SUSTAINABLE 3D PRINTING AEROGEL MATERIALS AND APPLICATION: A REVIEW

AUTHORS

Wenhuan Zhang[1], Yunyi Wang[1, 2], Jun Li[1, 2]

[1.] College of Fashion and Design, Donghua University, Shanghai 200051, China;

[2.] Key Laboratory of Clothing Design & Technology (Donghua University), Ministry of Education, Shanghai 200051, China

KEYWORDS

3D printing, Aerogel, Thermal management, Sustainable, Tissue engineering

ABSTRACT

Due to aerogel's network structure, specific surface area, and high porosity, SiO2 aerogel has excellent thermal insulation and inferior mechanical properties. It is challenging to accurately produce micro-objects and complex-shaped objects by traditional manufacturing methods because of their fragile mechanical properties. Three-dimensional (3D) printing can realize the design of performance requirements and manufacture unconventional structures. Publication data over the past six years about "3D printing thermal management materials" and "3D printing aerogel materials" all show a steady increase in the use of 3D printing technology, which is applied to the fields of material design and biomedicine. Furthermore, the related study pointed out its feasibility in functional clothing design applications. Based on this, the research progress of 3D printing aerogel materials is briefly analyzed in this study. Moreover, the more promising 3D printing technologies for fabricating aerogel materials are summarized and compared between extrusion and curing types. Compared with extrude 3D printing technology, light-curing 3D printing technology has low requirements for ink viscosity and viscoelasticity and has the advantages of fast printing speed and high printing accuracy. However, the 3D printing technology of aerogel materials is still in a period of rapid iteration, and technical bottlenecks still need to be overcome, such as the printing materials, the structure design, and the manufacturing process. In addition, the unique applicability of 3D printing aerogel materials in thermal insulation, dielectric material, and tissue engineering are discussed, as well as the application characteristics. It is worth mentioning that the excellent thermal insulation and mechanical properties of 3D printing materials, combined with flexible technology, are expected to be applied to functional protective clothing in the future, such as fire protection clothing and stab-resistant body armor. Based on the analysis, future trends are demonstrated, such as exploring the sustainability value of 3D printing technology thoroughly, improving the printing speed, developing 3D printing technology more adaptable to aerogel printing, and analyzing the influence of the controlled pore structure of 3D printing on its performance.

1 INTRODUCTION

Aerogel, a solid nano-material with a porous structure, is formed by replacing the liquid component in a wet gel with gas. Widely applied in areas such as thermal insulation, energy storage, catalysis, environmental treatment, and electromagnetic wave shielding, aerogels have seen diverse developments since the emergence of silica aerogel in 1931[1]. Among the various types of aerogels, silica-based aerogels have achieved significant progress, particularly in clothing research and applications[2, 3]. Studies have indicated that utilizing SiO2 aerogel composites can reduce the thickness and mass of firefighter suits by over 70% while ensuring equivalent thermal protection[4].

However, the inherent low density and strength of aerogels impose substantial limitations on their post-processing and handling capabilities[5]. Traditional aerogel preparation methods involve the formation of gels within specific molds, followed by solidification and drying (including ambient pressure drying, freeze drying, or supercritical drying) to eliminate the liquid component and yield aerogel materials. Notably, producing aerogel materials with intricate shapes necessitates custom-made molds, rendering this approach expensive and environmentally unsustainable[6, 7]. To address this challenge, there is a pressing need for novel, personalized, and customizable manufacturing technologies capable of producing aerogel materials with complex shapes in line with green and sustainable development principles.

Unlike traditional processing techniques, 3D printing technology for aerogel fabrication simplifies production and reduces manufacturing costs. Additionally, the macro-porous structure inside aerogels can be digitally controlled through computer-aided design, allowing adjustments of its internal properties such as adsorption, heat transfer, and conductivity. This capability makes aerogels suitable for applications in extreme environments. This paper reviews and summarizes the development of 3D printed aerogels, introducing 3D printing techniques applicable for aerogel preparation and elucidating the potential applications of 3D printed aerogels. Furthermore, the paper provides prospects for future directions and addresses the challenges in this field.

2 ANALYSIS OF THE KEYWORDS’ POPULARITY

This study conducted a literature review based on Web of Science using search terms “3D print*” and “thermal management material*” as well as “3D print*” and “aerogel*”. Publications from the years 2017 to 2022 were selected for analysis. Figure 1 illustrates the publication trends and research domains for both topics over the five years. The number of publications on 3D-printed thermal management materials and 3D-printed aerogels has steadily increased over the past five years. The sharp decline in 2020 is attributed to insufficient experimental conditions caused by the COVID-19 pandemic.

The results indicate that 3D printing technology has widespread applications in materials science, engineering, chemistry, nanotechnology, and biomedical fields, such as medical equipment and accessories design, image processing, and automated control. Particularly noteworthy is the acceptance of 3D printing technology in the fashion industry due to its independent and innovative clothing and apparel design techniques. Using 3D printing, patterns can be directly printed onto fabric without additional stitching or sewing operations. From individualized parts to unique and innovative clothing and accessories, 3D printing has created opportunities for producing personalized fashion items. This showcases the versatility and rapid adaptability of 3D printing technology.

The broad applicability and rapid adaptability of 3D printing technology in fashion design are demonstrated, indicating the feasibility of future research on applying related aerogel materials in functional clothing.

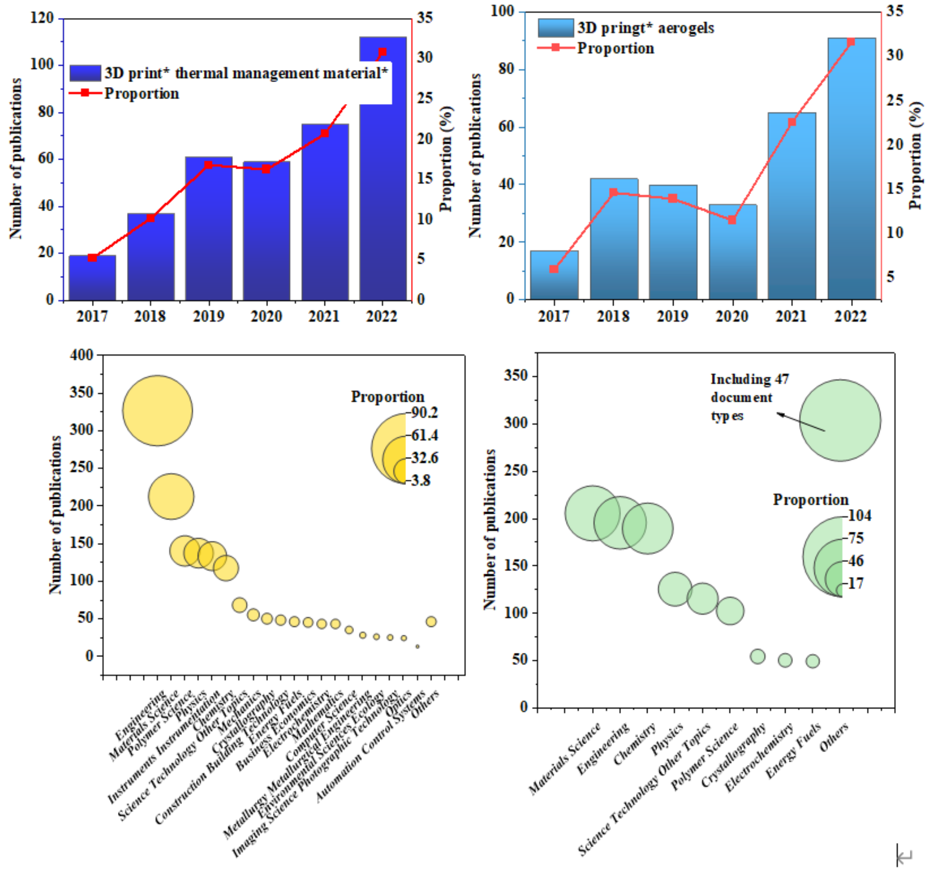

Fig 1. Search and analysis of keywords

3 3D PRINTING TECHNOLOGY

Three primary methods have been successfully employed in the 3D printing of aerogel materials: extrusion-based printing, cold field-assisted drop-on-demand (DOD) method, and photopolymerization-based printing. Photopolymerization 3D printing can be further categorized into stereolithography (SLA) and selective area photopolymerization (LCD) based on distinct printing principles.

(1) Extruded 3D printing technology

Extrusion-based 3D printing technology involves extruding and depositing high-viscosity ink through a nozzle onto the manufacturing platform, forming a stable printed structure [8, 9]. The essence of extrusion-based 3D printing lies where ink flows through the print nozzle and solidifies steadily on the platform. Therefore, the rheological properties of the ink are crucial for extrusion-based 3D printing[8]. Gel inks used in this method should exhibit the characteristics of pseudoplastic fluids, meaning that their viscosity decreases with increasing shear strain (shear thinning). This property allows the ink to extrude smoothly through the nozzle under shear stress. Extrusion-based 3D printing is currently the most widely used method and offers the most diverse range of printable materials in aerogel 3D printing.

(2) Light-curing 3D printing technology

Photopolymerization-based printing technology utilizes ultraviolet (UV) light to solidify photosensitive ink layer by layer, gradually forming the desired structure. This manufacturing technique primarily consists of two methods: Stereolithography (SLA) and Selective Area Photopolymerization (LCD)[10]. In SLA printing, a laser source scans the photosensitive ink along the designated path, curing it layer by layer. After completing one layer, the manufacturing platform moves, and another layer of uncured ink is applied on top of the cured ink, repeating these steps until a three-dimensional model is formed[11]. On the other hand, LCD printing employs a computer-controlled dynamic mask, typically a liquid crystal display (LCD screen), to selectively allow ultraviolet light to shine on the photosensitive ink, layer by layer, thus forming the three-dimensional geometric structure.

SLA and LCD technologies require photosensitive ink to fill the gaps formed on the moving manufacturing platform rapidly. Consequently, the viscosity of the photopolymerization ink should be relatively low to effectively and swiftly backfill the printing gaps. Compared to extrusion-based 3D printing technology, photopolymerization-based 3D printing requires lower viscosity and viscoelasticity of the ink. It offers advantages such as fast printing speed and high precision, making it a subject of significant research interest. However, due to the specific wavelength of light sources required for the photopolymerization process, developing inks suitable for photopolymerization-based 3D printing has been relatively slow. In contrast, the development of aerogels based on extrusion-based 3D printing technology is relatively advanced.

4 APPLICATION

Aerogel materials prepared through traditional template methods possess significant potential applications across various fields. However, the mechanical properties of aerogels produced using conventional methods are often insufficient for subsequent structural cutting and shaping, particularly in complex applications requiring intricate shapes and structures. Hence, the diversification of aerogel structures becomes crucial. Aerogels, characterized by their dispersed gas phase and nano-porous three-dimensional network structure, represent solid materials with extremely high porosity, specific surface area, remarkably low density, and thermal conductivity. Their thermal conductivity coefficient is even lower than that of static air at room temperature, measuring 0.025 $W/m/K^{-1}$[12]. Aerogels are renowned as the lightest solid materials with exceptional thermal insulation properties and find widespread applications in the military, transportation, aerospace, construction, and apparel industries. Aerogels are classified into inorganic and organic aerogels, constituting a diverse range of materials.

4.1 Applications in the field of thermal insulation

In the field of high-temperature thermal insulation, the printable oxide aerogels that have been developed primarily include SiO2 aerogels. Zhao et al. [13]successfully printed SiO2 aerogels using the DIW printing technique for the first time. The team uniformly dispersed silica aerogel powder with particle sizes ranging from 4 to 20 μm into a sol-gel solution of silica/1-pentanol. This mixture was then used to create printing ink. Then, the material was subjected to ammonia gas catalysis and supercritical drying, resulting in SiO2 aerogels. These aerogels had a specific surface area of 751 m2/g and a thermal conductivity of 0.016 W/m/K. However, the direct use of ammonia gas for catalysis can lead to environmental pollution. To reduce ammonia emissions, Wang et al.[14] presented a thermal curing 3D printing strategy. Urea was added to the SiO2 aerogel ink, which solidified through the coupled processes of urea thermal decomposition and ammonia catalysis. Building upon the successful printing of SiO2 aerogels, Maleki et al. [15] combined silk fibroin (SF) biopolymer extracted from silkworm cocoons with tetramethyl orthosilicate (TMOS) and 5-(trimethoxysilyl) pentanoic acid (TMSPA) additives to create printable gel inks. Subsequently, they used DIW printing and supercritical drying to produce compressible, thermally insulating, and flame-retardant SiO2-SF aerogels. These aerogels exhibited a low thermal conductivity ranging from 0.033 to 0.039 W/m/K and a compressive strain of up to 80%. Compared to pure SiO2 aerogels, the Young's modulus increased by three orders of magnitude. This high-performance hybrid aerogel, fabricated through printing, holds significant application value in thermal insulation.

In addition, Wang et al.[16] employed an extrusion-based coaxial 3D printer to create a thermally conductive, anisotropic composite aerogel composed of carbon nanotubes (CNTs) and carbon nanofibers (CNFs). The team filled two syringes with CNTs/CNFs mixed hydrogels and CNFs hydrogels, respectively. After extrusion according to the designed model, the hydrogels were placed on a low-temperature freezing stage for directional freezing, aligning the ice crystal growth direction with the printing path. Finally, the materials underwent freeze-drying to yield the composite aerogels. Experimental results showed that the longitudinal thermal conductivity of the aerogel was

0.025 W/m/K, and the radial thermal conductivity was 0.302 W/m/K. Although not yet carbonized into carbonaceous aerogels, this anisotropic thermal conductive composite aerogel holds significant potential in thermal management. However, these materials exhibit poor mechanical properties, limiting their practical applications. In the future, it is essential to enhance their mechanical properties while preserving their thermal insulation capabilities, thereby broadening their practical applications.

4.2 Applications in the field of dielectric

Yao et al.[17] utilized a composite gel ink of nanocellulose and SiO2 microspheres to fabricate 3D-printed carbide aerogels featuring a multi-level hierarchical porous structure. These aerogels exhibited an impressive specific surface area of up to 1750 m2/g. Additionally, their specific capacitance at -70 °C ranged from 71.4 to 148.6 F/g (at a low scan rate of 5 mV/s), approximately 6.5 times higher than that of bulk aerogels. Furthermore, the excellent compressibility of 3D-printed aerogel materials endowed them with a relative advantage in fields such as sensors and friction nanogenerators. This underscores the remarkable potential of 3D-printed aerogels, particularly in resolving the challenges posed by traditional methods in forming intricate electroactive materials. The intricate multi-level porosity structure of these aerogels expands their applicability in dielectrics, indicating their broader potential value in the field.

4.3 Applications in tissue engineering

Aerogel scaffolds derived from biomass materials such as cellulose and silk fibroin play a crucial role in tissue engineering. This significance stems from the interconnected, highly porous structure of aerogel scaffolds, which provides essential nutrients for cell growth and serves as a spatial template for cellular expansion. Consequently, aerogel scaffolds must possess specific mechanical properties and be manufactured into desired structures.

Mejuto et al.[18] employed alginate/hydroxyapatite (HA) composite gel ink and utilized 3D printing combined with supercritical carbon dioxide (ScCO2) drying to fabricate biocompatible 3D-printed aerogel scaffolds. In vitro scratch tests demonstrated that alginate/HA aerogel scaffolds with varying HA content stimulated the migration of mouse embryonic fibroblasts (BALB) effectively.

Kankala et al.[19] investigated gelatin/poly(lactic-co-glycolic acid) (PLGA) aerogel scaffolds in another study. Comparisons between 3D-printed and non-3D-printed aerogel scaffolds were conducted to evaluate their efficacy in in vitro cartilage regeneration. The results affirmed that 3D-printed aerogel scaffolds outperformed their non-3D-printed counterparts, highlighting their superior effectiveness in tissue regeneration. These findings underscore the pivotal role of 3D-printed aerogel scaffolds, exhibiting enhanced performance in tissue engineering applications compared to their non-3D-printed counterparts.

5 CONCLUSION AND FUTURE TREND

The development of aerogel materials spans over a century and has garnered significant attention across various fields. However, traditionally prepared aerogels using template methods exhibit a single structure, high economic costs, and face challenges in rapidly forming diverse customized structures, hindering their applications in thermal insulation, biology, electronics, and other fields. The advent of 3D-printed aerogel materials has effectively addressed these issues, incorporating structural optimization to achieve performance characteristics not present in traditional aerogels. Despite the progress made in recent years in the development of 3D-printed aerogels, researchers have gradually discovered and implemented diverse materials, complex structures, and multifunctionality. However, 3D-printed aerogels are still in their early stages of development and face numerous challenges in further advancement and application.

(a) Sustainability: Sustainability is a crucial research area that urgently needs further exploration within the 3D printing industry, focusing on developing eco-friendly materials and adopting circular economy models.

(b) Printing Speed: Standard extrusion-based printing methods involve stacking thin lines with a 0.2 to 1.0 mm thickness, resulting in relatively slow printing speeds (10 to 30 mm/s). This limitation hampers industrial-level production demands. Light-curing printing, especially LCD printing, offers considerably faster printing speeds, transitioning from surface to volume. However, challenges persist in preparing light-curable inks suitable for 3D-printed aerogels, necessitating in-depth research efforts.

(c) Structural Design: During the development of 3D-printed aerogels, researchers have found that the performance of aerogels (thermal conductivity, energy storage capacity) with designed multi-level pore structures changes due to the externally applied structure. So far, few studies have explored how optimizing these multi-level pore structures can yield unique properties distinct from or superior to traditional aerogels (geometric stretching, multi-level pores, etc.).

(d) Mechanistic Analysis: While the number of studies on 3D printing technology continues to grow, limitations in research have been acknowledged. Many studies focus on a limited range of materials, lack comprehensive information, lack depth, and involve small sample sizes, diminishing the overall understanding of experimental consistency. More research is needed to address these limitations and further explore this trending technology's potential.

6 REFERENCE

CHEN Z, LI J, LIU C, et al. Preparation of high solid loading and low viscosity ceramic slurries for photopolymerization-based 3D printing [J]. Ceramics International, 2019, 45(9): 11549-57.

CHAKRABORTY S, BISWAS M C. 3D printing technology of polymer-fiber composites in textile and fashion industry: A potential roadmap of concept to consumer [J]. Composite Structures, 2020, 248.

SMELIK A. Fractal Folds: The Posthuman Fashion of Iris van Herpen [J]. Fashion Theory, 2020, 26(1): 5-26.

TYCHANICZ-KWIECIEŃ M, WILK J, GIL P. Review of High-Temperature Thermal Insulation Materials [J]. Journal of Thermophysics and Heat Transfer, 2019, 33(1): 271-84.

ZHAO G, SHI L, YANG G, et al. 3D fibrous aerogels from 1D polymer nanofibers for energy and environmental applications [J]. Journal of Materials Chemistry A, 2023, 11(2): 512-47.

HAYASE G, NONOMURA K, HASEGAWA G, et al. Ultralow-Density, Transparent, Superamphiphobic Boehmite Nanofiber Aerogels and Their Alumina Derivatives [J]. Chemistry of Materials, 2014, 27(1): 3-5.

ALMEIDA C M R, GHICA M E, DURAES L. An overview on alumina-silica-based aerogels [J]. Adv Colloid Interface Sci, 2020, 282: 102189.

SKYLAR-SCOTT M A, MUELLER J, VISSER C W, et al. Voxelated soft matter via multimaterial multinozzle 3D printing [J]. Nature, 2019, 575(7782): 330-5.

HASSAN K, NINE M J, TUNG T T, et al. Functional inks and extrusion-based 3D printing of 2D materials: a review of current research and applications [J]. Nanoscale, 2020, 12(37): 19007-42.

VOGT B D. A Virtual Issue of Applied Polymer Materials: "3D Printing of Polymers" [J]. ACS Applied Polymer Materials, 2020, 2(6): 2102-4.

AKBARI M, SYDäNHEIMO L, JUUTI J, et al. Flash Reduction of Inkjet Printed Graphene Oxide on Flexible Substrates for Electronic Applications [J]. 2015 Ieee 15th International Conference on Nanotechnology (Ieee-Nano), 2015: 93-6.
PATIL S P, PARALE V G, PARK H-H, et al. Mechanical modeling and simulation of aerogels: A review [J]. Ceramics In-

ternational, 2021, 47(3): 2981-98.

ZHAO S, SIQUEIRA G, DRDOVA S, et al. Additive manufacturing of silica aerogels [J]. Nature, 2020, 584(7821): 387-92.
WANG L, FENG J, LUO Y, et al. Three-Dimensional-Printed Silica Aerogels for Thermal Insulation by Directly Writing Temperature-Induced Solidifiable Inks [J]. ACS Applied Materials & Interfaces, 2021, 13(34): 40964-75.

MALEKI H, MONTES S, HAYATI-ROODBARI N, et al. Compressible, Thermally Insulating, and Fire Retardant Aerogels through Self-Assembling Silk Fibroin Biopolymers Inside a Silica Structure-An Approach towards 3D Printing of Aerogels [J]. ACS Appl Mater Interfaces, 2018, 10(26): 22718-30.

WANG F, YANG Z, HU X, et al. Coaxial 3D printed anisotropic thermal conductive composite aerogel with aligned hierarchical porous carbon nanotubes and cellulose nanofibers [J]. Smart Materials and Structures, 2022, 31(4).

YAO B, PENG H, ZHANG H, et al. Printing Porous Carbon Aerogels for Low Temperature Supercapacitors [J]. Nano Lett, 2021, 21(9): 3731-7.

IGLESIAS-MEJUTO A, GARCIA-GONZALEZ C A. 3D-printed alginate-hydroxyapatite aerogel scaffolds for bone tissue engineering [J]. Mater Sci Eng C Mater Biol Appl, 2021, 131: 112525.

KANKALA R K, XU X M, LIU C G, et al. 3D-Printing of Microfibrous Porous Scaffolds Based on Hybrid Approaches for Bone Tissue Engineering [J]. Polymers (Basel), 2018, 10(7).