UV-curable acryl-polyurethane for Human Compatible flexural 3D Printing structures

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Abstract

An acryl-functionalized urethane prepolymer series with various compositions were synthesized using polyethylene glycol (PEG) and hexamethylene diisocyanate (HDI). Optimizing blending formulation for human-compatible 3D printing structures was based on MTT assays for cytotoxicity. The MTT assay was used to determine the biocompatibility of acryl-urethane (AU) resin for mammalian HaCaT cells. In the case of polyol, the most important component of the resin, treatment with poly(tetramethylene ether) glycol (PTMG) and polycaprolactone diol (PCL) induced concentration-dependent cytotoxicity, whereas PEG showed no cytotoxic effect. AU resin was designed by the addition of 2-hydroxyethyl methacrylate (2-HEMA) as a suitable material for digital light processing (DLP) 3D printing. The optimizing photo-initiator and additive were selected by UV-spectroscopy. The formulation containing the UV-curable AU resin and photo-curable additives was exposed to 405 μm UV radiation to produce the 3D structures. The effects of the photo-initiator/multifunctional acrylate value and UV absorptive power on the 3D printing performance were evaluated in terms of the mechanical properties and dimensional resolution. The surface properties of the 3D structures were tuned by controlling the photo-initiator type and composition in the AU resin. The resolution quality of the 3D printed wearable bands showed distinct differences by UV curing time, viscosity, and exposure amount. Overall, this UV-curable AU resin can be a promising prepolymer for the DLP printing of flexible photo-resin for biocompatible and photo-curable applications.

What is 3D Printing ?

Definition

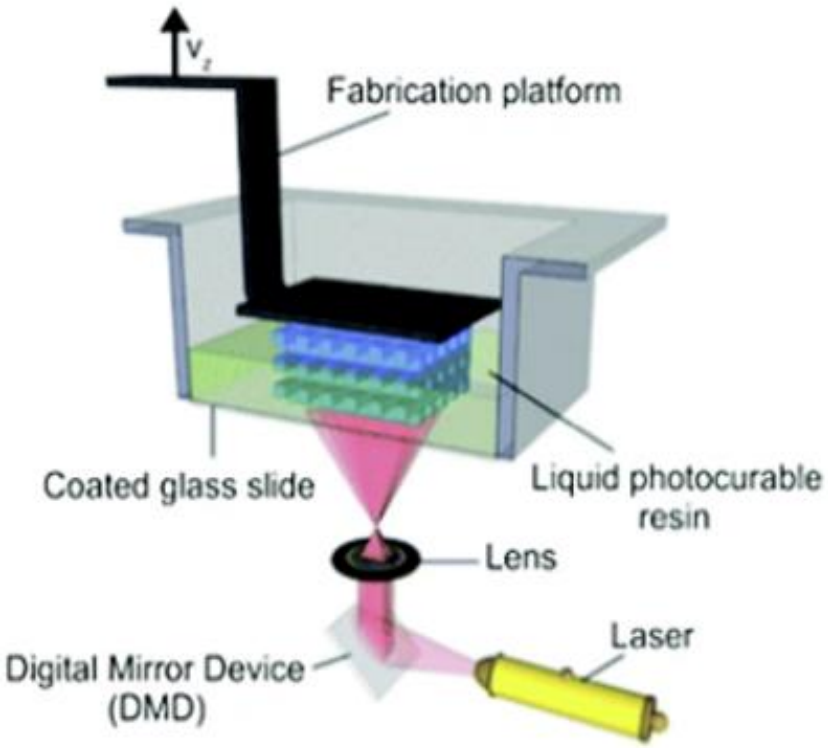
Process builds a three-dimensional object from a computer-aided design (CAD) model, usually by successively adding material layer by layer, which is also called additive manufacturing.

Modeling → Slicing → Printing → Finishing

Liquid	Filament	Powder	Sheet
SLA	FDM	SLS	LOM
DLP	MJM	3DP	
Polyjet			

Digital Light Processing (DLP)

DLP



- **Digital Light Processing**

  UV Curing

- **Elaborate printouts**
- **Fast printing speed**
- **Multiple products**
- **Miniaturization of product**
- **Expensive materials**
- **Resin toxicity**

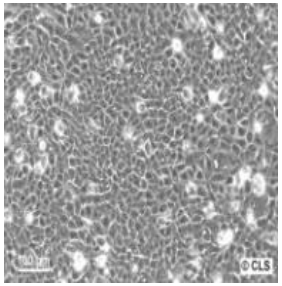
Cytotoxicity evaluation

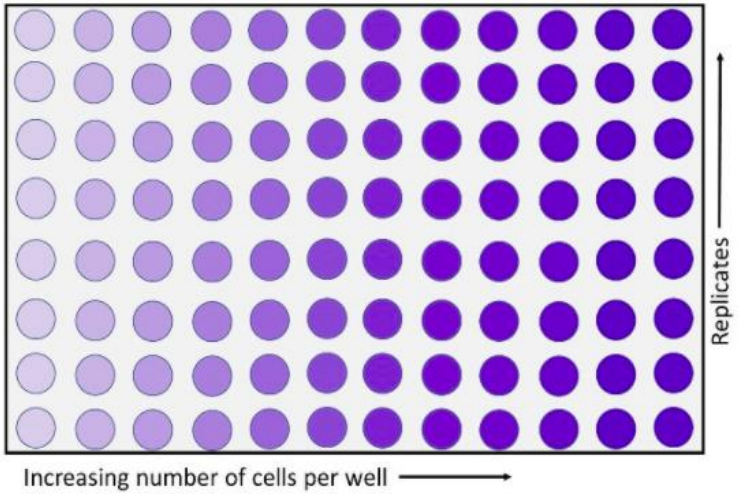
MTT Assay

☐ MTT Assay (ASTM E2149)

→ Human keratinocytes, HaCaT cells

-. Condition : DMSO, 37 ℃ , 5% CO_2

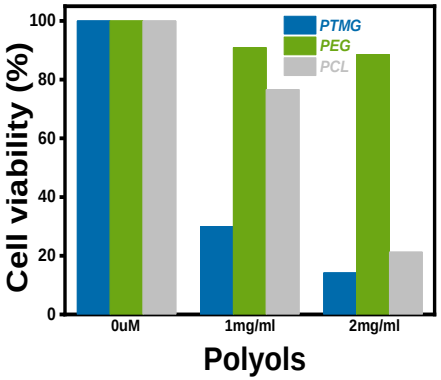


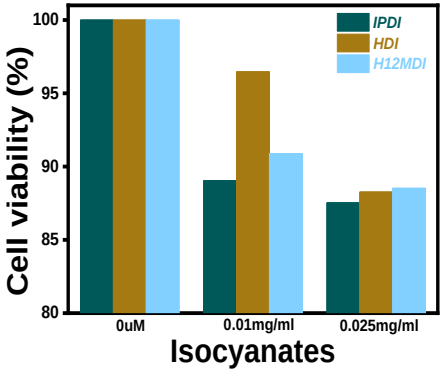


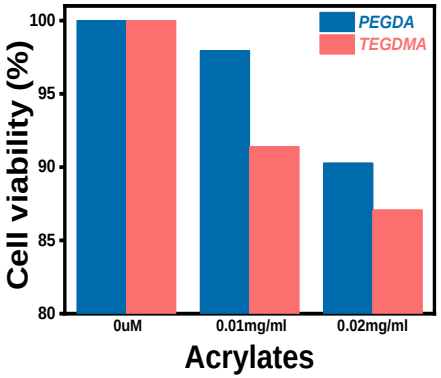
Materials

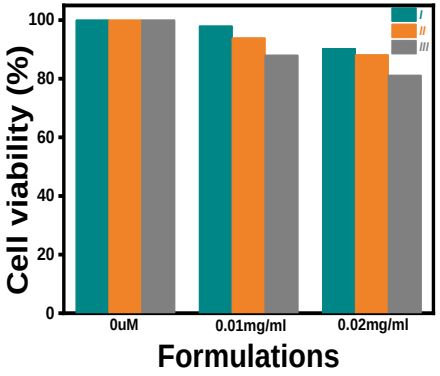
☐ Acryl-Urethane candidates

→ Polyol + Isocyanate + Acrylate



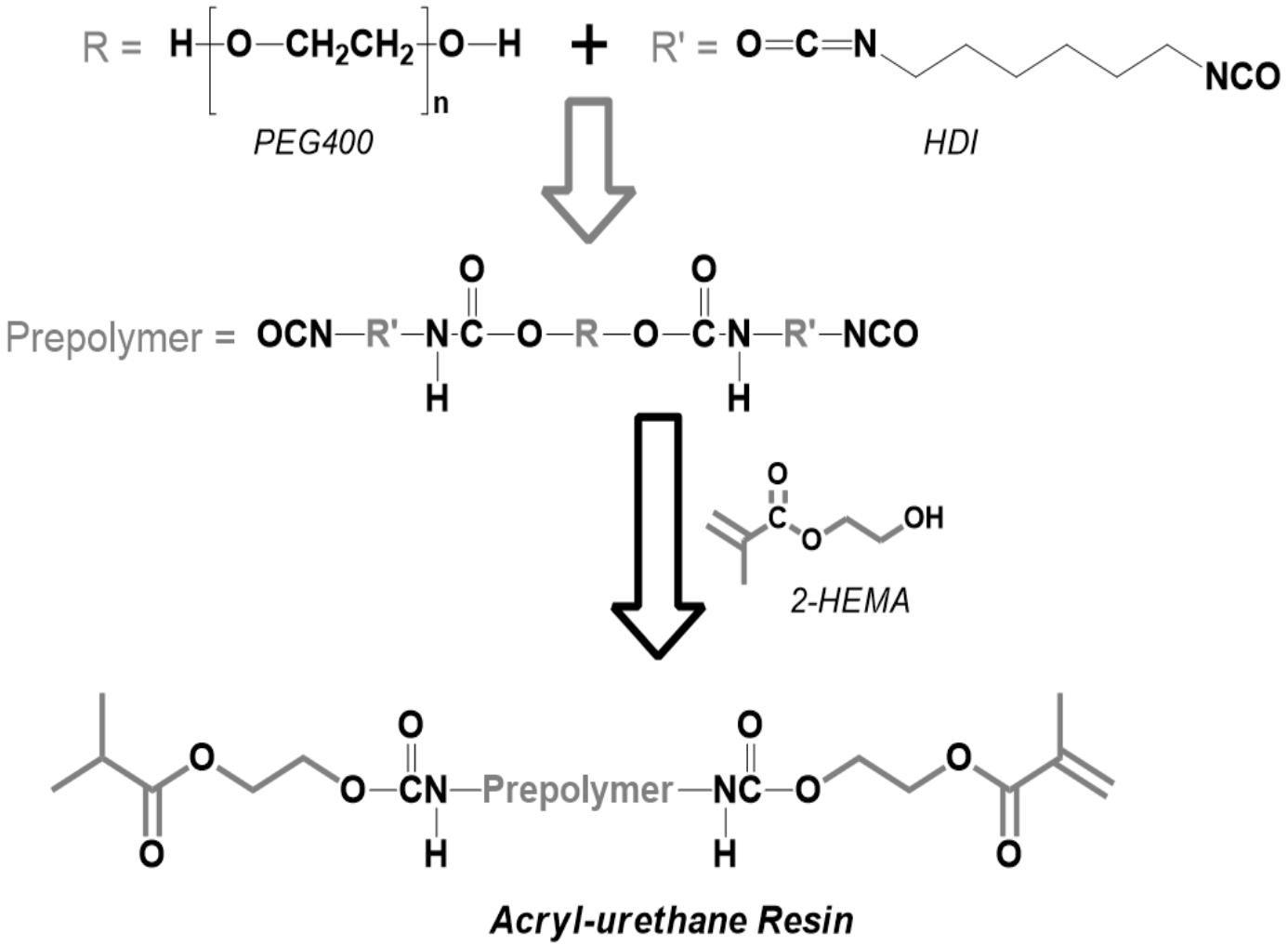






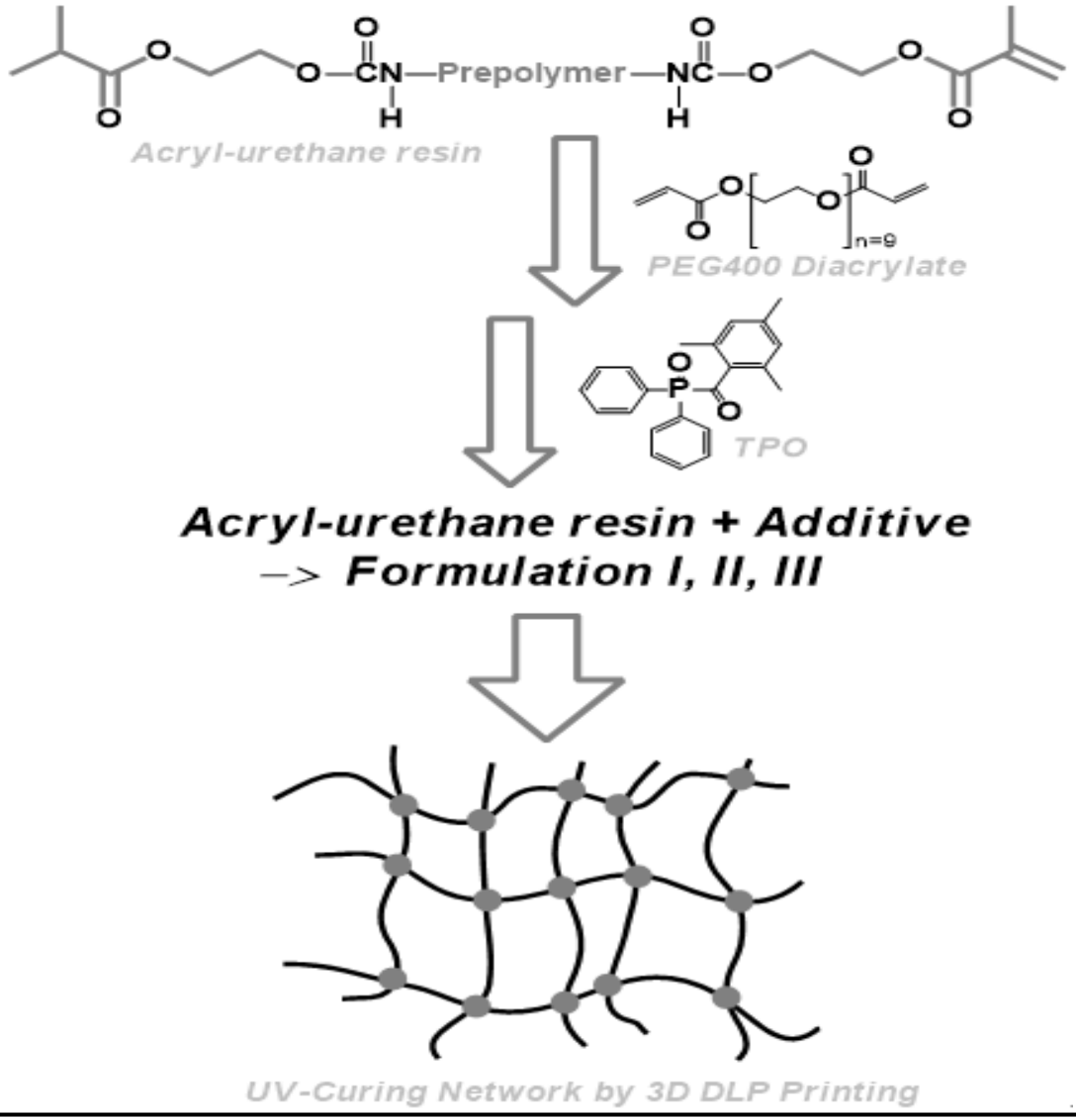
Synthesis of the acryl-urethane resin

Scheme



3D DLP printing process

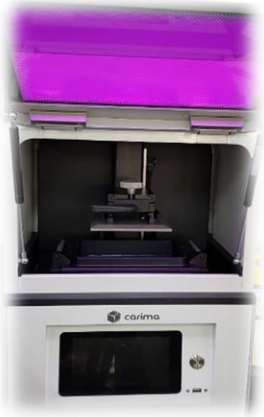
Scheme



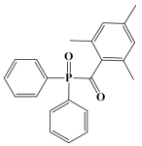
Optimization of 3D printing output conditions

DLP method (CARIMA IM2)

- **UV absorption** (Wavelength & Photoinitiator)



TPO



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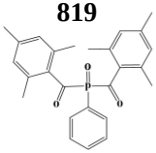
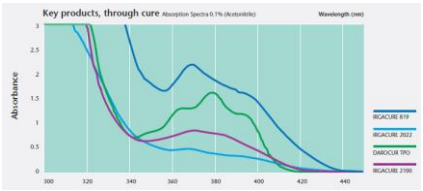
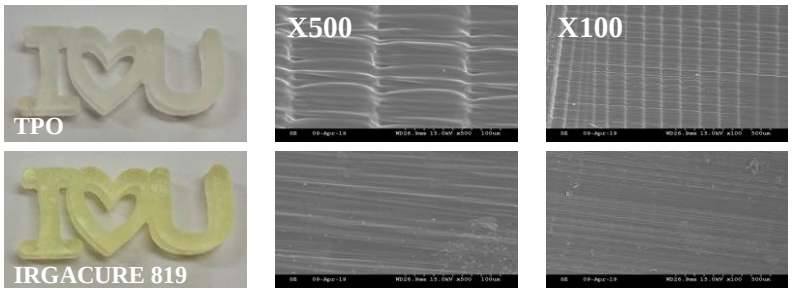




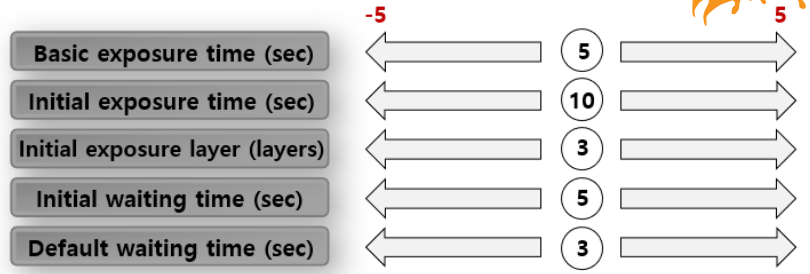
DLP Light source dominant wavelength band
: 385~405nm (→ Initiator selection)



Printing Condition

Critical Point

- **UV Energy** (Intensity & Tact time)

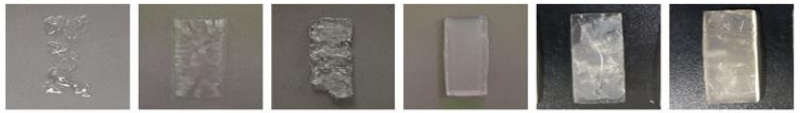


Exposure condition set-up according to time unit and light amount control

- Basic exposure time 5sec
- Initial exposure time 10sec
- Initial exposure layer 3layers
- Initial waiting time 5sec
- Default waiting time 3sec

Basic exposure time (sec)	3	4	4.5	**5**	10	15	30
Initial exposure time (sec)	5	5	5	**10**	15	30	60
printing	very bad	bad	not bad	**Good**	not bad	not bad	bad

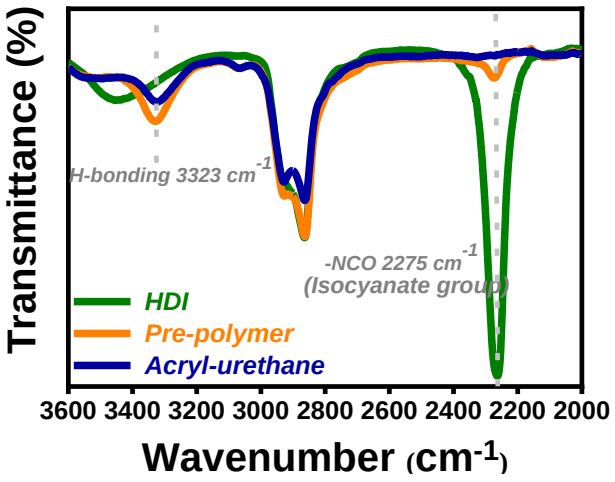
UV Energy (intensity, tact time)

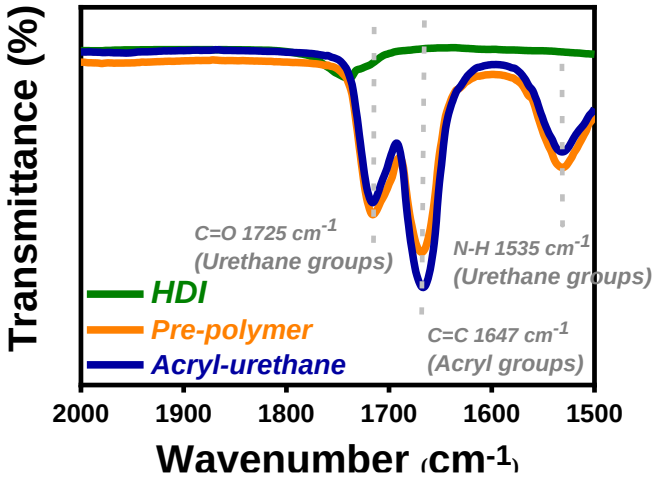


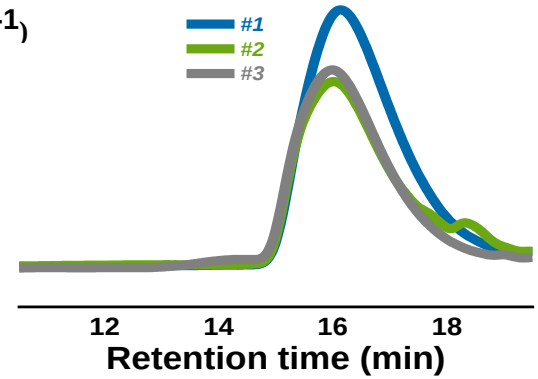
Synthesis Condition of Resin

Properties

☐ Synthesis Condition : FT-IR , GPC



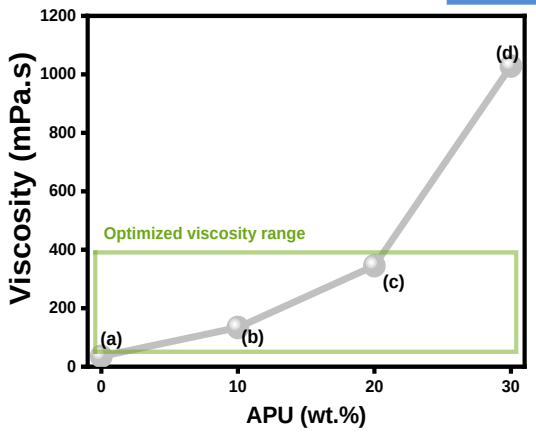


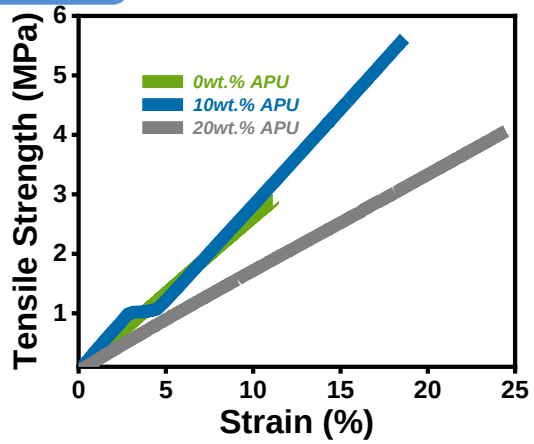


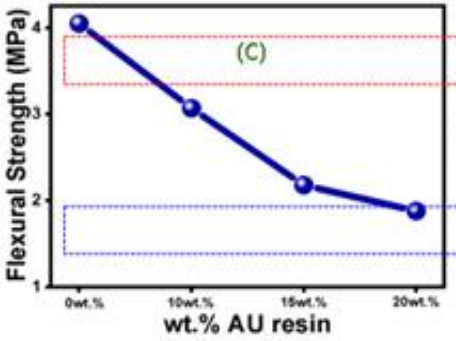
	M_n	M_w	PDI
Acryl-urethane #1	16073	26022	1.6
Acryl-urethane #2	16690	27004	1.6
Acryl-urethane #3	15316	24126	1.6

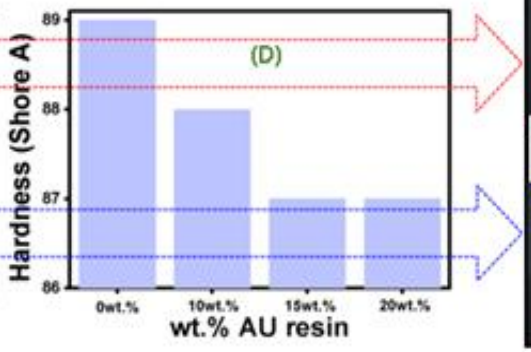
Mechanical properties of 3D architectures

Properties



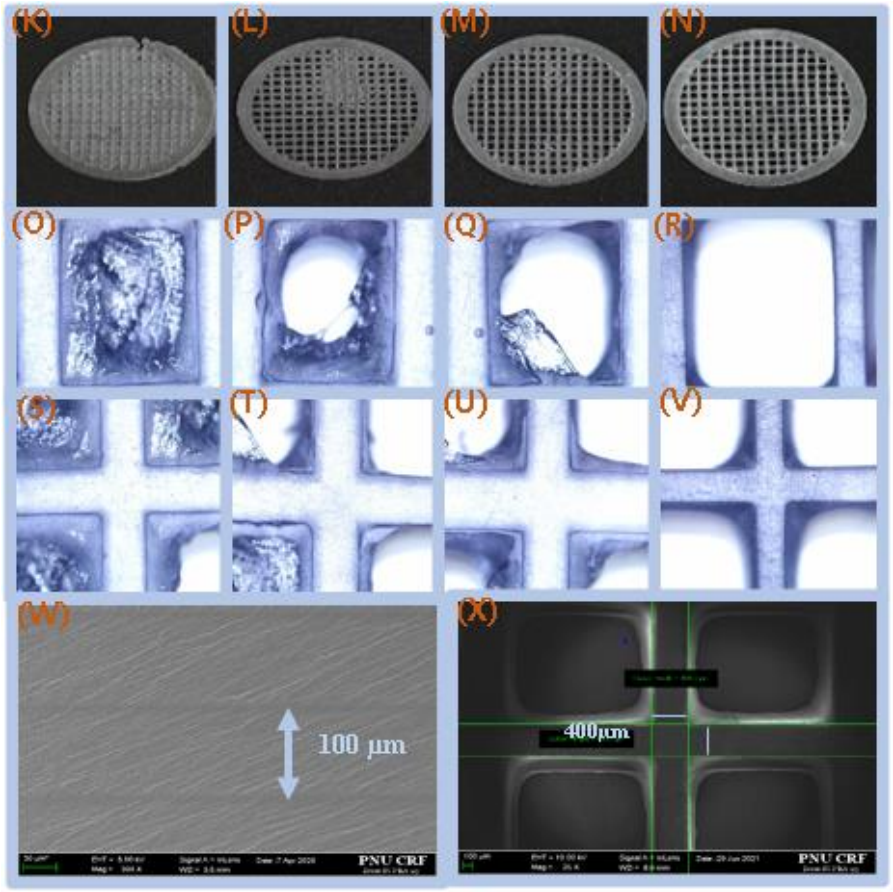






	Viscosity (mPa.s)	Stress (MPa)	Strain (%)	Hardness (Shore A)	Flexural Strength (MPa)
0wt. %	35.2	2.89	11.13	89	4.05
10wt. %	134.1	5.62	18.67	88	3.07
20wt. %	345.3	4.06	24.48	87	1.88

3D Printing procedure and SEM Images



Conclusion

Conclusion

- ☐ The successful synthesis acryl-urethane resin and UV-cured by DLP type 3D printer
- ☐ For biocompatibility, Resin was successfully formulated through cytotoxicity evaluation
- ☐ It showed excellent mechanical properties compared to the existing photocuring reference
- ☐ It was confirmed by SEM that the 3D printed structures were stacked well, and optimal exposure conditions were found
- ☐ With 3D Printing resin considering biocompatibility, more diverse applicability can be confirmed

Acknowledgement

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