# 3D-Printed Thermoset Biocomposites Based on Forest Residues by Delayed Extrusion of Cold Masterbatch

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## Objective

The objective of this work is to revalorize lignin and sawdust via 3D printing using bioepoxy as a carrier. However just the incorporation of these particles within the polymer matrix does not improve the rheological properties of the bioepoxy enough to be 3D printable. Keeping this in mind, we sought to shift the burden in 3D printing from materials to a processing method, so otherwise unprintable materials can be printed.

- We propose a new 3D-printing processing technique termed Delayed Extrusion of Cold Masterbatch (DECMA), which enables the 3D printing of thermoset biocomposites.
  - In this technique, the degree of curing of the ink is controlled via time/temperature conditions. Then, the resin is cooled down to stop the reaction and the printing is started.
  - We aimed to systematically investigate the printability of the biocomposite paste and assess the merits of the delayed extrusion, via DECMA.

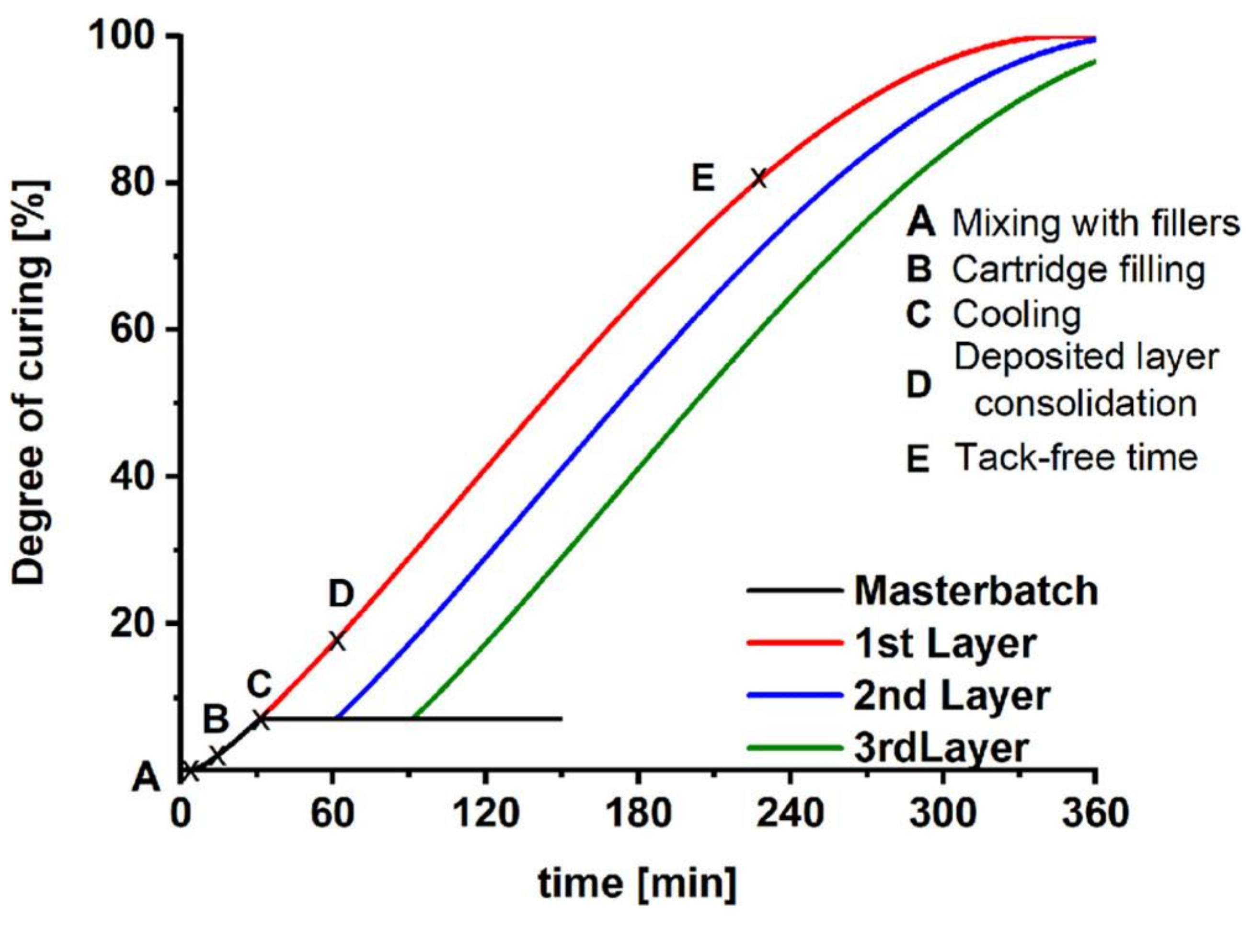



Figure 1. Schematic of the Delayed Cold Masterbatch approach. In the present diagram, three layers are presented, albeit more layers were deposited as part of this study. Segments A–B: wetting of fibers, B–C: consolidation of resin, point C: start of 3D printing, point D: deposition of the second layer, point E: tack free, the moment at which the resin is so cured that its losses adhesion.

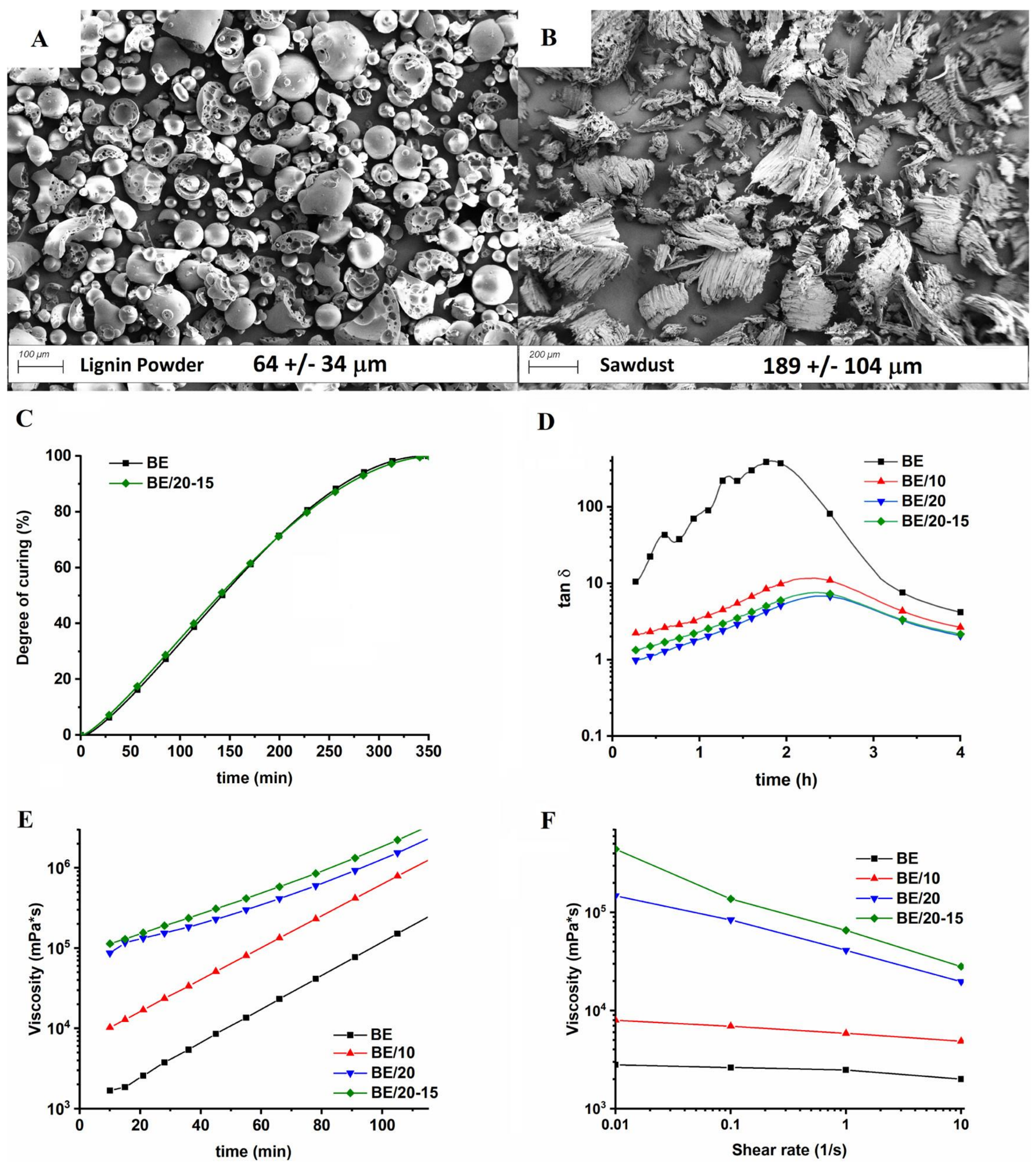
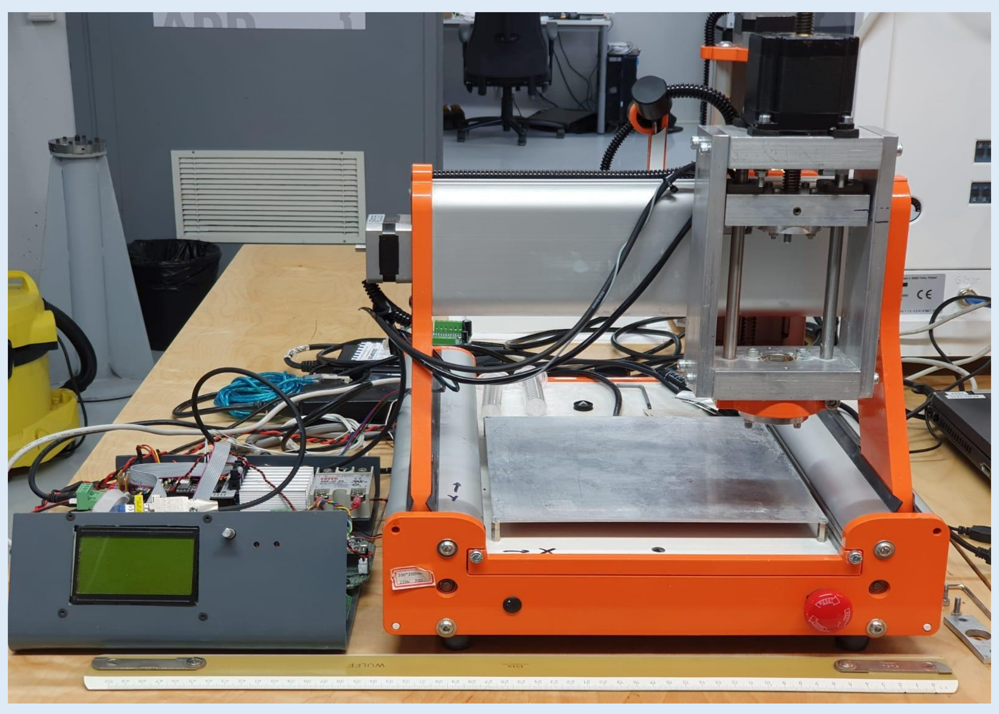



Figure 2. Characterization of materials (labeled as BE/sawdust%–lignin%). SEM images of (A) lignin powder, (B) sawdust, (C) curing kinetic of BE, and BE/20–15. (D) Loss factor (tan δ) of materials. (E) Evolution of the viscosity over time for BE and its composites. (F) Influence of the shear rate on material viscosity.

## Set-up

- The samples were 3D printed with an in-house developed piston-driven extrusion system to guarantee a constant paste dispensing speed.
- The paste extrusion process was performed at a piston speed (dispensing speed) 0.6 mL/min and a print speed of 200 mm/min.
- Objects were manufactured with a layer height of 1.5 mm, utilizing 2 mm nozzles.



*3D printer setup used in this study*

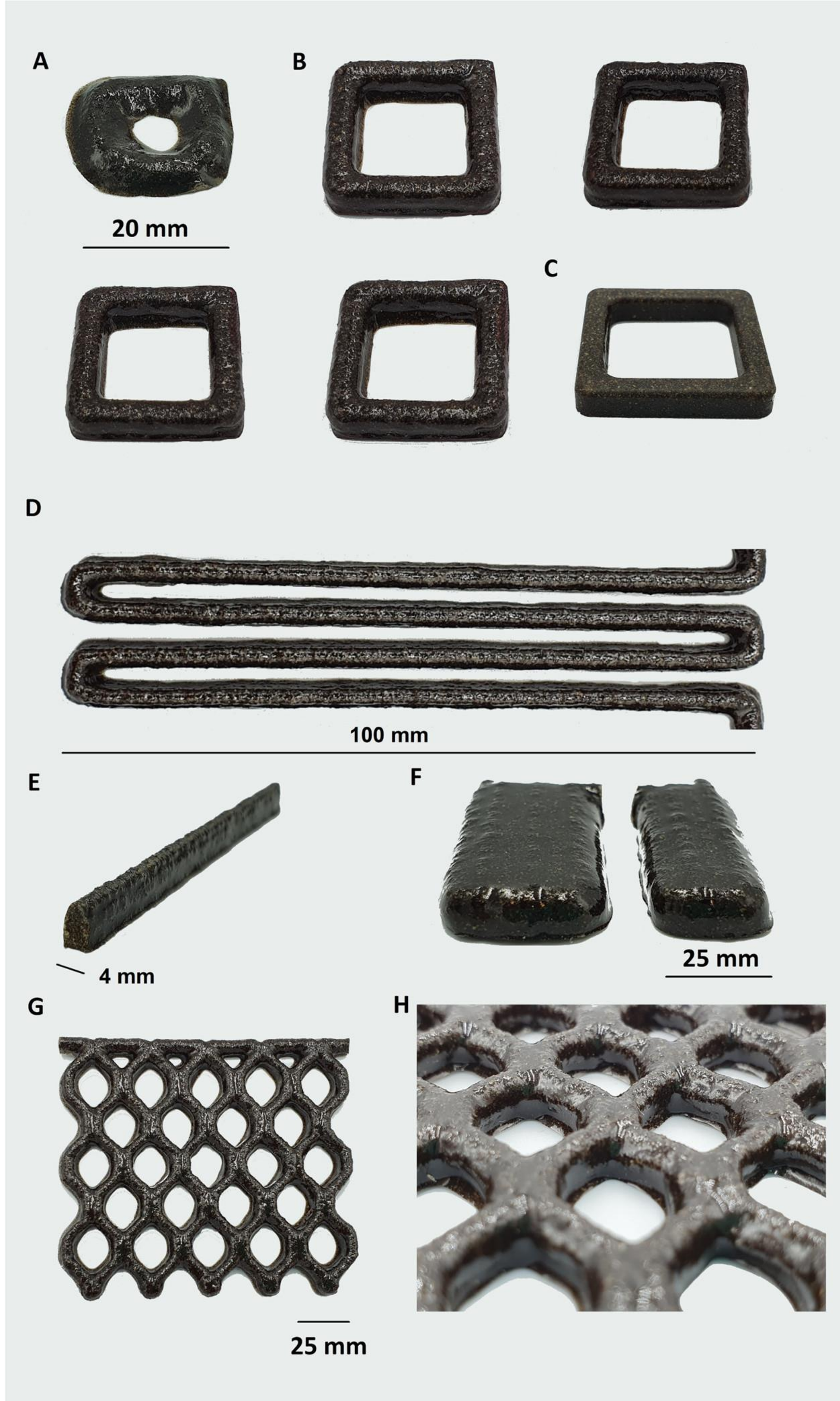



Figure 3. (A) Failed attempt to print open cuboid without the DECMA approach, (B) open-cuboid object printed with DECMA, (C) 3D-printed open cuboid that was post-processed via CNC machining, (D) continuous line 3D printing, (E) printed long continuous line, (F) line 3D printing at six and four adjoining lines, and (G, H) lattice scaffold—honeycomb structure. Unless otherwise noted, printed parts are five layers high and one layer width.

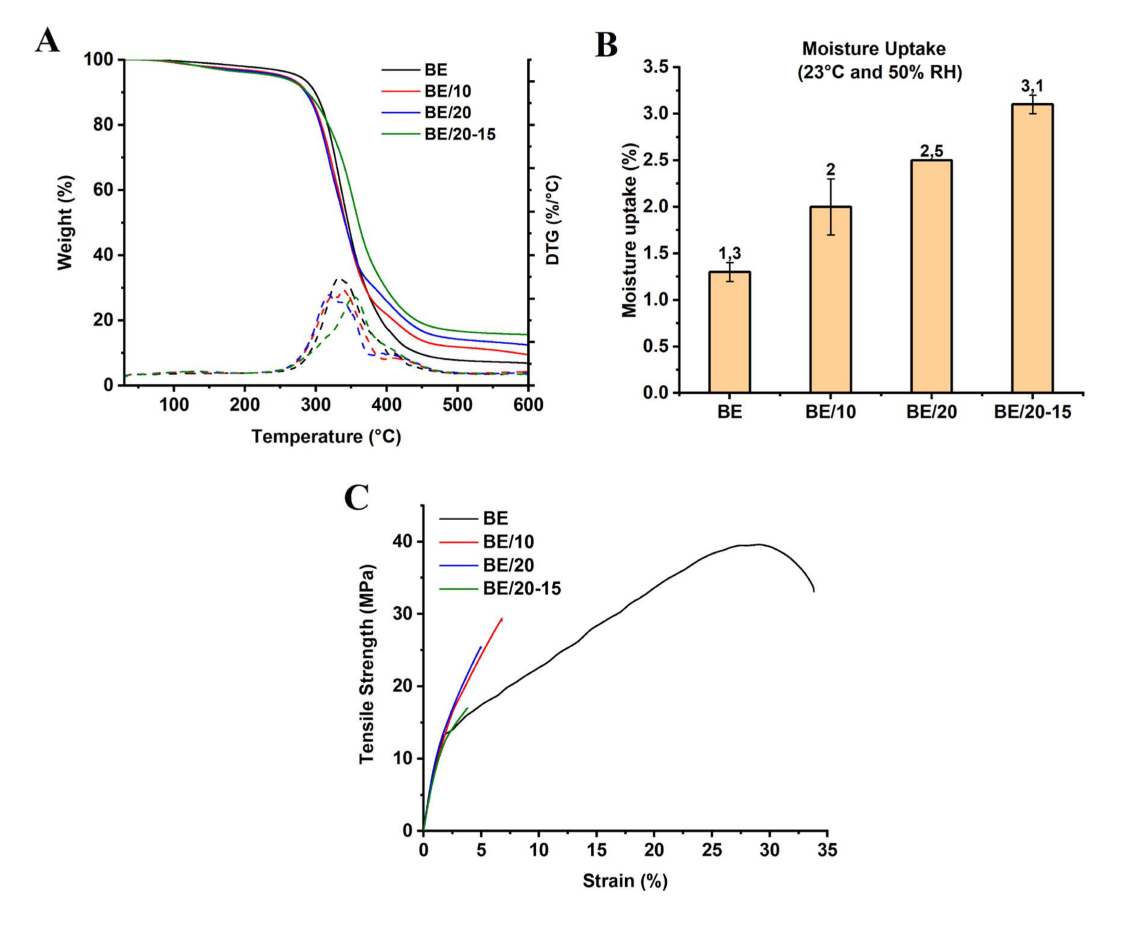



Figure 4. General properties of the material (A) TGA and dTG, (B) moisture uptake, and (C) mechanical properties.

## Conclusion

- A bioepoxy-based ink containing a 20% of sawdust and 15% of lignin (with a total bio-based content of 58–71%) was developed.
  - The incorporation of lignin and sawdust increased the starting viscosity of the mixture from 103 to 105 mPa·s and provided shear-thinning behavior without affecting the curing kinetic.
- It was found that the ink was not printable using the direct printing approach, but using DECMA, several parts (i.e., cuboids, adjoining lines, parallel lines, and honeycomb) were successfully printed.
- Additionally, 3D-printed parts could easily be machined, thereby showcasing potential for hybrid manufacturing.

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