Preparation of Graphene and the Uses in 3D Printing

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Abstract. The incorporation of graphene into 3D printing technology has brought a new perspective for several industries. This review explores the methods applied in creating graphene, including mechanical exfoliation and chemical vapor deposition. The significance for developing high-quality graphene in 3D printing is also discussed. Among the 3D printing processes, direct ink writing (DIW) is one of the most promising methods for fabricating graphene-based structures. The critical concerns of this technique are concerning with ink rheology and material purity. Meanwhile, contributions related to the other manufacturing techniques including fused deposition modeling (FDM) and stereolithography (SLA) are also discussed. The cost-effectiveness of FDM is still questioned. The challenge of the uniform dispersion of graphene in filaments has to be solved. SLA offers precision at the cost of complexity in resin formulation. While the incorporation of graphene significantly enhances the conductivity, mechanical strength, and thermal stability of 3D-printed materials, challenges regarding scalability and environmental impact still remain. In the future, further developments in graphene-based 3D printing techniques may concerning with the manufacturing from aerospace components to flexible electronics. The status and challenges of this technology are also pointed out in this work.

Keywords: 3D printing, graphene, preparation.

1. Introduction

3D printing technology, also known as additive manufacturing, refers to the process where a three-dimensional structure is created. It is highly valued because of its product can be fabricated with flexible designed structure. The 3D printing also has higher precision than the conventional techniques of manufacturing. There are three types of 3D printing which based on materials being used. 3D printing enables the use of computer-aided design (CAD) along with computer-aided manufacturing (CAM) for rapid and accurate production. This offers a new possibility for the manufacturing techniques.

In 3D printing, new paths have been discovered for three-dimensional fabrication of graphene. This ability of 3D printing opens up new opportunities for optimizing material properties in large scales. Among different techniques developed within 3D printing, direct ink writing (DIW) has emerged as one of the most widely used techniques in the fabrication of graphene-based structures. The preparation of graphene inks for 3D printing is critical and it needs to meet several requirements that could guarantee successful printing. These requirements encompass the formulation of stable and homogeneous dispersion to avoid nozzle clogging. Meanwhile, it should have the characteristics which allow smooth ejection through printing nozzles. Besides, rapid solidification after the deposition is also needed to facilitate multi-layer printing [1]. DIW is one of the main methods developed for the printing of personalized structures with graphene-based inks, with the assistance of a computer-controlled system. In this respect, the rheological properties of such inks are of paramount importance in guaranteeing the necessary flow and stability during the printing process [2]. While these additives help in the printing process, they may also compromise the purity and microstructure of graphene, which can lead to problems in the final product. In addition, laborious material preparation and high production costs further complicate the scalability of this process. Besides, the most outstanding techniques adopted in 3D printing with graphene are fused deposition modelling (FDM) and stereolithography (SLA). FDM is the extrusion of thermoplastic filaments infused with graphene, thus allowing a straightforward and low-cost means for fabricating components. However, difficulties arise in obtaining uniform graphene dispersion within the filament. In contrast, SLA uses laser to cure graphene-reinforced resins one layer at a time. It produces high-resolution structures with excellent surface finishes. While SLA can present good control of the microstructure from the printed parts, there is still some issues that this technique must face the challenges include the uniform dispersion of graphene and the photoreactive resin which is capable to sustain properties of graphene. FDM and SLA are two techniques that still contribute to the development of the use of graphene in 3D printing. While each of these techniques offers unique advantages, the time-consuming and labor-intensive material preparation processes limit their practical use. Therefore, a large number of researches are carried out around these technologies. In this work, preparation and applications of graphene in 3D printing are outlined in detail.

2. Graphene

Graphene has garnered significant interest due to its exceptional physical, chemical, and electrical properties. It displays high surface area, remarkable mechanical strength, thermal conductivity and electrical conductivity. Graphene is an ideal candidate for 3D printing. The synthesis of high-quality graphene usually employs exfoliation methods, which are essentials for extracting graphene sheets from bulk graphite.

2.1. Mechanical Exfoliation

Among the pioneering methods for graphene isolation was a process known as mechanical exfoliation or the scotch tape method. This method requires to peel graphite layers off by using adhesive tape. The graphene sheets are of high quality, but the yield is limited [3]. Mechanical exfoliation is still the benchmark for producing high-quality graphene due to its simplicity and effectiveness in yielding defect-free sheets [4].

2.2. Liquid-Phase Exfoliation

Liquid-phase exfoliation (LPE) is one of the most common methods. Graphite is dispersed in a solvent, followed by mechanical energy input through sonication or shear mixing. This would provide the needed conditions for layer separation. This methodology facilitates the generation of substantial amounts of graphene while it can remain a comparatively low density of defects [5]. The selection of solvent and the parameters governing exfoliation are critical factors that influence the quality and the yield of the graphene. For example, the incorporation of surfactant has the potential to improve the stability of graphene, thereby mitigating agglomeration and facilitating a greater concentration of exfoliated graphene [6].

2.3. Electrochemical Exfoliation

Chemical methods of exfoliation involve the oxidation of graphite to form graphite oxide, which is then reduced to yield graphene oxide.

This methodology facilitates the large-scale synthesis of graphene. However, it frequently leads to an increased number of defects and functional groups, which can negatively impact the electrical characteristics of the graphene [7]. Recent developments aimed at refining the oxidation and reduction processes to reduce defects [8]. Electrochemical exfoliation is regarded as an advantageous methodology owing to its capacity to generate high-quality graphene characterized by a reduced number of defects. This approach employs an electric field to introduce ions into graphite, thereby promoting the delamination of graphene layers. The procedure can be performed in a range of electrolytic solutions [9]. The conducted research illustrated that electrochemical exfoliation could produce graphene, characterized by a high level of electrical conductivity and stability. The graphene which is prepared by this method is good for application in energy storage and electronic applications [10].

2.4. Chemical Vapour Deposition (CVD)

CVD is another prominent method used for the preparation of high-quality graphene. Carbon-containing gases like methane are decomposed into high-temperature substrates of copper or nickel in this technique. The carbon atoms then rearrange to form a layer of graphene on the substrate surface. CVD is preferred for large-area, high-purity graphene films with the requisite thickness, which is necessary for the use of electronics. Nevertheless, such a method is more costly and complicated due to the requirement for the precise control of the processing conditions.

3. Applications of Graphene in 3D Printing

The distinctive properties of graphene make it an ideal material for elevating the performance of 3D printed products. As a result, using graphene in 3D printing make it possible to increase the ductility and the electrical conductivity. When using 3D printing technology to prepare graphene devices, new technologies are necessary, including DIW, FDM, and SLA. These technologies have been reported to have practical applications. Some practical examples produced by using these technologies are worthy of discussing.

3.1. Graphene-Based Inks

DIW is a multifunctional 3D printing technique, in which a material is extruded through a nozzle to create a structure layer by layer. Graphene-based inks are materials with dispersed particles of graphene in a solvent or polymer matrix. One of the pioneering methods for DIW uses poly (ionic liquid)-stabilized graphene nanoinks, which facilitate the 3D printing of graphene aerogels. This approach facilitates for the fabrication of structures that sustain their shape after deposition while exhibiting the necessary fluid characteristics during printing [1]. Viscous GO dispersion has been successfully used to print out geometries with high spatial resolution in applications such as microsized heaters [11]. Control over the viscosity and flow behaviour of these inks is particularly important to achieve the desired print quality and structural strength. Limitations still exists in the rheological ink properties which may affect the structural control at the microscale [12]. In order to prevent these issues, researchers have experimented using various printing environments. This method is proved to be effective in maintaining the integrity of the printed structures in subsequent necessary processing and etching. The resulting structures have high electrical conductivity, which makes them suitable for printing electronics, sensors, and energy storage devices. Besides, the mechanical properties of graphene are strong and flexible. This feature allows for its creation into the durable components that can endure the mechanical stress and deformation. DIW with graphene-based inks has been used to create supercapacitors, flexible circuits, and even biological scaffolds.

3.2. Graphene-Enhanced Filaments

Graphene nanoplatelets (GnPs) are one of the most common reinforcing materials in FDM processes. The composite, which is prepared by incorporation of GnPs into the thermoplastic polymer matrix, is proved to have mechanical properties. For instance, studies have shown that a synergistic interaction exist between the polyurethane and GnP which reinforces the tensile strength and elasticity on 3D printed composites [13]. This is significant because the effective dispersion of graphene in the polymer matrix will determine the overall performance of the printed parts. In this way, high-speed mechanical homogenization ensures homogeneous graphene distribution to maximize its reinforcement effects [14].

It was revealed by research that the addition of graphene can significantly enhance the thermal management of printed materials. For example, it was reported that graphene-filled thermoplastic polyurethane (TPU) composites depicted higher thermal conductivity and they were suitable in applications which require good heat dissipation performance. The filament preparation method is very critical. By using twin-screw extrusion together with melt blending, good dispersion of graphene can be achieved which can minimize voids in the filament.

In addition, the printing raster angle can affect the mechanical properties of FDM-printed parts. Studies revealed that this variation in the raster angle causes differences in tensile strength and flexural properties of parts [15]. The truth is that optimization of printing parameters is unavoidable to exploit graphene reinforcement fully in FDM.

Apart from mechanical and thermal improvements, graphene-filled filaments were being tried for their electrical conductivity. When graphene is added to polylactic acid (PLA), remarkable electrical conductivity can be achieved. It will be helpful in sensors and other electronic devices [16, 17]. It shows that even a small amount of graphene can enhance the electrical properties of the material significantly. Moreover, the utilization of graphene in FDM will contribute to sustainability within manufacturing. This is because it allows for more functions in the performance of the printed parts, thereby allowing the fabrication of lightweight and strong components. These attributes would potentially contribute to minimizing material usage and reducing manufacturing waste which is regarded as an objective of sustainable manufacturing practices [18, 19]. In other words, the adding of graphene in FDM filaments opens a promising route toward improvement of properties in 3D-printed materials. Further development concerning filament preparation techniques and increased understanding of graphene interactions with polymer matrices are continuous driving forces in this area. In turn, as the research develops, more and more possibilities of using graphene-enhanced FDM composites will surely be extended toward different applications, ranging from aerospace and automotive to electronics.

3.3. SLA-Printed Graphene-Reinforced Resins

SLA is a very high-precision 3D printing device, which uses a laser to install one layer of liquid resin at a time. By adding graphene into the resin, it is possible to get parts that have good mechanical performances and have good electrical conductivity.

For SLA, the main difficulty is the phenomenon of dispersing graphene within the resin. Graphene oxide (GO) is more efficient than pure graphene because it can be dispersed more easily in the resin. It can be converted to rGO after printing. The resin mixture must also be optimized to ensure that it retains its photo reactivity, allowing the laser to cure it properly.

SLA-printed parts with graphene reinforcement have better mechanical strength, stiffness, and thermal stability. The high degree of miniaturization and the fine-tuning of the shape of SLA permit the use of these parts for applications that require perfect accuracy in dimensions. These parts also can be electrically conductive so that they can be used in microelectronics, sensors, and other applications. SLA with graphene-reinforced resins is under development for the production of complex microstructures, such as biomedical devices. It opens the possibilities for miniaturized sensors, actuators, and other components.

4. Conclusion

The application of graphene in 3D printing developed rapidly in recent years. In the future, in-depth researches in this field will be focused on some issues that are need to be addressed urgently. The dispersion of graphene in 3D printing materials for all the current valid methods is largely limited. In addition, costly graphene production and the complexity in printing are also issues need to be solved. There should also be researches regarding methods for large-scale fabrication. Moreover, environmental impacts of graphene fabrication and disposal of graphene-enhanced 3D-printed parts would have to be addressed. This calls for the development of environmental-friendly manufacturing technologies.

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