

3D打印地质聚合物复合材料研究进展

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摘要

3D打印技术的应用有望引领工业革命4.0, 颠覆经济并提供设计定制。建筑行业正在迅速赶上这种现代技术, 生产混凝土3D打印机, 以提供健康的工作环境, 实现经济独立和建筑自由。地质聚合物被发现是建筑行业中用于3D打印水泥材料的有效替代品, 这可能有助于使其更加环保。本文全面回顾了打印工艺、性能要求和常见的3D打印混凝土技术。利用地质聚合物作为当今新兴环保混凝土化合物的合适混凝土材料, 用于现代建筑。文章还强调了用于3D打印的地质聚合物复合材料而必须克服的实际问题或潜在挑战。

关键词

3D打印, 增材制造, 地质聚合物

Research Progress of 3D Printing Geopolymer Composites Materials

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Abstract

The application of 3D printing technology is expected to lead the industrial revolution 4.0, subvert the economy and provide design customization. The construction industry is rapidly catching up with this modern technology and producing concrete 3D printers to provide a healthy working environment and achieve economic independence and building freedom. Geopolymers have been found to be effective substitutes for 3D printing cement materials in the construction industry, which may help to make them more environmentally friendly. This paper comprehensively reviews the printing process, performance requirements, and common 3D printing concrete tech-

nology. Geopolymer is used as a suitable concrete material for the emerging environmental protection concrete compound in modern buildings. The article also highlights the practical problems or potential challenges that must be overcome for geopolymers used for 3D printing.

Keywords

3D Printing, Additive Manufacturing, Geopolymer

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1. 前言

3D 打印混凝土是增材制造(AM)的一种，由于其可行性而在建筑领域越来越受欢迎。最简单和最常用的 3D 打印混凝土类型是基于挤出的混凝土打印：一种逐层混凝土挤出工艺，可以制造大中型土木工程结构，如人行天桥、办公楼、单层或多层房屋以及类似结构。大型 3D 打印混凝土结构的一些示例如图 1 所示。

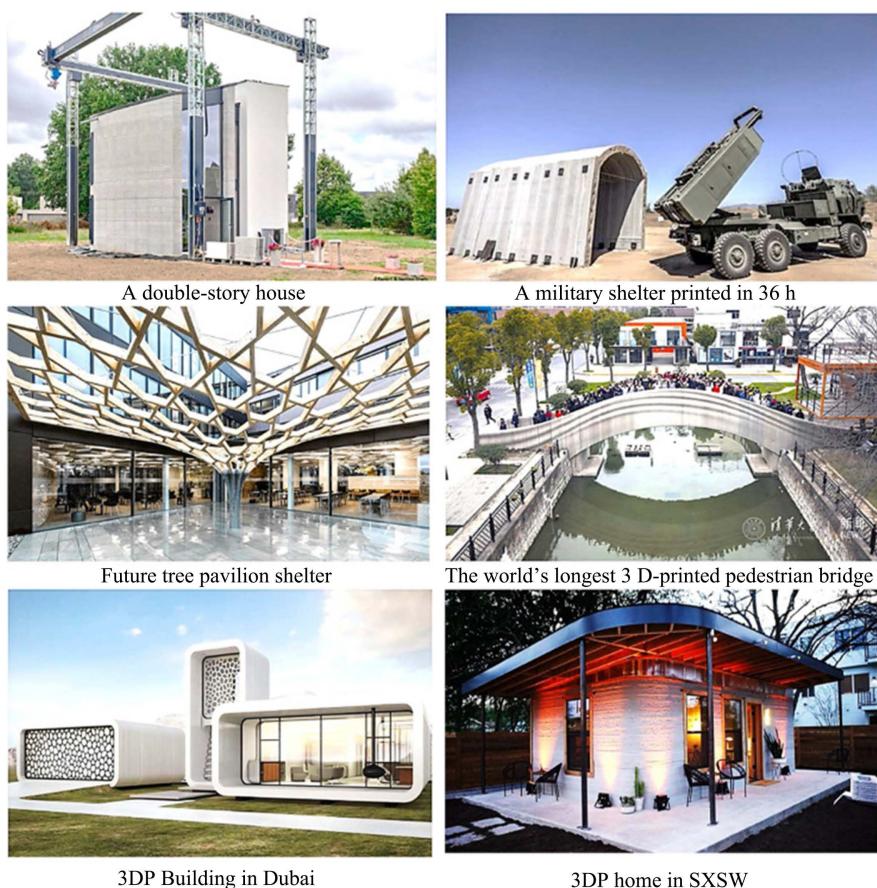


Figure 1. The latest example of large 3D printing concrete structure [1]

图 1. 大型 3D 打印混凝土结构的最新实例[1]

地质聚合物是无定形 3D 氧化铝 - 硅酸盐粘合剂材料,由 Davidovits 于 20 世纪 70 年代末首次命名和开发,通过 Al_2O_3 和 SiO_2 (例如偏高岭土)组成的原料与碱性介质(主要是碱金属氢氧化物/硅酸盐)反应生成[2][3]。当富含 Si 和 Al 的源材料被混合碱性溶液活化后,溶解的 Si^{4+}O_4 和 Al^{3+}O_4 四面体通过共享一个氧化物原子结合形成单体。单体相互作用形成地聚物,然后合成铝硅酸盐结构的 3D 网络。这种溶解和缩聚过程称为地聚合[4][5][6][7]。图 2 以简化形式显示了地质聚合过程。

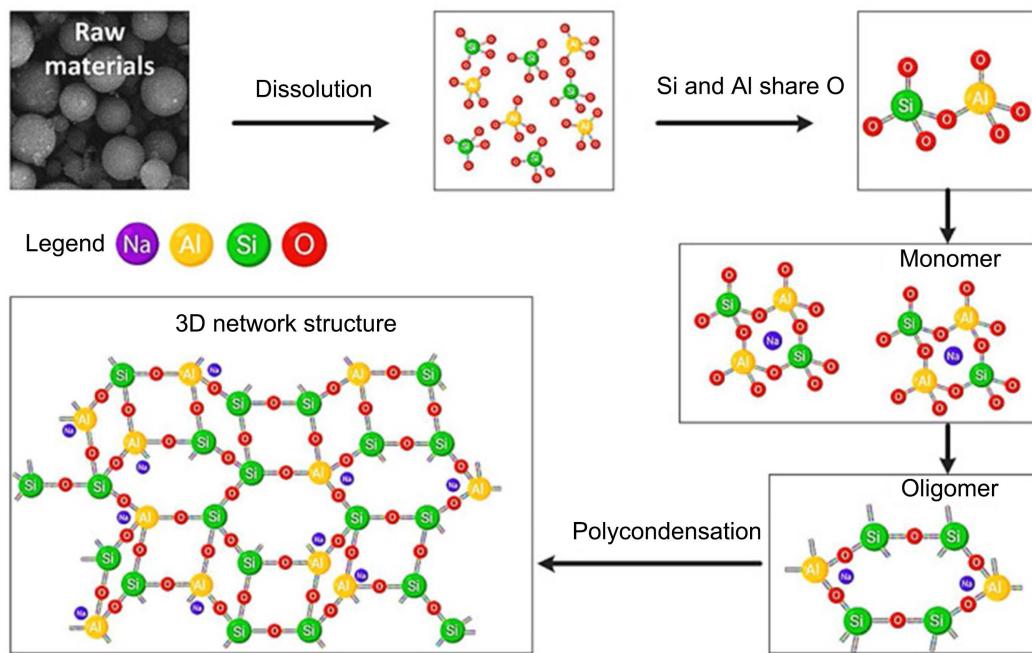


Figure 2. Simplified geological polymerization process [8]
图 2. 简化的地质聚合过程[8]

3D 打印技术和地质聚合物对这一创新的适应最近引起了越来越多的关注,因为它们对建筑行业的可持续发展战略产生了有意义的影响。文章还强调了用于 3D 打印的地质聚合材料而必须克服的理论问题或潜在挑战,以及基于先前研究和现有挑战的未来研究机会。

本文旨在探讨创新生产技术对地质聚合物复合材料性能和生态效率的影响。研究人员关注四个关键方面:1) 与传统材料相比,地质聚合物材料的优势;2) 3D 打印地质聚合物作为建筑材料的性能要求;3) 3D 打印地质聚合物材料的应用和发展方向;4) 未来的挑战。

该综述旨在进一步为该研究奠定基础,并描述研究见解、存在的差距以及未来的研究方向。

2. 3D 打印技术

2.1. 打印过程

在建筑中,增材制造(AM)工艺根据其性能参数分为两种主要类型,1) 粉末技术:该技术有资格生产高精度的复杂结构,使用这种方法通过在粉床上引入液体粘合剂来构建混凝土层,特别是沿着计算机辅助设计(CAD)模型给出的选择路径,以安全地保留粉末颗粒。完成后,多余的粘合剂粉末从构建平台上刮出,以产生几何形状的组件[9]-[15]。粉末印刷是一种生产小规模和复杂建筑元素的方法,如面板,室内结构和永久性模板,可以在打印完成后安装[16]。2) 基于挤压的技术:这是使用最广泛的 3D 打印技术,其中混凝土材料从放置在基座上的喷嘴依次挤压。基于挤压的技术通常用于工地的结构应用,例如

具有复杂几何形状的大型建筑构件。基于挤出的 3D 打印工艺技术分为混凝土印刷和轮廓工艺[17] [18] [19]。根据 Wang, Shen [20]的说法, 3D 打印混凝土混合料的打印过程分为三个步骤: 1) G 代码生成; 2) 材料准备和输送到打印机; 3) 打印步骤。首先, 使用计算机辅助设计应用程序创建 3D 模型。开发的模型以立体光刻(STL)格式生成, 这是 3D 打印领域广泛使用的格式。然后使用切片过程处理 3D 模型以制作 G 代码。将生成的 G 代码传递到内存即可完成模型生成过程。下一步是准备用于印刷的水泥材料成分。在准备原料的同时, 利用料斗 - 泵 - 喷嘴系统进行印刷过程。打印在计算机辅助设计应用程序中创建的建筑物即可完成该过程[21]-[26]。

2.2. 3D 打印的性能要求

在过去的几年中, 3D 打印技术因其成本效益和快速的构建速度而在建筑领域获得了广泛的关注[27] [28]。此外, 它还能够通过使用技术和数字建模来创建独立的结构组件, 从根本上改变传统的施工技术[29] [30]。3D 打印工艺分为四个阶段: 泵送、挤出、构建和强度发展。因此, 为了满足印刷标准, 3D 打印材料必须具有高流变和机械特性。以下是对特征的具体分析:

1) 泵送和挤出过程。泵送和挤出工艺提高了挤出性能, 挤出性定义为材料通过挤出机平稳流动而不结垢或破坏管道流动的能力。**图 3** 提供了示例。3D 打印建筑材料通过管道泵送, 并由挤出机头挤出; 因此, 在管道运输过程中, 它不能太厚导致阻塞管道[31] [32]。此外, 当混凝土混合料被泵送时, 它会在软管中分离, 产生有助于泵压降的润滑层[33] [34] [35]。该润滑层是由于剪切诱导的颗粒迁移而形成的, 当骨料从高剪切应力区域迁移时, 就会发生这种迁移。Kwon, Jang [36]发现沿管道横截面的速度分布, 大部分速度是在壁附近观察到的润滑层中产生的。然而, 不受控制的偏析会导致从混合物中挤出低质量的长丝。这可能会影响打印样本的硬化特性。由于大部分润滑层发生粘黏, 因此可能会出现收缩断裂, 从而使打印混凝土的耐久性降低。

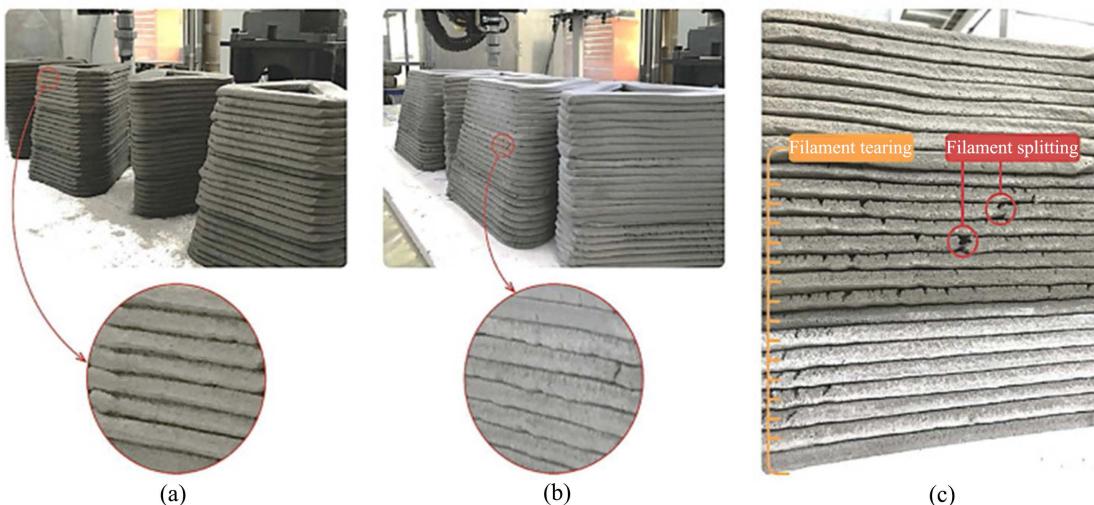


Figure 3. Use 40 × 10 mm rectangular nozzle for extrusion [37]

图 3. 使用 40 × 10 毫米矩形喷嘴进行挤压 [37]

2) 施工过程(良好的触变性能和形态保持性)。挤出后, 材料应在构建过程中根据挤出机尺寸保持其形状, 这可以使用称为形状保持因子的无量纲值进行量化。此外, 材料必须恢复其原始粘度, 以支持后续层施加的载荷, 并且使用无量纲因子作为触变性指数。根据 Bos, Kruger [38]的说法, 所应用的打印砂浆的材料特性是决定可建造性的重要参数。然而, 目前尚不清楚哪种材料特性最合适, 以及如何通过实

验确定它们[39] [40] [41]。

3) 发展强度的过程。3D 打印建筑材料必须具有足够的粘结强度和早期强度, 以便在后期层的压力下保持稳定[42] [43]。然而, 与任何结构一样, 需要足够的抗压强度和弯曲强度。普通水泥的早期强度低, 凝结时间长, 限制了其作为 3D 打印材料的使用。相比之下, 地质聚合物作为 3D 打印建筑材料具有巨大的前景, 因为它们具有更高的早期强度和冷凝率[44]-[50]。

3. 3D 打印地聚合物的发展进程

普通硅酸盐水泥早期强度低, 凝结时间长, 限制了其作为 3D 打印材料的应用。相比之下, 地聚合物材料由于其更大的早期强度和冷凝速率, 作为 3D 打印建筑材料具有巨大的前景[51] [52] [53] [54]。此外, 作为一种新型的绿色凝胶物质, 与硅酸盐水泥高能耗相比, 地聚合物因其节能环保的优点而引起了建筑行业的极大兴趣。一些研究人员对其进行了相关的研究, 以将其作为一种可持续的环保材料用于 3D 打印结构。地聚合物的流变性能与体积和粘度有关, 与新鲜混凝土相比, 3D 打印混凝土的工艺要求具有广泛的流变特性。Roussel [55] 观察到, 增加层间打印时间和触变性水平会降低 3D 打印混凝土混合物的层间粘结。触变性的水平被发现是冷关节的原因。因此, 鉴于 3D 打印混凝土混合料挤压前后不同的流变需求, 优化混凝土流变学是重要的。Lee, Kim [56] 表明, 对于地聚合物混合料的挤压能力, 屈服应力范围为 0.6~1.0 k 打印是可以接受的。Zhang, Wang [57] 研究了不同 Si/Na 比例碱活化 3D 打印 - 地聚合物混合物的屈服应力和结构积聚。已发现碱激活剂的 Si/Na 比对 3D 打印-地聚合物混合物的可造性和可挤压性有相当大的影响。作为开发的基础, 我们确定了增加碱激活剂的 Si/Na 比可以降低地聚合物混合物的粘度和屈服应力。根据 Nematollahi, Xia [58] 的研究, 当碱激活剂溶胶的 $\text{SiO}_2/\text{Na}_2\text{O}$ 比值为 3.22 时, 所得的地聚合物表现出可接受的和易性。

如前所述, 当碱激活剂溶胶的二氧化硅/氧化钠 $[\text{SiO}_2/\text{Na}_2\text{O}]$ 比为 3.22 时, 得到的地聚合物表现出可接受的强度、可接受的膨胀性和和易性, 以及良好的形状保持能力。此外, 由 50% 粉煤灰和 50% 矿渣制成的 3d 打印 - 地质聚合物混凝土的抗压强度为 25 MPa, 在很大范围内都能满足要求。Nematollahi, Xia [59] 认为, 当碱激活剂溶胶的 $\text{SiO}_2/\text{Na}_2\text{O}$ 比值为 3.22 时, 生成的地聚合物具有可接受的强度和膨胀性, 并具有良好的形状保持能力。Anda, Unluer [60] [61] [62] 研究发现, 当水灰比为 0.30, 活化剂/粘结剂比为 0.35 时, 添加 1% 的粘土具有较好的效果。Anda 和 Ruan [63] 的另一项研究中, 在碱活化渣和 0.4% 纳米粘土的混合体系中加入 2% 的水石墨苗, 水化性能得到改善, 大大提高了 3D 打印所需的结构积累速率。

总的来说, 低粘度和高屈服应力的材料可以用于 3D 打印混凝土, 地聚合物相比普通硅酸盐材料对材料的流变性能有着更高的要求。此外, 值得注意的是, 打印参数对界面或硬化特性的影响取决于材料混合物。配合比的设计也会影响混凝土的流变性能。在 3DP 混凝土配合比设计参数方面, 重要的是要牢记配合比的选择。

4. 未来的挑战

利用 3D 打印技术的建筑行业仍处于起步阶段, 在全面实施该技术之前, 必须解决几个障碍。最大的障碍之一是目前 3D 打印的稀缺性。总体而言, 虽然已经对 3D 打印生产进行了大量调查, 但缺乏适当的设计指南和标准测试技术, 正如研究人员所强调的那样[64]-[69]。此外, Mechtcherine, Tittelboom [70] 研究了增材制造的水泥材料在其硬化和硬化状态下的性能细节。根据作者的说法, 相关挑战与印刷材料的分层结构有关, 与传统浇注混凝土相比, 这导致更高程度的各向异性和不均匀性。因此, 在生产试样时, 必须考虑实际 3D 打印过程的特殊性。因此, 未来需要集中研究解决 AM 和 3D 打印技术的缺点, 包括可建造性, 流变学, 层间粘结和结构完整性。地质聚合物材料因其在环境和高温下的快速强度增长以

及其经济和环境效益[71]。

根据综述文献，研究人员在满足地质聚合物流变学标准方面取得了重大进展。即便如此，仍应考虑3D打印技术生产的结构细节、印刷性能以及固有问题(可构建性、层间粘合、结构完整性等)，并相互比较，以实现所需的流变特性。此外，值得注意的是，打印参数对界面或硬化特性的影响取决于材料混合物。此外，设计混合物会影响地质聚合物的流变性能。在3D打印配合料设计参数方面，重要的是混合料成分及其比例的选择将受到所应用3D打印技术的特定性能的限制。到目前为止，只有少数研究对3D打印纤维增强地质聚合物进行了研究。

5. 结论

本文对当前3D打印地质聚合物复合材料进行了全面综述。得出的结论如下：

- 1) 分析表明，3D打印地质聚合物制造方法，为制造高度复杂和多功能的结构提供了最新的可能性，显示出在环境修复，建筑行业和其他技术领域的应用前景。3D打印代表了地质聚合物材料制造的可持续方法，有助于降低浪费，能源消耗和CO₂排放。
- 2) 研究发现，基于挤出的3D打印作为目前地质聚合物材料制造中最普遍的技术，由于其相对较低的成本，简单性和高速生产，为建筑行业提供高度的设计灵活性。不过3D打印时间、打印作业的准确性和昂贵的大型打印机依然是制造地质聚合物的主要限制。
- 3) 地质聚合物制造的主要问题是各向异性现象，由于结构制造的层压方法，根据载荷方向表现出不同的机械行为。材料层之间的空隙形成会导致高孔隙率和层间粘合弱，从而降低3D打印地质聚合物的机械性能。这个问题需要改善方法以提高3D打印地聚合物中的层间附着力。打印地质聚合物结构层间区域的高孔隙率使其对冻融侵蚀、腐蚀性硫酸根以及碳酸化等的抵抗力降低，到目前为止，这些方面尚未得到调查。因此，需要进一步研究打印过程，以评估3D打印地质聚合物的长期耐久性。

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