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Muhammad Ali Kaleem

Department of Design and Manufacturing Engineering, National University of Sciences and Technology (NUST), Islamabad, Pakistan
Corresponding author. E-mail: alikaleem.pg@smme.edu.pk

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MANUFACTURING GRAPHENE BASED POLYMER MATRIX COMPOSITES (GPMCs) VIA 3D PRINTING (ADDITIVE MANUFACTURING): A REVIEW

The exponential increase in the potential applications of graphene has forced its inclusion in composites. Presently, composites containing graphene have been manufactured by many conventional processes. Since 3D printing (additive manufacturing) offers a wide range of advantages for manufacturing, researchers from the composite industry are now adopting novel techniques to manufacture graphene based composites via additive manufacturing. When selecting materials for composites, polymers stand out as the top choice for manufacturers because polymers require a low temperature to mold their shape and they are easy to handle when compared to ceramics and metals. Hence, substantial focus of the composite industry is now shifting towards manufacturing graphene based polymer matrix composites. In this regard, this paper provides a brief review of the 3D printing (additive manufacturing) processes which to date have been adopted to manufacture 'graphene based polymer matrix composites'. The promising physical properties of graphene based polymer matrix composites and the future prospects of functionalizing graphene in polymer based composites is also highlighted.

Keywords: **additive manufacturing (AM), graphene based polymer matrix composites (GPMCs), nanocomposites, fused deposition melting (FDM)**

INTRODUCTION

Graphene is called a wonder material due to its vast potential applications. Since its inception in 2004, graphene has become the focus of attention of researchers all around the globe. 'The Global and China Graphene Industry Report' highlighted that the graphene industry was worth 85 million USD in 2017. It was increased to 200 million USD in 2018 and is expected to exceed 1 billion USD in 2023 [1]. The more researchers became engaged in graphene study, the more significant properties of graphene emerged. Not only graphene alone but also GRMs (graphene related materials) exhibit outstanding physical properties. Therefore, graphene based composites have brought composite materials to a new level. Presently, graphene based ceramic, metal and polymer matrix composites have been fabricated successfully in various academic setups [2]. Table 1 presents an overview of the conventional methods used in manufacturing graphene based composites.

TABLE 1. **Conventional Methods for Fabricating Graphene Based Composites [2]**

Matrix	Techniques	Characteristics	Materials
Ceramic	Power processing	Ball milling or planetary ball milling	Alumina, silicon, nitride, zirconia and silica
	Sol-Gel processing	Creating a precursor	TiOC
	Colloidal processing	Producing a dispersion of graphene and ceramics to produce composites based on colloidal chemistry	Al_2O_3, Si_2N_3
Metal	Chemical synthesis	Hydrothermal preparation, reduction of GO and metal salt	Cu, Co, Ni and other metal materials
	Mechanical mixing	Physical force to mix graphene and metal	Mg, Al, Sn
	Electrodeposition	Using electric current to reduce dissolved metal cations and form a coherent metal coating on an electrode	Pure metal and alloy
	Self-assembly approach	Assembly fabricated with electrostatic attraction, covalent or non-covalent bonding	Al, Cu
Polymer	In-situ polymerization	Adding a suitable initiator to make a liquid monomer polymerize	PS, PMMA, PA6 and PVDF/ PMMA
	Solution compounding	Dispersed in a suitable covalent system, absorbing onto delaminated graphene sheets and creating a nanocomposite by evaporating solvent	PE-g-MA, PVA/graphene, PVC and PMMA/silica
	Melt compounding	High-shear mixing of graphene and molten thermoplastic polymer matrix	PP/graphene, HDPE/EG,PA6/EG, PLA/EG

Recently, a great deal of research work in fabricating graphene based composites has been done using additive manufacturing (3D printing) techniques. A brief summary of AM processes which can be employed to fabricate graphene reinforced composites is shown in Table 2 [2]. While keeping in mind the basic processes of AM and the physical capacity of polymers to mold their shape upon temperature manipulation, it is understandable that polymer matrix composites are the best choice for AM. Therefore, many experiments have been conducted to date to fabricate GPMCs in various academic setups. This study aims to give a brief review of the latest AM processes which have been employed so far to fabricate GPMCs. Moreover, it is highlighted that each fabricated GPMC exhibits a significant physical or electrical characteristic which may utilized for respectively specific applications in the industry.

TABLE 2. **AM processes for fabricating graphene based composites [2]**

Matrix	Powder bed fusion	Vat polymerization	Materials extrusion
GCMC	✓	×	✓
GMMC	✓	×	×
GPMC	✓	✓	✓

AM (3D PRINTING) TECHNIQUES FOR MANUFACTURING POLYMER MATRIX COMPOSITES

ASTM F42 is an international committee on AM (3D printing) technologies. The committee has categorized polymer composite manufacturing into seven different types [3]. Amongst these seven, four fundamental techniques are: powder bed fusion, material extrusion, vat photopolymerization and sheet lamination. A list of these techniques is shown in Figure 1.

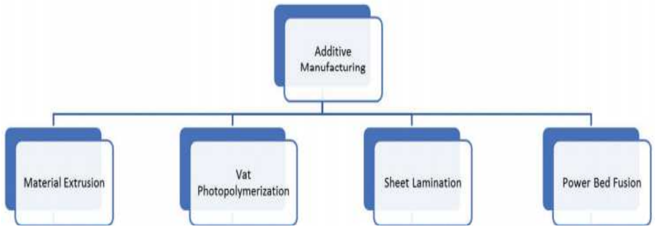

Fig. 1. Common AM techniques for manufacturing polymer matrix composites [3]

Powder bed fusion

In this technique, thermal energy is used to fuse selective regions of powdered materials [4]. If the used material is polymers, then the process is generally called selective laser sintering (SLS). Unlike SLM (selective laser melting) in which the whole powdered material is melted, SLS melts only selective surfaces of the powder particles, sintering the powdered particles to one another. Polymer resin can be added to the sintered material as a post processing step which helps make the composite stable. The process can be divided into four steps as highlighted in Figure 2.

Material extrusion

In this process the composite material is deposited in the form of a solid filament or formed paste [5]. The material is extruded using a nozzle. If the material is in melted form, then the process is called fused filament fabrication (FFF). On the other hand, if the material is in the form of a liquid paste, then it is called liquid deposition modelling [6]. In both techniques thin filaments of composite material are laid to form the layers of the composite. A general process of material extrusion through FFF is shown in Figure 3.

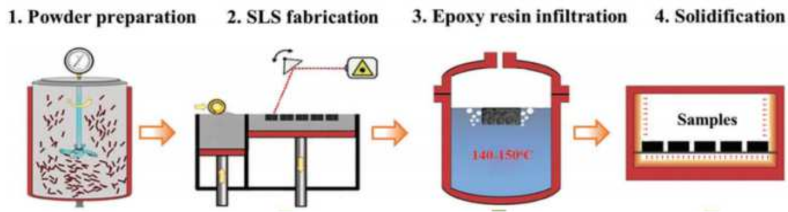

Fig. 2. Four steps of SLS technique (powder bed fusion) [4]

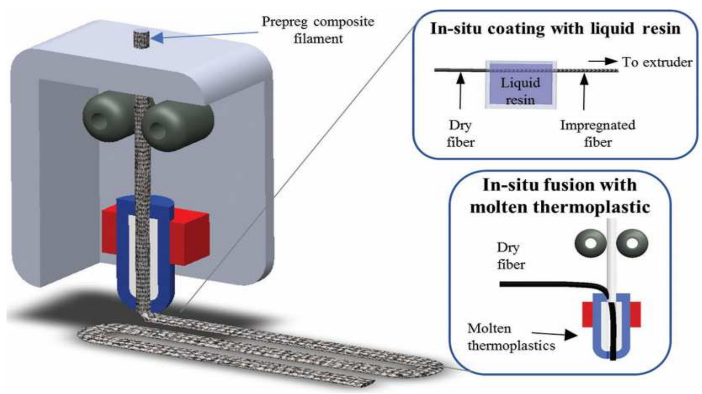

Fig. 3. Material extrusion technique [6]

Vat photopolymerization

In vat photopolymerization, UV light is used to cure photopolymer in a vat [7]. The most common practice of vat photopolymerization is called stereolithography (SLA). In this process the fibers are premixed with resin in a desired pattern [8]. The UV light cures the photopolymer on impact [9]. In SLA, a maximum of 60 vol.% fiber can be loaded in the resin [10]. The process is shown in Figure 4.

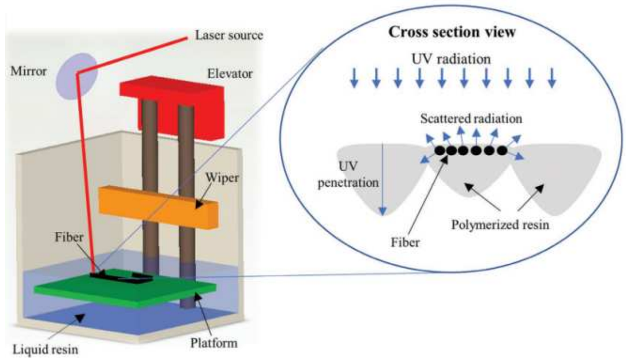

Fig. 4. Vat photo polymerization (stereolithography) [8]

Sheet lamination

This process involves bonding sheets to fabricate the required product [11]. Mostly a laser source is used to cut sheets of materials into the desired shapes. The shaped sheets are then stacked on one another and then bonded to each other by applying heat and pressure [12]. The process is shown in Figure 5.

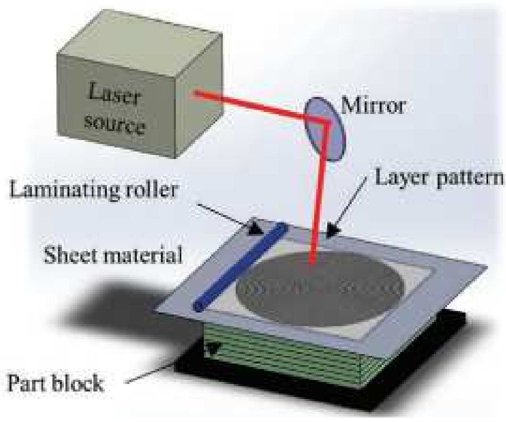

Fig. 5. Sheet lamination process [11]

CHALLENGES IN MANUFACTURING GRAPHENE POLYMER MATRIX COMPOSITES (GPMCs)

Polymers require a low temperature to mold their shape when compared to ceramics and metals [2]. Therefore, PLA [13], ABS [14], PVA [15] and epoxy [16] have been widely used in making polymer matrix composites. To fabricate GPMCs, nanofillers of graphene derivatives are added to polymers to enhance the mechanical and physical properties of the formed nanocomposites [17]. However, the following challenges are also observed in the fabrication of GPMCs via conventional methods:

a. Homogenous dispersion of graphene derivatives [2] in the polymer matrix.
b. The discovered dispersion techniques like ultrasonication [18], three roll milling [19, 20], high shear mixing [21], simple mechanical mixing [22], ball milling [23] and hot pressing [24] have some process deficiencies which are difficult to overcome in ambient conditions.
c. Phase separation between the polymer matrix and nanofillers [2].
d. Nozzle clogging due to the aggregation of graphene derivatives.

AM OF GRAPHENE POLYMER MATRIX COMPOSITES (GPMCs)

AM processes offer a better possibility of dispersing fibers due to the layer by layer deposition of the material. It is an additive technique in which material is added in a specifically required amount, thus minimizing waste and providing a near net surface finish. The following GPMCs have been fabricated using AM processes.

GPMCs using Thermoplastics

Thermoplastics can change their shape after melting and subsequent cooling. Examples of thermoplastic polymers include: polyamide, ABS [14], PLA [13], PVA [15], PMMA and PCL [2]. A review of the significant mechanical properties of graphene based thermoplastic polymer composites fabricated via AM is highlighted below.

PBT/Graphene Nanocomposites

Gnanasekaran used FDM (fused deposition modelling, a material extrusion process) to fabricate a graphene reinforced polybutylene terephthalate (PBT) matrix [25]. More than one print head was used in this process, which could fabricate more than one material while keeping the cost of manufacturing in check.

PVA/Graphene Nanocomposites

Shuai used the SLS technique to fabricate a 2.5 wt.% GO and PVA nanocomposite [26]. 150% improvement in tensile strength was observed when compared with pure PVA polymer. An increase of 60% in compressive strength was also observed.

PMMA/Graphene Nanocomposites

Mohan used 10 wt.% graphene in a polymethyl methacrylate (PMMA) solvent to produce a filament for the FDM technique [27]. The nanocomposite showed excellent electrical conductivity (electrical conductivity of 14.2 S cm^{-1}). The fabricated filament can be used in the semi-conductor industry.

PLG/Graphene Nanocomposites

A 3DP ink was developed by Jakus by adding PLG to 60 vol.% graphene [28]. The developed 3DG material had excellent electrical conductivity (800 S m^{-1}) with exceptional functional properties, which may have many applications in the semi-conductor industry. The processes are shown in Figure 6.

ricated nanocomposite had improved mechanical properties compared to pure PLA polymer.

PCL/Graphene Nanocomposites

Sayyar used the extrusion method to fabricate a PCL/graphene scaffold [36]. Young's modulus was increased by 140% and tensile strength was increased by 50% when compared to pure PCL polymer.

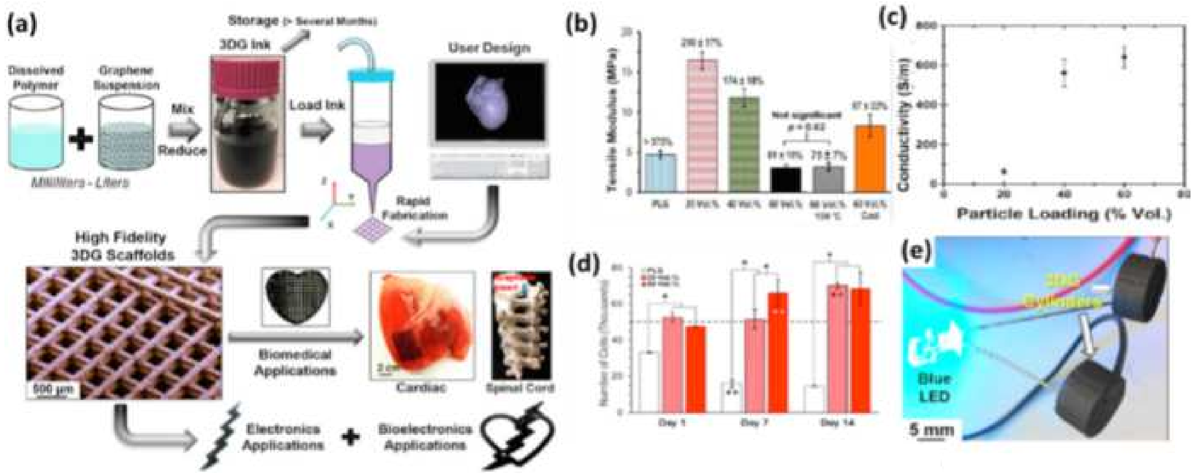

Fig. 6. (a-e): Processes involved in fabricating 3DP ink containing graphene, which may be used in material extrusion techniques [28]

ABS/Graphene Nanocomposites

FDM was used to fabricate an ABS+graphene nanocomposite [29]. The thermal and electrical conduction of the fabricated nanocomposite increased when compared to ABS alone [30]. It was observed that the tensile strength of the nanocomposite decreased considerably. The deficiency may be attributed to the inhomogeneous dispersion of graphene.

PVB/Graphene Nanocomposites

Huang developed a printable ink by combining GNP and polyvinyl butyral (PVB) [31]. The developed nanocomposite exhibited electrical anisotropic behavior.

Polyamide (PA)/Graphene Nanocomposites

An rGO (restricted graphene oxide) coated PA nanocomposite was developed by De Leon [32]. Some parts of modern electrostatic motors can be fabricated using the mentioned rGO coated PA nanocomposites. The nanocomposite was fabricated using the SLS technique.

PLA/Graphene Nanocomposites

Vernardou prepared a graphene reinforced PLA polymer nanocomposite by the FDM method [33]. The fabricated material showed excellent electrochemical behavior. Similarly, another graphene reinforced PLA polymer composite was fabricated by Foster [34]. The nanomaterial behaved like a superconductor and may have wide applications in battery manufacturing industries. Moreover, Chen worked on the same polymer and reinforced PLA with GO [35]. He observed that the fab-

GPMCs Using Thermosets

Thermosetting polymers upon taking their shape become highly stiff; however, they are generally found to be brittle. Graphene reinforcements can further enhance the strength and stiffness of thermosetting polymers but in most cases their brittleness remains the same [2]. Recently, AM techniques have emerged as outstanding methodologies for manufacturing thermosetting composites [4]. Researchers have fabricated the following graphene inclusive thermosetting polymers via AM.

Graphene Derivative Reinforced Photopolymer Resins

It has been observed that the thermo-mechanical properties of photopolymers can be increased by adding graphene derivatives but the weight percentage of graphene derivatives should be less than 5 wt.% [37]. The following properties of GO reinforced photopolymer resins have been researched in academic setups:

a. Korhonen developed a GO reinforced acrylic resin using the SLA technique [38]. He observed enhanced electrical conductivity in the developed composite. The photopolymer composite fabricated in a honeycomb pattern is shown in Figure 7.
b. Lin added 0.2 wt.% GO to a photopolymer and found a 60% increase in the tensile strength of the polymer [39].
c. Wang demonstrated that GO can make strong bonds with polymer matrices [37].
d. Zhou developed a methacrylate-polydiacrylate photopolymer reinforced GO composite using SLA. The composite displayed enhanced mechanical properties [40].

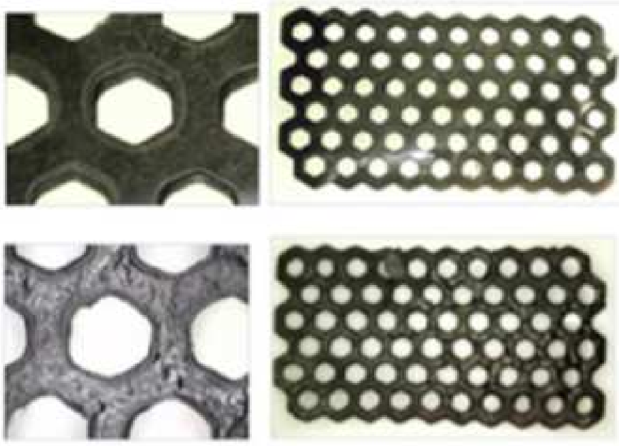

Fig. 7. GO-acrylic photopolymer composite in honeycomb pattern [38]

Epoxy/Graphene Nanocomposites

Compton developed an epoxy-graphene nanocomposite using DIW direct ink writing, a material extrusion process) [16]. The formed nanocomposite showed an almost 70% increase in stiffness. The material has an application in the packaging industry where electromagnetic shielding is required to protect sensitive electronic components.

THE WAY FORWARD - GRAPHENE BASED FUNCTIONALIZED COMPOSITES

It is understandable that the layer by layer fabrication method offers a greater possibility of aligning graphene nanofillers compared to conventional fabrication methods. Therefore, AM promises to enhance the mechanical strengths of graphene reinforced composites by imparting homogenous dispersion and aligning graphene derivatives. Researchers are now focusing on achieving greater efficacy by dispersing, aligning and controlling the graphene composition in the composites. Thus, the future of graphene based composites may generally be termed as graphene based functionally graded composites. The AM of graphene reinforced functionally graded materials is hence foreseeable as the focus of research in future manufacturing regimes. This idea of making GRM (graphene related materials) functionalized with other metals is not new. Udupa et al. [41] has already used a conventional mixing technique to manufacture CNT - aluminum functionally graded material as shown in Figure 8.

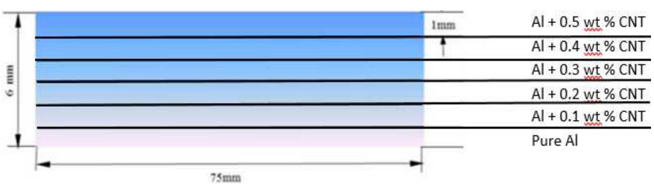

Fig. 8. Functionally graded composite (CNT + Al)

The hardness of the manufactured material was inspected for variation over a 6 mm length. The hardness of the fabricated functionally graded material varied from 26 HV (0.1 wt.% CNT) to 68 HV(0.5 wt.% CNT). Hence, this research provides manufacturers a way forward to functionalize graphene derivatives in polymer matrix composites to form functionally graded graphene polymer matrix composites (FG-GPMCs).

CONCLUSIONS

Having in mind the vast potentials of graphene, its inclusion in the future of the manufacturing industry is undeniable. AM is the future of manufacturing, therefore considerable focus has now shifted towards manufacturing graphene based composites via AM processes. Likewise, graphene based polymer matrix composites (GPMCs) possess a great potential for manufacturing compared to ceramics and metals because of the suitability of polymers for AM. This review paper has summarized the gist of research work related to manufacturing GPMCs, while the enhanced physical, mechanical and electrical properties of graphene based thermoplastics and thermoset composites are also highlighted. Each fabricated composite displays a significant property which may be exploited by material and manufacturing industries. This paper serves as a data bank for researchers in reviewing and channelizing the work done to date in the field of GPMCs. Moreover, it may also help to avoid any duplication of work that has already been carried out. The paper also highlights the possibility of functionalizing GPMCs to make functionally graded graphene based polymer matrix composites (FG-GPMCs).

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