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Effective Approaches for 3D printing on Grapheme based Nanocomposites

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Abstract

3D printing is also used to manufacture cutting edge nano-composite material, for example, high quality bulk graphene reinforced MMC's (metal matrix composite). MMC has become the object of favour in aerospace and national defence and it is irreplaceable. The mechanical property of most MMCs is dictated by their reinforcement fillers and Graphene has been considered as one of the most promising reinforcement fillers for metal matrix composites due to its mechanical roboustness. Numerous works of graphene reinforced MMCs have been reported ,which demonstrates that graphene indeed improves the mechanical ,thermal as well as electrical properties of composites. Here in different graphene content Gr-Al composites were prepared by laser 3D printing process. In this work it was found that maximum hardness was achieved when graphene content is wt. 2.5%. Unfortunately, further increasing graphene content would cause reducing of hardness. The mixture of graphene and aluminium powders was prepared by ball milling, and then sintered by the selective laser printing (3D printing technique) to fabricate bulk Gr-Al composites. The surface and cross – sectional SEM images, XRD patterns, and Raman spectroscopy verified not only the survival but also the distribution of graphene in Gr- Al composites. Vickers hardness results indicated that 2.5 wt.% graphene content samples have the best performance i.e. the maximum Vickers hardness. With grapheme sheets reinforcement, the composites Vickers hardness increases by nearly 75.3% compared with laser 3D printing pure aluminium. Nano-indentation was further use to determine the nano mechanical properties of the laser 3D printing composites .It was observed that under the same load pure Al samples had deeper penetration depth into the samples surface ,and 2.5wt%Gr- Alsamples had much less penetration depths on the contrast .This result was consistent with Vickers hardness value .These results indicate that graphene is a promising reinforcement material for aluminium matrix and laser based 3D printing technology can be used to prepare bulk Gr-Al composites.

Keywords Graphene, Nanocomposite, Laser Sintering, 3D printing.

INTRODUCTION

Additive manufacturing (AM) technique could provide a relatively simple and scalable method for advanced manufacturing of graphene-based electrodes for both supercapacitors as well as electrodes for other devices such as sensors and batteries. However, it remains challenging to produce the thick, high loading graphene-based electrodes required to achieve a high practical energy density in full devices. Herein, we introduce a powder-bed AM technique for the fabrication of crack-free, mm-thick graphene-based electrodes, with high surface area that can be printed in complex shapes. The raw powder used in this technique is thermally reduced graphene oxide (TRGO), prepared by rapid thermal expansion of graphene oxide. TRGO powder has an extremely low bulk density immediately after the rapid thermal expansion process and is too fluffy/lightweight to be used directly in the AM process. To densify this material and enhance the flowability required for the AM process, the powder was mixed with acetone and evaporative dried. A layer-by-layer fabrication process is conducted to build the 3D structure. There are two pistons, namely the feed bed and build bed, with adjustable heights in the chamber of the machine. The raw powder is first added to the feed bed with an even top layer of powder to provide the material required for the fabrication of the disks. Next, using a micro motion controller, the piston is translated upward according to the pre-adjusted layer thickness (for this study 100 mm) raising one layer of powder on top of the whole substrate. Then, a rotating roller moves pushing the exposed layer of powder forward to cover the build bed. The print head is subsequently directed to the top of the build bed to inject an aqueous-based binder .The print head strategically drops binder into the powder, to join powder particles. Layers of material are often then bonded to form an object. Finally the printed electrode was obtained which was a 3D printed disk. After the AM process, the free-standing disks were immediately assembled into supercapacitors. The electrodes, developed through AM, displayed a more porous microstructure compared to electrodes that were mechanically pressed to form powders. This leads to an interconnected pore structure which facilitated ion transport which improved conductivity (1).

In some cases, in order to improve the performance of the electrodes, the 3D-printed disks were impregnated with 150 mL of palladium nanoparticle dispersion at different concentrations like 1%(TRGO1),3%(TRGO3)and 9%(TRGO9). These nanoparticles are expected to bridge between adjacent powder agglomerates to reduce the contact resistance and improve electronic conduction capable of increasing the gravimetric and areal capacitance. Raising the concentration of palladium nanoparticles from 0% to 9% in TRGO to TRGO9 results in increased current density as well as making the CVs more rectangular. The rectangular shape of CV tells us that the capacitor is ideal. This change in shape of

CV is associated with the lower resistance in the electrodes. In comparison, the capacitive performance of TRGO9 electrodes is superior to their TRGO counterparts, which could be attributed to the reduced contact resistance affected by the palladium nanoparticles. This effect is more pronounced at higher scan rates such as 200 or 500 mV/s compares the specific capacitance and areal capacitance of all disks produced. The specific capacitance of the neat TRGO electrodes at 5 mV /s is 160 F/g, whereas palladium decorated electrodes (TRGO9) show a capacitance of more than 265 F/g. Although the capacitance drops at higher scan rates, a four-fold increase is observed at the scan rate of 200 mV/s between TRGO (9 F/g) and TRGO9 (34 F/g) electrodes. The areal capacitance obtained from TRGO9 electrodes is above 700 mF/cm^2 at 5 mV/s, which exceeds most of the reported values for graphene-based electrodes, which are typically of the thin film variety. Thus we can say graphene enhanced 3D printing and electrodes printed using this technique demonstrated high areal and gravimetric capacitance.

LITERATURE SURVEY

We construct graphene-based 3D structure by introducing direct ink writing method. Direct ink printing method, as an extrusion-based 3D printing technology, can be used to prepare desired 3D periodic structures. Direct ink writing has great freedom in material selection. Similarly, direct writing method provides high reliability for producing micro pattern with lightweight design. 3D printing technology has obvious advantages in material preparation, which can form a variety of geometric shapes based on the increase of structural complexity. The cellular network in the printed structure and ultra-light of graphene together determine the lightweight and high strength of graphene-based structure, which expect the graphene-based structure with excellent properties of graphene and gradually lightweight can be obtained by 3D printing technology. To prepare lightweight materials first we have to prepare graphene-based ink (homogeneous graphene dispersion). From the experiments it is seen that graphene sheets undergo severe agglomeration into spherical state .So dispersing graphene in organic solvents can simply open the agglomeration, but the difficulty of remove the dispersion medium clearly affect the properties of graphene in a certain extent, resulting in the application of graphene be limited. Graphene and ECG (ethylene glycol butyl ether) was added to ethanol .Then this solution was ultrasonicated to obtain graphene dispersion .Ethanol as low boiling point solvent ensures that the properties of graphene are not affected and the printed graphene-based structures can be achieved quickly. As soon as the graphene dispersion is obtained, the mixed solution of dibutyl phthalate and polyvinyl butyral is added as thickening agents to ensure the good adhesion between layers in the three- dimensional structure. Since the dispersion medium is gradually evaporated, the graphene dispersion turns into the slurry-like 3D printing ink. In order to push the ink flow out of the nozzle smoothly during the printing process and maintain the structure stable when forming on the substrate, the apparent viscosity of the inks should be studied .Apparent viscosity decreases with increase in shear force. The inks are subjected to a certain shear force when extruded from nozzle, which is negatively related to the diameter of the nozzle. When the inks are extruded, the small diameter of nozzle corresponds to a large shear force, and the corresponding apparent viscosity ensures the inks can smoothly extruded from the nozzle. Follow by forming on the substrate, the 3D printing ink exhibits large apparent viscosity in the absence of shear force, and the three-dimensional structure of the print molding remains stable.

3D printing technology can prepares a micro-size 3D structure precisely, and the structure has a large amount of macro-porous, which greatly reduces the weight of material while ensuring structural stability. As the graphene content increases, the apparent density of the 3D structure decreases while the uniformity of the graphene dispersion increases, which result in the printed graphene-based structure which are lightweight, flexible, providing the possibility of preparing high-strength and lightweight materials. The higher the graphene content of the 3D printing inks, the higher the stability of conductivity of the printed graphene-based structure. Therefore 3D printing graphene-based structure is a new method for obtaining structurally stable and lightweight with high-strength materials (2).

Additive manufacturing (AM) is a technology of building objects layer-by-layer based on computer aided design (CAD). This technology attracts strong interest from both industry and academic for the challenging possibility to build objects with complex shapes and minimal use of harmful chemicals at a reasonable speed. The most frequently used thermoplastic polymers are acrylonitrile–butadiene–styrene (ABS) and polylactic acid (PLA), but also polycaprolactone (PCL) and polycarbonate (PC) have been considered. One of the main limitations of this AM technique is related to the limited mechanical properties of the 3D printed parts. Development of composite materials could be a way to improve the mechanical properties of components produced by FDM. Adding nanomaterial such as carbon nanotubes, nanowires, and nanoparticles to matrices such as polymers, metals, and ceramics via AM has the potential to improve the performances of the resulting components.

Recently, graphene nanoplatelets (xGnP) are under investigation as potential reinforcing fillers for polymer based nanocomposites. Graphene nanoplatelets are ultrathin particles consisting of short stacks of graphene sheets. This kind of nano-filler has been used as multifunctional reinforcement, because it possesses 2D graphene stacked structure resulting in superior mechanical, electrical and thermal properties. Therefore, for thermoplastic nanocomposite filled with xGnP dramatic enhancements of Mechanical properties and thermal stabilities were reported.

QUASI-STATIC TENSILE TESTS

In general, it can be noted how the presence of graphene nanoplatelets promotes a remarkable increase of the elastic modulus of the ABS matrix, but slightly decreases its ultimate tensile strength.

DYNAMIC MECHANICAL RESPONSE AND COEFFICIENT OF THERMAL EXPANSION

Due to the xGnP addition in the ABS matrix, the storage modulus of CM, extrudate and FDM parts increases of about 30–50% with respect to the neat ABS below the Tg. The effect of xGnP nano-filler is manifestly more evident above Tg.

CREEP STABILITY

It is evident that the addition of graphene nanoplatelets can promote the reduction of creep compliance for each investigated process and build orientation. The role of nano-filler is to restrict the polymeric chain mobility, thus promoting a better creep stability.

Graphene nanoplatelets were successfully melt compounded in an ABS matrix by using a completely solvent-free process, and then extruded in filaments suitable for fused deposition modelling. Due to the processing constraints, the filler content was optimized at 4 wt%. The thermo-mechanical properties of neat ABS and its nanocomposites have been compared on samples obtained through various processing routes such as compression moulding, extrusion and fused-deposition modelling. In all cases, the presence of graphene nanoplatelets improved the tensile modulus of ABS. This positive effect was also verified along several different orientations in FDM samples. Concurrently, the presence of xGnP causes a slight reduction of ultimate tensile stress and strain at break for horizontal and vertical 3D built specimens and a more severe effect along perpendicular direction. Moreover, xGnP was also proven to reduce the coefficient of thermal dilation of 3D printed parts and to improve their stability under long lasting loads. In fact, the creep compliance significantly reduced by addition of the nano-filler. For FDM-printed parts the graphene nanoplatelets resulted to play the best reinforcement effect for horizontal and vertical orientation and to be less effective for perpendicularly printed specimens (3).

Preparation of inks with proper rheology performance is the key for extrusion-based 3D printing. In this work, extrusion-based 3D printing graphene oxide (GO)/geopolymer (GOGP) nanocomposite was reported for the first time. The addition of GO in a geopolymeric aqueous mixture (aluminosilicate and alkaline-source particles) dramatically changes its rheology properties, and enable the 3D printing that cannot be realized solely by geopolymer. Electrical conductivity was achieved after annealing, which is among the highest conductive ceramic nanocomposites. We expect that the rheology modification mechanism proposed in this study will facilitate the 3D printing of diverse materials, as well as the understanding of the interaction between GO and hydrophilic particles (4).

The addition of GO can dramatically change the rheological properties of geopolymer precursor, and enable the 3D printing of the ink based on GO/geopolymer (GOGP) mixture that cannot be realized by pure geopolymer. The GO nanosheets anchor themselves in geopolymer and encapsulate individual geopolymer grains to resist being pullout and at the same time, form a continuous 3D network throughout the whole nanocomposites (5).

It was found that the addition of GO can dramatically change the rheology of geopolymer precursors, and enable the 3D printing of geopolymer, which indicates a strong GO-HGPP interaction. This can be explained by the assumption that a thick layer of water film is formed in the confined space between GO and ASOP, which contribute greatly to the complex modulus of the mixture. The obtained geopolymer/GO nanocomposites exhibited good mechanical performance. It has also been shown that the HGPPs are encapsulated within films consists of GO layers, and after thermal reduction, the continuous GO films were converted to highly electrical conductive network, which can be used as the thermal source by joule heating. The unique properties of GO as it has been shown in this study will further expand the range of applications where GO can be used. In particular, this strategy makes it possible to explore the employment of GO as rheology property modifier by encapsulation, and enable 3D printing materials that were un-printable previously, and thus offer the opportunity to create new 3D printing materials(6)

3d-Printed Graphene -Al2O3 Composites with Complex Mesoscale Architecture Composites of rGO and AL2O3 were prepared by 3D printing technique and thermal reduction process. For which stable GO were prepared by Hummer's method from graphite powder. GO-AL2O3 structure were fabricated and thermally reduced in N2 atmosphere and the rGO sheet is evaluated in ceramic matrix by SEM, Raman spectroscopy and XRD analysis (7).

Graphene has unique features such as electrical, thermal, mechanical, and optical properties so we can make composites and enhance these properties AL2O3 has excellent properties including compression strength, hardness, wear resistance, chemical stability and so on at high temperature. GO in AL2O3 can improve some mechanical properties such as fracture toughness, bending strength, hardness and electrical conductivity (8).

3D printing is based on layer by layer deposition of ink through a syringe nozzle in design made by CAD. Advantages of this method is highly quality structure with complex architecture, high resolution and the ability to control the composition of the inks. High concentrated ceramics inks must have pseudo plastic and viscoelastic behavior to flow through nozzle and then retaining the cylindrical shape (9). For preparing graphene reinforced AL2O3 matrices with complex mesoscale architecture by using a 3D printing strategy. It developed and investigated the performance of highly-concentrated GO-AL2O3 inks with different GO concentration using the colloidal processing route. GO-AL2O3 composites were produced by the 3D printing technique and sintered under a reductive atmosphere at 1600C formation of reduced graphene oxide (rGO) (10).

SUMMARY

To fabricate the complex 3D structure a multilayer structure with square pores and periodicity in the X-Y plane and Z axis direction. Photographs of structure printed using 5wt% GO-AL2O3 ink. The printed 3D structure exhibit a high degree of uniformity and crack free surface. The sample was then sintered at 1600C in N2 atmosphere to carry out the reduction of the GO sheets and to get an rGO-Al2O3 composite with high mechanical stability. This temperature was selected as the best for sintering of our AL2O3 power and is also good for thermal annealing reduction of GO to rGO. Significant differences in the size of the sintered sample with regard to the initial patterned geometry. The sample exhibit a linear shrinkage of about 20% in all direction. This is mainly due to the sintering process as well as to the removal of polymeric additives, residual water and oxygenated functional groups during thermal treatment also significant weight loss in the composites. Sample exhibited a change in color after thermal treatment from yellowish color to clear grey. The change in color due to formation of rGO in composite. Optical images showed that these sintered composites had an interconnected network at meso scale level with well defined pores. SEM images showed the presence of rGO seeds in AL2O3 matrix. Finally the reduction of oxygen functional groups in the rGo-AL2O3 composite was confirmed using XRD and Raman analysis. This works provides an important step towards scalable fabrication of graphene-ceramic composite with complex meso scale architecture. It opens new avenues for their potential using application as capacitors, Aerospace components, electronics, sensors and catalyst support.

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REFERENCES

[1] Azhari, A., Marzbanrad, E., Yilman, D., Toyserkani, E. and Pope, M.A., 2017. Binder-jet powder-bed additive manufacturing (3D printing) of thick graphene-based electrodes. Carbon, 119, pp.257-266.

[2] You, X., Yang, J., Feng, Q., Huang, K., Zhou, H., Hu, J. and Dong, S., 2018. Three- Dimensional Graphene-Based Materials by Direct Ink Writing Method for Lightweight Application. International Journal of Lightweight Materials and Manufacture.

[3] Dul, S., Fambri, L. and Pegoretti, A., 2016. Fused deposition modelling with ABS– graphene nanocomposites. Composites Part A: Applied Science and Manufacturing, 85, pp.181-191.

[4] Zhong, J., Zhou, G.X., He, P.G., Yang, Z.H. and Jia, D.C., 2017. 3D printing strong and conductive geo-polymer nanocomposite structures modified by graphene oxide. Carbon, 117, pp.421-426.

[5] Tubío, C.R., Rama, A., Gómez, M., del Río, F., Guitián, F. and Gil, A., 2018. 3D-printed graphene-Al2O3 composites with complex mesoscale architecture. Ceramics International, 44(5), pp.5760-5767.

[6] Dul S, Fambri L, Pegoretti A. Fused deposition modelling with ABS–graphene nanocomposites. Composites Part A: Applied Science and Manufacturing. 2016 Jun 1;85:181-91.

[7] Tubío, C.R., Rama, A., Gómez, M., del Río, F., Guitián, F. and Gil, A., 2018. 3D-printed graphene-Al2O3 composites with complex mesoscale architecture. Ceramics International, 44(5), pp.5760-5767.

[8] Chou, S.L., Wang, J.Z., Choucair, M., Liu, H.K., Stride, J.A. and Dou, S.X., 2010. Enhanced reversible lithium storage in a nanosize silicon/graphene composite. Electrochemistry Communications, 12(2), pp.303-306.

[9] Chou, S.L., Wang, J.Z., Choucair, M., Liu, H.K., Stride, J.A. and Dou, S.X., 2010. Enhanced reversible lithium storage in a nanosize silicon/graphene composite. Electrochemistry Communications, 12(2), pp.303-306.

[10] Li, B. and Cao, H., 2011. ZnO@ graphene composite with enhanced performance for the removal of dye from water. Journal of materials chemistry, 21(10), pp.3346-3349.