Review Article

3D-printed stretchable conductive polymer composites with nano-carbon fillers for multifunctional applications
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Abstract: Carbon nanomaterials are widely used as substrate materials to prepare stretchable conductive composites due to their good stability, strong conductivity, and low price. In response to the demand for optimizing the performance of composite materials, various manufacturing methods for preparing carbon nanomaterial-reinforced stretchable conductive composite materials have emerged. Among them, 3D printing technology has the advantages of flexible processes and excellent product performance and has received widespread attention. This review focuses on the research progress of adding carbon nanomaterials as reinforcing phases to polymer materials using 3D printing technology. The application prospects of conductive polymer composites based on nanocarbon fillers in aerospace, energy storage, biomedicine, and other fields are prospected.

Keywords: carbon-based materials; 3D printing technology; polymer composites; structural design; electronic devices

1. Introduction

The stretchable conductive composite material prepared based on nano-carbon filler refers to a composite material that uses carbon material as a conductive filler. The key to stretchable conductive composites is the need to maintain the conductive network under large strains and recover its original properties after the strain is released. In general, flexible and elastic polymers have excellent stretch properties but poor electrical conductivity[1–4]. While carbon nanomaterials such as graphene, carbon nanotubes (CNT), and carbon black (CB) have high electrical conductivity[5], they have poor stretch properties[6,7]. Therefore, nano-conductive materials and stretchable polymers are usually mixed in a specific way to prepare stretchable conductive nanocomposites, which are applied to stretchable batteries, strain sensors, stretchable supercapacitors, and wearable medical device fields[8,9]. It is worth noting that, compared with metal conductive fillers, carbon materials have better stability and modification ability, a lighter weight, and a lower price, which makes it possible to achieve large-scale production to meet the growing demand for new electronic devices[10–18].

In recent years, 3D printing technology has developed very rapidly and has been widely used in many fields such as aerospace, biomedicine, and energy storage[19–26]. It is considered to be a promising new manufacturing molding technology[27]. 3D printing technology also provides new ideas for the preparation of polymer-based composite materials[28,29]. Combining 3D printing technology with the preparation of carbon nanomaterials/polymer-based composite materials can achieve rapid manufacturing of composite materials[30–32]. This provides a new path for the manufacture of products with complex structures. The addition of carbon nanomaterials makes 3D printing products have better mechanical properties, electrical properties, and functional characteristics, and it is also more convenient to prepare gradient functional products[33,34]. In
addition, the layer-by-layer manufacturing method of 3D printing inhibits the large-area agglomeration of carbon nanomaterials in the polymer matrix, which is more conducive to achieving uniform dispersion\cite{35}. As shown in Figure 1, the 3D-printed stretchable conductive polymer composites with nano-carbon fillers exhibit good mechanical and electrical properties, showing great application potential in the fields of electronics, aerospace, energy storage, and biomedicine. This review introduces the research on the formation of carbon nanomaterials/polymer matrix composites by 3D printing, briefly introduces the preparation methods of carbon nanomaterials/polymer matrix composites, and summarizes the 3D printing process and application fields.

Figure 1. A scheme of 3D-printed stretchable conductive polymer composites with nano-carbon fillers and their applications.

2. Classification of carbon-based polymer composites

Carbon materials are currently one of the most widely used materials due to their advantages such as low price, good stability, abundant raw material reserves, and good biocompatibility\cite{36}. It mainly includes graphite, carbon fiber, carbon black, graphene, graphyne, carbon nanotube, and fullerene (C$_{60}$). Graphite is the most common carbon material and is often used in corrosion-resistant materials, lubricating materials, refractory materials, and raw materials for preparing graphene oxide\cite{37}. Carbon fiber is a special fiber mainly composed of carbon elements\cite{38}. It has excellent mechanical strength and modulus along the fiber axis. Therefore, it is often used as a reinforcing material to combine with polymers, metals, or ceramics to prepare composite materials. C$_{60}$ is a new type of hollow molecule composed entirely of carbon. At present, it is mostly used as an electron transport layer in the field of organic solar cells, which can improve the photoelectric conversion efficiency of the cell\cite{39}. However, carbon black, graphene, and carbon nanotubes have smaller sizes and excellent electrical properties and belong to nanoscale conductive materials. Therefore, it is widely used in stretchable conductive nanocomposites.

2.1. Carbon black

As one of the most important carbon-based fillers, carbon black has been widely used in various industrial productions. This nanomaterial has a series of advantages, such as a high specific surface area, good chemical stability, high electrical and thermal conductivity, and low cost. Carbon black is mainly produced by the thermal decomposition or incomplete combustion of hydrocarbon compounds. The size, structure, and conductivity of carbon black particles are largely determined by the choice of raw material and method of manufacture. Carbon black particles have an amorphous and quasi-graphite structure, and the average particle
size of carbon black is 3–100 nm. It is worth noting that carbon black particles tend to agglomerate together to form aggregates, and these aggregates will form larger spatial network structure aggregates under the action of van der Waals force. Therefore, how to avoid the agglomeration of carbon black particles is the focus and difficulty of research. Recently, Bhagavatheswaran et al.\cite{40} successfully prepared composite materials by mixing carbon black and styrene-butadiene rubber, as shown in Figure 2(a–c). It is worth noting that the researchers prevented the agglomeration of carbon black by adding silica particles. The results showed that the composite had an electrical conductivity of 40 S m\(^{-1}\) and a maximum stretch of 200%, and its application in pressure sensors was explored. Niu et al.\cite{41} successfully prepared stretchable conductive composites using carbon black and polydimethylsiloxane, as shown in Figure 2(d–f). The research results show that the composite material has good electrical conductivity and mechanical stability, which can be used to assemble biological microchips. In addition, Song et al.\cite{42} used carbon black and carbon nanotubes mixed with polybutylene adipate/terephthalate (PBAT) to prepare composite materials, which were used as current collectors in aqueous lithium-ion batteries, as shown in Figure 2(g–i). The research results show that it can still work normally under 100% strain, and the electrical conductivity of the composite material can be significantly improved after adding carbon nanotubes.

Figure 2. (a) Development of a strong filler—filler network of the conducting carbon black particle. (b) Plot of electrical resistance for hybrid composites with different microsilica contents. (c) Resistance with strain\cite{40}. (d) Testing the circuit with LEDs to show the functionality of the bonded plate. (e) Quasi-static stretching and restoring at a rate of 1.5 mm min\(^{-1}\) for carbon black powder and PDMS (CPDMS). (f) Dynamic stretching characteristics of the CPDMS sample, peak-to-peak amplitude 1 mm, 50 Hz\cite{41}. (g) Steps for the fabrication of the carbon/polymer composite. (h) Fatigue test of the stretchable electrode containing the hybrid carbon/polymer composite under a strain of 200% that was repeated for 1000 cycles. The inset shows the tensile strength of the electrode as a function of the number of strain cycles, with the maximum value being 1000 cycles. (i) The relative discharge capacity of the stretchable aqueous rechargeable lithium-ion battery under various amounts of strain\cite{42}. 
2.2. Carbon nanotube

From the analysis of crystal structure, a carbon nanotube is a hollow cylindrical tubular structure formed by curling graphene sheets (hexagonal structure) according to a specific helical angle. There are two types of carbon nanotubes: (1) Single-walled carbon nanotubes (SWCNTs), which can be viewed as individual graphene sheets rolled into cylinders. (2) Multi-walled carbon nanotubes (MWCNTs), which can be viewed as stacks of multiple concentric layers of graphene. There are many methods for preparing carbon nanotubes, mainly including laser ablation, arc evaporation, chemical vapor deposition (CVD), etc. Carbon nanotubes are ideal materials for the preparation of composite materials due to their high modulus, high stiffness, high electrical conductivity, and low density. Recently, Shin et al. [43] prepared composites using MWCNTs obtained by chemical vapor deposition mixed with polyurethane. It is worth noting that almost no decrease in electrical conductivity of the composite is observed within a strain of 10%–20%, as shown in Figure 3(a,b). Sekitani et al. [44] prepared composite materials by mixing single-walled carbon nanotubes and fluorinated rubber, as shown in Figure 3(c–e). The as-prepared composites possess an electrical conductivity greater than 100 S cm\(^{-1}\) and stretchability exceeding 100%. A stretchable active-matrix display was successfully constructed based on this composite. Liu et al. [45] used reduced graphene oxide (rGO) and carbon nanotubes as conductive fillers and styrene-butadiene rubber as a polymer to prepare a composite material, as shown in Figure 3(f,g). The results of the study show that the electrical conductivity of the composite reaches 3.62 S cm\(^{-1}\) and can be stable under low tensile strain. More importantly, compared with carbon black conductive nanocomposites, their performance is significantly improved.

![Figure 3](image-url)

**Figure 3.** (a) Schematic diagram of the preparation method for the forest/polyurethane composite sheet. (b) Change in normalized resistance shown in the graph in going from the 10th to the 100th cycle as a function of the maximum applied strain. The first 10 cycles for each strain set were used to provide initial sample conditioning [43]. (c) Printed elastic conductors on a PDMS sheet. (d) Stretchability and conductivity as a function of SWCNT content. (e) A demonstration of a stretchable display that can be spread over arbitrary curved surfaces. The stretchable display is functional even when folded in two or crumpled, indicating excellent durability [44]. (f) Schematic illustration for preparation of rGO-CNT hybrid and styrene-butadiene rubber (SBR)/rGO-CNT composites. (g) Changes in electrical conductivity of SBR/GO-CNT and SBR/rGO-CNT composites under different strains [45].
2.3. Graphene

Graphene consists of a single layer of carbon atoms arranged in a two-dimensional honeycomb lattice, which can be deformed to obtain other carbon materials. Graphene has many excellent properties, such as a high specific surface area, high electrical conductivity and electron mobility, excellent thermal and chemical stability, and mechanical flexibility. In addition, graphene can obtain a variety of derivatives through the method of interface modification. For example, element-doped graphene is the basis for constructing self-supporting graphene composites, which endow the composites with excellent mechanical, electrical, and thermal properties. Recently, Chen et al. prepared graphene with a 3D structure by chemical vapor deposition, which was filled with polydimethylsiloxane to prepare a composite material, as shown in Figure 4(a–c). The composite material exhibits excellent electrical conductivity, making it useful as a stretchable conductor in various fields. Wang et al. prepared a stretchable graphene honeycomb composite structure using graphene foam and polydimethylsiloxane, as shown in Figure 4(d–g). The composite has a conductivity of 72 S m$^{-1}$. It is worth noting that a stretchable light-emitting display was successfully fabricated using this material as a circuit. In addition, Sun et al. prepared stretchable conductive fibers using graphene and polyurethane fibers, which can be used for strain sensors and stretchable conductors, as shown in Figure 4(h–k). However, the process of percolating 3D-structured graphene with polymers is usually complicated, which is not conducive to large-scale preparation.

Figure 4. (a) SEM image of graphene foam (GF). (b) A photograph of a bent GF/PDMS composite, showing its good flexibility. (c) Electrical conductivity of GFs and GF/PDMS composites as a function of the number of graphene layers. (d) Fabrication of GHCs and GHC sandwiches. (e) Graphene honeycomb (GHC) with $t$ ranging from 0.25 to 1 mm. (f) Schematic of a stretchable light-emitting display constructed using a GHC sandwich. (g) Photographs of the stretchable light-emitting display. (h) Schematic diagram of preparing the worm-shaped filaments. (i) Conductivity-strain curves. (j) Potential applications of strain-insensitive stretchy electronics. (k) Filament woven into fabric to conduct signals under wrist joint movements.
In recent years, researchers have improved the performance of stretchable conductive composites by adding carbon nanomaterials. However, there are still some issues that need to be addressed. The most crucial aspect is how to achieve uniform dispersion of carbon nanomaterials in polymer matrices. It is worth noting that the dispersion degree of carbon nanomaterials in polymers greatly affects the comprehensive performance of composite materials. Therefore, in order to fully utilize the excellent mechanical and electrical properties of carbon nanomaterials, it is necessary to develop new mechanisms, methods, and technologies to achieve uniform dispersion of carbon nanomaterials in polymers.

3. 3D printing process of carbon-based polymer composites

With the continuous development and improvement of 3D printing technology, various new 3D printing technologies emerge endlessly. In recent years, the preparation of carbon-based polymer composites by 3D printing technology has developed rapidly. At present, the 3D printing processes applicable to carbon-based polymer composites mainly include fused deposition modeling, inkjet printing, stereo lithography apparatus, and selective laser sintering. Different printing processes have corresponding advantages and disadvantages, which need to be selected comprehensively according to the characteristics of printing materials, process characteristics, and product uses.

3.1. Fused deposition modeling

Fused deposition modeling (FDM) is mainly suitable for the 3D printing of thermoplastic polymers and is currently the most commonly used 3D printing method. Specifically, this method requires the polymer to be prepared into a standard-diameter wire, and then the wire is transported to the nozzle by a stepping motor, heated, and melted for extrusion. Finally, the layers are stacked and bonded according to the desired shape on the substrate, and the desired molding is obtained after cooling and solidification. The fused deposition molding of the carbon-based polymer-based composite material can be performed by making the carbon-based polymer composite material prepared by melt mixing, solution mixing, etc. into a 3D printing wire. The addition of nano-carbon materials can not only enhance the mechanical properties of composite materials but also endow composite materials with excellent electrical, thermal, friction, and wear properties.

It is worth noting that acrylonitrile-butadiene-styrene copolymers (ABS) and polylactic acid (PLA) are the most commonly used polymers for FDM. Recently, Wei et al. prepared rGO/ABS and rGO/PLA composites by mixing polymers with graphene oxide (GO) by solution mixing and adding hydrazine hydrate for reduction, which were used for fused deposition molding after wire drawing, as shown in Figure 5(a–d). The research results show that the maximum amount of GO added can reach 5.6% (mass fraction, the same as below), and the electrical conductivity can reach $1.05 \times 10^{-3}$ S m$^{-1}$. The addition of carbon nanomaterials increases the glass transition temperature (Tg) of the polymer, so the 3D printing temperature needs to be increased appropriately compared with pure resin. Zhu et al. mixed 6% graphene nanosheets (GNPs) with nylon 12 (PA12) for fused deposition molding, as shown in Figure 5(e–j). The results show that the GNPs will be oriented during extrusion from the nozzle, which increases the thermal conductivity and elastic modulus of the composite along the direction of orientation by 51.4% and 7%, respectively, compared with compression molding. Fused deposition modeling not only has the advantages of a wide range of printing materials, easy operation, low equipment cost, easy operation, and fast printing speed, but it can also print different types of materials at the same time with multiple nozzles. Therefore, it is one of the most promising printing methods for industrial applications. However, this method also has shortcomings, including insufficient printing accuracy, blocked nozzles, uneven thermal stress, and low interlayer strength.
Figure 5. (a) Schematic illustration of fused deposition modeling in the 3D printing process. Inset is the graphene-based filament winding on a roller. The filament was deposited through a nozzle onto a heated building plate, whose temperature was set at 80 °C. (b) A typical 3D-printed model using 3.8 wt% G-ABS composite filament, scale bar: 1 cm. (c) Representative Raman spectra in prepared GO, rGO, ABS and G-ABS samples. (d) Electrical conductivity ($\sigma_c$) of G-ABS composites as a function of graphene loading. Inset is the four-probe schematic setup used in the $\sigma_c$ measurement. (e) Orientation of GNPs in the PA12 matrix during the FDM process. (f) XRD spectra of PA12 and PA12/GNPs nanocomposites with 2, 4, 6, 8, and 10 wt% GNPs compression-molded samples (10 mm × 10 mm × 4 mm). (g) TG (top) and DTG (bottom) curves of pure PA12 and PA12/GNPs nanocomposites with 2, 4, 6, 8, and 10 wt% GNPs. (h) TEM micrographs of PA12/6 wt% GNPs nanocomposites. (i) The MFI values, thermal conductivity ($\lambda$). (j) Tensile test results of pure PA12 and PA12/GNPs nanocomposites and their CM specimens, respectively.

3.2. Inkjet printing

Inkjet printing (Inkjet) has developed from a technology that was originally only used for text and picture printing to a rapid prototyping method. As an additive manufacturing technology, it has been widely used in electronic circuits, flexible devices, etc. In the commonly used piezoelectric inkjet printing process, the printing material is first dissolved or dispersed in a solvent to form “ink”. Then, according to the printing needs, the voltage is applied to the piezoelectric ceramic sheet to deform it, and the ink in the cavity is squeezed to be ejected drop by drop and accumulated layer by layer on the substrate to form the shape to be printed. Finally, the solvent setting is removed by heat treatment, freeze drying, and other post-processing methods. The high carrier mobility of carbon nanomaterials makes them very suitable for restoring the electrical conductivity of nanoelectronic devices, making flexible materials with excellent electrical conductivity and dielectric properties. Inkjet printing is a commonly used, convenient, and efficient preparation method. The addition of polymers can stabilize the ink, prevent carbon nanomaterials from precipitation and stratification, and also adjust the viscosity of the ink to make it in a range that is convenient for printing. It is worth noting that in order to adjust the viscosity of the ink, researchers found that polyvinylpyrrolidone (PVP) and ethyl cellulose (EC) could be added to the ink as stabilizers and viscosity regulators.

Recently, Lim et al. dissolved GO and polyvinyl alcohol (PVA) in water, mixed them, and then reduced them with hydrazine hydrate to prepare rGO/PVA ink, as shown in Figure 6(a–g). Finally, the electrodes of
organic field effect transistors were prepared by inkjet printing. The results show that the field-effect mobility of the rGO/PVA electrode printed by inkjet printing has been greatly improved compared with the traditional Au and PEDOT:PSS electrodes. García-Tuñon et al.\(^5\) grafted polymers on graphene oxide sheets to prepare pH-responsive surfactants. The research results show that the viscosity of the obtained ink can be adjusted by changing the pH, and finally, the continuous printing of three-dimensional molded objects can be realized through a 100 μm nozzle, as shown in Figure 6(h–j). Inkjet printing has the advantages of simple equipment, easy operation, and low cost. Therefore, it is very suitable for preparing micro-nano devices and electronic circuits. However, this method also has some defects, including the low strength of the prepared device, some defects after post-processing, and the device falling off the substrate.

Figure 6. (a) Inkjet-printed rGO/PVA electrodes. (b) XRD patterns of graphite, graphite oxide (GO), GO/PVA, and rGO/PVA composite. The insert shows photographs of well-dispersed GO/PVA (left) and rGO/PVA (right) suspensions. (c) rGO/PVA composite stably dispersed in a mixed solvent with DMF and water for three months (left) and rGO precipitated from the same medium (right). (d) Schematic illustration of the device structure. (Insert: Optical microscope image of inkjet-printed rGO-PVA composite electrodes, scale bar: 300 μm). (e) Photographs of rGO/PVA films with 5 and 20 layers fabricated by inkjet printing. (f) UV-vis spectra of rGO/PVA films with 5 and 20 layers fabricated by inkjet printing. Transmittance was measured at \(\lambda = 550\) nm. (g) Output characteristics of organic field-effect transistors based on different electrodes: Au (left), rGO/PVA (center), and PEDOT:PSS (right).\(^5\) (h) Sketch of the directed assembly mechanism. (i) Histogram showing a comparison of the viscosity and storage modulus (\(G'\)) of a GO suspension (1.75 wt%) without additives (left), a GO-branched copolymer surfactant (BCS) suspension with low graphene oxide concentration (1.75 wt%, LC, middle), and a highly concentrated GO/BCS ink (2.5 wt% GO, HC, right). The viscosity at a shear rate of 10 s\(^{-1}\) increases from 10 to nearly 50 Pa s. (j) Kinetics of self-assembly followed by a time sweep at a fixed strain (1%) and frequency (0.1 Hz).\(^5\)
3.3. Stereo lithography apparatus

Stereo lithography apparatus (SLA) is a molding method that uses photosensitive resin as the printing material. Specifically, the laser beam scans the surface of the liquid photosensitive resin according to the designed route to solidify a specific area of the photosensitive resin, thereby forming a cross-section of the model. Subsequently, the lifting table is moved down a small distance to solidify a new layer of section until a complete part is formed. Photosensitive resins generally include polymer monomers or prepolymer, photoinitiators, and other components\(^{59}\). The more commonly used types of photosensitive resins include unsaturated polyesters, epoxy acrylates, polyurethane acrylates, etc. When stereo lithography apparatus is used to form carbon nanomaterials/polymer-based composites, carbon nanomaterials are generally dissolved in a solvent and then added to a photosensitive resin or directly added to the resin for mixing, followed by photocuring\(^{60}\).

In recent years, Zhou et al.\(^{61}\) added GO to a phosphate buffered saline solution (PBS) of polyethylene glycol diacrylate (PEGDA) and methacrylated gelatin (GelMA) and then added a photoinitiator to form a photosensitive resin, as shown in Figure 7. Among them, GelMA and PEGDA are two commonly used photocurable biomaterials. It is worth noting that the addition of GO can promote the adhesion and growth of biological stem cells and induce stem cell differentiation. The research results show that the photosensitive resin can be used for photocuring to prepare biological scaffolds and promote the differentiation of human bone marrow mesenchymal stem cells to form cartilage tissue. In addition, there are some reports of adding carbon nanomaterials directly to commercial photosensitive resins for printing to improve their mechanical properties. And the polymer can also be removed by high-temperature post-treatment, followed by thermal reduction of GO to prepare a three-dimensional rGO structure. Stereo lithography apparatus has become one of the mainstream technologies in the current 3D printing market due to its high printing accuracy, excellent surface quality, and ability to form complex structures. However, the current bottleneck of this technology is mainly the high cost and the toxicity of the residual photoinitiator and uncured photosensitive resin. In addition, it is necessary to prevent carbon nanomaterials from settling out of the photosensitive resin during printing, resulting in an uneven distribution of carbon nanomaterials in the composite.

![Figure 7](image-url)

**Figure 7.** (a) Schematic diagram of a 3D-printed GO scaffold for promoting chondrogenic differentiation of human bone marrow mesenchymal stem cells (hMSCs). (b) and (c) SEM micrographs of GelMA-PEGDA scaffolds without GO and with GO (0.1 mg/mL). (d) Mesenchymal stem cell (MSC) proliferation on hydrogels with different compositions for 5 d. (e) MSC proliferation on GelMA-PEGDA scaffolds incorporated with different concentrations of GO for 5 d. (f) Adsorption profiles of bovine serum albumin (BSA) on GelMA-PEGDA scaffolds with and without GO (0.1 mg/mL) at different time points. (g) Collagen II. (h) Glycosaminoglycan (GAG) and (i) total collagen secretion of MSCs after chondrogenic differentiation on GelMA-PEGDA scaffolds without and with GO over three weeks\(^{61}\).
3.4. Selective laser sintering

Selective laser sintering (SLS) is a 3D printing method suitable for powder molding, mainly used for printing metal and ceramic powders, and can also be used for thermoplastic polymer powders\cite{62}. During the printing process, the barrel first rises a certain distance, and the powder spreading roller moves to spread a layer of powder material on the working platform\cite{63,64}. Then, the laser beam is emitted by the laser, and the powder in the selected area is fused and sintered according to the cross-sectional profile under computer control so that the layers are increased. Gaikwad et al.\cite{65} first melted and mixed carbon nanomaterials and nylon 11 (PA11) with a twin-screw extruder to granulate them, and then pulverized them at low temperature to form powders for selective laser sintering, as shown in Figure 8(c–e). The research results show that the addition of carbon nanomaterials not only improves the flexural modulus, Young’s modulus, and thermal stability of nylon 11, but also makes nylon 11 exhibit electrical conductivity, which can be used for static dissipation. Compared with other molding methods, the composite material obtained by selective laser sintering has better conductivity, and the amount of carbon nanomaterial required for electrostatic charge dissipation is small. In addition, carbon nanomaterials can enhance thermal conductivity, making the laser melting and sintering processes easier.

In addition, Shuai et al.\cite{66} first synthesized GO/PVA composite powder by the solution mixing method and then prepared biological scaffolds by selective laser sintering, as shown in Figure 8(a,b,f–h). Due to the strong hydrogen bond interaction between GO and PVA, the two are closely combined. The research results showed that the compressive strength, Young’s modulus, and tensile strength of the scaffold added with 2.5% GO/PVA were increased by 60%, 152%, and 69%, respectively, compared with the pure resin. The advantage of selective laser sintering is that there is a wide range of moldable materials, different types of powder materials can be mixed and sintered to form composite materials, no support structure is required, and the material utilization rate is high. At present, there are relatively few reports on the formation of carbon nanomaterials/polymer matrix composites by selective laser sintering. The reported research work mainly focuses on nylon-based materials, and future research can be extended to more types of composite materials.

In recent years, researchers have made significant progress in the preparation of carbon-based polymer composites through 3D printing. However, there are still some issues that need to be addressed. On the one hand, problems such as clogging nozzles and insufficient bonding force are likely to occur during the 3D printing process, which greatly affects the performance of carbon-based polymer composites. On the other hand, there are currently relatively limited types of polymers that can be used for 3D printing, which requires further expansion.

![Figure 8](image-url)
flexure modulus of PA11 and PA11/ nanographene platelet (NGP) nanocomposites. (e) Izod impact strengths[65]. (f) Compressive properties of GO-0.5, GO-1.5, GO-2.5, GO-3.5, and GO-4.5 stress-strain curves. (g) Compressive properties of GO-0, GO-0.5, GO-1.5, GO-2.5, GO-3.5, and GO-4.5 compressive strengths, and Young’s modulus. (h) Schematic representation of the PVA chains. (a), the GO sheets (b), and the GO sheet dispersion in the PVA matrix with various GO loadings (c) 0.5 wt%, (d) 2.5 wt%, and (e) 4.5 wt%[66].

4. Application of carbon-based polymer composites

4.1. Electronic field

As we all know, carbon nanomaterials have a large specific surface area and high carrier mobility, which makes them have great application potential in the field of electronics[67–71]. After compounding with a suitable polymer matrix, carbon nanomaterials can be used to prepare flexible electronic devices[72,73]. The application of 3D printing can conveniently and quickly form complex and exquisite electronic devices and can quickly integrate electronic components[74,75]. It is worth noting that one of the hot spots of graphene research in the field of electronics is the use of graphene in field-effect transistors (FETs). The higher carrier mobility of graphene makes the transistor made of graphene have a faster response speed, which can significantly increase the cut-off frequency of the transistor. In addition, due to the small thickness of graphene, the characteristic size of transistors can be reduced, and Moore’s law can be further continued[76], which is an important research direction in the field of integrated circuits in the future.

The 3D printing method used to prepare graphene FETs is mainly inkjet printing. Recently, Xiang et al.[77] deposited graphene on a Kapton flexible substrate by inkjet printing and used ionic liquid/copolymer gel as the gate dielectric layer to prepare FETs, as shown in Figure 9(a–c). Light-emitting diodes are optoelectronic devices that play an important role in communication, display, lighting, and other fields. Graphene has good transparent and conductive properties and can be used as an electrode material for light-emitting diodes. The researchers prepared graphene in a hydrogel state for inkjet printing[78]. In addition, electronic circuits prepared by 3D printing methods such as inkjet printing and fused deposition modeling can be used to connect various electronic devices, as shown in Figure 9(d–h).

![Figure 9](image-url)

Figure 9. (a) General fabrication procedures and signal output of graphene FET biosensor. (b) Graphene FET biosensor. (c) Epifluorescence staining with a fluorescently-tagged secondary antibody identifies areas of printed graphene successfully coated with...
a target-specific Norovirus capture antibody. Dotted white circles indicate the approximate area of primary antibody deposition\cite{77}. (d) Typical tapping mode AFM images (top) and the corresponding height cross-sectional profiles (bottom) of GO sheets in GO ink (0.1 mg/mL) and few-layered graphene oxide (FGO) sheets in FGO ink (0.1 mg/mL) deposited on mica substrate. (e) patterns printed on polyimide using FGO ink with a concentration of 5 mg/mL. (f) TGA curves of graphene oxide materials used in GO ink and FGO ink at a heating rate of 10 °C in an N\textsubscript{2} atmosphere. (g) CV measurements of the H\textsubscript{2}O\textsubscript{2} sensors. The three-electrode method to detect H\textsubscript{2}O\textsubscript{2} in 0.05 mol/L phosphate buffer solution (PBS) (pH 7.4) and 0.1 mol/L KCl. Shown in the inset is a bare-printed graphene electrode. (h) Cyclic voltammograms of GO (black) and Fe-c-GO adducts (the Fe and reduced graphene oxide hybrid adducts) (red) modified printed graphene electrodes in 5 mmol/L H\textsubscript{2}O\textsubscript{2}, 0.05 mol/L PBS (pH 7.4), and 0.1 mol/L KCl saturated with Ar at a 50 mV/s scan rate\cite{78}.

4.2. Aerospace field

In the field of aerospace, carbon-based polymer composites also show considerable application potential\cite{79}. Due to the excellent mechanical properties of carbon nanomaterials, adding them to polymer matrices may significantly improve mechanical properties such as tensile strength and elastic modulus\cite{80–82}. It is well known that bismaleimide, epoxy resin, and phenolic resin are commonly used resin matrices in the aerospace field\cite{83}. It is worth noting that after adding a small amount of carbon nanotubes, graphene oxide, or modified graphene to these resins, the mechanical properties are significantly improved. In addition to being used to improve mechanical properties, carbon nanomaterials can also be used as functional reinforcements. Carbon nanomaterials can form a conductive network in the polymer matrix to improve the conductivity of composite materials and can be used for static dissipative materials and lightning strike protection for aircraft\cite{84}. The addition of carbon nanomaterials to the polymer matrix can also enhance the thermal stability of the composite material, increase the carbon residue rate, and be used for ablation of heat-resistant materials, as shown in Figure 10(a–c). In addition, carbon-based polymer composites can be used for microwave absorption and electromagnetic shielding and are used in the field of aircraft stealth\cite{85}. Due to the excellent performance of carbon nanomaterials in terms of mechanical properties and functionality, carbon-based polymer composites can also be used as structural/functional integrated materials in future aircraft, as shown in Figure 10(d–g). The characteristics of 3D printing for rapid and precise forming of complex components, combined with the excellent functional properties of carbon-based polymer composites, will have great application potential in non-load-bearing parts of aircraft.

Figure 10. (a) Schematic representation of the fabrication process of polyurethane graphene nanocomposite films. (b) Variation in electrical conductivity with rGO loading in the thermoplastic polyurethanes (TPU) matrix. The inset shows the log(\sigma) vs. log(\rho − \rho_0)
plot. (c) Variation in the EMI shielding effectiveness with frequency for polyurethane/graphene (PUG) nanocomposites\cite{84}. (d) Schematic representation of the preparation of phenolic resin-based composite sheets containing different wt% of rGO, γ-Fe$_2$O$_3$ nanoparticles and carbon fibers in the organic medium. Variation of flexural strength and electrical conductivity as a function of wt% of (e) phenol resin, (f) carbon fiber, and (g) γ-Fe$_2$O$_3$ in rGO sheets\cite{85}.

4.3. Energy storage field

Based on the excellent electrical conductivity and low thermal expansion coefficient of carbon nanomaterials, researchers have mixed carbon nanomaterials with anode or cathode active materials to form 3D lithium-ion batteries or used thermally responsive inks to mix carbon nanomaterials and Cu powder to form supercapacitors. In-depth research on the potential application of high conductivity and low resistance properties of composite materials added with carbon nanomaterials in lithium-ion batteries and supercapacitors. Recently, Fu et al.\cite{86} put water-based ink into a syringe and extruded filaments to print them layer by layer to prepare electrodes, as shown in Figure 11(b–g). Then, the solidified electrode was freeze-dried and thermally annealed to obtain rGO. Lithium iron phosphate (LFP)/rGO and lithium titanium oxide (LTO)/rGO electrodes were prepared by the above 3D printing methods, respectively. Through the study of their electrochemical performance, it was found that when rGO was added, the two Li-ion batteries almost reached the theoretical capacity of LFP and LTO at a specific current density of 10 mA/g. Among them, the initial charge-discharge capacity of LTO/rGO is slightly higher than the theoretical capacity of LTO. After the 10th and 20th cycles of cycling, the charge-discharge curves of the two electrodes are close to stable, and LTO/rGO maintains low voltage hysteresis.

Rocha et al.\cite{87} used chemically modified graphene, a water-based thermal response formula mixed with Cu powder, and Pluronic F127 (thermal response ink) as reaction raw materials to prepare rGO/Cu electrodes with interlocking interfaces through 3D printing and heat treatment methods, as shown in Figure 11(h–j). The results showed that the electrode generated a Nyquist diagram with the same shape as an ideal supercapacitor, demonstrating good contact between the rGO electrode and the copper electrode. In addition, Shen et al.\cite{88} mixed sublimated sulfur and GO solution to concentrate to prepare ink and formed a sulfur copolymer-graphene structure (3DP-pSG) with periodic micro-lattices by extrusion 3D printing, as shown in Figure 11(a). It is found that the structure has a high reversible capacity of 812.8 mA h g$^{-1}$ and good cycle performance. Recently, researchers have found\cite{89,90} that when the content of carbon nanomaterials in polymer composites is higher, carbon nanomaterials can form more compact microstructures and well-connected conductive networks with lower electrical resistance. The above research work provides some guidance for the application of 3D-printed carbon-based polymer composites in the field of energy storage.
Figure 11. (a) Schematic demonstration of 3D printing sulfur copolymer-graphene (3DP-pSG) architectures. Aqueous GO suspension was homogeneously mixed with sublimed sulfur and concentrated into gel-like ink; then, 1,3-diisopropenylbenzene (DIB) was added to the ink and mixed homogeneously. As-prepared ink was placed into a 3 mL syringe and printed into layer-by-layer architectures. Afterward, the printed architectures were freeze-dried. Finally, sulfur copolymer was synthesized on the graphene nanowalls by thermal treatment at 200 °C [88]. (b) Charge and discharge profiles of the LFP/rGO half-cell at a specific current of 10 mA g⁻¹. (c) Rate profiles of the LFP/rGO half-cell at various specific currents. (d) Charge and discharge profiles of the LTO/rGO half-cell at a specific current of 10 mA g⁻¹. (e) Rate profiles of the LTO/rGO half-cell at various specific currents. (f) Cycling stability of the 3D-printed full cell. The inset is a digital image of the 3D-printed full cell consisting of LFP/rGO, LTO/rGO, and polymer electrolyte. (g) Charge and discharge profiles of the 3D-printed full cell [86]. (h) SEM images at the reduced chemically modified graphene (rCMG)/Cu interface. (i) Typical Nyquist plot of a carbon–carbon supercapacitor. It includes the high- to low-frequency behavior of a supercapacitor with the equivalent circuits (Rₛ is the high-frequency resistance, Rᵢ is the resistance of the active material/current collector interface, Cᵢ is the interface capacitance with the dispersion parameter αᵢ, R(ω) is a part of the supercapacitor resistance depending on the frequency, and C(ω) is the supercapacitor cell capacitance) and (j) Nyquist plots recorded from 100 kHz to 10 mHz for the three-electrode (blue) and symmetric (black) systems in EMI-TFSI electrolyte, with their corresponding magnification of high and mid-frequency response [87].

4.4. Biomedical field

Many researchers use 3D printing technology to make biocompatible polymer materials and carbon nanomaterials into hydrogels, 3D scaffolds, and catheters [91–93]. Then, through in vitro experiments to simulate its impact on bone tissue, nerve tissue, and cell proliferation, it was found that low-content carbon nanomaterials are non-toxic to biological cells [94–96]. Similarly, carbon nanomaterials have good biocompatibility, which can not only enhance the stiffness of biomaterials but also promote cell proliferation [97,98]. This provides great prospects for research in tissue engineering and biomedicine [99].

The development of 3D printing to manufacture hydrogel structures has made it possible to mass-produce engineered cartilage tissues. Recently, Wang et al. [100] used NaOH solution to treat 3D-printed poly(ε-caprolactone) (PCL) scaffolds with low concentrations of graphene, as shown in Figure 12(b). The results of the study showed that the scaffolds treated with NaOH were more biocompatible with cells. Cheng et al. [101] connected a 3D bioprinted microinjection system with a biopolymer reservoir, using chondrocytes to seed
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GO/chitosan hydrogels, as shown in Figure 12(c,d). The results of the study showed that, compared with pure hydrogel, the 3D-printed GO/hydrogel tissue had thicker new cartilage after transplantation into cartilage tissue. In addition, Chen et al.\cite{102} dissolved thermoplastic polyurethane (TPU) and graphene oxide (GO) in dimethylformamide (DMF) and polyactic acid (PLA) in dichloromethane (DCM), respectively, as shown in Figure 12(a,g–j). Then, the mixture is precipitated and dried using an extruder to make a composite filament, which can be used directly in an FDM printer. The results of the study showed that the mechanical properties and thermal stability of the composites added with GO were significantly improved, and the scaffolds showed good biocompatibility with NIH\textsubscript{3}T\textsubscript{3} cells. Sayyar et al.\cite{103} successfully prepared polytrimethylene carbonate (PTMC)/carbon nanomaterial composites by extrusion deposition 3D printing method, as shown in Figure 12(e,f). Through the comparison experiment before and after the addition of carbon nanomaterials, it was found that there was no significant difference in the DNA content of cells on the two scaffolds. This shows that the addition of carbon nanomaterials has no effect on the number of cells. Therefore, carbon-based polymer composites have important application prospects in the field of biomedical materials, especially in the development of new conductive scaffolds for tissue engineering.

Figure 12. (a) TPU/PLA/GO nanocomposites filament preparation and FDM printing process\cite{102}, (b) Top surface and cross-section scanning electron microscope images of neat PCL and 0.78 wt\% pristine graphene scaffolds treated and untreated with NaOH\cite{100}, (c) Toluidine staining of hydrogel + BMP7 + GO-np transplanted in cartilage of rat knees. (d) Toluidine staining of hydrogel + BMP7 + transplanted in cartilage of rat knees. In the region of interest, the neogenetic cartilage of the hydrogel + BMP7 was thinner than hydrogel + BMP7 + GO-np (graphene oxide nanoparticles) (yellow arrow), and no neogenetic chondrocytes were observed in the hydrogel + BMP7 group (red arrow)\cite{101}, (e) Effect of electrical stimulation (ES) on mesenchymal stem cell (MSC) numbers relative to unstimulated controls. Results are shown as a fold difference relative to the unstimulated control after five days of ES. (f) Cell number measured at two time points (donor 2)\cite{103}, (g) Differential scanning calorimetry (DSC) curves of samples at different GO loadings. (h) S compression testing curves of samples of different GO loadings. (i) L compression testing curves of samples of different GO loadings. (j) Compression modulus of L and S compression testing of samples of different GO loadings\cite{102}.

5. Conclusions and perspectives

Carbon-based polymer matrix composites and 3D printing are two research directions that have developed rapidly in recent years. Combining the two and taking advantage of their respective advantages can provide an effective solution for the complex structural molding of carbon-based polymer composites. Therefore, stretchable conductive nanocomposites prepared using carbon-based fillers provide a new research direction for next-generation electronic devices. However, the research and application of stretchable conductive polymer composites based on nanocarbon fillers are still in their infancy and still face many problems and challenges. It mainly includes the following three aspects: (i) In the existing composite methods, the dispersion of carbon nanomaterials in the polymer carrier is poor, which results in the inability to fully utilize the excellent
mechanical and electrical properties of carbon nanomaterials; (ii) Problems such as nozzle clogging and insufficient bonding force are prone to occur during the 3D printing process, which greatly affects the performance of carbon-based polymer composite materials; (iii) The types of polymers currently available for 3D printing are relatively limited, which requires further expansion.

Future research on stretchable conductive polymer composites based on nanocarbon fillers will mainly focus on the following aspects: (i) Choose a suitable mixing method and use certain chemical additives to improve the dispersion of conductive fillers in the polymer. (ii) A variety of carbon nanomaterials are used together to construct a stable and efficient conductive network. (iii) Carbon nanomaterials have strong modification ability and can be modified according to specific applications. (iv) Miniaturization and large-scale fabrication of stretchable electronic devices can be achieved by developing novel printing techniques. Through the summary of the existing research, it is believed that the stretchable conductive polymer composites prepared based on nano-carbon fillers can be used in many fields, such as stretchable electronic devices, which promotes the progress of related research fields.

Author contributions

CZ and RL contributed equally. CZ, RL, and RM proposed the topic of the work. HL, LW, YW, and RW were responsible for image beautification. BF, ZW, ZS, and RW revised the literature and provided the content. Correspondence should be addressed to RM. All authors have read and agreed to the published version of the manuscript.

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Conflict of interest

The authors declare no conflict of interest.

References


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