SPE Plastics Research Online
10.2417/spepro.006953

Integrating nanoparticles into 3D-printed structures

Jenniffer Bustillos, Daniela Montero, Pranjal Nautiyal, Archana Loganathan, Benjamin Boesl, and Arvind Agarwal

Understanding the processing–structure–property relationship of 3D-printed composites reinforced with 2D nanomaterials enables the development of scaffold structures with enhanced performance.

In recent years, 3D printing has attracted attention as a fast and reliable manufacturing route for developing the complex geometries often required for patient-specific implants and scaffolds.[1] However, the functionality of 3D-printed structures is often hindered by the limited variety of commercially available starting feedstock materials. Fortunately, the introduction of nanoparticles—i.e., graphene, boron nitride nanoplatelets (BNNPs), and carbon nanotubes—to the 3D-printing feedstock has been found to provide composite materials with enhanced mechanical, electrical, and thermal properties. For instance, the uniform dispersion of graphene in polymer matrices has been proven to result in electrically conductive composites with superior mechanical properties.[2] Similarly, the addition of BNNP to polymeric matrices has been shown to improve the compressive strength of biocompatible scaffold structures.[3,4]

Among the available 3D-printing methods, fused deposition modeling (FDM) and stereolithography (SLA) have gained attention due to their facile procedures and commercial availability. The potential of graphene and its derivatives for use as a nanofiller in thermoplastic filament (i.e., that is used in FDM) has been explored for a number of applications, such as printed flexible circuits, and thermal and mechanical-reinforced composites.[1,5,6] Likewise, the development of composites for the SLA printing process has included nanoparticles with different morphologies—e.g., 0D silicon dioxide, 1D attapulgite, and 2D organic montmorillonite—added to the UV curable resin as feedstock material.[7,8] Despite the success of these preliminary studies, the influence of nanoparticle additives on the printing and curing processes, as well as the resulting properties of the composites, is not well understood. Furthermore, the addition of 2D nanoparticles to the 3D-printing processes will necessitate modifications in the processing parameters that depend on the intrinsic properties of the filler used.

In our work, we have therefore investigated the influence of nanoparticles on composite structures fabricated using 3D-printing techniques.

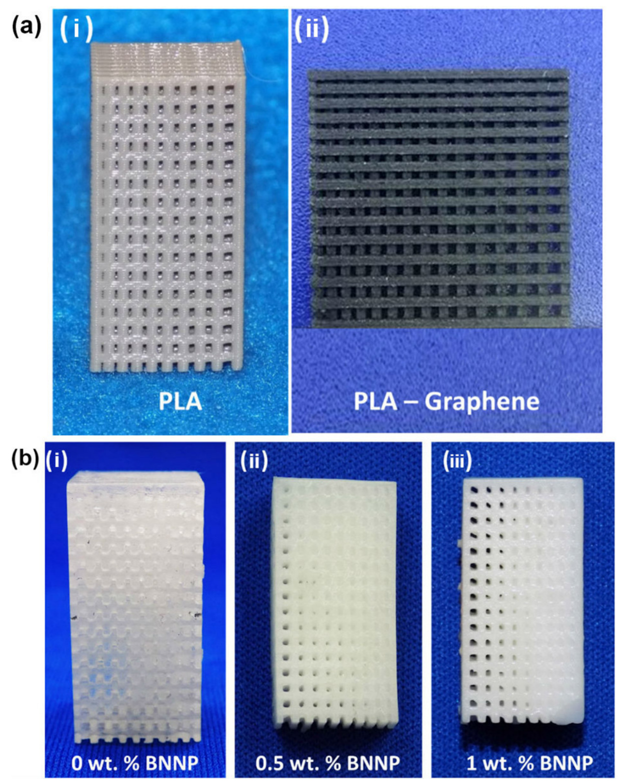

Figure 1. *(a) Macroscopic images of scaffold structures 3D-printed by fused-deposition modeling, with dimensions of $20 \times 20 \times 3mm^3$ and a graded pore size ($400 - 850\mu m$), comprised of (i) poly(lactic) acid (PLA) and (ii) PLA/graphene. (b) Macroscopic images of scaffold structures 3D-printed by stereolithography (SLA), with dimensions of $12.7 \times 12.7 \times 25.4mm^3$ and a graded pore size ($400 - 850\mu m$), comprised of (i) a pure photosensitive polymer, and the photosensitive polymer with (ii) 0.5wt% and (iii) 1wt% boron nitride nanoplatelets (BNNPs).*

Specifically, we used FDM and SLA to fabricate polymer-based nanocomposites with functional fillers (graphene and BNNPs, respectively). We then probed the behavior of these samples under mechanical

Continued on next page

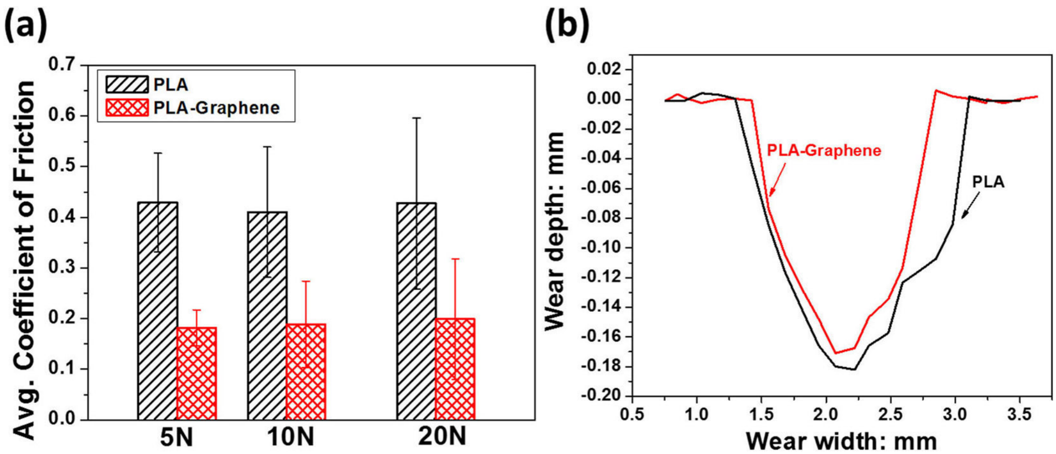

Figure 2. *(a) Average coefficient of friction of FDM-printed PLA and PLA/graphene composites during ball-on-disk tribological tests. (b) Cross-sectional depth profiles of worn tracks in the PLA and PLA/graphene composites at a normal load of 20N.*[9]

stress to determine whether such techniques are suitable for the desired application (i.e., the development of patient-specific implants and scaffolds). We used commercially available poly(lactic) acid (PLA) and PLA/graphene filaments in the extrusion of dense scaffold structures with a graded porosity, as shown in Figure 1(a).[9] We also investigated the influence of adding 2D-layered BNNPs to a photosensitive polymer (PSP) resin when printed via the SLA printing process: see Figure 1(b).

The layer-by-layer curing process of SLA printing enables the manufacture of structures with a higher layer resolution (∼0.02mm) compared with FDM (∼0.1mm). The prime challenges associated with adding nanoparticles to the UV-curable resin include a change (due to agglomeration) in the viscosity and the refractive index of the resin. These factors will govern the curing process and the properties of the resulting composite. Furthermore, commercially available SLA printers emit UV-rays with a wavelength of 405nm. Because BNNPs are characterized by a low transmittance within the UV-region, the chance of experiencing incomplete curing is therefore enhanced in composites with higher BNNP content (i.e., 1wt% or greater).[10]

In the fabrication of PLA/graphene samples via FDM, we found that the samples exhibited a higher cooling rate during their extrusion.[11] We propose that this higher cooling rate occurs as a result of graphene's high thermal conduction (2000–4000W/mK). Consequently, we observed (through tribological studies) that the 3D-printed composites exhibited a decrease in crystallinity (by ∼8%) as compared with neat PLA. Furthermore, we found that the lower crystallinity in PLA/graphene acted as a lubricant, thus promoting the dissociation of graphene sheets.

We then investigated the response of the FDM-printed PLA/graphene composites to frictional forces, with the aim of demonstrating the potential of 3D printing as a novel manufacturing technique for load-bearing structures. We also studied the viscoelastic behavior (creep) of the samples.[9] We thus found that the PLA/graphene composite exhibited a reduced coefficient of friction (by ∼21%) compared with neat PLA: see Figure 2(a). Additionally, the composites exhibited an enhanced wear resistance (of around 14%), due to lower wear depth, at loads of 20N: see Figure 2(b). Finally, we measured a higher strain-rate-sensitivity index in the PLA/graphene composites (0.27) as compared to neat PLA (0.19), indicating that the composites had superior resistance to creep-induced deformations.[9]

In summary, we have demonstrated the potential of 3D-printing processes (FDM and SLA) for the development of nanocomposites with good mechanical and structural properties. We integrated 2D nanomaterials—graphene (via FDM) and BNNPs (via SLA)—into polymers (PLA and a PSP, respectively) and then 3D-printed scaffold samples. In the case of the 3D-printed BNNP/PSP samples, we found that a higher layer resolution was achieved (∼0.02mm) compared to the PLA/graphene samples. However, the optical properties of the BNNP/PSP composites had a high dependence on the BNNP agglomeration at higher volume fractions. In the PLA/graphene composites, we observed a reduced coefficient of friction and an enhanced wear resistance compared with neat PLA. The processing challenges inherent to the FDM method include the influence of graphene's high thermal conductivity on the extrusion behavior and the resulting properties of the composite. In the next stage of our investigations, we will evaluate the tribological behavior of PLA/graphene and PSP/BNNP 3D-printed nanocomposites in simulated body fluids. We also intend to work toward the development of other advanced nanocomposite systems via 3D printing.

Continued on next page

Author Information

Jenniffer Bustillos, Daniela Montero, Pranjal Nautiyal, Archana Loganathan, Benjamin Boesl, and Arvind Agarwal
Department of Mechanical and Materials Engineering
Florida International University (FIU)
Miami, FL

Jenniffer Bustillos is an undergraduate researcher. She is pursuing research in nanocomposites and advanced materials processing, including 3D printing.

Daniela Montero obtained her BS in mechanical engineering from FIU, where her research focused on 3D-printed nancomposites.

Pranjal Nautiyal is a PhD student in materials engineering. His research focuses on nanomaterials, including graphene and boron nitride, and in situ nanomechanics.

Archana Loganathan is a PhD student in materials engineering. Her research interests are in boron nitride and other 2D nanomaterials.

Benjamin Boesl is an assistant professor. His research interests are focused on advanced materials and in situ nanomechanics.

Arvind Agarwal is a professor. His current research interests include surface engineering, materials processing, nanoindentation, nanotribology, and carbon-nanotube-, BNNT-, and graphene-reinforced composites and coatings.

References

1. X. Wei, D. Li, W. Jiang, Z. Gu, X. Wang, Z. Zhang, and Z. Sun, *3D printable graphene composite*, **Sci. Rep. 5**, pp. 1–7, 2015. doi:10.1038/srep11181
2. G. Mittal, V. Dhand, K. Y. Rhee, S.-J. Park, and W. R. Lee, *A review on carbon nanotubes and graphene as fillers in reinforced polymer nanocomposites*, **Ind. Eng. Chem. Res. 21**, pp. 11–25, 2015. doi:10.1016/j.jiec.2014.03.022
3. B. Farshid, G. Lalwani, M. S. Mohammadi, J. Simonsen, and B. Sitharaman, *Boron nitride nanotubes and nanoplatelets as reinforcing agents of polymeric matrices for bone tissue engineering*, **J. Biomed. Mater. Res. Part B Appl. Biomater. 105**, pp. 406–419, 2015. doi:10.1002/jbm.b.33565
4. M. S. R. N. Kiran, K. Raidongia, U. Ramamurty, and C. N. R. Rao, *Improved mechanical properties of polymer nanocomposites incorporating graphene-like BN: dependence on the number of BN layers*, **Scripta Mater. 64**, pp. 592–595, 2011. doi:10.1016/j.scriptamat.2010.12.007
5. D. Zhang, B. Chi, B. Li, Z. Gao, Y. Du, J. Guo, and J. Wei, *Fabrication of highly conductive graphene flexible circuits by 3D printing*, **Synth. Metals 217**, pp. 79–86, 2016. doi:10.1016/j.synthmet.2016.03.014
6. S. Dul, L. Fambri, and A. Pegoretti, *Fused deposition modelling with ABS–graphene nanocomposites*, **Compos. Part A 85**, pp. 181–191, 2016. doi:10.1016/j.compositesa.2016.03.013
7. Z. Weng, Y. Zhou, W. Lin, T. Senthil, and L. Wu, *Structure-property relationship of nano enhanced stereolithography resin for desktop SLA 3D printer*, **Compos. Part A 88**, pp. 234–242, 2016. doi:10.1016/j.compositesa.2016.05.035
8. G. Postiglione, G. Natale, G. Griffini, M. Levi, and S. Turri, *UV-assisted three-dimensional printing of polymer nanocomposites based on inorganic fillers*, **Polym. Compos**, pp. 1662–1670, 2015. doi:10.1002/pc.23735
9. J. Bustillos, D. Montero, P. Nautiyal, A. Loganathan, B. Boesl, and A. Agarwal, *Integration of graphene poly(lactic) acid by 3D printing to develop creep and wear-resistant hierarchical nanocomposites*, **Polym. Compos.**, 2017. doi:10.1002/pc.24422
10. T. Takahashi, H. Itoh, and M. Kuroda, *Structure and properties of CVD-BN thick film prepared on carbon steel substrate*, **J. Cryst. Growth 53**, pp. 418–422, 1981. doi:10.1016/0022-0248(81)90092-0
11. E. Pop, V. Varshney, and A. K. Roy, *Thermal properties of graphene: fundamentals and applications*, **MRS Bull. 37**, pp. 1273–1281, 2012. doi:10.1557/mrs.2012.203