Dean&Francis

ISSN 2959-6157

Applications of Graphene Composite Materials in 3D Printing

Shanglin Yang[1, *]

[1]Department of Information, Mechanical and Electrical Engineering, Shanghai Normal University, Shanghai, China

*Corresponding author: 1000534770@ smail.shnu.edu.cn

Abstract:

With the advancement of technology, 3D printing has transformed manufacturing in various aspects and has received widespread attention and research over the past few years, being regarded as the beginning of a whole new era. However, current mainstream materials cannot meet the growing demand for lightweight, high-strength applications, leading to an increasing societal demand for new materials. One such material is graphene, which has attracted considerable attention due to its enormous specific surface area and outstanding mechanical properties. Graphene sheets are extremely thin, approximately one atom thick, but they lack ideal rheological properties and tend to aggregate and stack in solvents. To address this issue, graphene composite materials have emerged. The innovation of graphene composites in the field of 3D printing holds great promise. By refining manufacturing techniques, optimizing materials, and overcoming key limitations, graphene composites have the potential to revolutionize manufacturing, enabling the realization of high-performance devices in the future.

Keywords: 3D Printing; Graphene; composite materials; applications.

1. Introduction

With the advancement of technology, 3D printing has transformed production and manufacturing across all aspects of society. Not only does 3D printing reduce material waste and lower costs, but it can also produce structures that traditional manufacturing methods cannot achieve. The key to 3D printing lies in the materials. Currently, polymers such as polylactic acid (PLA) and acrylonitrile butadiene styrene copolymer (ABS) are the most commonly used materials [1]. Their advantages include relatively low cost, availability, and moldability. However, one of the biggest issues is that when printing porous structures, conventional printing materials often fail to provide adequate material strength, leading to a significant reduction in structural strength, which cannot meet the growing demand for lightweight, high-strength applications [2].

A promising alternative is two-dimensional carbon materials, which have attracted widespread attention due to their large specific surface area and excellent mechanical properties, becoming a new direction for printing materials. Among them, graphene stands out

ISSN 2959-6157

the most. However, graphene sheets are extremely thin, approximately one atom thick, and do not possess ideal rheological properties, making them prone to aggregation in solvents, forming stacked states rather than uniform dispersion. During the printing process, if graphene cannot be evenly distributed, it may result in inconsistent performance of the printed parts. address this issue, graphene-based composite materials emerged in response to the issue [3].

This paper aims to summarize graphene composite materials from aspects of properties and preparation, providing a theoretical foundation for their application in the field of 3D printing. It will first introduce the basic properties of graphene composite materials, then describe the preparation of different types of graphene composite materials, followed by discussing the applications of graphene composite materials in various 3D printing fields. Finally, it will introduce the limitations and future prospects of graphene-based composite materials in the 3D printing field.

2. Commonly Used Graphene Composites in 3D Printing and Their Preparation

Leveraging the high specific surface area and anisotropy of graphene nanosheets and make a further processing, mixing graphene with metals, polymers, and ceramics, following by layer-by-layer printing to construct 3D structures, has become a new research direction. However, graphene has some drawbacks, such as its tendency to aggregate due to its layered structure and the risk of burning or oxidation at high temperatures. Therefore, how graphene can improve the properties of the matrix material is worthy of in-depth research. Currently, reports indicate that graphene-added composites have potential applications in energy electronics, biomedicine, and aerospace, among other fields, although many issues still require further investigation [4].

2.1 3D Printed Graphene-Reinforced Polymer Composites

Adding a small amount of an appropriate reinforcing phase to polymers can significantly enhance the performance of the base material. Researchers have utilized 3D printing technology to incorporate graphene into polymer matrices, discovering its great potential to improve the properties of polymer materials. After modification and reduction, graphene can form nanoscale dispersion within the polymer matrix, thereby enhancing the mechanical, thermal, and electrical properties of the polymer.

For graphene-polymer composites, the large specific surface area and superior performance offer excellent structural and functional systems. Using AFM nanoindentation techniques, the intrinsic strength of perfect graphene sheets is 130 GPa, and their elastic modulus is 1.0 TPa. Therefore, graphene is an excellent choice for mechanical reinforcement in polymer nanocomposites [5]. Oriented distribution of graphene nanosheets ensures that the interface between the reinforcing material and the matrix material is uniformly distributed throughout the composite, maximizing stress transfer through the interface. Chandrasekaran et al. [6] studied the mechanism by which oriented graphene can enhance the toughness of composites, as illustrated in Fig 1.

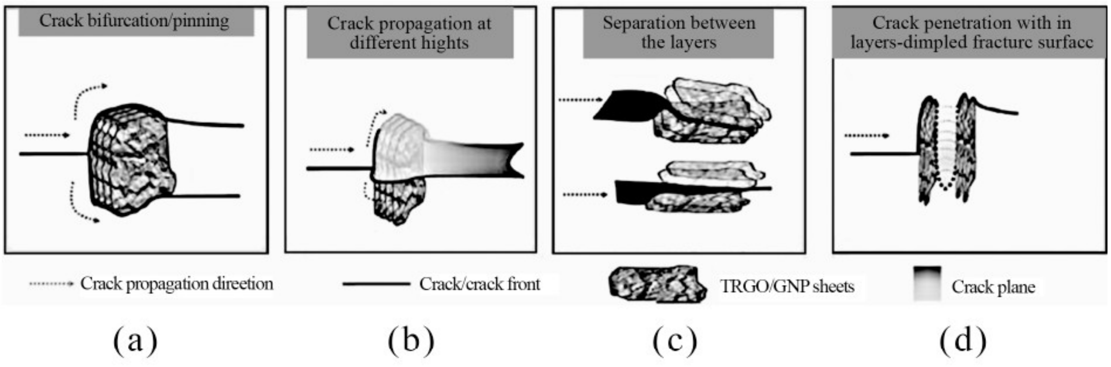

Fig.1 Schematic on the interaction of crack front with graphene particles[6]

To enhance the thermal stability of functional polymers, materials with superior thermal properties, such as graphene matrix fillers, can be incorporated. For instance, adding 1% of functionalized graphene sheets to polyacrylonitrile can increase the glass transition temperature by approximately 40°C, significantly improving the strength, modulus, and thermal stability of the polymer, far surpassing those of carbon nanotube-modified polymer composites [7].

Graphene is a single layer of pure carbon atoms arranged in a honeycomb lattice. Even when cut into elements as narrow as 1 mm, it retains excellent electrical conductivity. Graphene sheets can provide pathways for electron transfer, making the composite material conductive. Adding high-conductivity graphene as a filler to the polymer matrix can greatly enhance the electrical conductivity of the base material.

The interaction mechanisms of graphene-polymer composites are related to the polarity, molecular weight, hydrophobicity, and reactive groups of the polymer, as well as the properties of graphene/graphite and the solvent. There are three primary methods for preparing graphene-polymer composites [8]. The first is in-situ interlayer polymerization, where graphene or modified graphene is dispersed in a liquid polymer monomer. An initiator is added to disperse the graphene, and then polymerization is initiated by heating or radiation. The second method is solution interlayer polymerization, which requires that the polymer or prepolymer is soluble, and that the graphene or modified graphene sheets can swell or disperse in the solution. The third method is melt interlayer polymerization, which does not require a solvent. Graphite, graphene, or modified graphene is directly mixed with the molten polymer.

2.2 3D Printed Graphene-Reinforced Metal Matrix Composites

Research has shown that the performance of graphene-reinforced metal matrix composites is directly related to the dispersion of graphene. At the same time, numerous studies have indicated that, regardless of the dispersion of graphene in metals, the strength and corrosion resistance of the composites are enhanced compared to the raw materials. However, the electrical conductivity is closely related to the selection of raw materials.

The introduction of graphene significantly enhances the tensile strength and yield strength of the material and improves its ductility. This enhancement is positively correlated with the uniformity of graphene distribution in the matrix. The main mechanisms by which graphene reinforces the metal matrix include grain refinement, dislocation pinning, and stress transfer. During plastic deformation, graphene can pin dislocations, preventing their slip. Under external forces, graphene helps the metal matrix share the load, thereby enhancing the overall load-bearing capacity of the material [9]. Additionally, in corrosive environments, the introduction of reinforcing phases typically reduces the corrosion resistance of the matrix, but the addition of graphene can actually enhance the corrosion resistance of the matrix.

In terms of electrical conductivity, graphene/metal composites prepared from graphite exhibit lower resistivity than pure metals. However, composites made from graphene oxide may show increased resistivity. Although the electrical conductivity of graphene oxide improves after reduction, the change in resistivity is limited due to incomplete reduction. Moreover, the electrical conductivity of graphene/metal composites is influenced by the material's density. Generally, higher density means fewer internal pores, resulting in better electrical conductivity of the graphene-metal composite [10].

There are three common preparation methods. The first is the melt metallurgy method [11], which involves adding the reinforcing phase to molten metal or alloy and continuously stirring to ensure thorough mixing and obtain the composite material. The hardness, yield strength, and ultimate tensile strength of the composite material are significantly improved. However, due to the high melting points of metals, prolonged stirring at high temperatures can lead to interfacial reactions between graphene and the matrix, forming metal oxides and carbides, which increase material brittleness. Simple stirring methods also fail to adequately disperse the reinforcing phase in the matrix, leading to graphene agglomeration and a higher number of pores in the composite, reducing its performance. Therefore, the melt metallurgy method is more commonly used for preparing composites with metals like Mg and Al, which have lower melting points.The second method is the powder metallurgy method [12], which involves thoroughly mixing graphene or graphene oxide powders with metal powders, followed by shaping and processing the composite powders to obtain the desired composite material. The powder metallurgy method offers advantages such as simple process, lower cost, and controllable types and amounts of reinforcements. However, it also has limitations, such as the easy destruction of graphene structure under pressure and difficulty in controlling the density of the composite material, which require further research and improvement.

The third method is the chemical synthesis method [13], which uses the chemical reaction between the precursor of the reinforcing phase and metals, metal ions, or metal oxides to synthesize the composite material. Graphene is generated during the reaction process rather than being physically mixed with the matrix. This method results in good interfacial bonding between graphene and the matrix and uniform dispersion of graphene. However, the process is complex and requires high standards for equipment and production.

2.3 3D Printed Graphene-Reinforced Ceramic Matrix Composites

Traditional ceramic matrix composites use one-dimen-

ISSN 2959-6157

sional carbon fibers and ceramic whiskers as reinforcing phases. However, these materials tend to distribute unevenly in the ceramic matrix and are prone to agglomeration. In contrast, graphene offers significant advantages, as it can be more evenly dispersed in the ceramic matrix. Coupled with its excellent mechanical and physicochemical properties, graphene has great potential for enhancing the overall performance of the material.

After 3D printing three-dimensional graphene structures, chemical vapor infiltration (CVI) is used to introduce a SiC matrix between the graphene sheets. The resulting three-dimensional graphene/SiC composites maintain a porous structure, as shown in Fig 2.

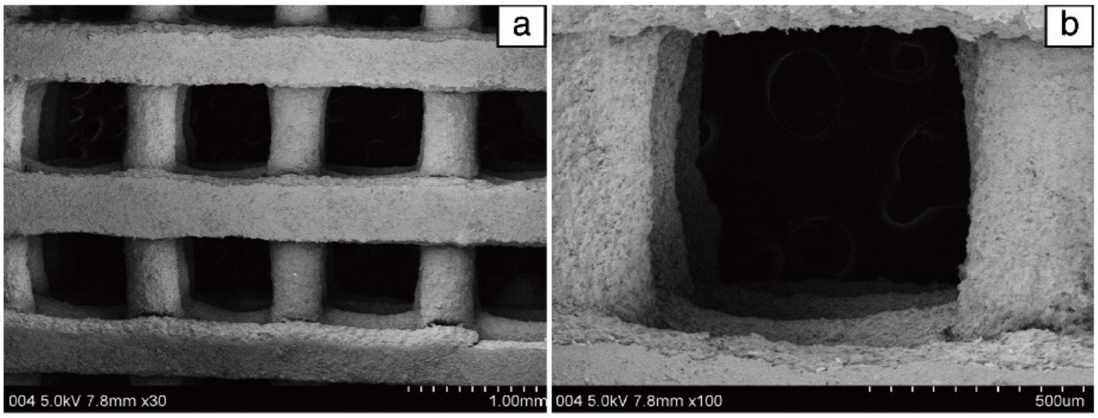

Fig.2 SEM images of 3D graphene/SiC composites[14]

The dispersion of graphene in the ceramic matrix directly affects the performance of graphene/ceramic composites. Currently, there is limited research on methods for dispersing graphene in ceramic matrices. However, the methods for dispersing carbon nanotubes in ceramic matrices are relatively mature, and these methods can be adapted for graphene dispersion. The main methods currently applied are powder processing and colloidal forming. In powder processing, ultrasonic degradation methods are used to disperse graphene, which is then mixed with ceramic powders. Ball milling or high-energy ball milling is subsequently used to obtain a well-dispersed graphene-ceramic powder mixture. In colloidal forming, ceramic powder colloidal solutions and graphene colloidal solutions are mixed and then uniformly dispersed using magnetic stirring or ultrasonic homogenization. From a mechanical property perspective, since graphene itself possesses excellent mechanical properties, its uniform dispersion in the ceramic matrix can significantly enhance the mechanical properties of the ceramic matrix. In terms of electrical properties, graphene's inherent excellent conductivity and its ability to form a uniform distribution in the ceramic matrix mean that its addition can also significantly improve the electrical conductivity of the ceramic matrix.

3. 3D Printing Techniques for Graphene Composite Materials

The development of composite materials has placed higher demands on the 3D printing field. With the advancement and perfection of 3D printing technology, the processes for 3D printing graphene-based materials can primarily be divided into Selective Laser Sintering (SLS), Binder Jetting Technology (BJT), Fused Deposition Modeling (FDM), and Direct Ink Writing (DIW).

3.1 Selective Laser Sintering (SLS)

As shown in Fig 3, selective laser sintering involves formulating graphene/ceramic composite powders into a shear-thinning composite slurry, which is extruded from a nozzle under pressure into filaments. These filaments are scanned along pre-set printing paths and deposited layer by layer to create graphene/ceramic composite materials with specific structures. The laser sintering technique allows the powder to solidify during the part manufacturing process without the need for support structures, and it is mainly used for the formation of metal and thermoplastic materials.

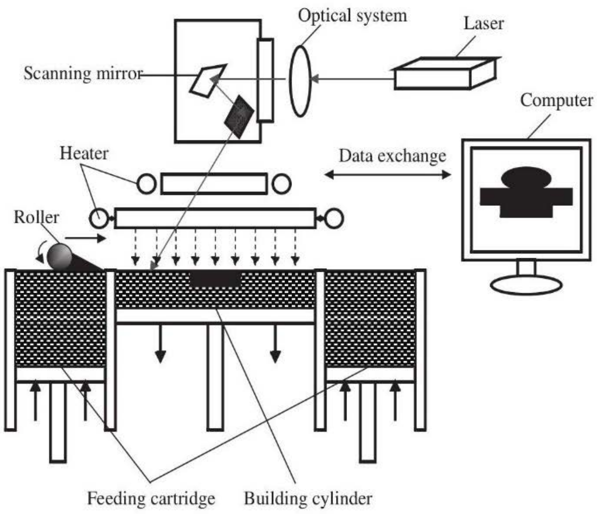

Fig. 3 Schematic of the selective laser sintering process[15]

3.2 Fused Deposition Modeling (FDM)

Thermoplastic filament materials are extruded through a movable nozzle, primarily for structural purposes. Fillers are added to prepare novel filaments with special functionalities (such as thermal conductivity and electrical conductivity), thereby expanding the application range of FDM-printed components.

3.3 Binder Jetting Technology (BJT)

Binder Jetting is a powder bed-based additive manufacturing technology that uses powder materials as the base material. In this process, no additional polymer is required to aid in the shaping of the printed graphite powder. Instead, after the powder is laid down, a binder is sprayed through the print head to bind the graphite powder into the desired shape. BJT offers several advantages, including high efficiency, low cost, material reusability, and the absence of support structures. This technology enables the moldless formation of graphite products, resulting in preforms with controllable structural properties.

4. Applications of 3D Printed Graphene-Based Composite Materials

Graphene, with its outstanding properties and diverse modification methods, has demonstrated broad potential in various fields and has become a focal point in recent years. By combining graphene with other materials, the strengths of each can be maximized. Meanwhile, 3D printing technology has made it possible to manufacture complex and precise structures, further expanding the potential of composite materials in various application areas.

4.1 Microwave Absorption

With the advancement of technology, electromagnetic pollution has become increasingly severe, and designing “thin, light, strong” microwave absorbing materials has gained significant attention. Graphite, carbon fibers, and graphene are typical dielectric loss microwave absorbing materials. Among these, graphite is abundant, has a low density, and is highly adaptable to various environments, making it particularly advantageous in microwave absorption. The exceptional performance of absorptive materials is largely attributed to artificial structures. 3D printing technology can selectively reduce the dielectric matrix, making the absorbers lighter, and can design complex and innovative structures to achieve superior absorption performance.

4.2 Energy Storage

Currently, most materials used for 3D printing electrodes are conductive thermoplastics, which have poor electrochemical responsiveness and are not suitable for electrochemical sensing applications. Graphite and its composites, with their unique thermal stability and electrochemical activity, can compensate for these deficiencies. Graphene, with its ultra-large specific surface area and excellent electrical conductivity, has gained significant attention in the energy sector. 3D-printed graphene-based composites are widely used in lithium-ion batteries and supercapacitors. Graphene-based composites are now an indispensable part of the energy storage field.

4.3 Biomedical Applications

The application of graphene in the biomedical field has also attracted considerable attention from researchers.

ISSN 2959-6157

Graphene exhibits excellent biocompatibility and antibacterial properties. Graphene oxide (GO) has abundant oxygen-containing functional groups on its surface, making it easy to modify and fix drugs, suitable for drug delivery. Graphene's outstanding photothermal conversion capability in the near-infrared region makes it useful for photothermal cancer therapy. It can also be used to enhance the wear resistance of artificial bone tissues and joints when formulated into composites. GO films can promote cell adhesion, enhancing cell proliferation and differentiation, making them suitable for biological scaffolds. 3D-printed graphene/polymer composites have been extensively studied in the biomedical field, primarily for the fabrication of biological scaffolds. Common printing methods include inkjet printing, fused deposition modeling, and stereolithography.

5. Limitations and Prospects of 3D Printing Graphene-Based Composite Materials

The application of 3D printing technology in the field of graphite and its composites has provided possibilities for optimizing the macrostructure of graphite and its composites, enhancing their applications in multiple fields. However, 3D printing technology still faces several challenges and issues in the molding and preparation of graphite and its composites.Firstly, due to the inherent properties of graphite materials, the 3D printing techniques available for graphite are limited, and most are still in the laboratory research stage, not yet put into practical production. Secondly, graphite and its composites are typically conductive, which can lead to thermal runaway during the printing process, especially when using BJT (Binder Jetting Technology). Conductive powders may affect the electrical circuits of the printing equipment, placing higher demands on the printing devices. Additionally, devices made from graphite composites using 3D printing often suffer from poor surface quality and low mechanical strength, requiring post-processing (such as impregnation and surface coating) to improve the quality of the devices.
To address these issues, the following directions can be pursued for the development of 3D printing of graphite and its composites. First, developing and expanding the types of graphite composites. It is necessary to achieve more diverse performance and applications. This requires adjusting the ratios of composite materials and developing new composites to enhance material performance while adapting to different printing technologies. Considering economic benefits and environmental factors, it is also essential to develop eco-friendly materials and combine graphite materials with other renewable resources to promote green and sustainable development. Second, the development of new printing equipment and supporting devices. It is crucial as the demand from application sectors continues to grow. High-performance, high-efficiency, and high-precision graphite 3D printing equipment are urgently needed. Research should focus on developing large-scale, high-precision, and mass-production-capable printing devices tailored to the characteristics of graphite materials for practical production. Finally, develope the post-processing technologies for 3D printed graphite. 3D-printed graphite green bodies often have low density and poor mechanical properties. In addition to improving these issues through material design and preparation, it is important to optimize post-processing techniques based on the characteristics of 3D-printed bodies to further enhance the density, strength, and other mechanical properties of graphite prints to meet application requirements. Specific areas for in-depth research include post-processing techniques, process optimization, and the design of post-processing materials.

6. Conclusion

In summary, graphene-based composite materials hold great potential in the field of 3D printing and are expected to be applied in various aspects of production and manufacturing in the future. In recent years, with the continuous improvement of 3D printing technology and the discovery of new graphene composites. Compared to existing materials, the combination of the two has demonstrated greater malleability, better mechanical and electrical properties, and a wider range of applications In the foreseeable future. Still, the 3D printing and large-scale production of graphene-based composites still face challenges, which require ongoing research and innovation. It is hoped that this article will provide readers with a more comprehensive understanding of the applications of graphene composites in the 3D printing field.

References

[1] Wang Chao, Chen Jifei, Feng Tao, et al. Development of 3D Printing Technology and Its Material Application Progress [J]. China Foundry Equipment & Technology, 2021, 56(06):38-44.
[2] Yang Jianming, Tang Yang, Gu Hai, et al. Research and Application Status of Porous Structures Prepared by 3D Printing [J]. Materials Reports, 2018, 32(15):2672-2682.
[3] Kuang Da, Hu Wenbin. Research Progress on Graphene Composite Materials [J]. Journal of Inorganic Materials, 2013, 28(03):235-246.
[4] Shi Yufei, Li Xiaoli, He Tianyi, et al. Research Progress

of Graphene-based Materials in the Field of 3D Printing. Electroplating & Finishing, 2023, 45(07):74-83.
[5] Lee C G, Wei X D, Kysar J W, et al. Measurement of the Elastic Properties and Intrinsic Strength of Monolayer Graphene. Science, 2008, 321, 385–388.
[6] Chandrasekaran S, Sato N, Tölle F, et al. Fracture Toughness and Failure Mechanism of Graphene-Based Epoxy Composites [J]. Composites Science & Technology, 2012, 72(15):1854-1860.
[7] Ren Cheng, Wang Xiaojun, Li Yongxiang, et al. Research and Application of Graphene Composite Materials [J]. Modern Chemical Industry, 2015, 35(01):32-35. [8] Xu Jing, Xing Yue, Hao Sijia, et al. Research Progress on 3D Printing Formation of Graphene/Polymer Matrix Composites [J]. Journal of Materials Engineering, 2018, 46(07):1-11.
[9] Zhou W, Dong M, Zhou Z, et al. In situ formation of uniformly dispersed Al4C3 nanorods during additive manufacturing of graphene oxide/Al mixed powders, Carbon, 2019, 141:67.
[10] Wu Z S, Zhou G, Yin L C, et al. Graphene/Metal Oxide Composite Electrode Materials for Energy Storage [J]. Nano Energy, 2012, 1(1):107-131.
[11] CHEN L Y, HIROMI K, FEHRENBACHER A, et al. Novel Nanoprocessing Route for Bulk Graphene Nanoplatelets Reinforced Metal Matrix Nanocomposites [J]. Scripta Materialia, 2012, 67(1):29-32.
[12] WANG J Y, LI Z Q, FAN G L, et al. Reinforcement with Graphene Nanosheets in Aluminum Matrix Composites [J]. Scripta Materialia, 2012, 66(8):594-597.
[13] LIU G, ZHAO N Q, SHI C S, et al. In-Situ Synthesis of Graphene Decorated with Nickel Nanoparticles for Fabricating Reinforced 6061Al Matrix Composites Materials Science and Engineering: A, 2017, 699:185-193.
[14] Yang Jinshan, Huang Kai, You Xiao, et al. 3D Printing of Three-Dimensional Graphene and Its High-Performance Ceramic Matrix Composites Chinese Journal of Materials Research, 2018, 37(08):590-596.
[15] He Yuyu, Liu Yi, Zhang Yunyun, et al. Research Progress on 3D Printing of Graphite and Its Composite Materials Journal of Materials Engineering, 2024,1-10.