THERMAL CONDUCTIVITY OF BORON NITRIDE AND GRAPHENE NANOCOMPOSITES IN FDM PRINTING

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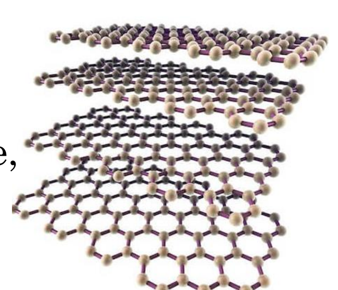
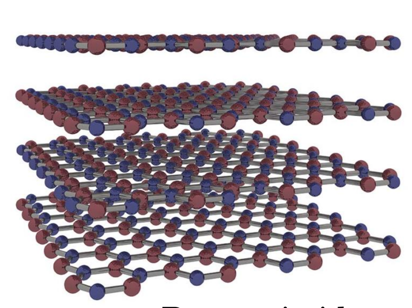
Introduction

- The thermal conductivity of printing materials in fused deposition modeling (FDM) is crucial to the printability of the material and to the quality of fusion between extruded threads[1].
- Thermoplastics like polylactic acid (PLA) and polypropylene (PP) are often used in FDM printing due to their plasticity when heated and rigidity when cooled, but suffer from poor thermal properties, which limits the utility of 3D printing.
- Polymer nanocomposites formed from the dispersion of conductive nanoparticles in polymer matrices can exhibit higher thermal conductivities than pure polymers while still maintaining a degree of thermoplasticity[2].
- Graphene nanoplatelets (GNP) are known to exhibit high thermal conductivity and to improve the thermal properties of polymers when introduced into the polymer matrix.
- Boron nitride (BN) nanoparticles may offer a viable alternative to carbon in polymer nanocomposites for FDM printing, since BN is similar in structure to graphene, has a large thermal conductivity, and is a nontoxic lubricant at high temperatures[3].



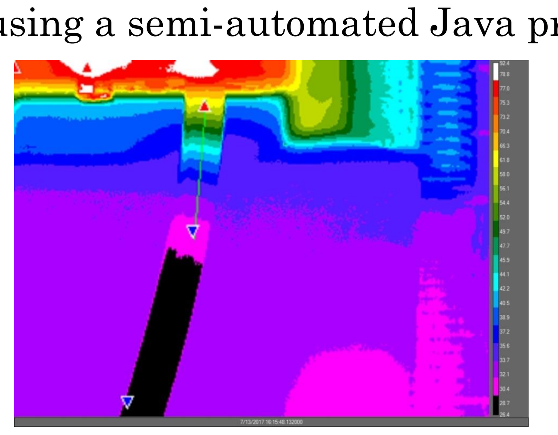
Graphene



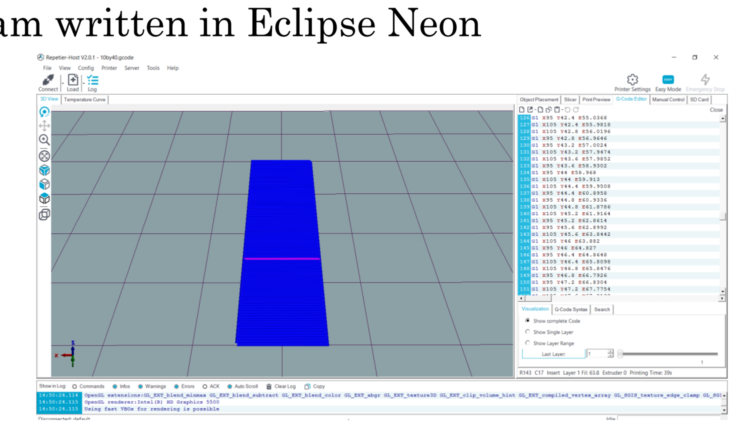
Boron nitride

Materials & Methods

- PLA 4042D and PP of molecular weight 250,000g/mol were blended in a Brabender melt-mixer with commercial boron nitride and graphene H-5 nanoplatelets at concentrations of 5, 10, and 20wt%
- Pure and composite materials were pelletized in a Brabender Granulator and extruded through a single phase Filabot Extruder
- The transfer of heat from an aluminum heating block through the filaments was imaged using a FLIR A300C IR camera with 4X lens magnification
- Custom G-code to control orientation of threads in printed samples was generated using a semi-automated Java program written in Eclipse Neon

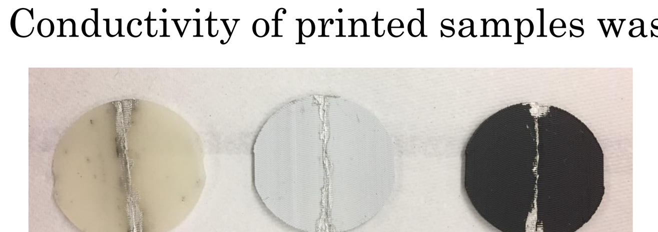


IR image of thermal profile of pure PP filament



Custom G-Code for oriented printing written in Repetier-Host V2.01

- Two oriented semicircles were printed for PLA, 90/10 PLA/BN and 90/10 PLA/GNP and the halves were then joined together with a Circuitworks conductive circuit pen
- Conductivity of printed samples was tested using a thermal conductivity meter

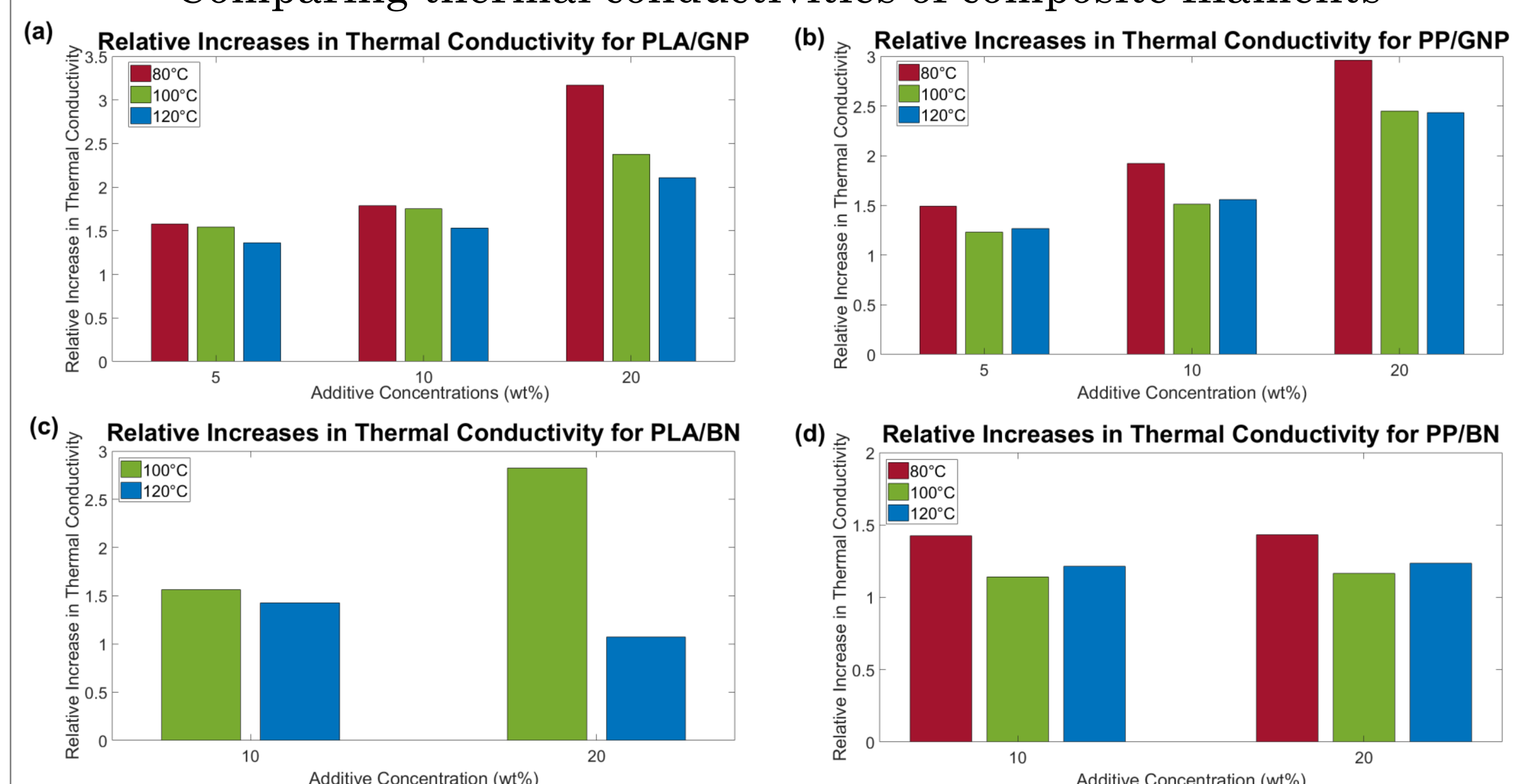


Oriented circular samples for thermal conductivity testing for pure PLA (left), 90/10 PLA/BN (middle), and 90/10 PLA/GNP (right)

- Rectangular oriented samples were printed, freeze fractured to 1cm squares, and sputter coated with gold in preparation for scanning electron microscopy (SEM)
- SEM was then used to take high resolution photos of the surface morphology and cross-sections of printed samples

Results & Discussion

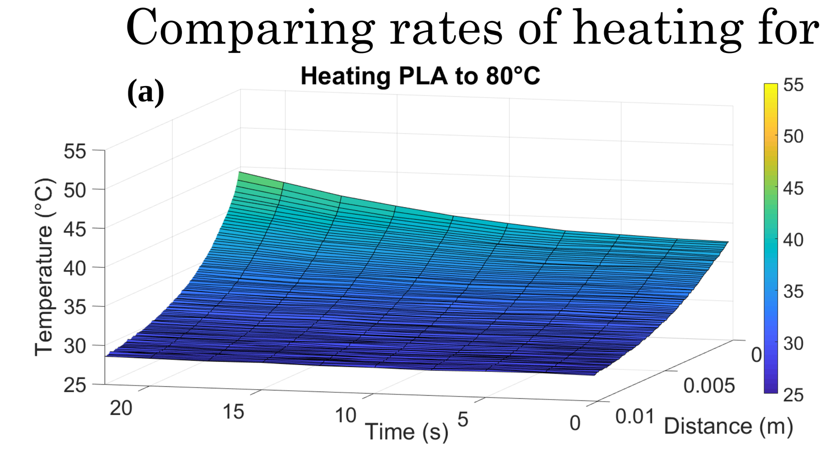
Comparing thermal conductivities of composite filaments

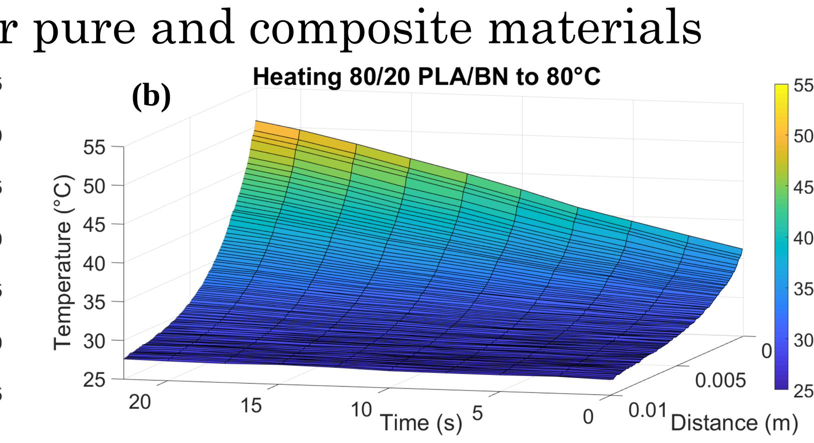


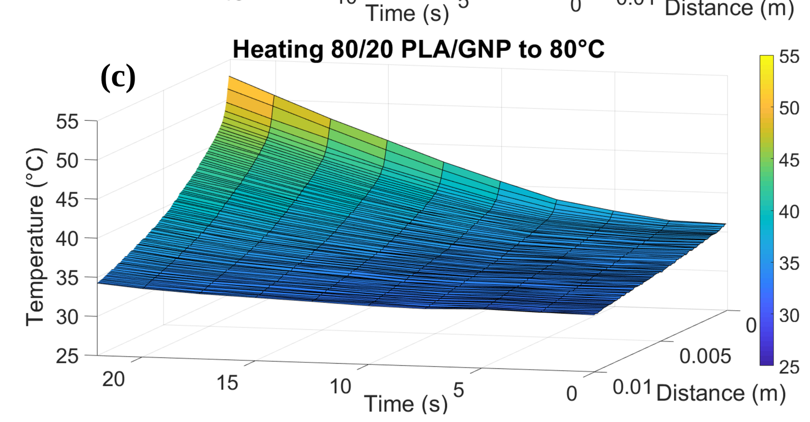
Relative increases in thermal conductivity of composite filaments for (a) PLA/GNP, (b) PP/GNP, (c) PLA/BN, and (d) PP/BN at varying additive concentrations and heating block temperatures

- Both GNP and BN consistently improved the thermal properties of the pure polymers PLA and PP under all conditions tested
- At 20wt% and 80°C, GNP increased the thermal conductivity of PLA by 217% and, at 20wt% and 100°C, BN increased the thermal conductivity of PLA by 182%
- Decreases in thermal conductivity corresponding to increasing temperature can be explained by polymer deformation at higher temperatures near the glass transition

Comparing rates of heating for pure and composite materials





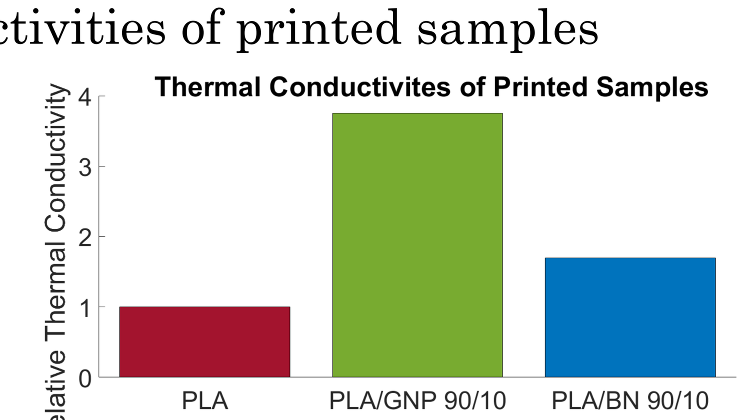


Surface plots representing the relationship between temperature, time, and distance from the heating block for (a) PLA, (b) 80/20 PLA/BN, and (c) 80/20 PLA/GNP

- Both composite materials heated far quicker than the pure PLA and heat travelled much further down the filament in the same amount of time

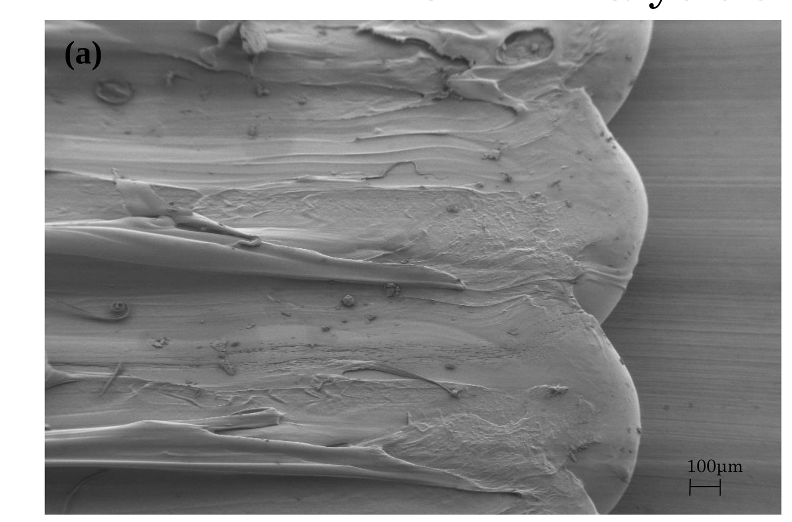
Comparing thermal conductivities of printed samples

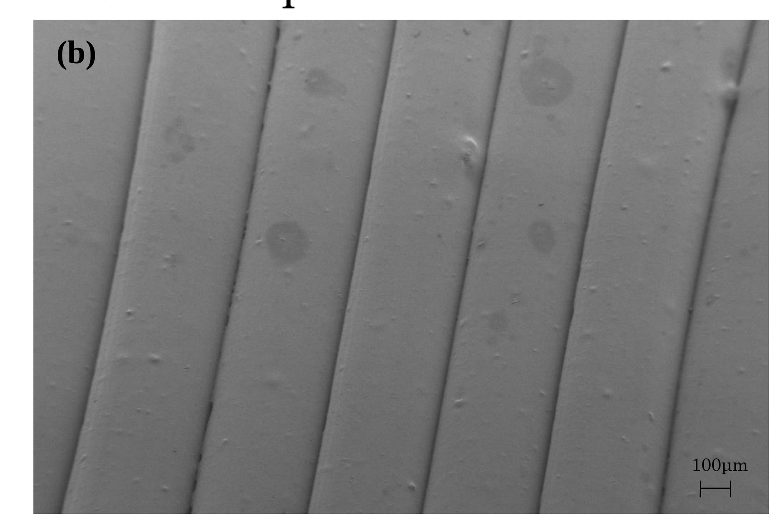
- At 10wt% GNP and BN increased the thermal conductivity of printed PLA by 276% and 70%, respectively



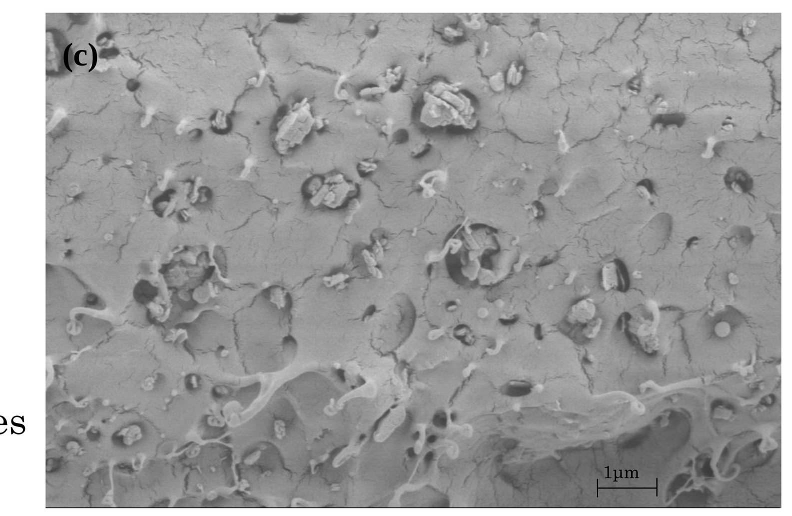
Thermal conductivity of printed samples as measured by thermal conductivity meter

SEM Analysis of Printed Samples





SEM images at 150 X magnification of fusion between extruded threads in printed samples of (a) PLA and (b) 90/10 PLA/BN and (c) an image at 30 kX magnification of a cross-section of 90/10 PLA/BN



- Better fusion and fewer surface defects were observed in the printed sample containing BN nanoparticles than in the pure PLA sample
- Previous results affirm that BN composites heat up quicker than pure PLA, which implies that, during the printing process, material deposition and fusion occurred at higher temperatures in the composite samples, which may explain this improvement in surface quality
- The ridges between each pass of the nozzle and the rough surface quality observed in the pure PLA sample can thus be attributed to poor thermal properties
- The cross-sectional image reveals that the alignment of BN nanoparticles is parallel to the direction of heat transfer which is known to contribute to greater heat conductance
- In the sample containing BN nanoparticles, the observable network of nanoparticles is well-dispersed and oriented

Conclusion

- While GNP composite materials performed better than those containing BN in thermal conductivity tests, the introduction of BN nanoparticles to the polymer matrices of thermoplastics PLA and PP was still very beneficial to the materials' thermal properties, nearly tripling thermal conductivity in some cases.
- BN nanocomposite materials may be better suited to FDM printing than pure polymers for applications requiring good mechanical strength, since better fusion between threads was observed in samples containing BN, or large thermal conductivities, since the introduction of BN nanoparticles significantly increased the thermal conductivity of printed PLA.
- In the fabrication of thermally conductive nanocomposite materials for FDM printing, BN nanoparticles present a viable non-carbon alternative to GNP since they similarly affect the thermal properties of thermoplastics and improve the printability of pure polymers.

References

1. Sun, Q., Rizvi, G. M., Bellehumeur, C. T., & Gu, P. (2008). Effect of Processing Conditions on the Bonding Quality of FDM Polymerfilaments. Rapid Prototyping Journal, 14(2), 72-80. doi:10.1108/13552540810862028.
2. Ebadi-Dehaghani H., & Monireh Nazempour (2012). Thermal Conductivity of Nanoparticles Filled Polymers. Smart Nanoparticles Technology. Dr. Abbass Hashim (Ed.). InTech, doi:10.5772/33842.
3. Kostoglou, Nikolaos & Polychronopoulou, Kyriaki & Rebholz, Claus. (2015). Thermal and chemical stability of hexagonal boron nitride (h-BN) nanoplatelets. Vacuum. 112. 42-45. 10.1016/j.vacuum.2014.11.009.