Fabrication of Photo-curable Polyurethane-Acrylate for 3D Printing based on Viscosity and UV Curing time

WonBin Lim, Ji-Hong Bae, Chanhyuk Jee, Byung Joo Kim,
Jin Gyu Min, Chang Min Seo, PilHo Huh*
Department of Polymer Science and Engineering, Pusan National University,
Busan 609-735, South Korea

***** *pilho.huh@pusan.ac.kr***

Abstract

Nowadays, 3D printers have been undergone much attention in all fields of industry. The photo-curing resins which ranging from rigid to flexible, are successfully prepared using the synthesis of Polyurethane-Acrylate. It will be used for according to the application through the measurement of flexural strength and hardness. The intrinsic viscosity of the photo-curable monomer and polymer is measured to target the molecular weight of the material. The photo-curing polymer is produced through physical or chemical reaction, and the curing time and physical properties of the material are adjusted according to the purpose. It can be controlled the ratio of the photo initiator and polymer. For example, Thermoplastic polyurethane (TPU) series based on polyethylene glycol(PEG) as a polyol and hexamethylene diisocyanate (HDI) as a isocyanate were synthesized as a function of molecular weight formulation. After that, PU-acryl will be synthesized by attaching hydroxyethyl-methacrylate(HEMA) and used for DLP 3D printing by controlling the content ratio of photo-initiator and addition multifunctional acrylate.

What is 3D Printing ?

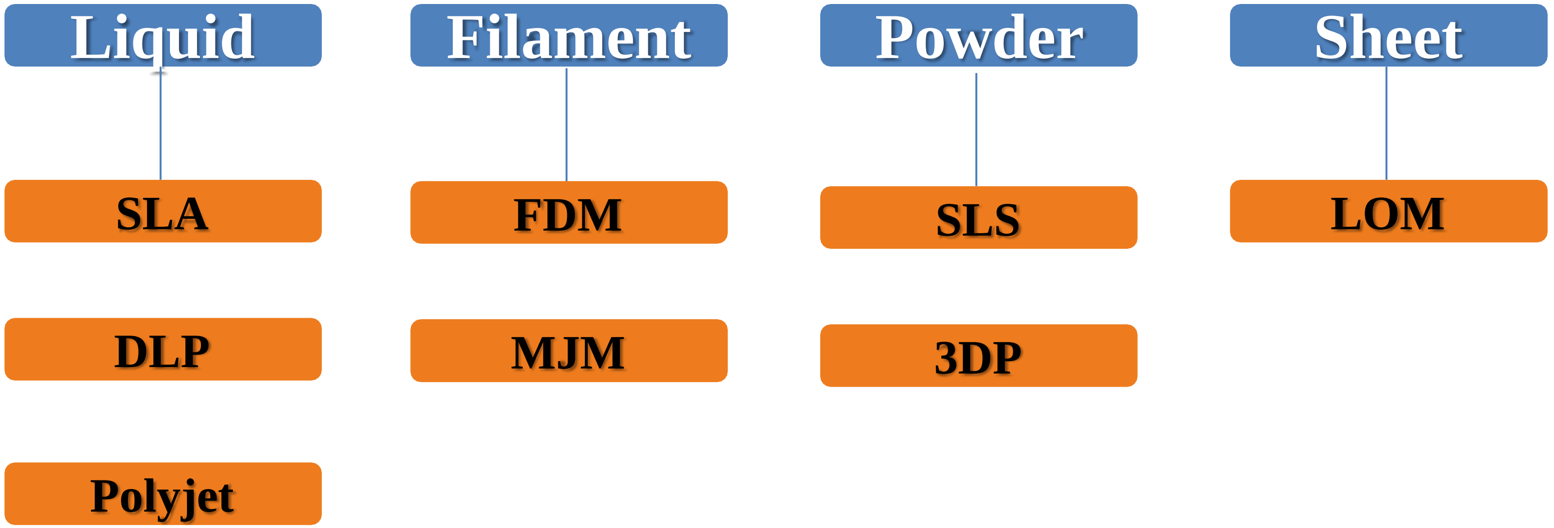
Definition

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.

Materials

- **Plastics : Nylon, Polyamide, PLA, ABS, Thermoplastic Polyurethane etc.**
- **Resins : CLIP, CE- Cyanate Ester, Prototyping Acrylate etc.**
- **Multicolor(composite material)**
- **Metals : Aluminium, Cobalt, Stainless, Titanium**

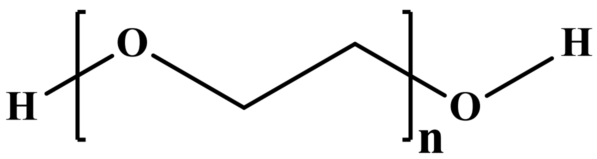
Classification of 3D printing according to methods and materials



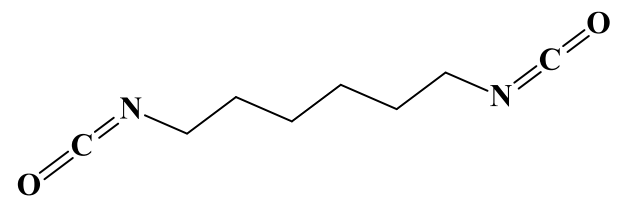
Experimental

Materials

- Polyol : PEG(Polyethylene glycol)

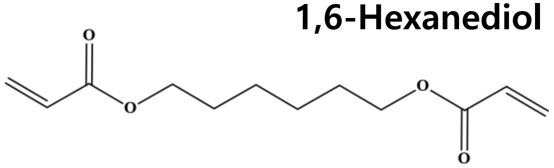


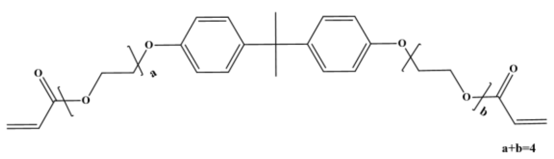
- Isocyanate : HDI(Hexamethylene diisocyanate)



- Acrylate :

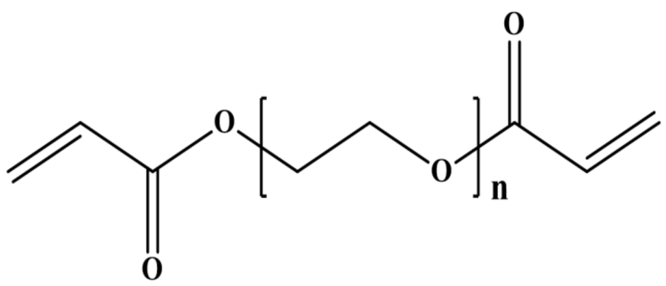
1,6-Hexanediol Diacrylate





Bisphenol A $(EO)_4$ Diacrylate

- Addition Acrylate :
  PEG(Polyethylene glycol) Diacrylate

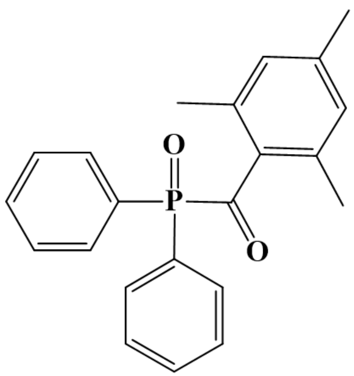


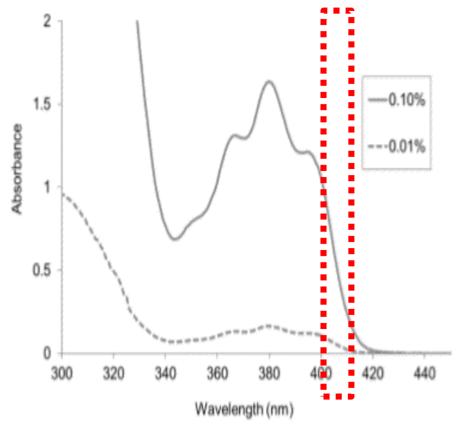
Experimental

Photo Initiator

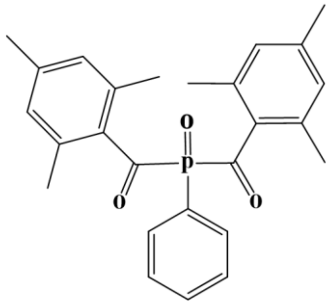
DLP(Digital Light Processing)

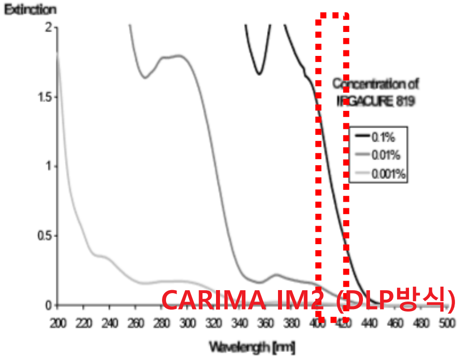
- TPO : Diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide





- IRGACURE 819 : Bis(2,4,6-trimethylbenzoyl)-phenylphosphineoxide)





CARIMA – IM2

Wavelength: 385~405nm

Design of 3D Printing materials

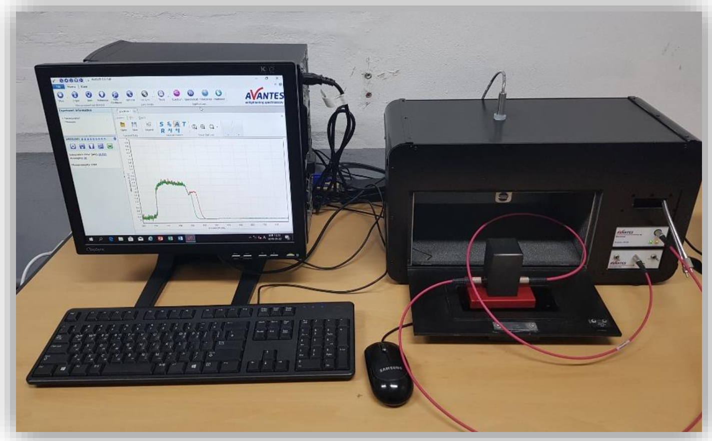
☐ UV absorbance

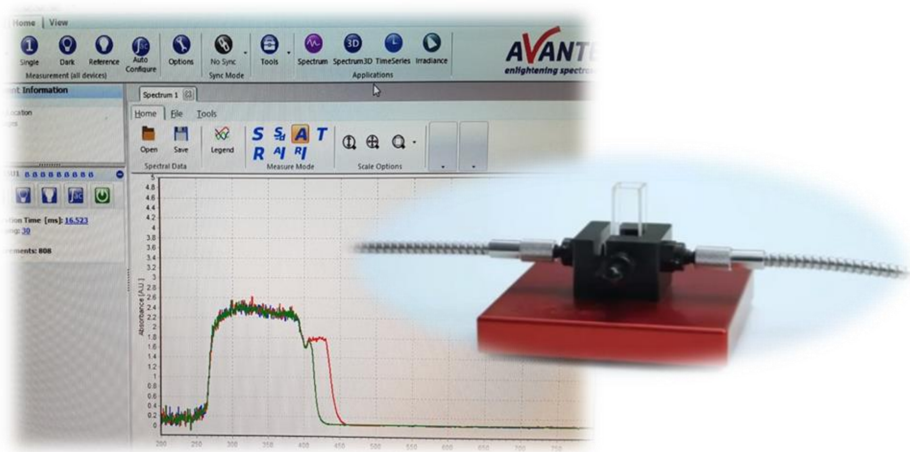
- **Spectrometer :** AvaSpec-2048L
- **light source :** AvaLight-DHc
- **Sampling kit :** Cuvette holder

Analysis of Monomer

Analysis of Additive

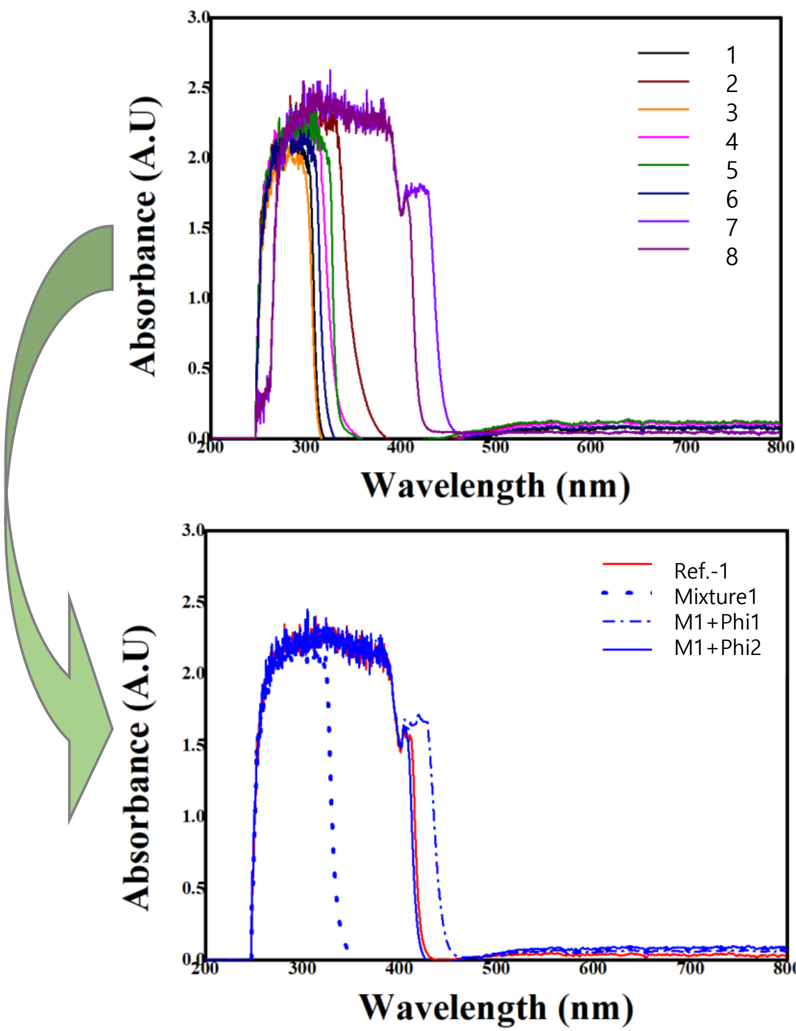
Reference vs. New Design Material





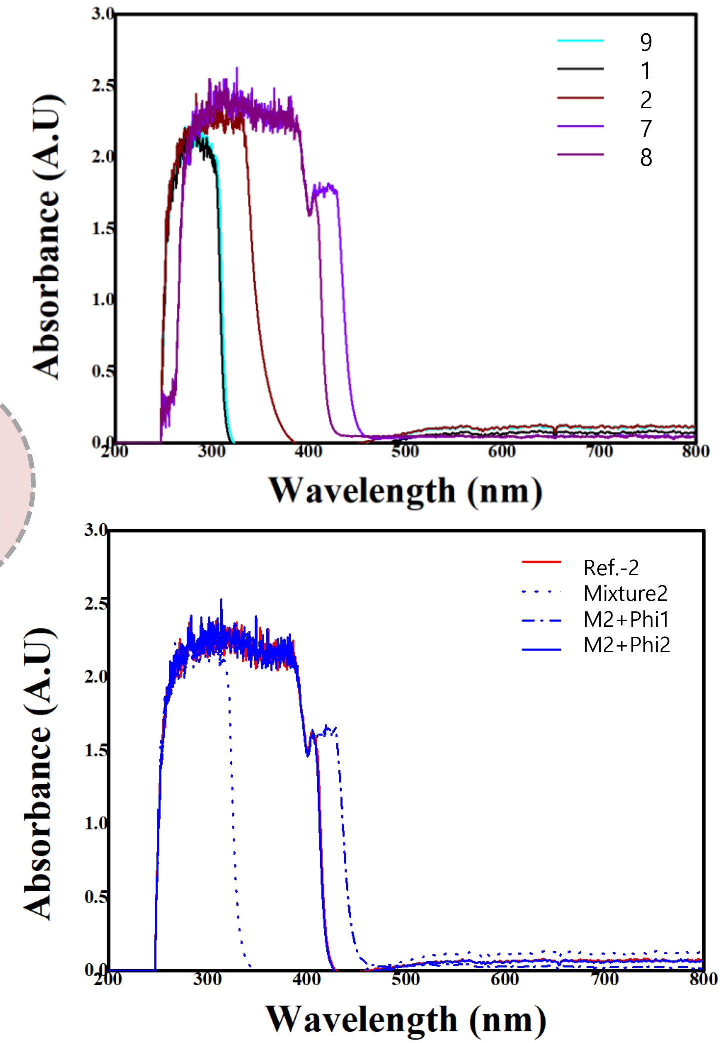
Design of 3D Printing materials

New Material 1



Target wavelength 385~405nm

New Material 2



Analysis of Viscosity

LAMY RM 100 PLUS CP2000

	CONDITION
SHEAR RATE	$50s^{-1}$
DURATION	60sec
TEMPERATURE	25℃

VISCOSITY

SAMPLE	VISCOSITY
M1	435.8mPa.s
M2	297.2mPa.s
Reference	139mPa.s
M1+Phi1	**104mPa.s**
M1+Phi2	**89.7mPa.s**
M2+Phi1	**87.4mPa.s**
M2+Phi2	**82.7mPa.s**

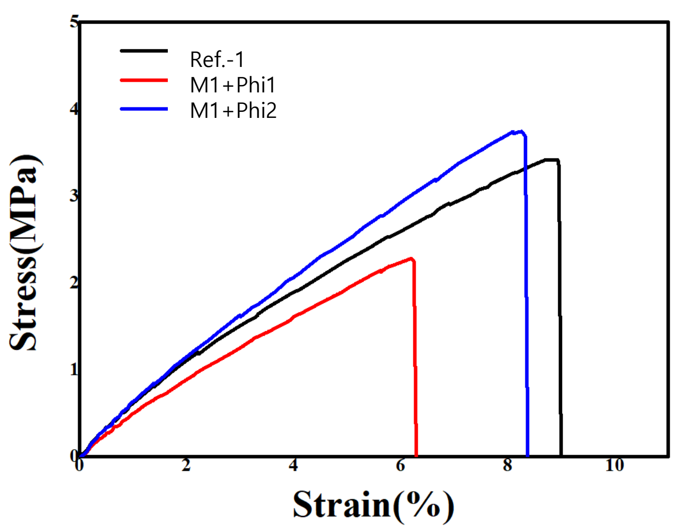
Analysis of UTM

□ Young's Modulus

- New Material-1: Ref. vs. [w/Phi2] Stress 9.6%↑ / Strain 7.5%↓
- New Material-2: [w/Phi1] Stress 434.5%↑ / Strain 13.9%↓

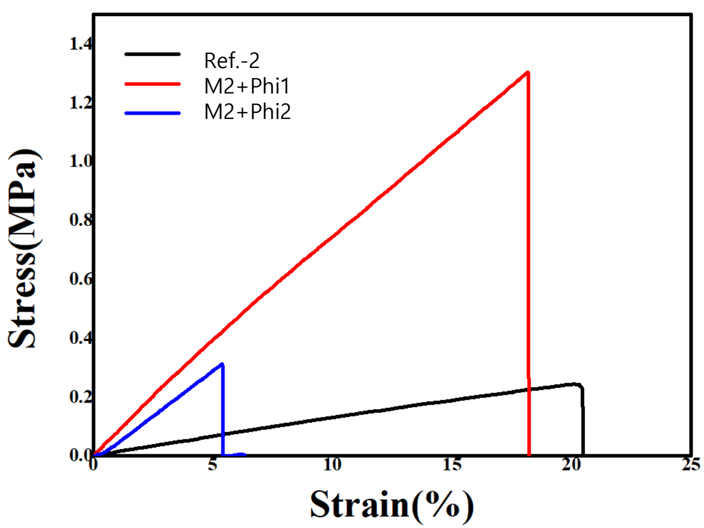
New Material-1

	Young's Modulus (Mpa)	Maximum Stress (Mpa)	Percent Strain(%)
Ref.-1	0.3820	3.4150	8.9376
M1+Phi1	0.3682	2.2814	6.1957
M1+Phi2	0.4531	3.7441	8.2632

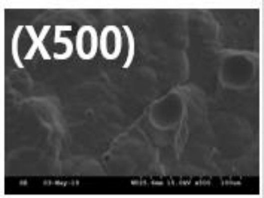
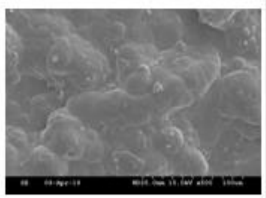
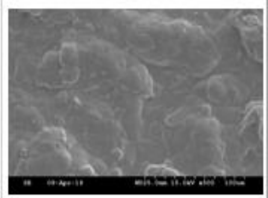
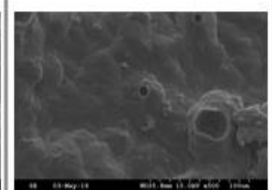
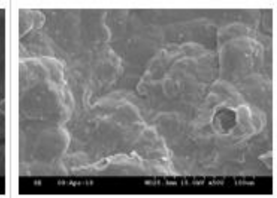
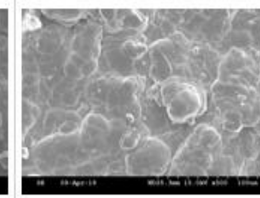
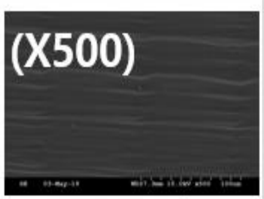
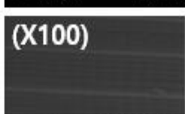
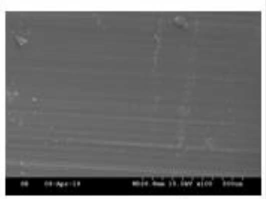
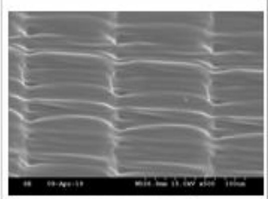
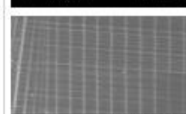
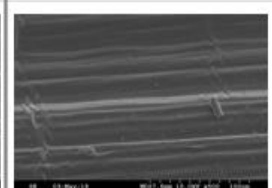
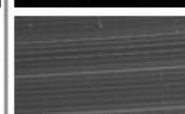
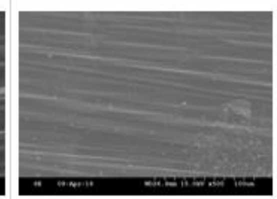
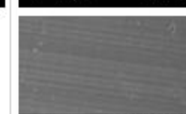
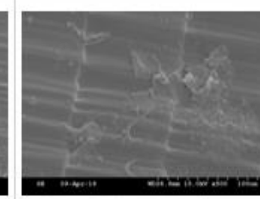
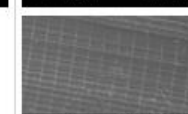


New Material-2

	Young's Modulus (Mpa)	Maximum Stress (Mpa)	Percent Strain(%)
Ref.-2	0.0110	0.2440	21.4020
M2+Phi1	0.0700	1.3041	18.4270
M2+Phi2	0.0490	0.3121	6.3289



Analysis of SEM

	New Material 1			New Material 2		
	Ref.-1	M1		Ref.-2	M2	
		Phi1	Phi2		Phi1	Phi2
Properties	○	◎	○	○	◎	○
Sticky	△	○	○	△	○	○
Sample						
Front						
side	 	 	 	 	 	 

Conclusions

- The successful synthesis Acryl-polyurethane and UV-cured by the photo-initiator
- The special optical properties of the Acryl-polyurethane after UV-curing
  (UV transmittance : 83 to 90%)
- The increase of percentage strain and tensile strength after UV-curing
- The thermal properties were measured using DSC
  (T_g =-52°C, T_m =199°C)
- To demonstrate potential applications of 3D printer materials

Acknowledgement

This work was supported by the National Research Foundation of Korea(NRF)
(No. NRF-2019R1A2C1087953)