

水泥基材料超疏水改性方式以及改性材料

姚 铃

重庆交通大学土木工程学院, 重庆

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摘 要

水进入水泥基材料内部会引发冻胀开裂、化学侵蚀、碳化等问题, 导致结构严重破坏, 造成巨大的安全隐患和经济财产损失。对水泥基材料进行超疏水改性使得改性后的新型建筑材料具备更加优异的性能。本文综述了水泥基材料的两种超疏水改性方式(表面超疏水改性和整体超疏水改性); 常用超疏水改性材料及其作用机理。最后, 对水泥基材料超疏水改性的研究进行了归纳总结并对未来研究工作进行了展望。

关键词

超疏水性水泥基材料, 表面超疏水改性, 整体超疏水改性

Superhydrophobic Modification of Cement-Based Materials and Modified Materials

Ling Yao

School of Civil Engineering, Chongqing Jiaotong University, Chongqing

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Abstract

The infiltration of water into cement-based materials can cause a range of problems including frost heave cracking, chemical erosion, carbonization, and other structural damage that may lead to significant safety risks and economic losses. To address this issue, superhydrophobic modification can be used to improve the impermeability, frost and ice resistance, and UV resistance of cement-based materials. This paper reviews two methods of superhydrophobic modification, surface superhydrophobic modification and global superhydrophobic modification, that have been used to modify cement-based materials. The paper also examines commonly used superhydro-

phobic modified materials and their mechanisms of action, the effects of superhydrophobic modification on the mechanical energy of cement-based materials for these materials. Finally, the research on superhydrophobic modification of cement-based materials is summarized, and future research prospects are discussed.

Keywords

Superhydrophobic Cement-Based Materials, Surface Superhydrophobic Modification, Overall Superhydrophobic Modification

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1. 引言

水泥基材料由于其优异的力学性能和耐久性能成为世界上使用最广泛的建筑材料[1], 但由于其亲水性, 环境中的水很容易携带腐蚀性物质通过混凝土孔隙进入混凝土内部, 导致钢筋腐蚀或其他耐久性问题[2] [3] [4], 因此, 有效防止水渗透对提高混凝土耐久性、延长建筑使用寿命至关重要。

过去几十年, 降低水胶比和增加胶凝材料是两种常见的增强水泥基材料耐久性的方法[5], 但是这两种方法存在明显缺陷: 降低了水泥基材料流动性、增加了水泥基材料硬化后的开裂风险。因此, 基于“荷叶效应” [6] [7], 研究人员提出了有效增强水泥基材料耐久性的方法——水泥基材料超疏水改性。

本文从超疏水改性方式、超疏水改性材料两个方面综述国内外超疏水水泥基材料的研究进展, 以期对超疏水水泥基材料的科学研究和工程实际运用提供借鉴和参考。

2. 超疏水改性方式

根据润湿性理论模型, 研究人员通过构造粗糙结构和降低表面能对水泥基材料进行疏水改性, 根据改性方式可以将水泥基材料的超疏水改性分为表面超疏水改性和整体超疏水改性, 表面超疏水改性是通过在混凝土表面的孔壁上附着疏水剂实现, 形成连续的保护层以增强混凝土凝结硬化后的耐久性; 整体超疏水改性通常将疏水混合物与水泥基材料融合, 从而实现水泥基材料的整体超疏水改性。评价超疏水改性效果, 可以通过检测水泥基材料的水接触角(WCA)、滚动角(SA), 当满足 $150^\circ < CA < 180^\circ$, 同时 $SA < 10^\circ$ 时, 认为材料具备超疏水性能。

2.1. 表面超疏水改性

总结近年来混凝土表面超疏水改性的研究[8] [9], 表面超疏水改性可以归纳为以下三种主要类型: 1) 喷涂[10]: 通过喷涂在表面沉积富含微纳米颗粒的疏水悬浮液, 如图 1 所示; 2) 浸渍[11]: 将样品浸入含有纳米颗粒的疏水性有机溶液或水乳液中, 如图 2 所示; 3) 刷涂[12]: 通过刷涂将聚合物和水泥浆体覆盖在混凝土表面, 如图 3 所示。

从生产工艺来看, 表面超疏水改性主要通过喷涂、刷涂和浸渍三种方式实现, 工艺简单、操作灵活, 适应性强, 可以根据具体的应用场景采用不同的疏水剂和纳米材料。但表面改性存在明显的缺点: 涂层与固体表面之间的粘合强度低、涂层易开裂、表面改性水泥基材料无法保证长期耐久性(有机硅烷分子与混凝土表面之间的化学键长时间暴露在水中会被降解) [13]。所以考虑表明超疏水改性前要做好充分的表

面评估和准备，否则容易出现疏水材料与水泥基材料粘结力不足、疏水材料浸渍深度不够、水泥基材料表面形态不满足疏水条件等情况。

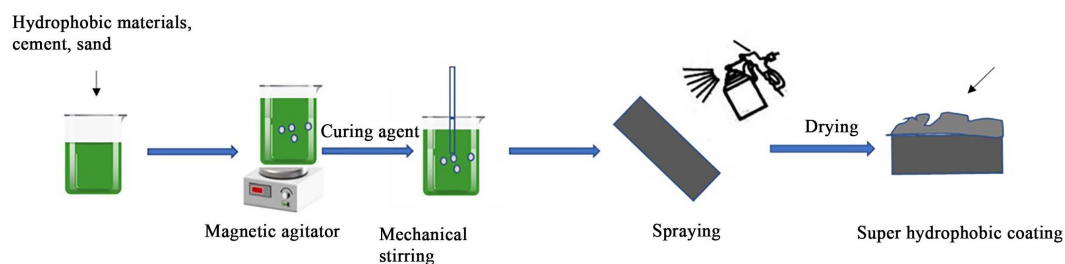


Figure 1. Preparation process diagram of superhydrophobic spraying

图 1. 超疏水喷涂制备工艺示意图

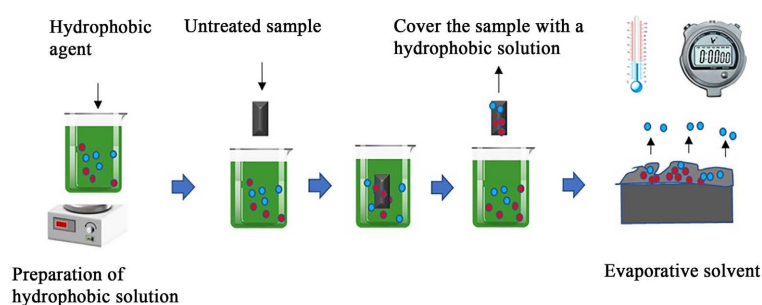


Figure 2. Preparation process diagram of superhydrophobic coating impregnation

图 2. 超疏水涂层浸渍制备工艺示意图

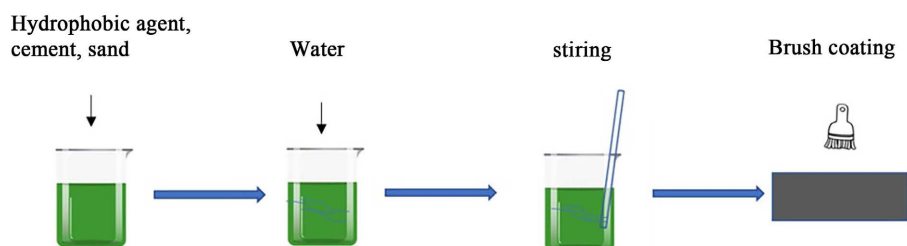


Figure 3. Preparation process diagram of superhydrophobic brush coating

图 3. 超疏水刷涂制备工艺示意图

2.2. 超疏水整体改性

针对混凝土开裂、涂层老化和剥落使得新暴露出来的结构显示原来的亲水性问题，表面改性难以解决。在这种情况下研究人员提出了在水泥基材料成型过程中添加疏水材料，即所谓的整体改性，其制备工艺如图 4 所示。整体超疏水改性所制得的混凝土在表层脱落或破坏时通过简单的表面研磨处理即可恢复超疏水性能，整体超疏水改性方式包括：直接掺加疏水剂[14] [15] [16] [17]和使用经疏水改性的胶凝材料[18]，这两种方式受外界的影响小，但造价成本较高。

3. 超疏水改性剂

目前水泥基材料超疏水改性所用的改性剂有很多，改性剂配合不同制备工艺改性效果各有不同，在两种超疏水改性方式中，常用的疏水剂包括硅烷、硅氧烷、硬脂酸等，常用构造粗糙度的纳米级颗粒有

二氧化硅、偏高岭土[19]、硅藻土等纳米颗粒。下面对常用的疏水改性剂(硅烷和硅氧烷、硬脂酸)和二氧化硅纳米颗粒进行详细介绍。

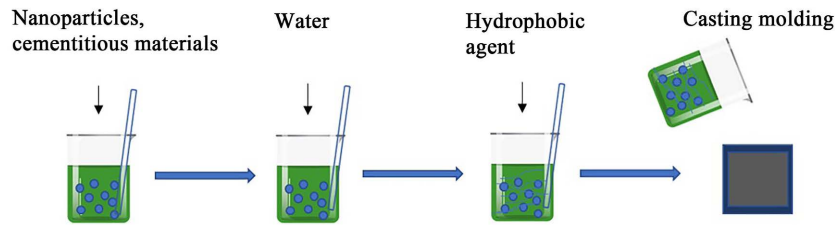


Figure 4. Schematic diagram of the overall superhydrophobic preparation process

图 4. 整体超疏水制备工艺示意图

硅烷和硅氧烷凭借其小分子结构特点,可以渗透到水泥基材料致密结构中,通过与胶凝材料发生反应进而对水泥基材进行疏水改性[20]。由于聚二甲基硅氧烷(PDMS)优异的化学惰性、无毒、成本适中、生物相容性和环境友好性而经常用于制备超疏水混凝土,相关综述总结了 PDMS 的其他显著优势[9]: 1) PDMS 含有柔性 Si-O-Si 骨架,能够适当抵挡外部冲击; 2) PDMS 的低粘度使改性基材具有更好的抗渗性; 3) PDMS 分子的 -OH 基团与无机材料发生的水解缩合反应使得 PDMS 能更好键合在水泥基材上。硅烷和聚二甲基硅氧烷因以上优异性能,用作疏水改性剂深受研究人员喜爱,表 1 总结了近几年硅烷和硅氧烷用于水泥基材料疏水改性。

Table 1. Silane and siloxane used for hydrophobic modification of cement materials

表 1. 硅烷和硅氧烷用于水泥材料疏水改性

疏水剂	表面粗糙结构	改性方式	接触角/滚动角	性能	参考文献
硅烷、硅氧烷	纳米二氧化硅	喷涂	$CA = 162.0^\circ \pm 3^\circ / SA = 5^\circ \pm 1^\circ$	超疏水、耐磨损	[21]
1H, 1H, 2H, 2H-全氟癸基三乙氧基硅烷	—	刷涂	$CA = 157^\circ / SA = 2.8^\circ$	超疏水、抗渗、抗冰、机械磨损	[15]
三乙氧基辛基硅烷	砂纸打磨	刷涂	$CA = 158^\circ$	超疏水、自清洁、耐磨损	[13]
聚二甲基硅氧烷	二氧化钛、纳米二氧化硅	刷涂	$CA = 155.2^\circ / SA = 5.8^\circ$	超疏水、抗紫外线、发光	[22]
聚二甲基硅氧烷	聚乙烯醇基纤维	砂浆涂层	$CA = 164^\circ / SA = 2.5^\circ$	超疏水、自清洁	[23]
聚二甲基硅氧烷	氧化镁	内掺	$CA > 150^\circ / SA < 10^\circ$	超疏水、自清洁、可回收	[24]
聚二甲基硅氧烷	硬脂酸钙、羟丙基甲基纤维素	内掺	$CA = 153^\circ$	超疏水、自清洁、耐腐蚀	[25]

硬脂酸(STA)分子中的羧基可以接枝到水泥基材料的羟基上形成长链烷基,长链烷基可以显著降低表面能,所以硬脂酸是一种超疏水性改性的常用材料[26] [27] [28]。Charikleia 等人[29]通过使用硬脂酸和造纸污泥制备超疏水粉末,通过研究不同链长的脂肪酸得出硬脂酸产生的疏水性最高。此后,大量学者将硬脂酸用于水泥基材料的超疏水改性,Wang [30]通过将水泥石样品浸入 STA 溶液中,采用简单的浸渍法

制得超疏水水泥石(SCS)。Lei [31]采用 STA 和铜网制备超疏水混凝土, 探明了在 STA 含量为 0.8 g 时, 超疏水混凝土 CA 和 SA 分别达到 159°和 5°的最优值。其中, STA 主要通过和混凝土中的羟基接枝, 形成疏水尾链; 此外, 水泥水化产物再进一步与 STA 反应生成硬脂酸钙, 增加了额外的粗糙度。表 2 总结了近几年硬脂酸用于水泥基材料疏水改性。

Table 2. Stearic acid used for hydrophobic modification of cement materials
表 2. 硬脂酸用于水泥材料疏水改性

疏水剂	表面粗糙结构	改性方式	接触角/滚动角	性能	参考文献
硬脂酸	硬脂酸钙	浸渍	CA = 167.2°/SA = 4.2°	超疏水、耐腐蚀	[30]
硬脂酸	铜网	内掺	CA = 159°/SA = 5°	超疏水、耐腐蚀、耐磨损	[31]
硬脂酸	-	涂层	CA = 155.7°	超疏水、抗渗	[32]
硬脂酸	砂纸打磨	内掺	CA = 155.2 ± 2°/SA = 8.5°	超疏水、自清洁、耐磨损	[33]

纳米级颗粒用于水泥基材料超疏水改性不仅能够构建表面微纳米级粗糙结构, 还能细化水泥基材料内部孔隙, 提高水泥基材料抗渗性能。其中, 纳米二氧化硅(NS)因其化学稳定性、易于制备和大小可控的优点被广泛使用。NS 的加入可以降低水泥水化物在表层区域的 Ca/Si 比, 随着 Ca/Si 比的降低, 硅酸钙水合物(C-S-H)凝胶的刚度和内聚强度可以显著提高[34]。此外, 通过在改性水泥基材料的过程中掺入 NS 可以解决硅烷超疏水改性水化延缓和强度降低的问题, 研究表明, 二氧化硅纳米颗粒附着在混凝土表面, 形成微纳米级粗糙结构, 创造了超疏水改性条件; 其次, 火山灰效应与水泥水化产物 C-S-H 凝胶反应堵塞混凝土孔隙, 降低吸水率提高水泥基材料力学性能[17]。特别的, 纳米二氧化硅掺入超疏水泡沫混凝土可以起到稳定气泡的作用[25], 机理如图 5 所示。表 3 总结了近几年纳米二氧化硅用于水泥基材料超疏水改性。

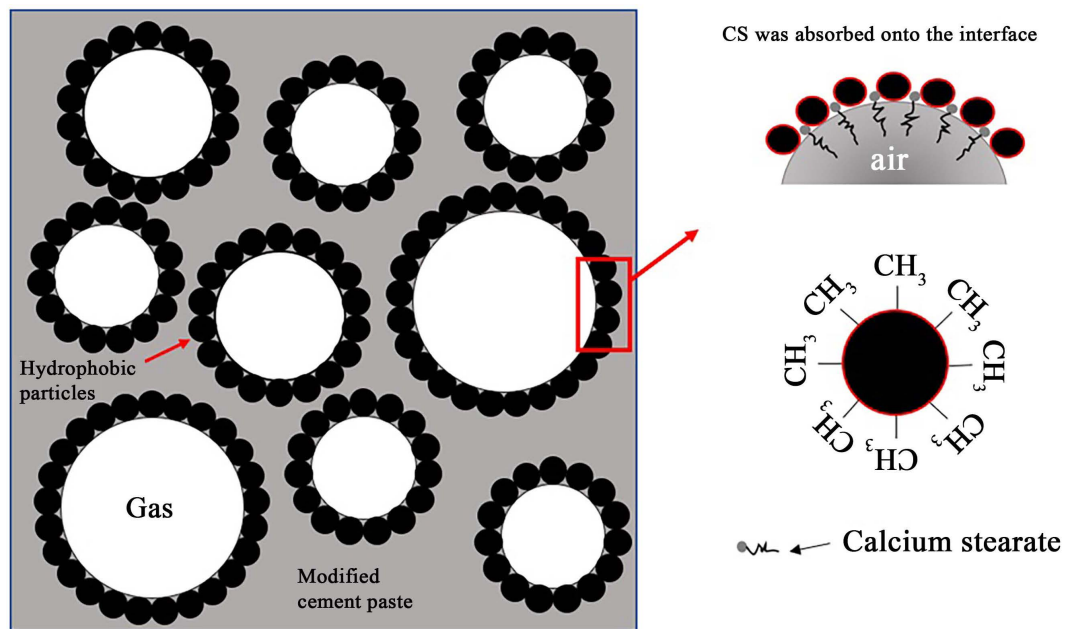


Figure 5. Construction diagram of porous hydrophobic interface of foamed concrete [25]
图 5. 泡沫混凝土孔隙疏水界面构建示意图

Table 3. Nano silica used for hydrophobic modification of cement materials
表 3. 纳米二氧化硅用于水泥材料疏水改性

疏水剂	表面粗糙结构	改性方式	接触角/滚动角	性能	参考文献
氟硅烷	纳米二氧化硅	喷涂	CA = 150.7°	超疏水、防冰、除冰	[35]
氟硅烷	纳米二氧化硅	喷涂	CA = 165.5°	超疏水、抗冰	[36]
氟烷基硅烷	纳米二氧化硅	喷涂	CA = 152.3° ± 0.5°	超疏水、抗渗	[37]
聚二甲基硅氧烷	纳米二氧化硅	刷涂	CA = 149°	疏水	[38]
聚二甲基硅氧烷	二氧化钛、 纳米二氧化硅	刷涂	CA = 155.2°/SA = 5.8°	超疏水、抗紫外线、 发光	[22]
异丁基三乙氧基硅烷	纳米二氧化硅、 硬脂酸钙	内掺	CA > 150°	超疏水	[16]

4. 结语

超疏水水泥基材料的应用提高了结构的耐久性，有利于提高混凝土建筑物的使用寿命，减少了后期的维护成本和可能存在的内在隐患。本文介绍了水泥基材料超疏水改性方式、疏水改性材料，并得出以下结论：

- 1) 水泥基材料的表面超疏水改性和整体超疏水改性均能提高水泥基材料的疏水性能。
- 2) 一般表面超疏水改性和整体超疏水改性选用的疏水剂不同，但大多采用硅烷、硅氧烷、硬脂酸、二氧化硅纳米颗粒等，其中不同的疏水剂使水泥基材料附带的性能各异。

上述结论可以为超疏水改性水泥基材料提供一定的借鉴和参考，接下来可以继续从以下几个方面开展深入研究：

- 1) 整体超疏水改性中，超疏水改性剂的直接掺入，或经超疏水改性的骨料的掺入是否会对水泥基材料流变性能产生影响，目前相关文献对这一研究较少涉及。
- 2) 有没有其他材料可以代替现有的硅烷及硅氧烷一类材料，降低超疏水泡沫混凝土的制造成本，可以展开进一步的研究。

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