STRUCTURAL CHANGES IN POLYAMIDE-6/CARBON FIBER 3D-PRINTED COMPOSITE

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Can we create stronger, more versatile robotic components?

- Why does a 3D-printed composite exhibit increased mechanical strength after annealing?
- What is changing at the structural level that accounts for this increase?
- How can we best study and verify this change?

Fig. 1. The material used is a proprietary nylon-6/carbon fiber (CF) composite (Onyx)

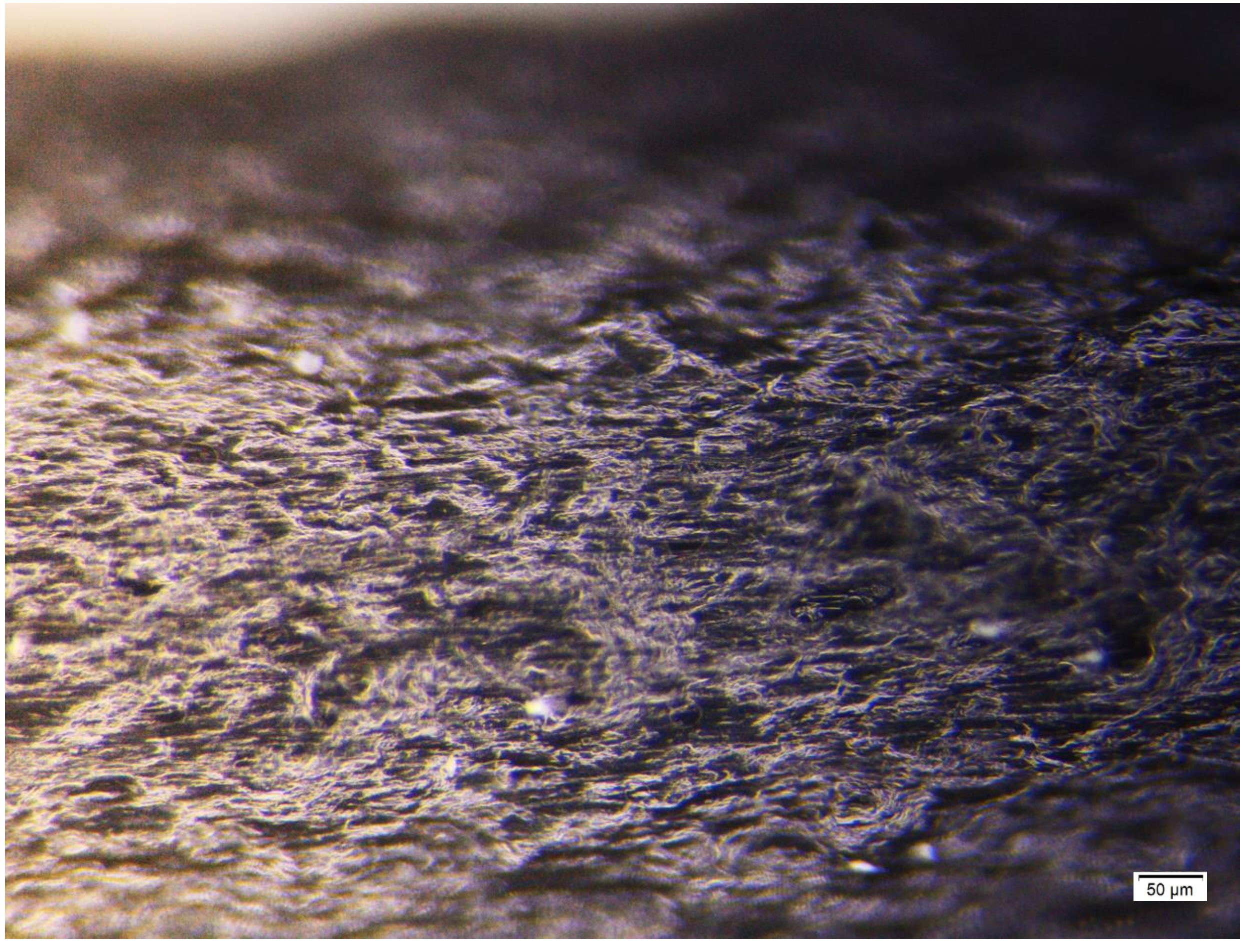

Fig. 2. Specimen printed to ASTM D790 standard for flexural testing

Previous research finds two mechanisms by which strength could increase

- Increase in crystallinity of polymer
- Change in surface chemistry of carbon fiber resulting in better interfacial adhesion with the polymer matrix
- **Our hypothesis:**

  Annealing reduces or eliminates voids/gaps in specimen

Specimens that were manually fractured or cut were difficult to image due to the short focal distance of the optical microscope

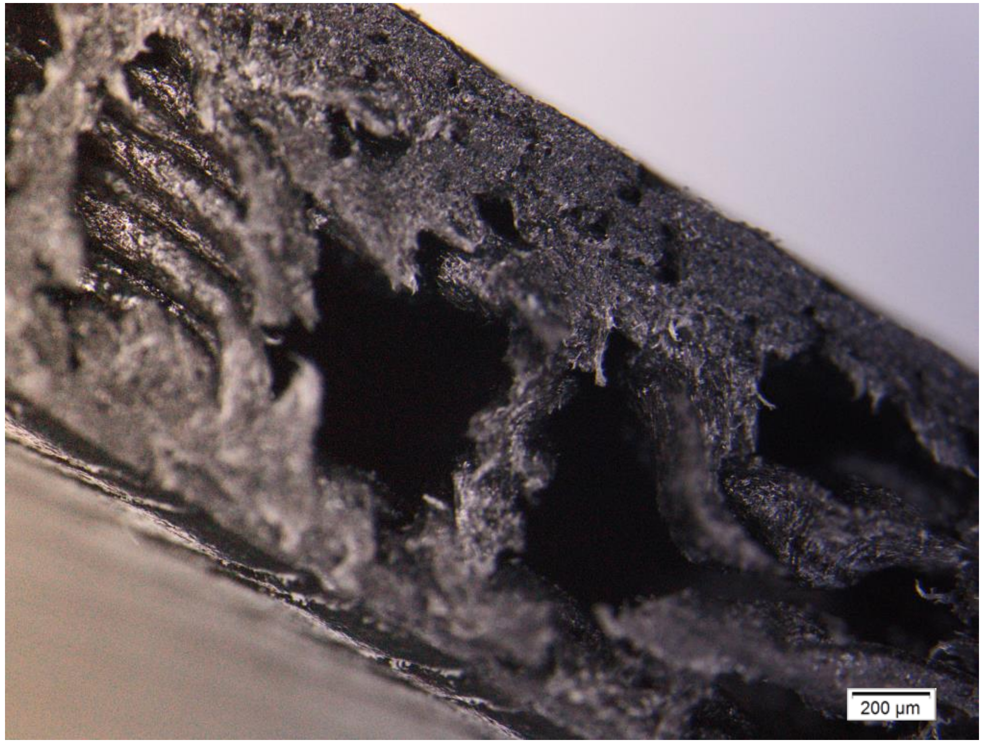

Fig. 3. Specimen cut with a pair of scissors shows significant surface deformation.

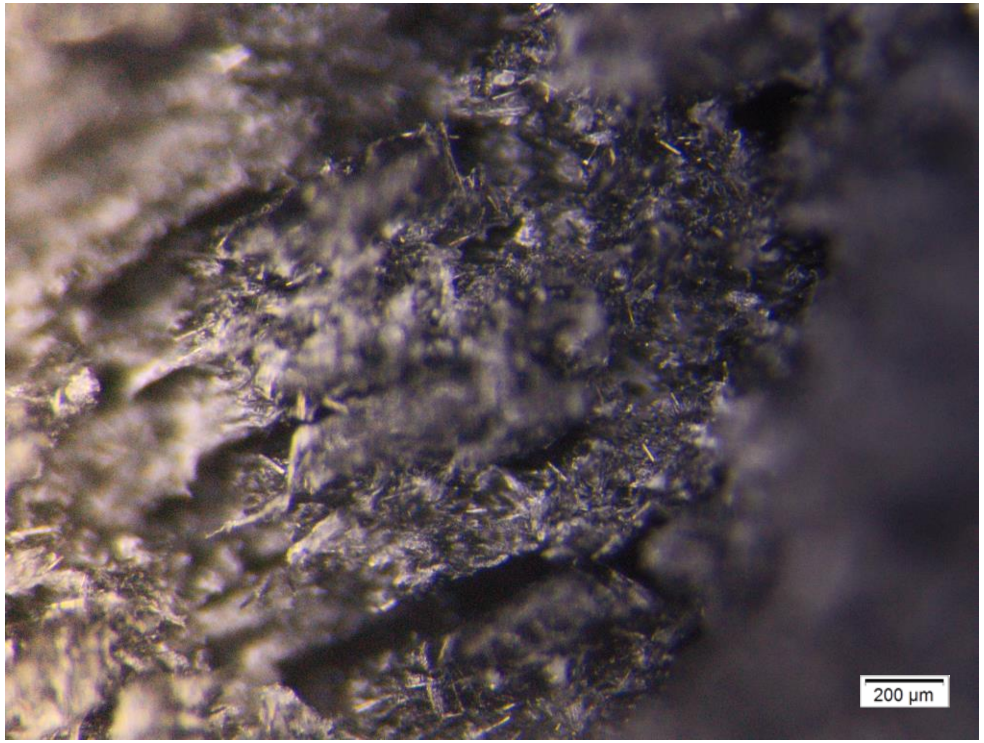

Fig. 4. Topography of manual fracture varies significantly making optical microscopy difficult.

Fig 5. Specimens mounted in epoxy resin in preparation for optical imaging

Before and after sample preparation

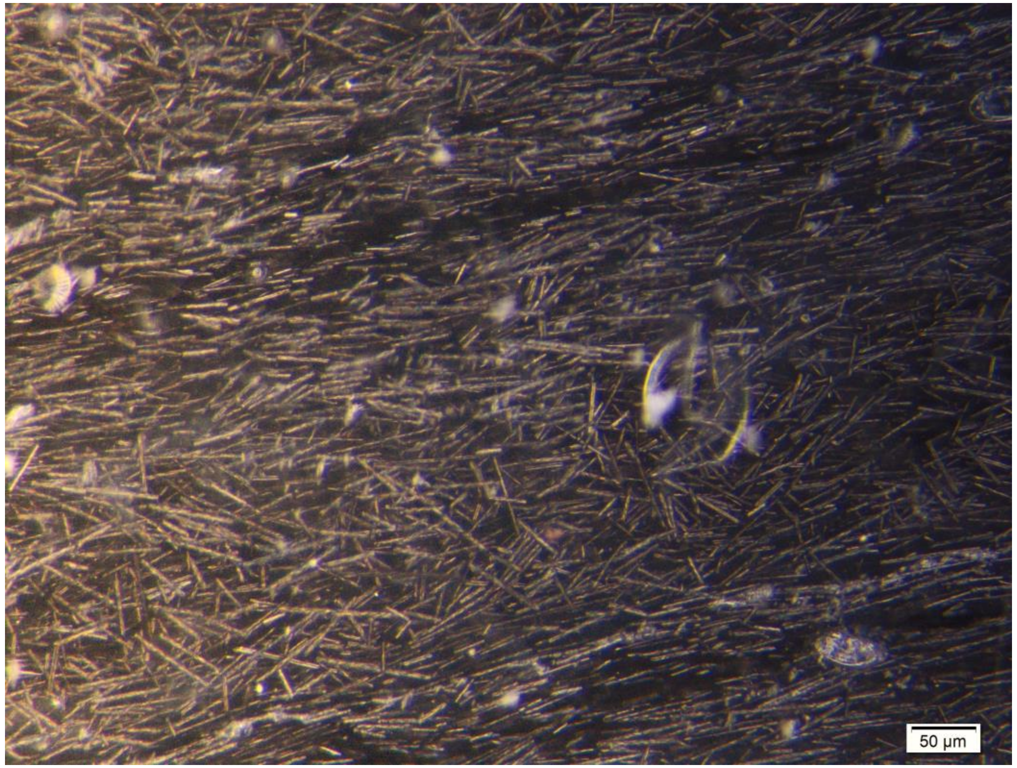

Fig. 6. Broadside of annealed specimen pre-preparation showing carbon fibers suspended in polymer matrix.

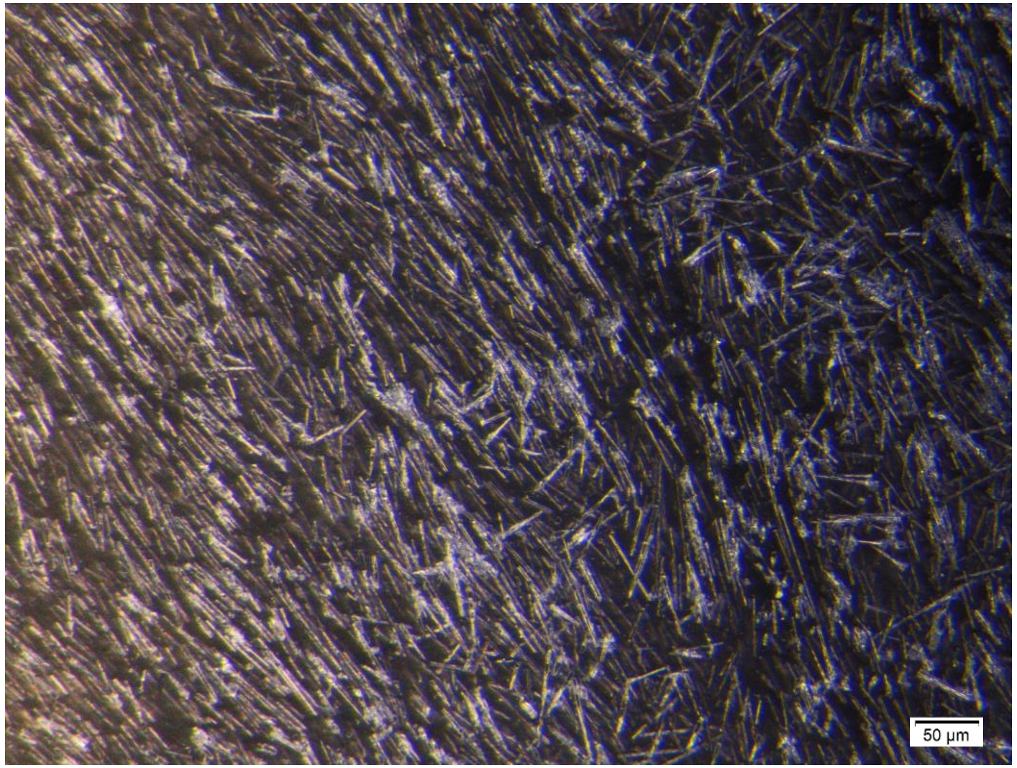

Fig. 7. Maximum resolution achievable via optical microscopy gives no substantive new information.

Cross-section shows significant surface deformation after preparation

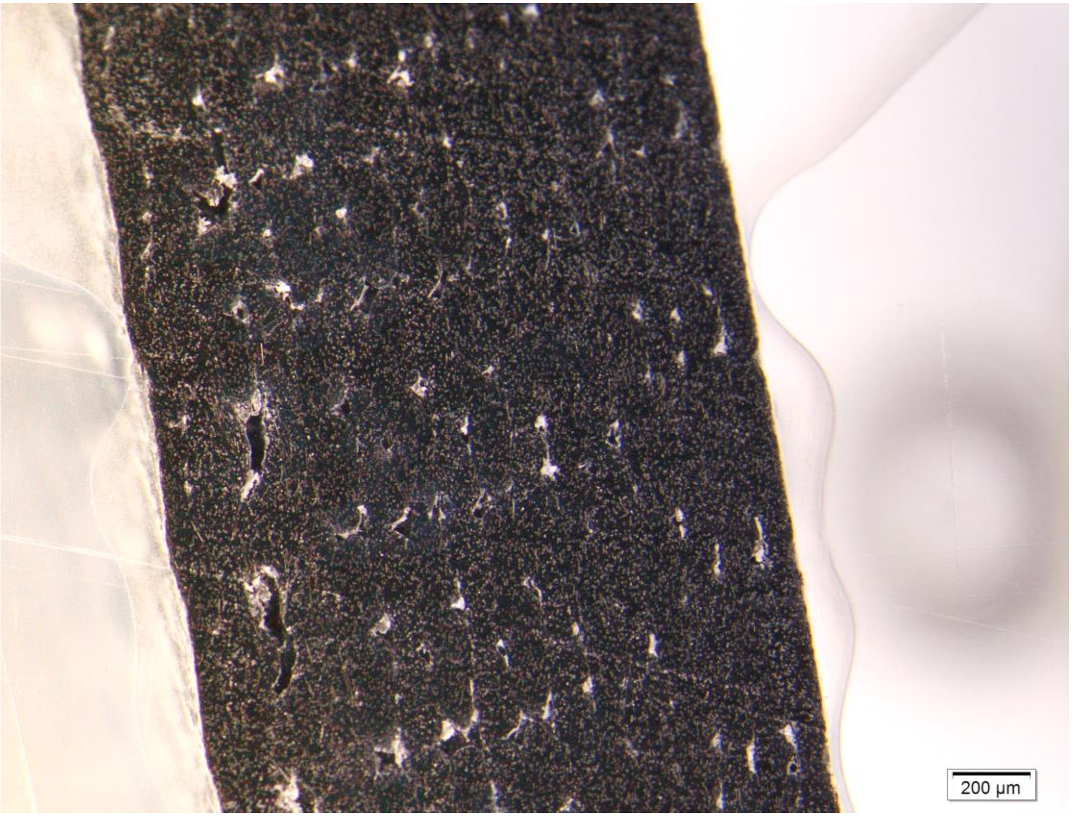

Fig. 8. Voids (darkest areas) still present after annealing.

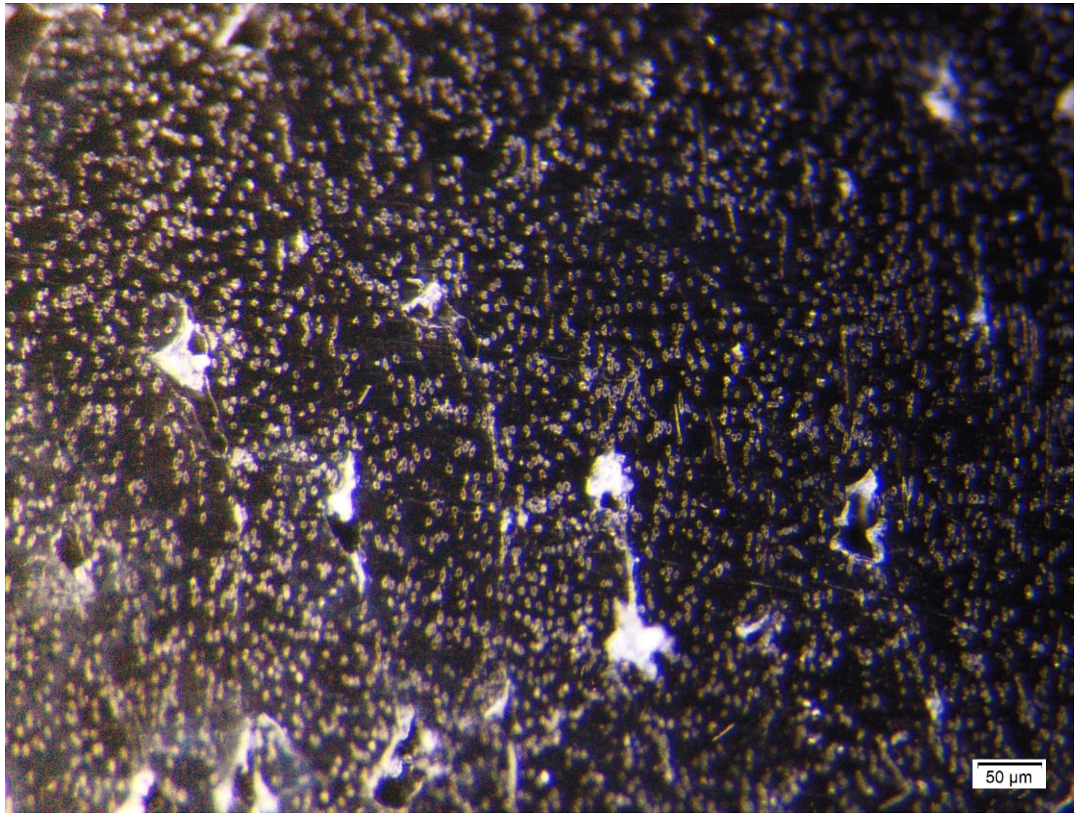

Fig. 9. Epoxy (lightest areas) ground into soft polymer matrix during preparation. Smaller ellipses are cross-sections of carbon fibers.

Measurements were taken pre- and post-annealing with calipers to study any potential macroscopic changes in structure

	Avg. Change	Avg. % Difference
Length (mm)	-0.27	-0.22
Width (mm)	-0.0066	-0.051
Thickness (mm)	0.0036	0.12
Mass (g)	-0.0085	-0.15
Density (g/cm^3)	0.00018	0.031

Table 1. 100% in-fill, vertically-printed specimens exhibited more variation in dimensional changes.

	Avg. Change	Avg. % Difference
Length (mm)	-0.62	-0.49
Width (mm)	-0.047	-0.37
Thickness (mm)	-0.025	-0.77
Mass (g)	-0.088	-1.6
Density (g/cm^3)	0.00030	0.038

Table 2. 100% in-fill, horizontally-printed specimens exhibit greater – and more consistent – shrinkage.

No change was observed in layer thickness pre- and post-annealing

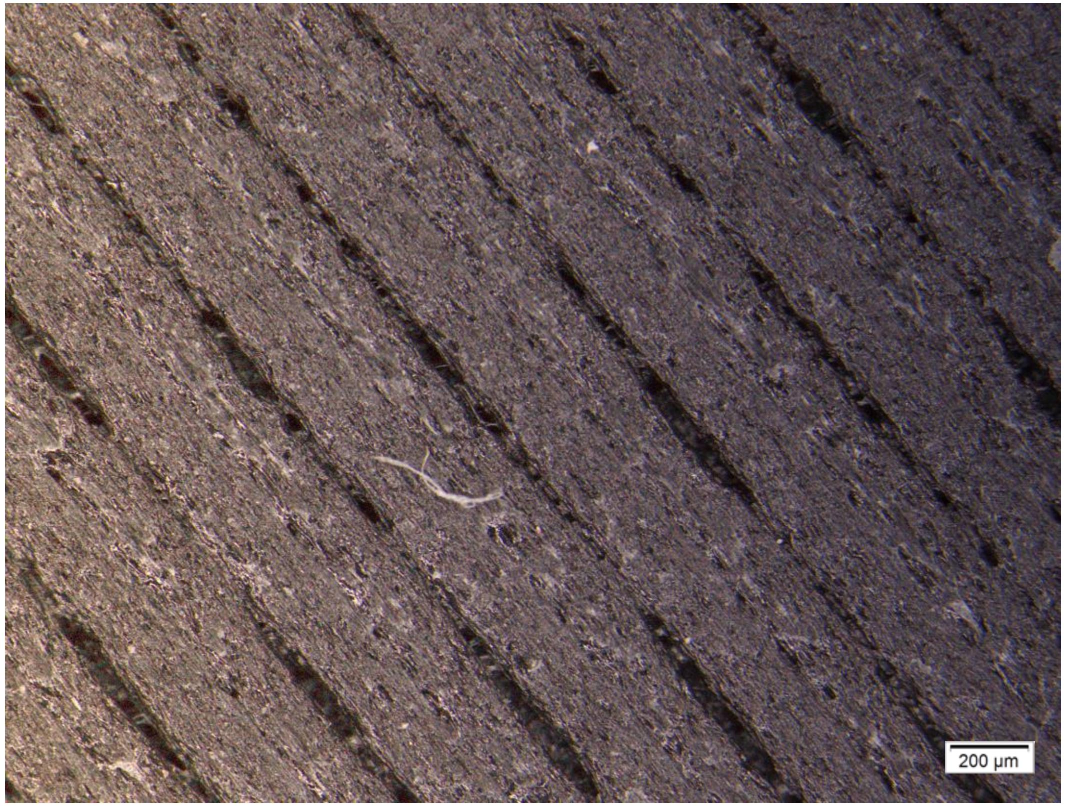

Fig. 10. 100% in-filled specimen pre-annealing

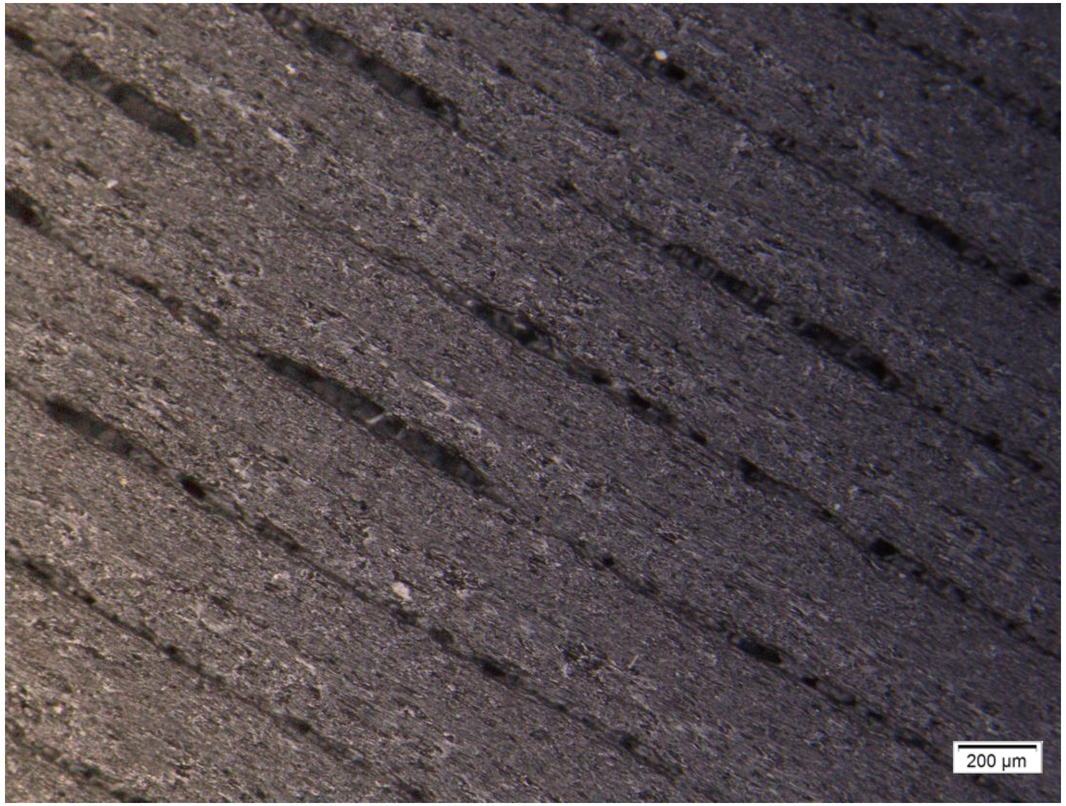

Fig. 11. Same specimen post-annealing

No change in gaps of specimens printed at 37% in-fill

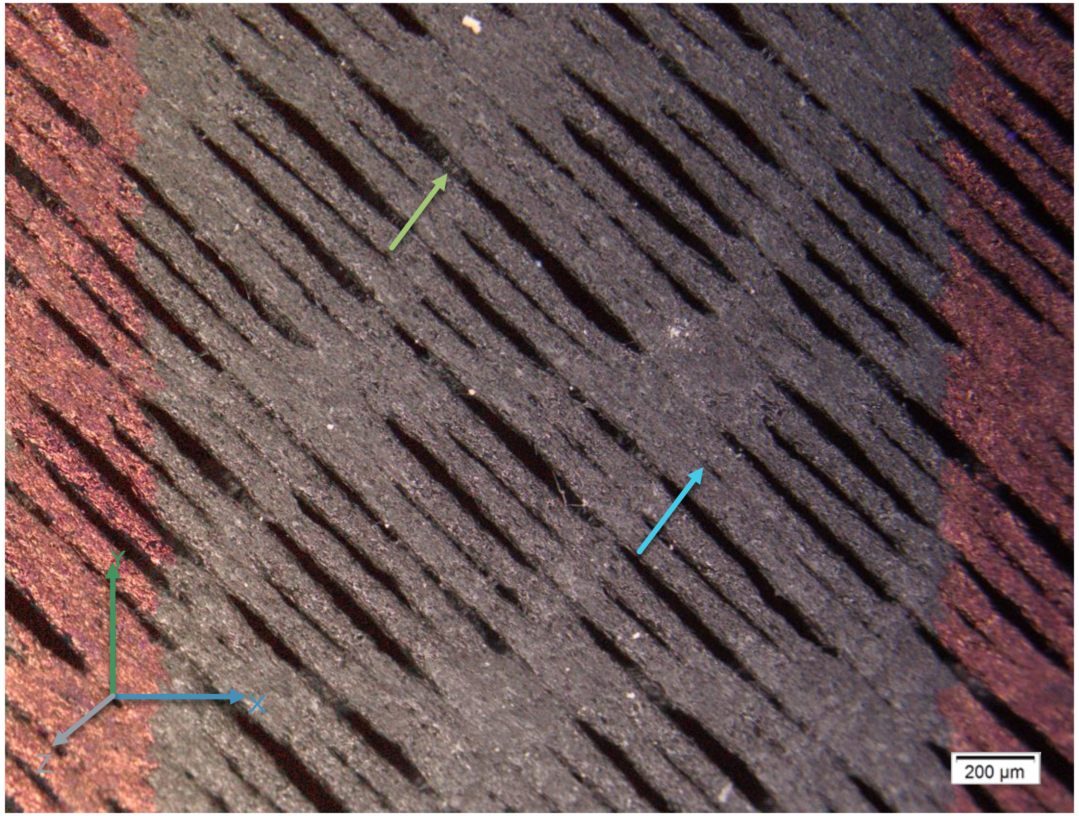

Fig. 12. Pre-annealing

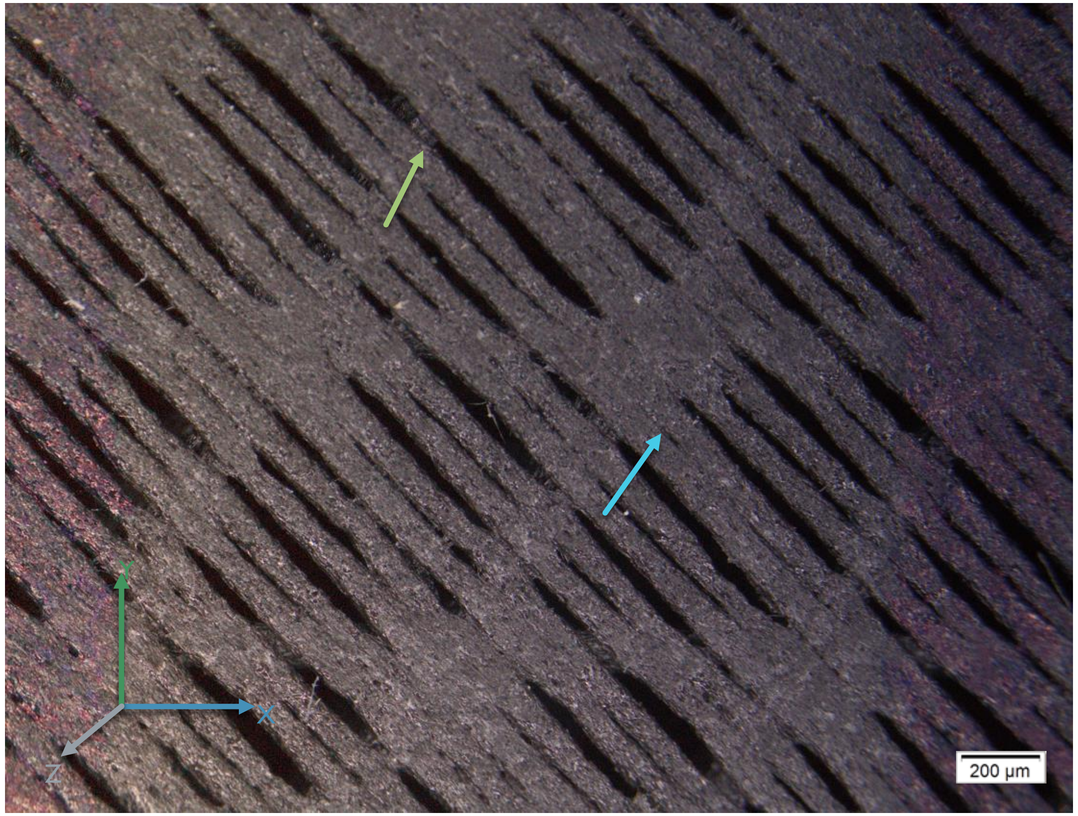

Fig. 13. Post-annealing

What do we know?

- It shrinks and it gets stronger

CHALLENGES/LIMITATIONS

- Optical microscopy is useful for identifying areas of interest but does not necessarily give us enough information to make any conclusions regarding how or why specimens become stronger post-annealing.
- Polymers are notoriously difficult to prepare for microscopy, increasing the likelihood of substantial surface deformation, rendering specimens useless.

RECOMMENDATIONS FOR FUTURE RESEARCH

- Continue studying how specimens shrink after annealing
  - Larger specimens at different dimensions
- Use X-ray diffraction to study composition and crystallinity
- Pie in the sky – three-dimensional imaging to study voids

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REFERENCES

- J. Mendoza, "Three Point Flexural Test on Annealed Onyx 3D Print Material," 2019.
- N. Murthy, R. Bray, S. Correale and R. Moore, "Drawing and annealing of nylon-6 fibres: studies of crystal growth, orientation of amorphous and crystalline domains and their influence on properties," *Polymer*, vol. 36, no.20, pp. 3863-3873, 1995.
- T. K. Chaki, J. P. Rath and D. Khastgir, "Change in fiber properties due to the heat treatment of nylon 6 tire cords," *Journal of Applied Polymer Science*, vol. 108, pp. 3960-3967, 17 March 2008.
- D. Zhishuang, Z. Baoyan, S. Fenghui, M. Li, Z. Zuoguang and G. Yizhuo, "Effect of heat treatment on carbon fiber surface properties and fibers/epoxy interfacial adhesion," *Applied Surface Science*, vol. 257, no. 20, pp. 8457-8461, 1 August 2011.
- R. L. J. Clark, *Influence of the Interphase on the Mechanical Properties of Nylon 66 Composites*, Blackburg, VA: Virginia Polytechnic Institute and State University, 1996.
- B. F. Jogi, M. Sawant, P. K. Brahmankar, D. Ratna and M. C. Tarhekar, "Study of Mechanical and Crystalline Behavior of Polyamide 6/Hytrel/Carbon Nanotubes (CNT) based Polymer Composites," *Procedia Materials Science*, vol. 6, pp. 805-811, 2014.
- "ASTM D790: Standards test methods for flexural properties of unreinforced and reinforced plastics and electrical insulating materials," ASTM International, West Conshohocken, 2003.
- L. C. Sawyer and D. T. Grubb, Polymer Microscopy, 2nd ed., Oxford: Chapman & Hall, 1996.

THANK YOU

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