微胶囊智能自修复材料研究进展

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摘 要 微胶囊自修复材料是由生物体受伤愈合机制启发所构建的智能自修复体系。微胶囊自修复材料可智能地实现自身能量和物质的补充,在一定程度上增强材料的机械性能,延长材料的使用寿命。研究了自修复微胶囊的制备工艺,以及微胶囊自修复材料的自修复机理和自修复体系,简要概述了自复效果的评价方法。展望了微胶囊自修材料的发展前景。

关键词 微胶囊,自修复,裂纹,自修复体系

Research progress of microcapsule intelligent self-healing material

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Abstract Microcapsule self-healing material is an intelligent self-healing system inspired by the mechanism of organism wound healing. The microcapsule self-healing material can realize its own energy and material replenish intelligently, to a certain extent, enhance the mechanical properties of material and prolong the service life. The preparation technology of microcapsule, self-healing mechanism of microcapsule and self-healing system were studied, and the evaluation method of self restoring effect was briefly summarized. The development prospect of microcapsule self-healing materials was prospected.

Key words microcapsule, self-healing, crack, self-healing system

智能自修复材料可对外部环境和内部状态的信息加以识别和处理,并催动材料自身做出适应环境的响应,从而有效增加材料的使用寿命,强化各项性能。受智能自修复材料的优良特性所吸引,许多发达国家和著名科研机构相继投入大量精力对此展开研究[1-3]。

智能自修复材料主要通过材料物质和能量的自补充实现修复,根据补充方式不同可分为本征型和埋覆型两种。本征型属于分子级别的自修复[4],无需额外补充修复剂,但是一般需要外界能量补充[5],可修复裂纹的范围相对较小。埋覆型智能修复材料相对于本征型具有设计灵活、裂纹修复范围大的特点,可实现材料的完全自修复。根据修复剂的存在方式埋覆型智能自修复材料分为空芯纤维型、微胶囊型和脉管型 3 种[6-8]。微胶囊型相对于空芯纤维型、脉管型具有更好的应用前景。微胶囊制备工艺更加简单,技术成熟,可工业化生产,包覆修复剂种类较多。同时,微胶囊对材料基体的机械性能影响小,对裂纹的感知效果好。笔者主要介绍了近期微胶囊自修复材料的研究进展和突破性工作。

1 微胶囊型自修复材料的修复机理

微胶囊智能自修复材料是利用微胶囊技术模仿生物体皮肤组织受伤愈合机制。皮肤组织受到损伤后,血液流出并结痂,细胞汇集到伤口处生成新组织,从而修复伤口[9]。生物体愈合功能的实现要有能量、物质的补充和遗传信息的控制,而复合材料不具备生命体征,因此需要人为对其构建自修复机制。

White 等[10]根据生物体的感知和激励功能,提出微胶囊型自修复材料的 3 个阶段:(1)感知阶段,即基体中裂纹扩展迫使自修复微胶囊破裂;(2)运输阶段,即微胶囊释放所包覆的修复剂进入裂纹;(3)执行阶段,即修复剂与基体中预先埋覆的催化剂接触,并在催化剂作用下发生化学反应,交联固化进而修复裂纹。该理论受到了广泛认可,并且以此设计出了大量的微胶囊型自修复材料。

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2 微胶囊的制备工艺

微胶囊是直径在微米级的球形小颗粒，根据不同的应用需求可包覆固体、液体和气体，应用范围十分广阔[11-12]。

2.1 自修复微胶囊的合成工艺要求

自修复微胶囊也是微胶囊技术的应用领域之一[13]，自修复微胶囊壁一般为致密的高分子材料，芯材为修复剂、催化剂或固化剂等。

自修复微胶囊的制备过程复杂，会受到各种因素的干扰。制备自修复微胶囊所需保证的基本要素有：(1)合成工艺应与芯材相容；(2)微胶囊必须有足够长的保质期，同时保证与树脂基体可以良好结合；(3)微胶囊在合成过程中必须保证囊壁致密且不受破坏，阻止修复剂扩散至外界。

2.2 自修复微胶囊的制备方法

自修复微胶囊的制备方法众多，根据其自身特性和应用背景可大致分为化学法和物理法。常见的自修复微胶囊制备方法见表 1[14-18]。

表 1 常见的自修复微胶囊制备方法

制备方法	壁材	芯材
乳液聚合法	脲醛树脂、聚甲基丙烯酸甲酯等	疏水物质
界面聚合法	脲醛树脂、聚氨酯等	疏水或亲水物质
溶胶-凝胶法	聚正硅酸乙酯、聚甲基丙烯酸甲酯等	疏水物质
溶剂蒸发法	聚醋酸乙烯酯、聚乙烯醇缩甲醛等	疏水或亲水物质

目前，研究者大多采用尿素-甲醛原位聚合制备脲醛树脂自修复微胶囊。根据制备过程中是否制备尿素-甲醛预聚体，可将该方法分为一步法和两步法。

一步法[19]是将壁材、芯材材料制成 pH＝3.5 的乳液，并向其中加入一定量的甲醛水溶液后，直接合成自修复微胶囊。一步法的实质是乳液聚合，无需制备预聚体，所得微胶囊形貌好，但所用乳化剂的价格较高。

两步法的实质是界面聚合。首先在碱性条件下，合成尿素-甲醛预聚体，然后在酸性条件下，尿素-甲醛预聚体和尿素在界面缩聚生成脲醛树脂囊壁。Yuan 等[20-21]对两步法的工艺进行了系统研究，考察了尿素与甲醛投料比、搅拌速度、升温速率及乳化剂的种类和用量等因素对制备脲醛树脂自修复微胶囊的影响。

3 微胶囊自修复材料体系

微胶囊自修复材料经过多年发展形成了多种修复体系，根据结构不同可简单分为单微胶囊体系和双微胶囊体系。按照微胶囊反应修复类型又可分为反应物/催化剂型、环氧树脂/固化剂型、溶剂自修复型和点击化学型等。

3.1 反应物/催化剂型

反应物/催化剂型自修复体系是修复剂在催化剂作用下聚合实现自修复。White 等[22]将包覆有双环戊二烯(DCPD)的微胶囊埋覆在含有格拉布催化剂的基体中，成功制备了微胶囊自修复材料。之后，陆续有人对该体系进行了深入研究和优化[23-25]，涉及修复反应的速率、格拉布催化剂的保护与改性等方面。目前，该体系的研究已拓展到工程领域，应用于修复混凝土结构[26]。DCPD/格拉布催化剂修复体系的优点为可在室温下实现自修复，缺点是催化剂价格昂贵，而且容易失活。

此外，Keller 等[27-28]利用微胶囊分别包覆乙烯功能化聚二甲基硅氧烷(PDMS)、铂催化剂与聚二甲基硅氧烷共聚体构建双微胶囊自修复体系，成功实现了基体的自修复。Cho 等[29-30]在包覆有二月桂酸二丁基锡催化剂的微胶囊加入乙烯基酯树脂和修复剂混合制备的基体材料，微胶囊破裂释放的催化剂与基体中修复剂接触发生反应实现自修复。Hondred 等[31-32]先以桐油甘油三酯为修复剂，再由强路易斯酸三氟化硼乙醚催化发生阳离子聚合反应修复裂纹，但该催化剂易失活，后又改为使用稀土三氟甲磺酸酯作催化剂。反应物/催化剂型自修复体系对修复环境要求较高，限制其进一步发展。

3.2 环氧树脂/固化剂型

环氧树脂/固化剂型修复体系根据微胶囊应用方式可分为双微胶囊自修复体系和单微胶囊自修复体系。

双微胶囊自修复体系是将环氧树脂和固化剂分别用微胶囊包覆，再按一定比例分散于基体中。其优势在于能实现室温自修复，缺点在于设计和制备过程均较为复杂，双微胶囊体系需要优化两种微胶囊粒径及含量关系才能达到最佳修复效果。Jin 等[33-34]成功制备出环氧树脂微胶囊和改性脂肪族胺固化剂微胶囊，修复效率最高可达 91%。

单微胶囊自修复体系，即微胶囊包覆环氧树脂，而固化剂分散于基体中。Yin 等[35-36]采用 $CuBr_2(2\text{-}MeIm)_2$ 咪唑金属盐络合物作为潜伏固化剂。该固化剂在 130℃修复温度下可解离出咪唑络合物和微胶囊释放的环氧树脂发生反应，自修复效率可达 111%。潜伏性固化剂的研究重点是降低催化反应

温度,但是不宜低于室温,否则易和基体在室温下发生反应,失去潜伏效果。Coope 等[37]提出以路易斯强酸三氟甲基磺酸钪作为潜伏性固化剂,可将修复温度降至 45℃,但修复效率也随之降低。Liao 等[38-39]将上述两种体系应用于环氧树脂自修复涂层,获得了良好的自修复效果和防腐性能。

3.3　溶剂自修复型

溶剂自修复型是利用有机溶剂的溶胀作用实现自修复,该自修复体系具有结构设计简单、反应温度低等特点。Caruso 等[40-41]最先提出了采用有机溶剂作为修复剂,并且制备了包覆氯苯微的微胶囊。环氧树脂基体的氯苯微胶囊质量分数为 20%时,修复效率为 82%。由于氯苯毒性较高,后将其替换为小毒性的苯乙酸乙酯。Ma 等[42-45]提出以汉森溶解度参数预测溶剂的修复效果,探讨苯乙酸乙酯微胶囊含量和粒径对环氧树脂基体力学性能和修复效果的影响,修复效率可达(98±11)%。

3.4　点击化学型

点击化学是通过小单元拼接,快速实现有机合成,具有反应高效稳定、副产物污染小[46]的优点。目前,点击化学应用于微胶囊自修复材料有叠氮化物-炔烃反应、狄尔斯-阿尔德反应。

Gragert 等[47]利用三炔丙基胺和三臂星型叠氮遥爪聚异丁烯制备自修复微胶囊,将两种微胶囊和质量分数为 2%的 $CuBr(PPh_3)_3$ 催化剂添加到聚异丁烯树脂中,成功实现了自修复功能。Pratama 等[48]进一步研究发现将质量分数为 10%的马来酰亚胺微胶囊添加到呋喃功能化环氧树脂中,在室温下两者发生狄尔斯-阿尔德反应,修复率可达 71%。

3.5　其他

微胶囊自修复体系还可以借助空气和水分实现修复。目前的报道主要是基于干性油氧化成膜和有机硅氧烷水解形成硅烷膜这两种反应实现自修复,例如包覆有亚麻油[49]、桐油[50]、1H,1H,2H,2H-全氟辛基三乙氧基硅烷[51]和聚二甲基硅氧烷[52]修复剂的自修复微胶囊。

4　自修复效率的评价

自修复材料可实现损伤修复并在一定程度上恢复材料的力学性能。自修复效率用于材料在不同损伤方式下的恢复情况进行评价。

4.1　静力试验

静力试验是验证自修复材料结构强度和修复效率的重要手段。以断裂韧性为例,利用材料恢复前后的断裂韧性参数可定量计算自修复效率[53]。各种悬梁臂试样以及其对应作用结果见表 2[54-61]。

表 2　种悬梁臂试样以及其对应作用结果

试样名称	作用
哑铃型拉伸梁	利用断裂伸长、屈服点等计算修复效率,但受到干扰因素较多
单边切口梁(SENB)	根据裂纹修复前后的长度对修复效率进行定量计算
梯形双悬梁臂(TDCB)	克服三点弯曲试验中裂纹长度难以测量的缺陷
宽锥形双悬梁臂(WTDCB)	提供单个裂纹用以测量断裂韧性
双悬梁臂(DCB)	可在不同几何形状和载荷下进行测试

4.2　冲击试验

在冲击试验中冲击材料时,材料及支撑夹会具有动态响应。通常利用低速冲击试验研究材料的自修复效率,通过摆锤式冲击试验机分别测定试样修复前后的冲击能量(E),用以计算材料的自修复效率[62-63]。

Patel 等[64]对 DCPD/格拉布催化剂型微胶囊自修复材料进行了低速冲击试验,发现微胶囊自修复材料的修复效率可达 51%,抗压强度显著恢复。

5　总结与展望

微胶囊自修复材料设计简单、制备方便,可有效修复裂纹,延长材料的使用寿命,但也存在很多亟需解决的问题:(1)目前,自修复微胶囊受合成工艺的限制致使芯材的选择十分有限,需进一步研究优化或开发新的制备工艺以应对上述问题;(2)在微胶囊的修复机理方面,未能解答材料裂纹拓展刺穿自修复微胶囊的机理以及微胶囊几何性质对修复效果的影响。目前,对于微胶囊自修复材料的研究已经日趋成熟,相信在不久以后一定可以推广使用。

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