococcus*)菌株 36，其在 40 d 内可以使 PP 失重达 6.4%[65]。*R. ruber* C-208 可以以每周 0.9%的降解速率降解 PE，同时，该菌株在培养 56 d 后，PE 的失重率达 7.5%[31]；2022 年同济大学马杰团队在湖底沉积物中分离得到了 1 株降解 PS 的 *B. cereus* CH6，孵育 50 d 后，该菌对 0.5 g PS 的降解率达 10.7%，并且研究发现在降解过程中细菌胞外蛋白质浓度和酯酶活性出现由低到高的变化[66]。此外，还有很多细菌对聚烯烃类塑料具有降解作用，例如海洋细菌食烷菌(*Alcanivorax* sp.) 24 可以在 34 d 内使 LDPE 的分子量从 122 kg/mol 降低到 83 kg/mol[67]；*A. borkumensis* 与未经处理的 LDPE 膜孵育 7 d 后失重率达 3.5%。

昆虫肠道中分离到了一系列可以降解聚烃类塑料的细菌，2018 年研究者在黄粉虫中分离到产酸克雷伯氏菌(*Klebsiella oxytoca*)、费格森埃希菌(*Escherichia fergusonii*)及芽孢杆菌(*B. cereus*) Reborn，这 3 株菌的共培养物对 PE、PP、PS、PVC 都具有降解作用[50]。2019 年，Ren 等使用以 PE 为唯一碳源的培养基从 *G. mellonella* 幼虫肠道中筛选到了肠杆菌(*Enterobacter* sp.) D1[40]，PE 膜经过菌悬液处理 14 d 后表面出现凹陷、裂纹、羰基和醚官能团，培养上清液经色谱分析也发现了与 PE 生物降解相关的代谢物；2020 年，研究发现昆虫肠道分离到的不动杆菌(*Acinetobacter* sp.) NyZ450 和 *Bacillus* sp. NyZ451 与 PE 膜共培养 30 d 后，检测到 PE 膜分子量明显下降，FTIR 也显示 PE 膜表面被氧化[68]；2022 年研究者在昆虫肠道中分离得到了 1 株可以降解 PVC 的变栖克雷伯菌(*Klebsiella* sp.) EMBL-1，经过 90 d 培养后，PVC 膜的重量损失达 19.6%，分子量也明显下降[58-59]。

3 聚烯烃塑料的生物降解机制

聚烯烃塑料的生物降解是一个复杂的过程，可以简单概括为在生物及非生物因素的共同作用下，塑料聚合物的分子量逐渐下降，产生的小分子降解物进入细胞内参与物质代谢，最终转变为碳源和能量供细胞生长。通常将生物降解过程分成 4 个阶段：定殖、解聚、同化和矿化(图 3)[69]。

3.1 定殖

定殖是指微生物在塑料表面形成生物膜的过程。生物膜的形成是塑料生物降解的第 1 阶段，同时也是必要阶段[70]。微生物通过分泌多糖等物质可以牢固附着在塑料表面，例如具有 PE 降解活性的 *R. ruber* 在与 PE 共培养时形成了三维的“蘑菇状”生物膜[31]。生物膜的形成可以降低塑料的浮力和疏水性[71]，增加微生物分泌的酶与塑料底物的接触面积，该阶段塑料膜

表面可能会出现劣化、孔洞等。此外，一些非生物因素也会引起塑料表面物理化学性质的变化，如紫外线照射、机械损伤和极端温度等。经过非生物因素处理后的聚烯烃塑料更加有利于微生物降解，例如来自链霉菌(*Streptomyces* sp.) K30 的乳胶清除蛋白 Lcp_{K30} 对紫外线照射处理过的 PE (UVPE)和 PP (UVPP)有明显降解效果，具体表现为 FTIR 观察到 UVPE 和 UVPP 膜上有新的官能团产生，如−OH 和−C=O；SEM 显示酶处理后的 UVPE 和 UVPP 膜明显变粗糙，出现裂纹和凹坑；GPC 也观察到分子量的下降[72]。2022 年有研究者利用漆酶介质体系氧化 UVPE 膜，并通过 GC-MS 检测到降解产物油酸和鲨烯[73]。

3.2 解聚

形成生物膜后塑料表面会发生劣化，微生物会通过分泌胞外酶催化聚烯烃塑料化学键的断裂，降低其分子量并释放小分子物质。目前认为氧化还原反应是破坏聚烯烃塑料 C−C 主链的主要方式，虽然具体反应机制仍不清楚，但该过程往往伴随自由基的产生，漆酶、锰过氧化物酶、烷烃羟化酶等均被报道对聚烯烃塑料具有降解作用(表 3)。

真菌中具有聚烯烃类塑料降解能力的酶主要是过氧化物酶和氧化酶等[82-84]。例如哈茨木霉(*Trichoderma harzianum*)中的漆酶和过氧化物酶在 PE 降解过程中发挥了重要作用，在与 PE 膜孵育 10 d 后,质量分别减少了 0.5%和 0.6%[85]，同时 FTIR 检测到了羧酸、醛、芳烃、醇、酯、醚和烷基卤化物等特征基团。2022 年江南大学吴敬团队发现来源于杏鲍菇(*Pleurotus eryngii*)的过氧化物酶对紫外线照射过的 PE 具有降解作用，通过 GC-MS 检测到了醛、酮、醇和酸等降解产物，利用 SEM 和 FTIR 观察到 PE 膜表面变得粗糙褶皱并且有新的官能团产生[86]。在大肠杆菌中异源表达并纯化来源于白腐真菌(*Gelatoporia subvermispora*)的锰过氧化物酶，与经过紫外线照射的 PE 膜孵育后，膜表面出现刻蚀，亲水性也明显增强，同时检测到了醛、酮等小分子化合物[87]。除 PE 外，来自 *P. chrysosporium* 的木质素过氧化物酶对 PVC 具有降解效果，经纯酶处理后，PVC 的重

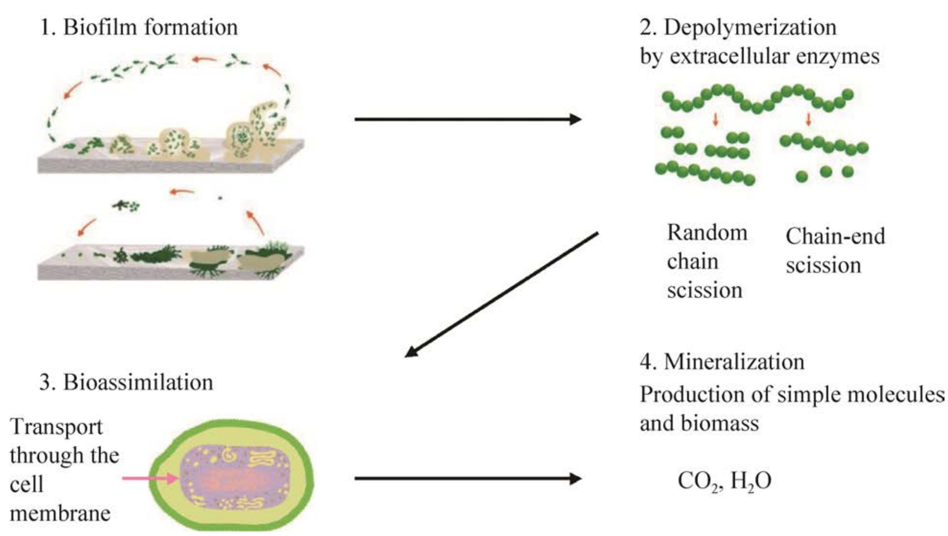

图 3 聚烯烃塑料的生物降解过程[69]

Figure 3 The biodegradation process of polyolefin plastics[69].

表 3　对聚烯烃类塑料具有降解作用的酶

Table 3　Enzymes capable of degrading polyolefin plastics

Enzyme	Isolated source	Plastic type	Incubation time	Degradation effect	References
Manganese peroxidase	*P. chrysosporium*	PE film	12 days	Molecular weight decreased	[74]
Soybean peroxidase	Soybean	HDPE film	2 hours	–	[75]
Laccase	*R. ruber* C208	LDPE film	30 days	Weight loss: 2.5%	[76]
Alkane hydroxylase	*Pseudomonas* sp. E4	LDPE film	80 days	Weight loss: 19.3%	[77]
Demetra	The saliva of *Galleria mellonella* larvae	PE film	90 min	Detect 2-ketones	[78]
Ceres	The saliva of *Galleria mellonella* larvae	PE film	90 min	Detect 2-ketones	[78]
Hydroquinone peroxidase	*Azotobacter beijerinckii* HM121	PS film	20 min	Molecular weight decreased	[79]
Alkane hydroxylase	*A. johnsonii* JNU01	PS powder	7 days	Confirmed by SEM and FTIR	[80]
Laccase	*Botrytis aclada* and *Bacillus subtilis*	UVPE film	24 hours	Detect oxygen-containing products	[73]
Lignin peroxidase	*P. chrysosporium*	PVC film	4 weeks	Weight loss: 31%	[81]

量减少 31.0%[81]。细菌中也发现了一些对聚烯烃塑料具有降解作用的酶，如 *Pseudomonas* sp. E4 AlkB 家族的烷烃羟化酶，在 80 d 内将低分子量聚乙烯(low molecular weight polyethylene, LMWPE)中 19.3%的碳转化为 CO_2[77]。2022 年，来自西班牙最高科学理事会生物学研究中心的 Federica Bertocchini 团队发现 *G. mellonella* 的唾液能够快速氧化并降解 PE。通过对唾液成分的深入研究，最终发现了 2 种属于苯酚氧化酶家族的酶 Demetra 和 Ceres，在室温条件下短时间内对 PE 膜表现出了降解活性，同时通过 FTIR 检测到了新官能团 C−O−C 和 C−COO[78]。

氧化酶对聚烯烃塑料的生物降解普遍遵循自由基氧化原理。例如漆酶将电子从有机物转移至分子氧，而血红素过氧化物酶使用 H_2O_2 作为底物进行氧化还原反应，这一过程会产生活性氧自由基(羟基自由基·OH 和超氧阴离子自由基 O_2^{-}·)[88]。自由基在化学上也称“游离基”，是含有 1 个不成对电子的原子团，由于化学键中的电子必须成对出现，因此自由基需要夺取其他物质的 1 个电子，使自己成为稳定的物质，这种现象称为“氧化”。2021 年，研究人员通过量子化学模拟和计算探究了羟基自由基·OH 和超氧阴离子自由基 O_2^{-}·对 PE 的氧化作用。结果表明 C6 模式底物上的氢原子可以转移到·OH 上，形成烷烃自由基 R·和 1 分子水，这种氢原子的转移会引发烷烃的裂解反应，R·与 O_2 反应后产生过氧自由基 ROO·，通过计算 ROO·与烷烃 RH 和 R·反应的活化能，发现这 2 种反应都可以在常温常压下自发进行，进一步氧化产生 ROOH 和 ROO^{-} (图 4)[89]。

以 *P. chrysosporium* 的锰过氧化物酶(MnP)为例[84]，MnP 的活性位点包括 Asp179、Ala79、Ser78、Arg42、Glu35、Glu143、Glu39、Asn81、His46、Phe45、Pro142，丙酸血红素和 2 个水分子(图 5A)，在含有 H_2O_2 的酸性条件下发挥催

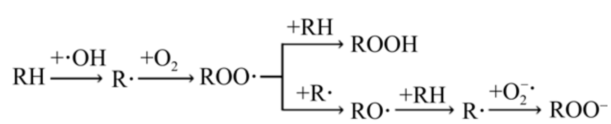

图 4　烷烃氧化反应途径[89]

Figure 4　The oxidation reaction pathway of alkanes[89].

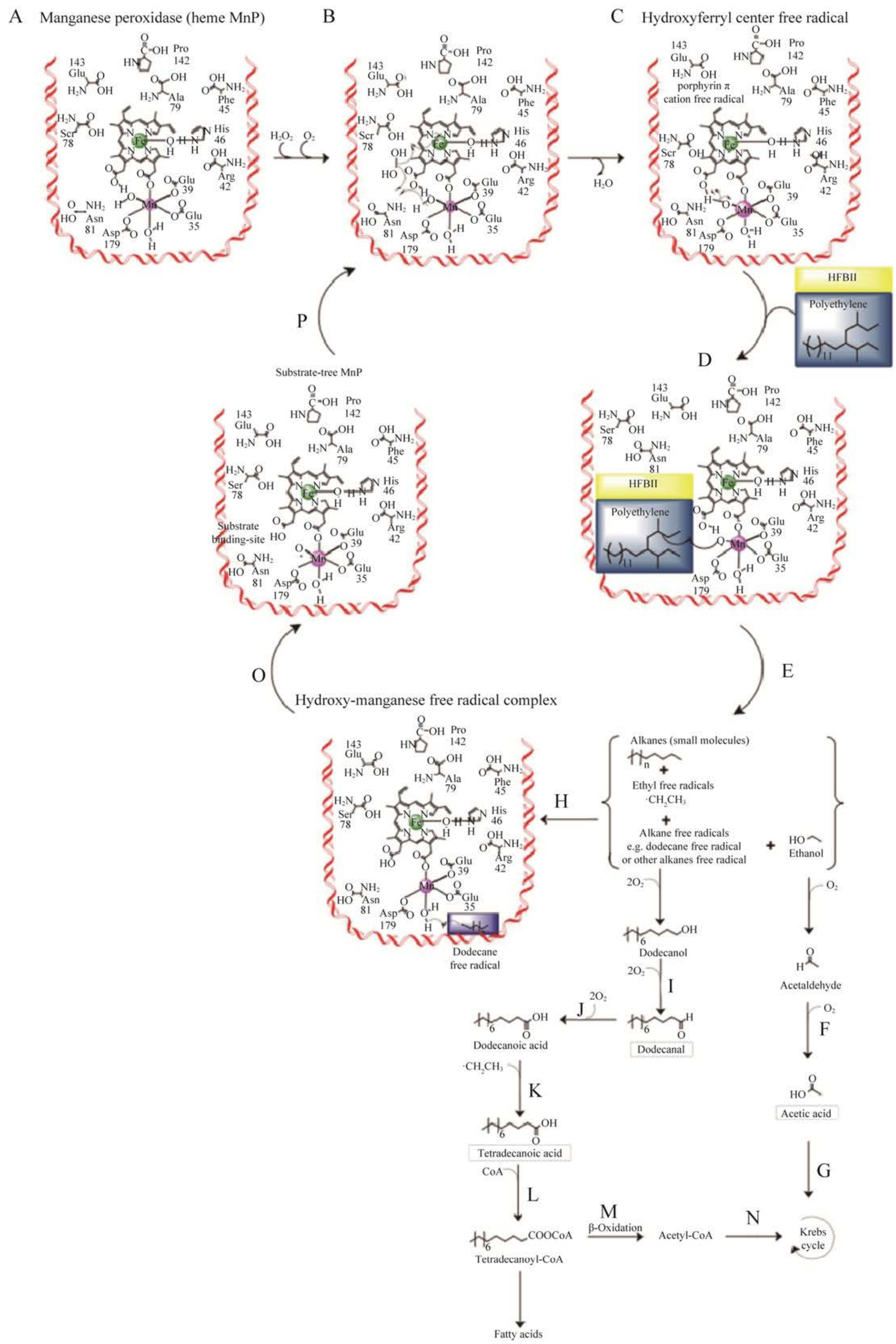

图 5 ***Phanerochaete chrysosporium*** **中潜在的 PE 生物降解机制[84]**

Figure 5 Potential mechanisms of PE biodegradation in *Phanerochaete chrysosporium* [84].

化作用。H_2O_2 作为氧化剂通过均裂释放出 2 个 ·OH，其中 1 个·OH 与 MnP 上的氢结合，另 1 个 ·OH 与 Fe^{2+}结合，释放出 1 分子的水(图 5B)；然后铁-卟啉配合物发生均裂生成卟啉-π-阳离子自由基和羟基铁中心自由基，其中卟啉-π-阳离子自由基与羟基铁中心自由基的氢结合，羟基铁中心自由基上丙酸中的氧与水中氢共价结合生成氧锰自由基(图 5C)；随后 PE 进入 MnP 的活性位点，与氧锰自由基的氧反应生成氧铁-MnP 自由基复合物(图 5D)；最后 PE 在 MnP 的作用下分解成小分子，如烷烃、烷烃自由基等(图 5E)。

3.3 同化

同化是指聚烯烃塑料解聚过程产生的小分子物质被细胞吸收并参与生化代谢的过程。聚烯烃塑料分子量降低后增加了被细胞膜上受体识别的可能性，可以通过细胞膜转运进细胞内参与物质代谢。聚烯烃类塑料结构与烷烃相似，可以参照烷烃的同化途径[90]。以图 5 为例，PE 生物解聚过程中产生的烷烃和烷烃自由基，可以进入细胞并发生一系列氧化反应，它们会依次氧化为醛(图 5I)和羧酸(图 5K)，最后与辅酶 A 反应生成酰基辅酶 A 经 β 氧化生成乙酰辅酶 A，进入矿化阶段。

3.4 矿化

矿化是聚烯烃塑料生物降解的最后一步，是指塑料解聚后的分子在微生物细胞内经过物质代谢，最终氧化生成 CO_2、N_2、CH_4 等物质或积累生物质的过程[91]。以图 5 为例，同化过程将进入细胞内的烷烃代谢生成乙酰辅酶。接着进入矿化阶段，乙酰辅酶 A 会通过三羧酸循环矿化成 CO_2 和生物质(图 5O)，完成整个聚烯烃塑料的生物降解过程。

4 总结与展望

聚烯烃类塑料作为 1 种由 C−C 键骨架构成的高分子聚合物，具有多样的化学结构及物理特性，且难以被生物降解。虽然目前已经发现一些微生物甚至昆虫具有聚烯烃塑料的降解能力，但目前生物降解效率仍然较低，其中涉及的酶和底物较多，具体的生物降解机制及关键酶仍有待明确。探究聚烯烃类塑料的生物降解机制并提高其生物降解效率是未来的主要研究方向。以下 3 个问题需要重点关注：(1) 目前生物降解聚烯烃塑料的表征手段虽然很多，但标准模糊，大部分仍停留在定性层面，如通过电子显微镜观察微生物对于塑料膜的侵蚀时，通常局限在塑料膜局部的表面变化，难以衡量对于塑料整体的降解效果，并且受主观因素影响较大。另外，一些环境因素及塑料添加剂也会干扰对于聚烯烃塑料生物降解效果的判断。针对该问题，应建立更加系统规范的聚烯烃塑料生物降解表征方法，通过多个维度衡量微生物对于聚烯烃塑料的生物降解能力，如宏观层面的塑料形态变化、物理性质变化、重量损失和微观层面的物质组成变化等，尤其是采取合适的降解产物分析方法，明确生物降解过程产生的小分子降解物，这将有利于后续生物降解机制的研究。(2) 聚烯烃类塑料化学结构高度稳定、疏水性强，这些材料特性决定了单纯依靠微生物作用可能难以实现高效的生物降解。针对该问题，通过一些绿色的物理化学方法，对聚烯烃塑料进行预处理，如增加材料的比表面积、疏水性，甚至通过化学氧化技术添加羟基等更易水解的化学基团，可以明显提升聚烯烃塑料的生物可降解性。再与生物降解技术有机结合，引入对应的生物降解途径，优化整个降解工艺，提高整体的降解效率。(3) 目前聚烯烃塑料的生物降解研究主要集中在降解微生物的筛选鉴定方面，具体的生物降解机制，尤其是发挥作用的关键酶，还有待深入研究。针对该

问题，应结合基因组、转录组、代谢组等多组学技术，深入分析聚烯烃降解微生物的遗传特性，挖掘生物降解相关的关键酶。从分子层面解析聚烯烃塑料的生物降解机制，并通过蛋白质工程技术提高关键酶的催化活性，进而推动聚烯烃塑料的绿色高效循环利用。

REFERENCES

[1] RODRIGUES MO, ABRANTES N, GONÇALVES FJM, NOGUEIRA H, MARQUES JC, GONÇALVES AMM. Impacts of plastic products used in daily life on the environment and human health: what is known?[J]. Environmental Toxicology and Pharmacology, 2019, 72: 103239.

[2] da COSTA JP. The 2019 global pandemic and plastic pollution prevention measures: playing catch-up[J]. Science of the Total Environment, 2021, 774: 145806.

[3] ORTIZ D, MUNOZ M, NIETO-SANDOVAL J, ROMERA-CASTILLO C, de PEDRO ZM, CASAS JA. Insights into the degradation of microplastics by Fenton oxidation: from surface modification to mineralization[J]. Chemosphere, 2022, 309: 136809.

[4] 郭鸿钦，罗丽萍，杨宇航，王宇萌，陆遥力，赵鑫，胡筱敏. 利用昆虫取食降解塑料研究进展[J]. 应用与环境生物学报, 2020, 26(6): 1546-1553.
GUO HQ, LUO LP, YANG YH, WANG YM, LU YL, ZHAO X, HU XM. Research progress on plastic degradation by worms[J]. Chinese Journal of Applied and Environmental Biology, 2020, 26(6): 1546-1553 (in Chinese).

[5] KADAC-CZAPSKA K, KNEZ E, GREMBECKA M. Food and human safety: the impact of microplastics[J]. Critical Reviews in Food Science and Nutrition, 2022: 1-20.

[6] GEYER R, JAMBECK JR, LAVENDER LAW K. Production, use, and fate of all plastics ever made[J]. Science Advances, 2017, 3(7): e1700782.

[7] 张彤，刘盼，王倩，梁泉峰，祁庆生. 降解石油基塑料的微生物及微生物菌群[J]. 生物工程学报，2021, 37(10): 3520-3534.
ZHANG T, LIU P, WANG Q, LIANG QF, QI QS. Degradation of petroleum-based plastics by microbes and microbial consortia[J]. Chinese Journal of Biotechnology, 2021, 37(10): 3520-3534.

[8] ALI SS, ELSAMAHY T, AL-TOHAMY R, ZHU DC, MAHMOUD YAG, KOUTRA E, METWALLY MA, KORNAROS M, SUN JZ. Plastic wastes biodegradation: mechanisms, challenges and future prospects[J]. Science of the Total Environment, 2021, 780: 146590.

[9] CHAMAS A, MOON H, ZHENG JJ, QIU Y, TABASSUM T, JANG JH, ABU-OMAR M, SCOTT SL, SUH S. Degradation rates of plastics in the environment[J]. ACS Sustainable Chemistry & Engineering, 2020, 8(9): 3494-3511.

[10] REDDY MS, YAMAGUCHI T, OKUDA T, TSAI TY, NAKAI S, NISHIJIMA W, OKADA M. Feasibility study of the separation of chlorinated films from plastic packaging wastes[J]. Waste Management, 2010, 30(4): 597-601.

[11] GLAS D, HULSBOSCH J, DUBOIS P, BINNEMANS K, de vos DE. End-of-life treatment of poly(vinyl chloride) and chlorinated polyethylene by dehydrochlorination in ionic liquids[J]. ChemSusChem, 2014, 7(2): 610-617.

[12] ARTHAM T, DOBLE M. Biodegradation of aliphatic and aromatic polycarbonates[J]. Macromolecular Bioscience, 2008, 8(1): 14-24.

[13] ZHANG Y, PEDERSEN JN, ESER BE, GUO Z. Biodegradation of polyethylene and polystyrene: from microbial deterioration to enzyme discovery[J]. Biotechnology Advances, 2022, 60: 107991.

[14] GAJENDIRAN A, KRISHNAMOORTHY S, ABRAHAM J. Microbial degradation of low-density polyethylene (LDPE) by *Aspergillus clavatus* strain JASK1 isolated from landfill soil[J]. 3 Biotech, 2016, 6(1): 1-6.

[15] KHRUENGSAI S, SRIPAHCO T, PRIPDEEVECH P. Low-density polyethylene film biodegradation potential by fungal species from Thailand[J]. Journal of Fungi, 2021, 7(8): 594.

[16] KHAN S, ALI SA, ALI AS. Biodegradation of low density polyethylene (LDPE) by mesophilic fungus '*Penicillium citrinum*' isolated from soils of plastic waste dump yard, Bhopal, India[J]. Environmental Technology, 2022: 1-15.

[17] CHAUDHARY AK, VIJAYAKUMAR RP. Effect of chemical treatment on biological degradation of

high-density polyethylene (HDPE)[J]. Environment, Development and Sustainability, 2020, 22(2): 1093-1104.

[18] SANGALE MK, SHAHNAWAZ M, ADE AB. Potential of fungi isolated from the dumping sites mangrove rhizosphere soil to degrade polythene[J]. Scientific Reports, 2019, 9: 5390.

[19] MUNIR E, HAREFA RM, PRIYANI N, SURYANTO D. Plastic degrading fungi *Trichoderma viride* and *Aspergillus nomius* isolated from local landfill soil in Medan[J]. IOP Conference Series: Earth and Environmental Science, 2018, 126: 012145.

[20] GAO RR, LIU R, SUN CM. A marine fungus *Alternaria alternata* FB1 efficiently degrades polyethylene[J]. Journal of Hazardous Materials, 2022, 431: 128617.

[21] ZHANG JQ, GAO DL, LI QH, ZHAO YX, LI L, LIN HF, BI QR, ZHAO YC. Biodegradation of polyethylene microplastic particles by the fungus *Aspergillus flavus* from the guts of wax moth *Galleria mellonella*[J]. Science of the Total Environment, 2020, 704: 135931.

[22] LOU H, FU R, LONG TY, FAN BZ, GUO C, LI LL, ZHANG J, ZHANG GC. Biodegradation of polyethylene by *Meyerozyma guilliermondii* and *Serratia marcescens* isolated from the gut of waxworms (larvae of *Plodia interpunctella*)[J]. Science of the Total Environment, 2022, 853: 158604.

[23] SANGEETHA DEVI R, RAJESH KANNAN V, NIVAS D, KANNAN K, CHANDRU S, ROBERT ANTONY A. Biodegradation of HDPE by *Aspergillus* spp. from marine ecosystem of gulf of mannar, India[J]. Marine Pollution Bulletin, 2015, 96(1/2): 32-40.

[24] VIVI VK, MARTINS-FRANCHETTI SM, ATTILI-ANGELIS D. Biodegradation of PCL and PVC: *Chaetomium globosum* (ATCC 16021) activity[J]. Folia Microbiologica, 2019, 64(1): 1-7.

[25] ALI MI, AHMED S, ROBSON G, JAVED I, ALI N, ATIQ N, HAMEED A. Isolation and molecular characterization of polyvinyl chloride (PVC) plastic degrading fungal isolates[J]. Journal of Basic Microbiology, 2014, 54(1): 18-27.

[26] BRANDON AM, GARCIA AM, KHLYSTOV NA, WU WM, CRIDDLE CS. Enhanced bioavailability and microbial biodegradation of polystyrene in an enrichment derived from the gut microbiome of *Tenebrio molitor* (mealworm larvae)[J]. Environmental Science & Technology, 2021, 55(3): 2027-2036.

[27] PENG BY, SU YM, CHEN ZB, CHEN JB, ZHOU XF, BENBOW ME, CRIDDLE CS, WU WM, ZHANG YL. Biodegradation of polystyrene by dark (*Tenebrio obscurus*) and yellow (*Tenebrio molitor*) mealworms (Coleoptera: Tenebrionidae)[J]. Environmental Science & Technology, 2019, 53(9): 5256-5265.

[28] KIM SY, KIM HG, SONG SH, KIM NJ. Developmental characteristics of *Zophobas atratus* (Coleoptera: Tenebrionidae) larvae in different instars[J]. International Journal of Industrial Entomology, 2015, 30(2): 45-49.

[29] BOMBELLI P, HOWE CJ, BERTOCCHINI F. Polyethylene bio-degradation by caterpillars of the wax moth *Galleria mellonella*[J]. Current Biology, 2017, 27(8): R292-R293.

[30] PIVATO AF, MIRANDA GM, PRICHULA J, LIMA JEA, LIGABUE RA, SEIXAS A, TRENTIN DS. Hydrocarbon-based plastics: progress and perspectives on consumption and biodegradation by insect larvae[J]. Chemosphere, 2022, 293: 133600.

[31] SIVAN A, SZANTO M, PAVLOV V. Biofilm development of the polyethylene-degrading bacterium *Rhodococcus ruber*[J]. Applied Microbiology and Biotechnology, 2006, 72(2): 346-352.

[32] Koutny M, AMATO P, MUCHOVA M, RUZICKA J, DELORT ANNE-MARIE. Soil bacterial strains able to grow on the surface of oxidized polyethylene film containing prooxidant additives[J]. International Biodeterioration & Biodegradation, 2009, 63(3): 354-357.

[33] MONTAZER Z, HABIBI-NAJAFI MB, MOHEBBI M, OROMIEHEI A. Microbial degradation of UV-pretreated low-density polyethylene films by novel polyethylene-degrading bacteria isolated from plastic-dump soil[J]. Journal of Polymers and the Environment, 2018, 26(9): 3613-3625.

[34] PEIXOTO J, SILVA LP, KRÜGER RH. Brazilian Cerrado soil reveals an untapped microbial potential for unpretreated polyethylene biodegradation[J]. Journal of Hazardous Materials, 2017, 324: 634-644.

[35] MEHMOOD CT, QAZI IA, HASHMI I, BHARGAVA S, DEEPA S. Biodegradation of low density

polyethylene (LDPE) modified with dye sensitized titania and starch blend using *Stenotrophomonas pavanii*[J]. International Biodeterioration & Biodegradation, 2016, 113: 276-286.

[36] AZEKO ST, ETUK-UDO GA, ODUSANYA OS, MALATESTA K, ANUKU N, SOBOYEJO WO. Biodegradation of linear low density polyethylene by *Serratia marcescens* subsp. marcescens and its cell free extracts[J]. Waste and Biomass Valorization, 2015, 6(6): 1047-1057.

[37] AUTA HS, EMENIKE CU, FAUZIAH SH. Screening of *Bacillus* strains isolated from mangrove ecosystems in Peninsular Malaysia for microplastic degradation[J]. Environmental Pollution, 2017, 231: 1552-1559.

[38] DELACUVELLERIE A, CYRIAQUE V, GOBERT S, BENALI S, WATTIEZ R. The plastisphere in marine ecosystem hosts potential specific microbial degraders including *Alcanivorax borkumensis* as a key player for the low-density polyethylene degradation[J]. Journal of Hazardous Materials, 2019, 380: 120899.

[39] KYAW BM, CHAMPAKALAKSHMI R, SAKHARKAR MK, LIM CS, SAKHARKAR KR. Biodegradation of low density polythene (LDPE) by *Pseudomonas* species[J]. Indian Journal of Microbiology, 2012, 52(3): 411-419.

[40] REN L, MEN LN, ZHANG ZW, GUAN FF, TIAN J, WANG B, WANG JH, ZHANG YH, ZHANG W. Biodegradation of polyethylene by *Enterobacter* sp. D1 from the guts of wax moth *Galleria mellonella*[J]. International Journal of Environmental Research and Public Health, 2019, 16(11): 1941.

[41] YANG J, YANG Y, WU WM, ZHAO J, JIANG L. Evidence of polyethylene biodegradation by bacterial strains from the guts of plastic-eating waxworms[J]. Environmental Science & Technology, 2014, 48(23): 13776-13784.

[42] 涂晨, 刘颖, 周倩, 骆永明. 一种聚乙烯塑料高效降解菌及其分离筛选方法和应用: CN110257310A[P]. 2019-11-26.
TU C, LIU Y, ZHOU Q, LUO YM. Polyethylene plastic efficient degrading bacterium and separating and screening method and application thereof: CN110257310A[P]. 2019-11-26 (in Chinese).

[43] MOHAN AJ, SEKHAR VC, BHASKAR T, NAMPOOTHIRI KM. Microbial assisted high impact polystyrene (HIPS) degradation[J]. Bioresource Technology, 2016, 213: 204-207.

[44] YANG Y, YANG J, WU WM, ZHAO J, SONG YL, GAO LC, YANG RF, JIANG L. Biodegradation and mineralization of polystyrene by plastic-eating mealworms: part 2. role of gut microorganisms[J]. Environmental Science & Technology, 2015, 49(20): 12087-12093.

[45] SEKHAR VC, NAMPOOTHIRI KM, MOHAN AJ, NAIR NR, BHASKAR T, PANDEY A. Microbial degradation of high impact polystyrene (HIPS), an e-plastic with decabromodiphenyl oxide and antimony trioxide[J]. Journal of Hazardous Materials, 2016, 318: 347-354.

[46] MOR R, SIVAN A. Biofilm formation and partial biodegradation of polystyrene by the actinomycete *Rhodococcus ruber*[J]. Biodegradation, 2008, 19(6): 851-858.

[47] JEON HJ, KIM MN. Isolation of mesophilic bacterium for biodegradation of polypropylene[J]. International Biodeterioration & Biodegradation, 2016, 115: 244-249.

[48] FONTANELLA S, BONHOMME S, BRUSSON JM, PITTERI S, SAMUEL G, PICHON G, LACOSTE J, FROMAGEOT D, LEMAIRE J, DELORT AM. Comparison of biodegradability of various polypropylene films containing pro-oxidant additives based on Mn, Mn/Fe or Co[J]. Polymer Degradation and Stability, 2013, 98(4): 875-884.

[49] ARKATKAR A, JUWARKAR AA, BHADURI S, UPPARA PV, DOBLE M. Growth of *Pseudomonas* and *Bacillus* biofilms on pretreated polypropylene surface[J]. International Biodeterioration & Biodegradation, 2010, 64(6): 530-536.

[50] 徐东遐, 成金花. 从黄粉虫幼虫分离的具有塑料降解活性的微生物及利用其的塑料降解方法: CN111094543A[P]. 2020-05-01.
XU DY, CHENG JH. Microorganism with plastic degradation activity isolated from *Tenebrio molitor* larvae and its plastic degradation method thereof: CN111094543A[P]. 2020-05-01 (in Chinese).

[51] JAIN K, BHUNIA H, SUDHAKARA REDDY M. Degradation of polypropylene-poly-L-lactide blend by bacteria isolated from compost[J]. Bioremediation Journal, 2018, 22(3/4): 73-90.

[52] 黄和, 张立慧, 赵金娣, 王盼琳, 阮永强. 一株高效降解聚丙烯的冷杆菌及其降解菌剂和应用: CN113061546A[P]. 2022-11-25.
HUANG H, ZHANG LH, ZHAO JD, WANG PL, RUAN YQ. A strain of psychrophilic bacteria with high efficiency in degrading polypropylene and its degrading agent and application: CN113061546A[P]. 2022-11-25 (in Chinese).

[53] 黄和, 王盼琳, 张立慧, 李秀娟, 徐晴. 聚丙烯高效降解菌株 LICME 200610 WZH-4 及其生产的菌剂和应用: CN112175862A[P]. 2021-01-05.
HUANG H, WANG PL, ZHANG LH, LI XJ, XU Q. Polypropylene high-efficiency degrading strain LICME 200610 WZH-4 and its production and application: CN112175862A[P]. 2021-01-05 (in Chinese).

[54] 黄和, 张立慧, 赵金娣, 王盼琳, 阮永强. 一株高效降解聚丙烯的葡萄球菌及其降解菌剂和应用: CN112877259A[P]. 2021-06-01.
HUANG H, ZHANG LH, ZHAO JD, WANG PL, RUAN YQ. A strain of *Staphylococcus* highly degrading polypropylene and its degrading bacterial agent and application: CN112877259A[P]. 2021-06-01 (in Chinese).

[55] GIACOMUCCI L, RADDADI N, SOCCIO M, LOTTI N, FAVA F. Polyvinyl chloride biodegradation by *Pseudomonas citronellolis* and *Bacillus flexus*[J]. New Biotechnology, 2019, 52: 35-41.

[56] KHANDARE SD, CHAUDHARY DR, JHA B. Bioremediation of polyvinyl chloride (PVC) films by marine bacteria[J]. Marine Pollution Bulletin, 2021, 169: 112566.

[57] MALEKI RAD M, MOGHIMI H, AZIN E. Biodegradation of thermo-oxidative pretreated low-density polyethylene (LDPE) and polyvinyl chloride (PVC) microplastics by *Achromobacter denitrificans* Ebl13[J]. Marine Pollution Bulletin, 2022, 181: 113830.

[58] ZHANG Z, PENG HR, YANG DC, ZHANG GQ, ZHANG JL, JU F. Polyvinyl chloride degradation by a bacterium isolated from the gut of insect larvae[J]. Nature Communications, 2022, 13: 5360.

[59] 鞠峰, 张哲. 一种降解塑料的克雷伯氏菌株及其用途: CN113151102A[P]. 2021-12-10.
JU F, ZHANG Z. A *Klebsiella* strain degrading plastics and its application: CN113151102A[P]. 2021-12-10 (in Chinese).

[60] KIM MY, KIM C, MOON J, HEO J, JUNG SP, KIM JR. Polymer film-based screening and isolation of polylactic acid (PLA)-degrading microorganisms[J]. Journal of Microbiology and Biotechnology, 2017, 27(2): 342-349.

[61] CHANDRA P, ENESPA, SINGH DP. Microplastic Degradation by Bacteria in Aquatic Ecosystem[M]//Microorganisms for Sustainable Environment and Health. Amsterdam: Elsevier, 2020: 431-467.

[62] 杨丽娟, 张献, 冯旭, 苟红梅, 林袁. 一种肺炎克雷伯氏菌及其在降解聚乙烯中的应用: CN114456991A[P]. 2022-05-10.
YANG LJ, ZHANG X, FENG X, GOU HM, LIN Y. A *Klebsiella pneumoniae* and its application in polyethylene degradation: CN114456991A[P]. 2022-05-10 (in Chinese).

[63] 黄和, 李安妮, 张雨萱, 乔杰, 盛义杰, 叶盛雪, 陈嘉怡, 陈春利, 李秀娟, 张立慧. 莴苣不动杆菌、含有该菌的菌剂及它们的应用以及降解塑料的方法: CN114958645A[P]. 2022-08-30.
UANG H, LI AN, ZHANG YX, QIAO J, SHENG YJ, YE SX, CHEN JY, CHEN CL, LI XJ, ZHANG LH. Acinetobacter lettuce, bacterial agents containing the bacteria and their application, and methods for degrading plastics: CN114958645A[P]. 2022-08-30 (in Chinese).

[64] 邵宗泽, 刘仁菊, 赵素芳. 高效降解聚苯乙烯塑料的戈登氏菌属菌株: CN115109717A[P]. 2022-09-27.
SHAO ZZ, LIU RJ, ZHAO SF. High efficient degradation of polystyrene plastics by *Gordon*: CN115109717A[P]. 2022-09-27 (in Chinese).

[65] AUTA HS, EMENIKE CU, JAYANTHI B, FAUZIAH SH. Growth kinetics and biodeterioration of polypropylene microplastics by *Bacillus* sp. and *Rhodococcus* sp. isolated from mangrove sediment[J]. Marine Pollution Bulletin, 2018, 127: 15-21.

[66] 马杰, 袁建华. 具有聚苯乙烯塑料降解活性的微生物及利用其降解塑料的方法: CN114891671A[P]. 2022-08-12.
MA J, YUAN JH. Microorganism with polystyrene plastic degradation activity and the method of using it to degrade plastics: CN114891671A[P]. 2022-08-12 (in Chinese).

[67] ZADJELOVIC V, ERNI-CASSOLA G, OBRADOR-VIEL T, LESTER D, ELEY Y, GIBSON MI, DORADOR C, GOLYSHIN PN, BLACK S, WELLINGTON EMH, CHRISTIE-OLEZA JA. A mechanistic understanding of polyethylene biodegradation by the marine bacterium *Alcanivorax*[J]. Journal of Hazardous Materials, 2022, 436: 129278.

[68] YIN CF, XU Y, ZHOU NY. Biodegradation of polyethylene mulching films by a co-culture of *Acinetobacter* sp. strain N_yZ450 and *Bacillus* sp. strain N_yZ451 isolated from *Tenebrio molitor* larvae[J]. International Biodeterioration & Biodegradation, 2020, 155: 105089.

[69] BHER A, MAYEKAR PC, AURAS RA, SCHVEZOV CE. Biodegradation of biodegradable polymers in mesophilic aerobic environments[J]. International Journal of Molecular Sciences, 2022, 23(20): 12165.

[70] URBANEK AK, RYMOWICZ W, MIROŃCZUK AM. Degradation of plastics and plastic-degrading bacteria in cold marine habitats[J]. Applied Microbiology and Biotechnology, 2018, 102(18): 7669-7678.

[71] LOBELLE D, CUNLIFFE M. Early microbial biofilm formation on marine plastic debris[J]. Marine Pollution Bulletin, 2011, 62(1): 197-200.

[72] ZHANG H, KONG DM, WANG L, XIA W, YAO CY, WU J. Degradation of UV-pretreated polyolefins by latex clearing protein from *Streptomyces* sp. strain K30[J]. Science of the Total Environment, 2022, 806: 150779.

[73] YAO CY, XIA W, DOU MD, DU YY, WU J. Oxidative degradation of UV-irradiated polyethylene by laccase-mediator system[J]. Journal of Hazardous Materials, 2022, 440: 129709.

[74] IIYOSHI Y, TSUTSUMI Y, NISHIDA T. Polyethylene degradation by lignin-degrading fungi and manganese peroxidase[J]. Journal of Wood Science, 1998, 44(3): 222-229.

[75] ZHAO JC, GUO ZA, MA XY, LIANG GZ, WANG JL. Novel surface modification of high-density polyethylene films by using enzymatic catalysis[J]. Journal of Applied Polymer Science, 2004, 91(6): 3673-3678.

[76] SANTO M, WEITSMAN R, SIVAN A. The role of the copper-binding enzyme-laccase-in the biodegradation of polyethylene by the actinomycete *Rhodococcus ruber*[J]. International Biodeterioration & Biodegradation, 2013, 84: 204-210.

[77] GYUNG YOON M, JEONG JEON H, NAM KIM M. Biodegradation of polyethylene by a soil bacterium and *AlkB* cloned recombinant cell[J]. Journal of Bioremediation & Biodegradation, 2012, 3(4): 1000144.

[78] SANLUIS-VERDES A, COLOMER-VIDAL P, RODRIGUEZ-VENTURA F, BELLO-VILLARINO M, SPINOLA-AMILIBIA M, RUIZ-LOPEZ E, ILLANES-VICIOSO R, CASTROVIEJO P, AIESE CIGLIANO R, MONTOYA M, FALABELLA P, PESQUERA C, GONZALEZ-LEGARRETA L, ARIAS-PALOMO E, SOLÀ M, TORROBA T, ARIAS CF, BERTOCCHINI F. Wax worm saliva and the enzymes therein are the key to polyethylene degradation by *Galleria mellonella*[J]. Nature Communications, 2022, 13: 5568.

[79] NAKAMIYA K, OOI T, KINOSHITA S. Non-heme hydroquinone peroxidase from *Azotobacter beijerinckii* HM121[J]. Journal of Fermentation and Bioengineering, 1997, 84(1): 14-21.

[80] JOLIVALT C, MADZAK C, BRAULT A, CAMINADE E, MALOSSE C, MOUGIN C. Expression of laccase IIIb from the white-rot fungus *Trametes versicolor* in the yeast *Yarrowia lipolytica* for environmental applications[J]. Applied Microbiology and Biotechnology, 2005, 66(4): 450-456.

[81] KHATOON N, JAMAL A, ALI MI. Lignin peroxidase isoenzyme: a novel approach to biodegrade the toxic synthetic polymer waste[J]. Environmental Technology, 2019, 40(11): 1366-1375.

[82] WEI R, ZIMMERMANN W. Microbial enzymes for the recycling of recalcitrant petroleum-based plastics: how far are we?[J]. Microbial Biotechnology, 2017, 10(6): 1308-1322.

[83] SÁNCHEZ V. Fungal potential for the degradation of petroleum-based polymers: an overview of macro- and microplastics biodegradation[J]. Biotechnology Advances, 2020, 40: 107501.

[84] SANTACRUZ-JUÁREZ E, BUENDIA-CORONA RE, RAMÍREZ RE, SÁNCHEZ C. Fungal enzymes for the degradation of polyethylene: molecular docking simulation and biodegradation pathway proposal[J]. Journal of Hazardous Materials, 2021, 411: 125118.

[85] SOWMYA HV, RAMALINGAPPA, KRISHNAPPA M, THIPPESWAMY B. Degradation of polyethylene by *Trichoderma harzianum*—SEM, FTIR, and NMR analyses[J]. Environmental Monitoring and Assessment, 2014, 186(10): 6577-6586.

[86] 夏伟, 吴敬, 窦明德, 姚从禹, 杜妍怡, 陈晟. 一种多功能过氧化物酶在聚乙烯降解中的应用: CN114888054A[P]. 2022-08-12.
XIA W, WU J, Dou MD, YAO CY, DU YY, CHEN S. Application of a multifunctional peroxidase in polyethylene degradation: CN114888054A[P]. 2022-08-12 (in Chinese).

[87] 吴敬, 夏伟, 窦明德, 姚从禹, 杜妍怡, 陈晟. 一种白腐真菌锰过氧化物酶在聚乙烯降解中的应用 CN113897378A[P]. 2022-01-07.
WU J, XIA W, DOU MD, YAO CY, DU YY, CHEN S. Application of manganese peroxidase from a white rot fungus in polyethylene degradation: CN113897378A[P]. 2022-01-07 (in Chinese).

[88] LI HQ, AGUIRRE-VILLEGAS HA, ALLEN RD, BAI XL, BENSON CH, BECKHAM GT, BRADSHAW SL, BROWN JL, BROWN RC, CECON VS, CURLEY JB, CURTZWILER GW, DONG S, GADDAMEEDI S, GARCÍA JE, HERMANS I, KIM MS, MA JZ, MARK LO, MAVRIKAKIS M, et al. Expanding plastics recycling technologies: chemical aspects, technology status and challenges[J]. Green Chemistry, 2022, 24(23): 8899-9002.

[89] JIANG QX, LI ZY, CUI ZH, WEI R, NIE KL, XU HJ, LIU L. Quantum mechanical investigation of the oxidative cleavage of the C–C backbone bonds in polyethylene model molecules[J]. Polymers, 2021, 13(16): 2730.

[90] JENO HJ, KIM MN. Functional analysis of alkane hydroxylase system derived from *Pseudomonas aeruginosa* E7 for low molecular weight polyethylene biodegradation[J]. International Biodeterioration & Biodegradation, 2015, 103: 141-146.

[91] ZEENAT, ELAHI A, BUKHARI DA, SHAMIM S, REHMAN A. Plastics degradation by microbes: a sustainable approach[J]. Journal of King Saud University-Science, 2021, 33(6): 101538.

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