

Sustainable materials for additive manufacturing of active release devices

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Introduction

Additive manufacturing (AM) has seen significant advances in recent years, and now encompasses various techniques, including stereolithography (SLA). SLA is a well-established technique, which constructs objects layer by layer using a photoactive resin and a light source. While these techniques have facilitated rapid prototyping and innovation, there is a pressing need for more sustainable materials to reduce the reliance on petrochemical-based resins as AM adoption grows.

Aim: To explore the printability of poly(glycerol) 4 and 6 (meth)acrylates as sustainable and functional resin alternatives. Determine the printability of Jasmine lactone as a sustainable resin.

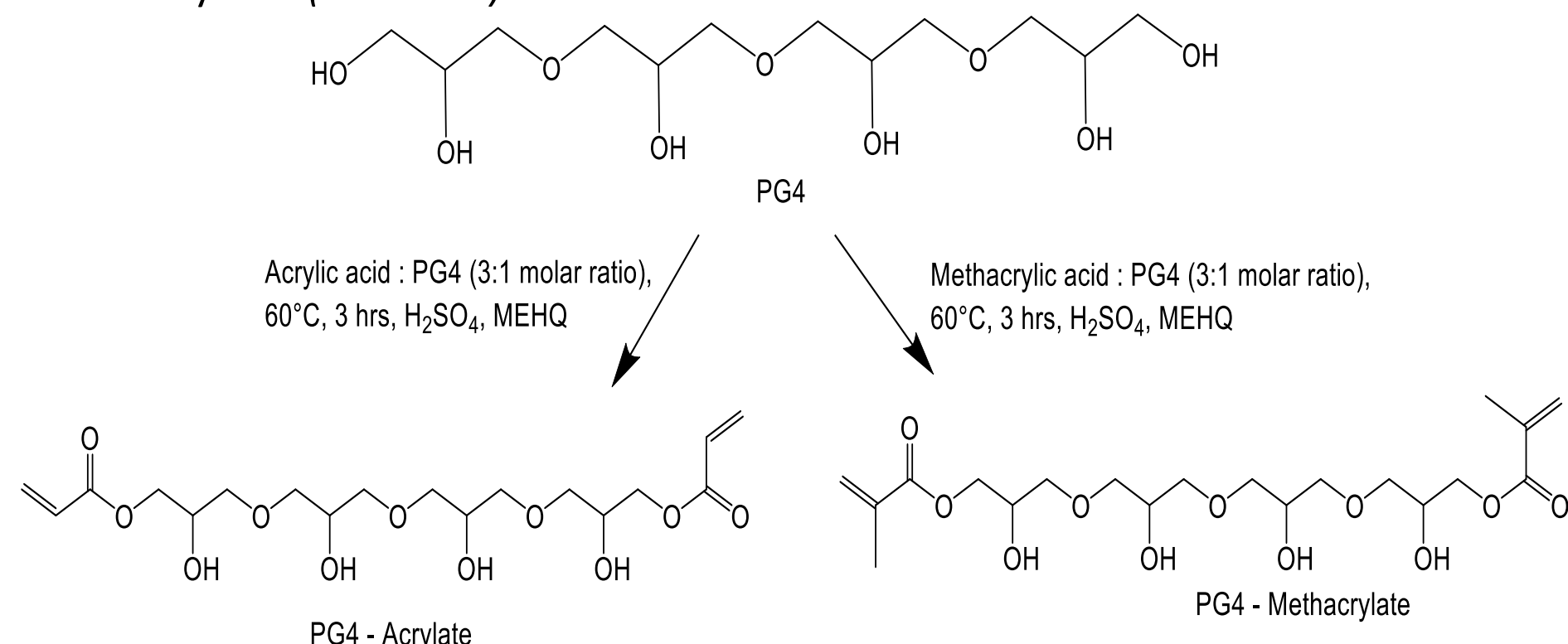


Figure 1, Image of 3D SLA printer

PhD worked funded by Velcro thus printability of sustainable resins for hook and loop systems will be explored.

Methodology – Polyglycerol Meth(acrylate)

The range of polymeric materials available for printing remains limited, with the majority sourced from petrochemical feedstocks. Glycerol is a by-product of the biodiesel industry and can be polymerised to produce polyglycerol (PG)¹. Polyglycerols were selected as the major component of the resin as they are viscous, biodegradable, transparent, biocompatible, renewably sourced, and can be functionalised with polymerisable moieties such as acrylates (*scheme 1*).

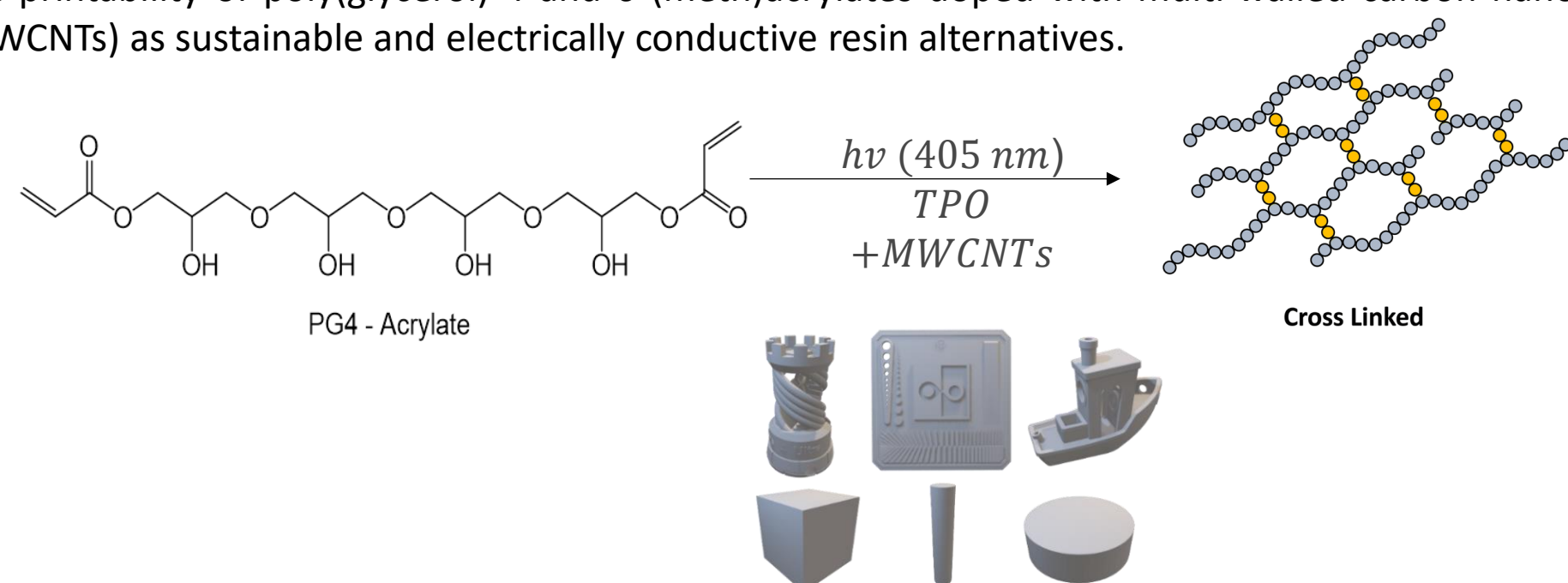


Scheme 1, Synthesis of PG4 - Acrylate

SLA printing was conducted using a Elegoo Mars 4 Ultra, initially printing was completed using PG4 Acrylate and PG4 Methacrylate. Further work was then completed using Glycerol 1,3 diacrylate with the addition of PEGDA 250 and photo-absorber to increase printing resolution for hooks and loops.

Methodology – Carbon Nanotubes (CNTs)

The printability of poly(glycerol) 4 and 6 (meth)acrylates doped with multi-walled carbon nanotubes (MWCNTs) as sustainable and electrically conductive resin alternatives.



Scheme 2, 3D SLA printing of MWCNTs at 0.125 wt% of various STL models

Results – PG Resin

High resolution 3D printed scaffolds from stereolithography can be produced using Polyglycerol (meth)acrylates (Figure 2). These scaffolds exhibit structural precision, and tuneable mechanical properties, making them suitable for various applications, including biomedical implants.

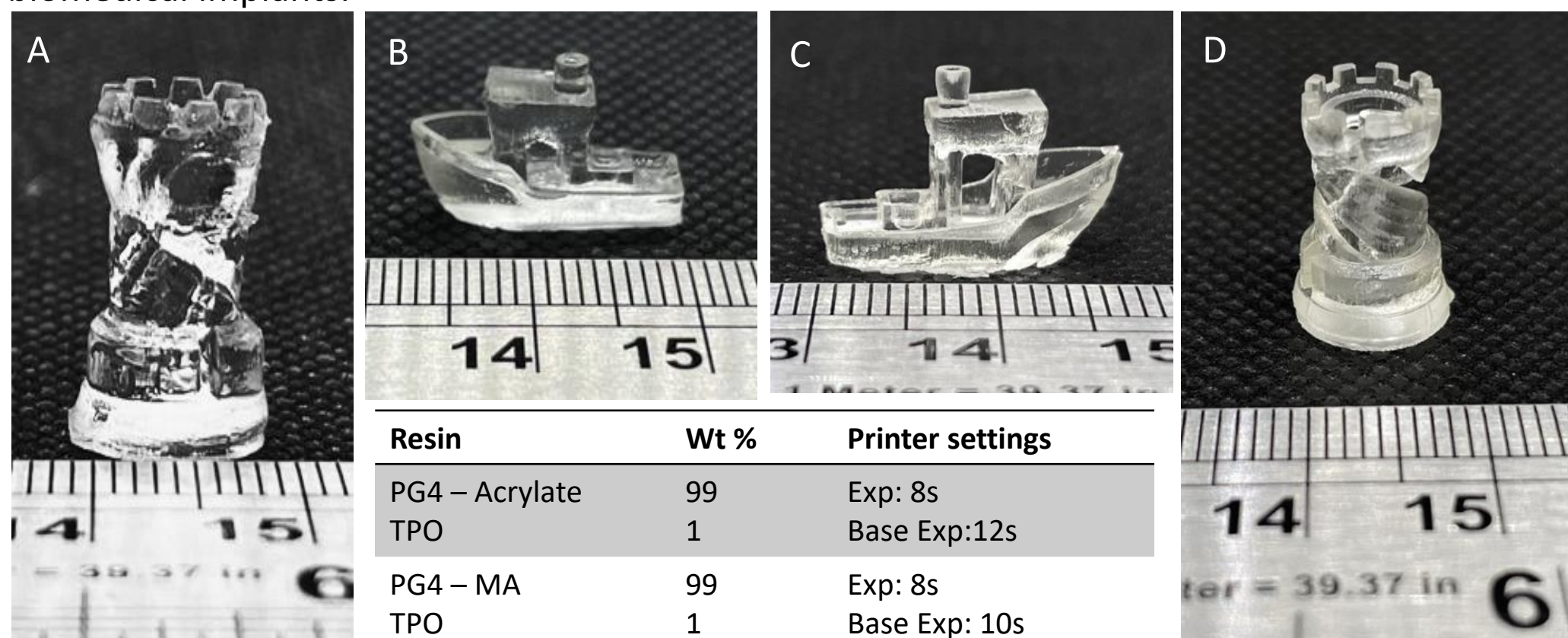


Figure 2, (A) Rook of PG4 – Acrylate (B) Boat of PG4 – Acrylate (C) Boat of PG4 – MA (D) Rook of PG4 – MA.
Table 1, Resin material for SLA Printed rook and boats

Results – MWCNTs

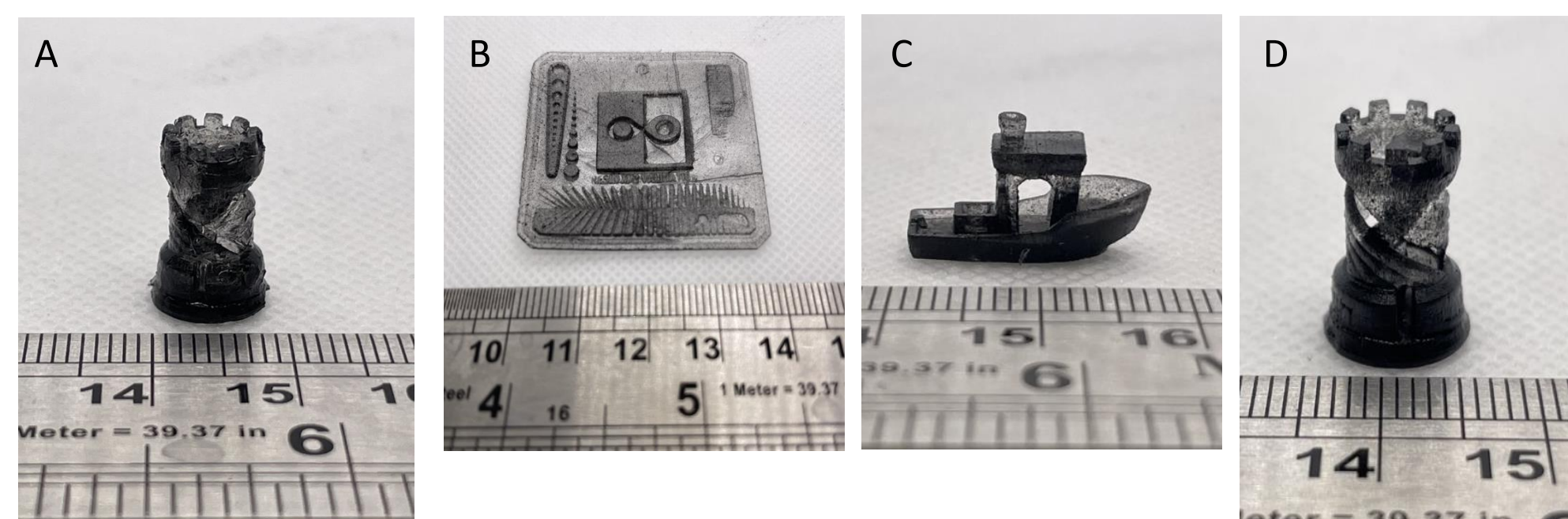
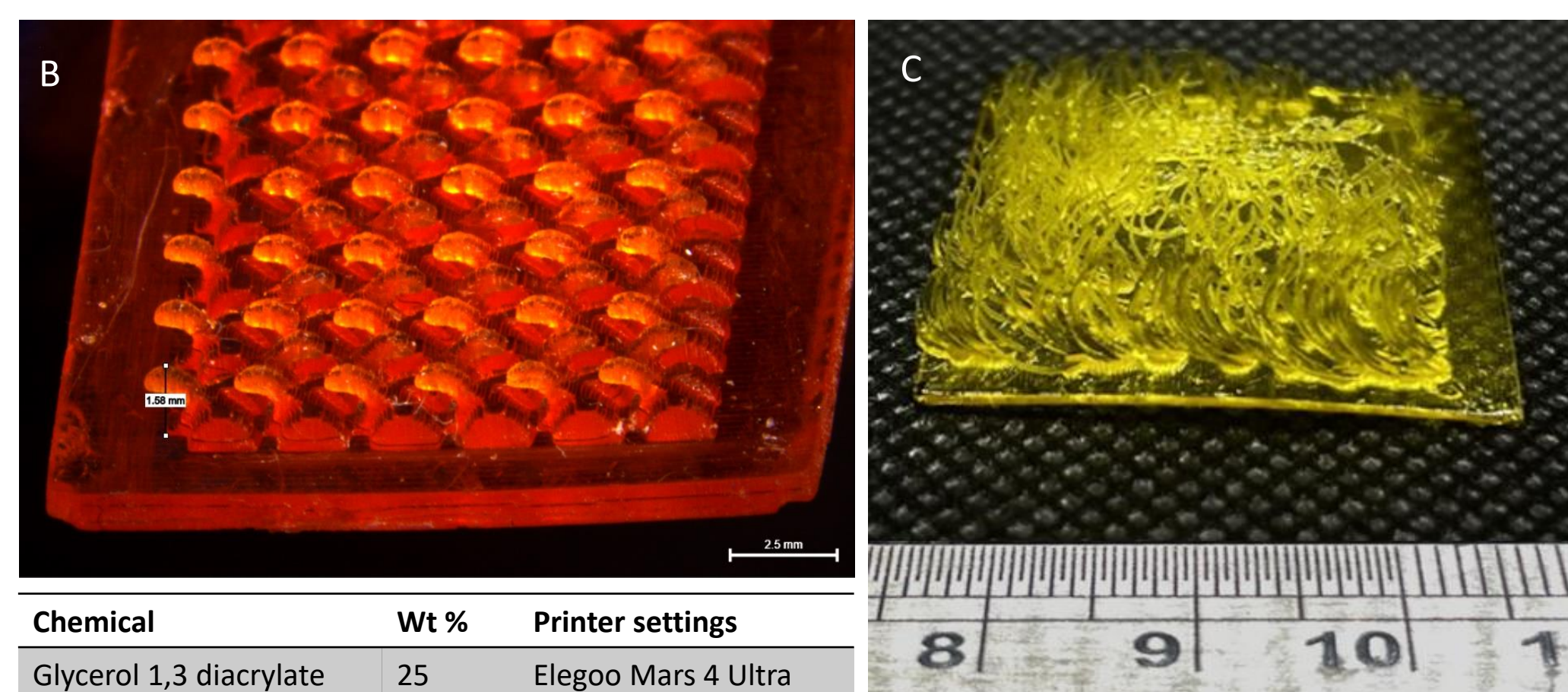
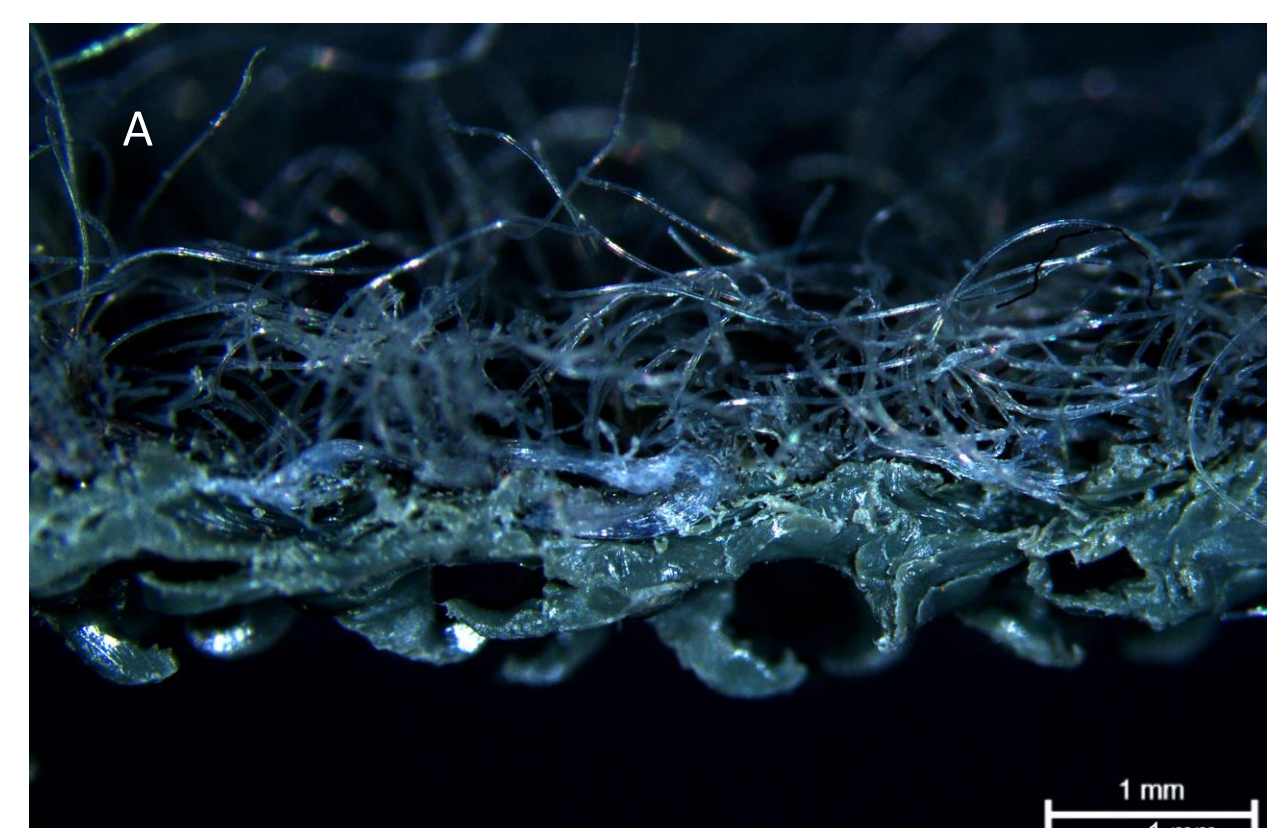


Figure 3, (A) Rook of PG4 – Acrylate 0.125 wt % (B) Validation matrix of PG4 – Acrylate 0.125 wt % (C) Boat of PG4 – MA 0.125 wt % (D) Rook of PG4 – MA 0.125 wt %

From the printability screening it can be seen that PG4 (meth)acrylates have better resolution than the PG6 analogues as they do not suffer from significant shrinkage/warping. The best performing resin in terms of printability and resolution was PG4 methacrylate with an MWCNT content of 0.125 wt % (Figure 3). These printed parts were shown to have pressure sensing capabilities as their conductivity increased with increasing pressure.

Results – Printing hooks and loops

Optical microscope images were taken of the desired Velcro (*Figure 4A*). Glycerol 1,3 diacrylate with the addition of PEGDA 250 and photo-absorber to increase printing resolution for hooks and loops. The preliminary results are shown below (*Figure 4B & 4C*).



Chemical	Wt %	Printer settings
Glycerol 1,3 diacrylate	25	Elegoo Mars 4 Ultra
PEGDA 250	73.95	Exp: 15s
Sudan I / Tartrazine	0.05	Base Exp: 30s
TPO	1	

Figure 4, (A) Optical microscope of Velcro hook and loops (B) SLA printed hooks (C) SLA printed loops. Table 3, Resin material for SLA Printed hooks and loops (Figure 4B and 4C)

Conclusion

Polyglycerol meth(acrylates) can be successfully used to produce intricate geometries using SLA. The resin system offers tuneable mechanical properties depending on the use (meth)acrylate systems. Additionally further functionalities can be added such as MWCNT to develop printed scaffolds with electrical conductivity.

Future work

1. Use of Micro Stereolithography (PμSL) to achieve required dimensions for hook and loop systems
2. Additional use of a crosslinker for increased flexibility of hook and loops
3. Active ingredient added along with release mechanisms investigated

References

1. Krumins, E., Lentz, J. C., Sutcliffe, B., Sohaib, A., Jacob, P. L., Brugnoli, B., Cuzzucoli Crucitti, V., Cavanagh, R., Owen, R., Moloney, C., Ruiz-Cantu, L., Francolini, I., Howdle, S. M., Shusteff, M., Rose, F. R. A. J., Wildman, R. D., He, Y., & Taresco, V. (2024). Glycerol-based sustainably sourced resin for volumetric printing. *Green Chemistry*, 26(3), 1345–1355.