Direct Printing of Thermal Management Device Using Low-Cost Composite Ink

Nam Nguyen, Eric Melamed, Jin Gyu Park,* Songlin Zhang, Ayou Hao, and Richard Liang

This work presents a new method for fabricating thermal devices, such as heat sinks, using a 3D printing technique and lightweight composite ink. The method focuses on formulating composite inks with desired properties and direct ink writing for manufacturing. The ink undergoes two phases: phase one uses low viscosity epoxy to provide viscoelastic properties and phase two provides the fillers consisting of carbon fiber and graphite nanoplatelets to provide high thermal conductivity and structural properties. By combining these functional materials, 3D structures with a high thermal conductivity (≈2 W m⁻¹ K⁻¹) are printed for thermal management applications with the storage modulus of 3000 MPa and a density only 1.24 g cm⁻³. The results show that by carefully tailoring functional properties of the ink, net-shape multifunctional structures can be directly printed for thermal management device applications, such as heat sinks.

1. Introduction

Formulating composite ink to yield desired properties is the key for 3D printing thermal management devices, such as heat exchangers, heat sinks, and gap fillers. Direct ink writing can produce lightweight functional devices with improved durability and reliability.[1–3] These composite thermal devices can potentially replace conventional metal devices, which are subject to corrosion and manufacturing constraints.[4–6] Recently, the need for increased power density for the next generation electronic devices is driving the research of advanced composite materials for improved thermal control and reliability.[7–9] Researchers are focusing on low cost, lightweight and thermally conductive composite materials to dissipate heat more effectively.[8–11]

Conventional approaches have been explored by embedding thermally conductive fillers within a polymer matrix to make thermal conductive materials.[12] Several techniques have been investigated, such as high shear mixing,[13–15] self-assembly of fillers,[16–18] alignment of high aspect ratio fillers,[19–21] and filler functionalization.[22,23] Common fillers are metal, ceramic, and nanostructures such as carbon nanotubes, graphene, silver nanowire.[6,12,24] Among these, nanostructured fillers are demonstrating excellent properties due to their high aspect ratio and large surface to volume ratio. Although adding fillers increases thermal conductivity, high filler concentration increases the viscosity of the polymer mixture, which reduces the processability and requires more complicated manufacturing techniques.[25] Therefore, traditional processing methods are restricted to only a few methods, such as casting, hot rolling into thin films,[3] or hot press molding.[26] These techniques not only limit the product shape, but also increase the manufacturing cycle time. Therefore, despite the recent advances in thermal management, developing a high thermally conductive polymer composite and a practical manufacturing technique for thermal management devices are critically important.

Emerging 3D printing technology is capable of building net-shape complex structures at a lower cost[27,28] and enables fabricating structures with multifunctionality, which potentially opens new applications. Types of 3D printing techniques include fused deposition modeling,[29] ink jet printing,[30,31] stereolithography,[32,33] and direct ink writing.[34–36] Among these techniques, direct ink writing is widely used in various fields because of its simple setup and room temperature processing. This technique uses air pressure to push an ink solution through a nozzle, which is directed using computer control. Recently, direct ink writing has been used to produce functional products, such as lightweight cellular structures, shape memory composites, and sensors. However, using direct ink writing for fabricating lightweight thermal devices has not been reported. The most recent work used a stereolithographic 3D printer to create a composite heat sink.[37] However, this technique is limited to photopolymers, while direct writing can be applied to a wide range of materials.

For this work, we formulated a composite ink to directly manufacture thermal devices. We designed and printed a heat sink using direct ink writing to demonstrate the effectiveness of our nonmetal composite ink and direct writing approach. The results from this work open a new method for producing low-cost thermal devices using direct ink writing with lightweight and corrosion resistance features.

The challenges with printing thermal devices using the direct ink writing are formulating the ink with both shear thinning rheological behavior and high thermal conductivity.[36,38] Ink with proper shear-thinning properties allow it to flow smoothly through the nozzle[26,36] and a stable 3D structure can be achieved without collapsing after making contact with the substrate.[2] High thermal conductivity is also critical for...
thermal devices to more rapidly dissipate the generated heat. In addition, ink should have a long shelf life at room temperature to ensure the ink remains stable for an extended period.

For this research, we made ink using an EPON Resin 862 with a hydrid filler of milled carbon fiber and graphite nano-platelets. Several different pattern designs for thermal management were printed, including thermal interface materials and heat sink. The mechanical and thermal properties of the materials and printed devices were evaluated.

2. Results and Discussion

2.1. Ink Formulation and Printing Process

Utilizing nanostructured fillers for modified rheology behaviors and building thermal conductive paths are critical for ink formulation to produce both effective 3D printed structures and enhanced thermal conductivity.[39,40] In this research, we also used a similar approach. Our fillers were graphite nanoplatelets and milled carbon fibers since we sought to produce lightweight high thermal conductivity devices for thermal management applications. We used carbon fiber to maintain a low viscosity of mixed ink, while maintaining the mechanical properties and proper shear thinning properties (Figure 1a,b). To formulate the ink, we began by mixing graphite nanoplatelets with EPON 862 resin. Then, we added the milled carbon fibers. The fillers were added in small increments, then mixed in a planetary centrifugal mixer (Thinky mixer) for 2 min. Finally, the latent curing agent was added to the ink. After carefully tailoring the composition for printing, the resulting material consisted of 7.1 wt% curing agent, 7.6 wt% carbon fiber, 9.3 wt% graphite nanoplatelet, and 75.9 wt% EPON 862. This hybrid ink's viscosity was $2.5 \times 10^4$ Pa s at low shear rate 0.001 s$^{-1}$.

Figure 1a shows the formulated ink, which was loaded into a 5cc syringe. The syringe was connected to an air pressure control and mounted to the 3D CNC stage (Zen Toolworks CNC). The printed paths and geometries were programmed using a G-code script. To achieve a large extrusion filament and high printing rates, we used tips with diameters of 100–250 $\mu$m. As a result, we printed various 3D structures that did not collapse. Figure 1b–d shows the process. Printed parts were cured at 150 $^\circ$C for 2 h and then removed from the polytetrafluoroethylene (PTFE) substrate.

2.2. Properties of Printed Samples

Figure 2 shows scanning electron microscopy (SEM) images of fractured and polished samples, which display the multiscale fillers graphite nanoplatelets and milled carbon fibers. The low magnification image shows the distribution of graphite nanoplatelet and milled carbon fiber, as presented in Figure 2a.
The physical properties of printed samples were measured. The electrical conductivity of printed samples was 0.11 ($\pm$ 0.02) S m$^{-1}$. Dynamic mechanical analyzer (DMA) measurements of the printed hybrid composite sample revealed a storage modulus about 3000 MPa, which was an $\approx 50\%$ improvement compared to 2112 MPa in control sample of EPON 862 with latent curing agent (Figure 3a,b), due to the high modulus carbon fiber in hybrid composite. The results of storage modulus indicate that the hybrid ink can be used for structural thermal devices. Figure 3c shows that thermal diffusivity of both printed hybrid ink composite and pure epoxy after curing. The diffusivity of printed hybrid ink composite was $\approx 2$ times higher than that of epoxy control sample. The thermal conductivity of printed hybrid ink composite was $\approx 2$ W m$^{-1}$ K$^{-1}$ at room temperature, as shown in Figure 3d, which was $\approx 10$ times higher than that of the epoxy control sample (about 0.2 W m$^{-1}$ K$^{-1}$). The strong enhancement of thermal properties is attributed to the use of hybrid filler. The surrounding polymer matrix is known to provide a large thermal interface resistance due to the phonon mismatch between polymer and fillers.[41] To reduce the thermal resistance, the hybrid filler approach is becoming a widely used technique to synergistically increase the electrical and thermal conductivity properties of polymer composites.[13,42,43]

As shown in Figure 2b, the presence of carbon fibers among graphite structures could bridge the contacts among graphite clusters. Our thermal conductivity results were comparable to some commercial products and recently published outcomes, but with a lower density of 1.24 g cm$^{-3}$.[43–46]

2.3. Heat Transfer Simulation of Printed Heat Sink

We fabricated a heat sink as a device demonstration. Figure 4a shows the printed and cured heat sink made of hybrid composite ink with dimension of 5 mm ($D$) $\times$ 22 mm ($W$) $\times$ 22 mm ($H$). To check the heat dissipation capability, we placed it on the hot plate ($80^\circ$C) and measured the temperature distribution with IR camera (Figure 4c). The temperature gradient was around 40$^\circ$C between the hot plate and the end of heat sink. We also simulated the heat sink performance with finite element analysis using Abaqus software. The heat sink block was meshed with 8-node linear heat transfer brick (DC3D8) elements and Equation (1) shows the governing heat transfer model used in the simulation[47]

$$k \left( \frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} + \frac{\partial^2 T}{\partial z^2} \right) - hA(T - T_{amb}) = 0 \tag{1}$$

where $k$ is the thermal conductivity (W m$^{-1}$ K$^{-1}$), is the heat generation per unit volume (W m$^{-3}$), $h$ is the convective heat transfer coefficient (W m$^{-2}$ K$^{-1}$), $A$ is the surface area (m$^2$), and $T$ is the temperature (°C). Figure 4d shows the simulation results based on the parameters from the experiments in Section 2.2, where $k$ is 2 W m$^{-1}$ K$^{-1}$ and $h = 10$ W m$^{-2}$ K$^{-1}$. The simulation results showed a temperature gradient of 40 °C with heat flux ranging from $3.3 \times 10^{-4}$ to $1.3 \times 10^{-2}$ W mm$^{-2}$, as shown in Figure 4b. The simulation results...
had a temperature range that was consistent with the IR camera result of printed sample as presented in Figure 4c.

To compare the performance of the printed heat sink with the epoxy heat sink, we used a mold to make the Epon 862 heat sink instead of printing since Epon 862 has a low viscosity, which is not suitable for printing 3D structures. Figure 4e IR camera image shows the heat sink made of epoxy underwent a larger temperature difference (47 °C) compared to the printed heat sink (40 °C) due to lower thermal conductivity. The corresponding simulation results in Figure 4f with low thermal conductivity also matched the IR camera image, which indicates that the printed heat sink’s thermal performance was better than the epoxy heat sink. In general, by using direct ink writing, we can design and print net-shaped and custom-made thermal devices, such as heat sinks, gap fillers, or thermal interface materials. Using this printing method of composite ink can save cost and manufacturing time.

3. Conclusion

We formulated functional ink with graphite nanoplatelets and milled carbon fiber to fabricate thermal management devices using direct ink writing. The formulated hybrid composite ink with latent curing agent that demonstrated printable capabilities with a long shelf life and demonstrated a thermal conductivity of 2 W m⁻¹ K⁻¹ with storage modulus of 3000 MPa. We successfully printed different devices, such as heat sinks and thermal gap fillers to demonstrate the process. The printed heat ink demonstrates net-shape manufacturing and adequate thermal
dissipation features. These properties can be further improved by controlling the carbon fiber alignment direction under different extruding conditions. This work could open new methods to fabricate low cost and high performance thermal devices.

4. Experimental Section

4.1. Materials

EPON Resin 862 was purchased from Hexion and used as the main polymer matrix because it offers low viscosity for ink formulation and good mechanical strength. Milled carbon fibers were polyacrylonitrile (PAN) based fibers ZOLTEK PX35 from Zoletk Toray. Milled fiber has a 99+% carbon content obtained from high temperature batch graphitization process and was free of any sizing with thermal conductivity around 70 W m\(^{-1}\) K\(^{-1}\). XGnP Graphene Nanoplatelets, with an average size of 25 µm, were purchased from XG Sciences and consisted of short stacks of graphene sheets with an in-plane thermal conductivity around 3000 W m\(^{-1}\) K\(^{-1}\) and a through-plane thermal conductivity of 6 W m\(^{-1}\) K\(^{-1}\). Latent curing agent Ajicure PN-40 was purchased from A&C Catalysts. This latent curing agent is an amine epoxy adduct type that increases the ink shelf life with high glass transition temperature and allows the ink to remain stable at room temperature for weeks. Figure 5 illustrates the ink preparation and device manufacturing processes.

4.2. Characterization

Viscosity of ink was measured using concentric cylinder cone in the rheometer (MCR302, Anton Paar, Austria). A Laser Flash Apparatus (E40, FLIR) was used to obtain thermal images of the heat sink, and Abaqus 6.13 was used to for finite element analysis of the printed heat sink with quantitative thermal conductivity.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

3D printing, advanced composite, carbon fiber, hybrid inks, thermal management

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