Synthesis of photo-activating acryl-polyurethane containing multifunctional monomer for high strength and biocompatible 3D printing materials

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Abstract

A UV curable acryl-polyurethane is successfully prepared by a combination of poly(tetramethylene ether) glycol (PTMG) and 1,4-butanediol (1,4-BD) as polyols, 4,4'-methylene bis(phenylisocyanate) (MDI) as an isocyanate, pentaerythritol triacrylate and triethyleneglycol dimethacrylate (TEGDMA) as multifunctional monomers and benzophenone was used to photoinitiator for UV curing to optimize the physical property of the 3D structure. The crosslinking step of acryl-polyurethane elastomers were processed using the exposure to 385~405nm UV radiation. The structure of the resulting acryl-polyurethane was evaluated by fourier transform infrared spectroscopy (FT-IR), gel permeation chromatography (GPC). The tunable UV absorbance of acryl-polyurethane was adjusted through the material design. The mechanical properties such as tensile strength, elongation and modulus were evaluated by universal testing machine. And flexural strength and hardness were measured by durometer and ISO test machine. The surface resolution-quality of the 3D structure was analyzed by field emission scanning electron microscope (FESEM).

3D Print

- Definition: processes used to create a three-dimensional object in which layers of material are formed under computer control to create an object

- Materials of 3D printing

  -Plastics : Polyamide(PA), ABS, PLA, Thermoplastic Polyurethane etc.

  -Resins : CLIP, CE- Cyanate Ester, Prototyping Acrylate etc.

  -Multicolor(composite material)

  -Metals

- Many Applications:

  Medical - Bio-printing, Medical devices, Pills

  Industry - Aerospace, Car's body, Architectures, Apparel etc.

Amman Girrbach Group
Align Techology
Dentwise

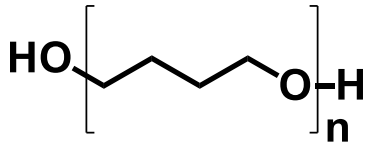
Materials of 3D printing & classification according to output method

Binder Jetting	3DO(CJP) Ink-jetting S-printer M-printer	Combined by spraying the powder material and adhesive → Metal, polymer, ceramic
Material Jetting	Polyjet Ink-jetting MJP	Spray liquid material through printing nozzle and cure with ultraviolet → Polymer, wax
Material Extrusion	FDM (FFF)	Form objects with nozzles using heat on solid materials → Polymer, wood
Direct Energy Deposition	Direct Metal Deposition Laser Deposition Electro Bea Direct Melting	Form materials by directly depositing or melting materials with a laser or electron beam → Metal (powder), wire
Powder Bed Fusion	DMLS (DMP) SLM EBM SLS	Placing powder material on the bed and selectively melting by irradiating laser or electron beam → Metal, polymer, ceramic
Photo Polymerization	SLA DLP	Curing liquid materials by light and laser irradiation → Polymer, ceramic

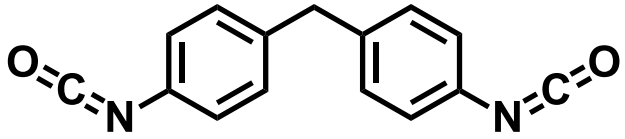
Experimental

- Materials

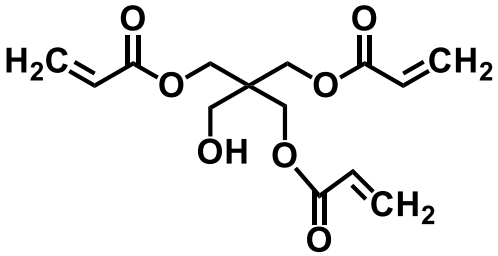
-Polyol : PTMG (poly(tetramethylene ether) glycol)



-Isocyanate : MDI (methylene diphenyl diisocyanate)

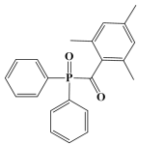


-Acyrlate : Pentaerythritol triacrylate



- UV crosslinker

TPO



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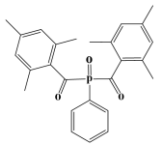
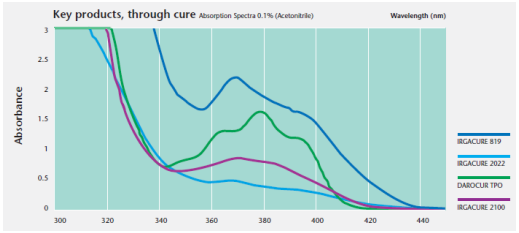
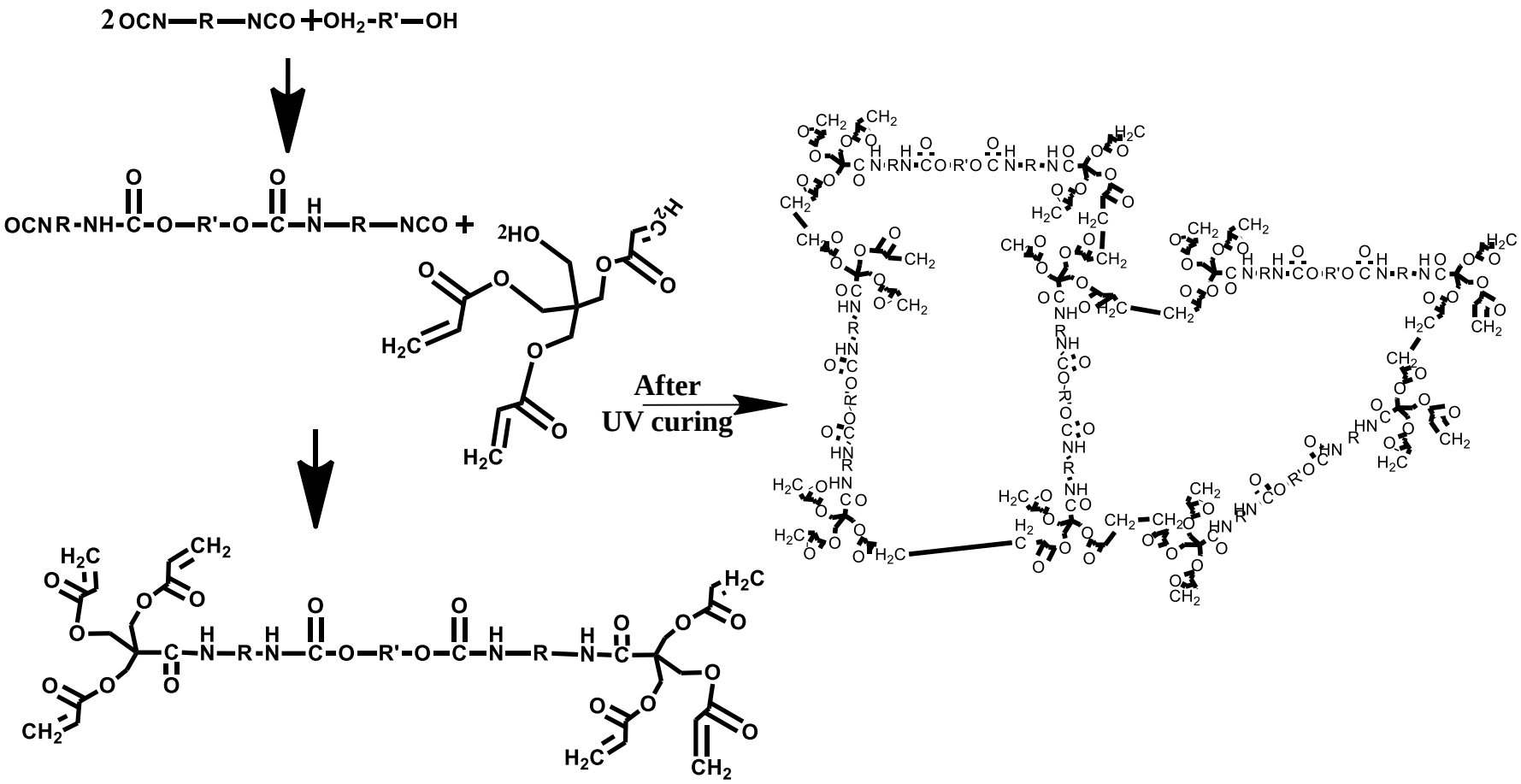




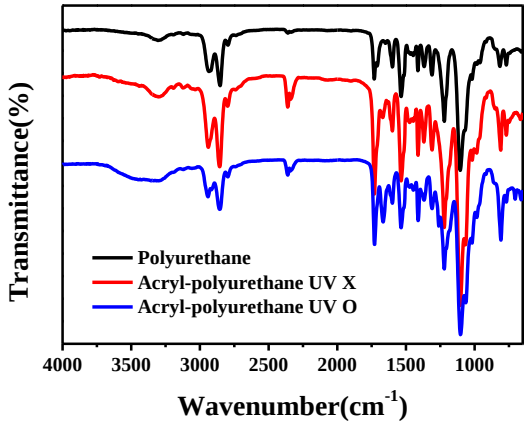
Scheme

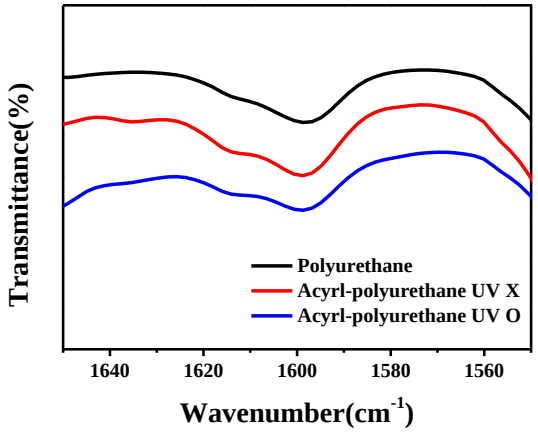


Analysis of FT-IR & GPC

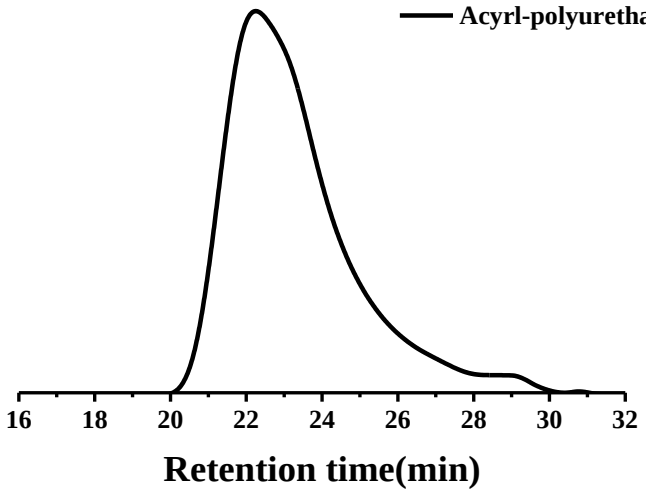
-. PU → Acryl-polyurethane : Appear of functional peak CC double bond around 1620cm^{-1}

-. Before and After UV : Reduce of functional peak CC double bond around 1620cm^{-1} and intermolecular crosslinked by UV-curing





	M_n	M_w	PDI
Acryl-polyurethane	10200	27320	2.68

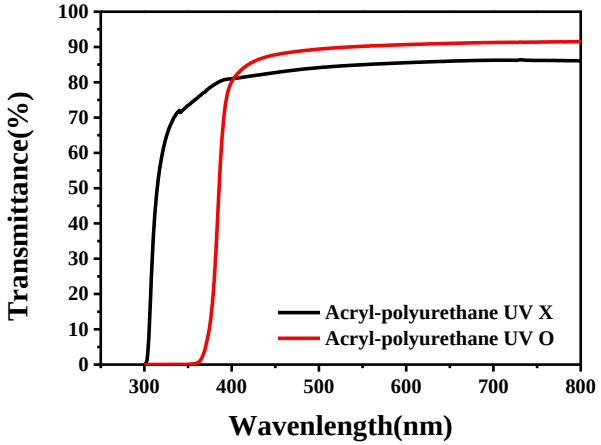


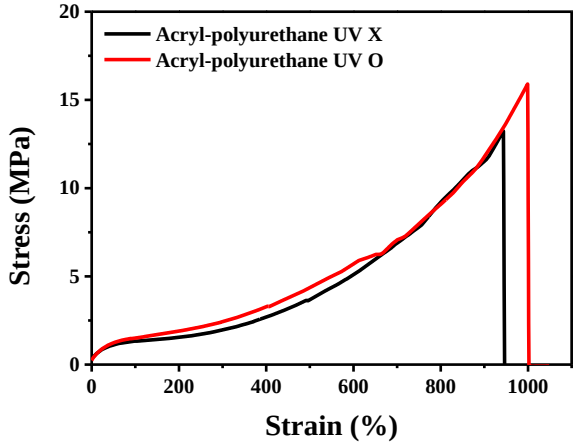
Analysis of UV Transmittance & UTM & DSC

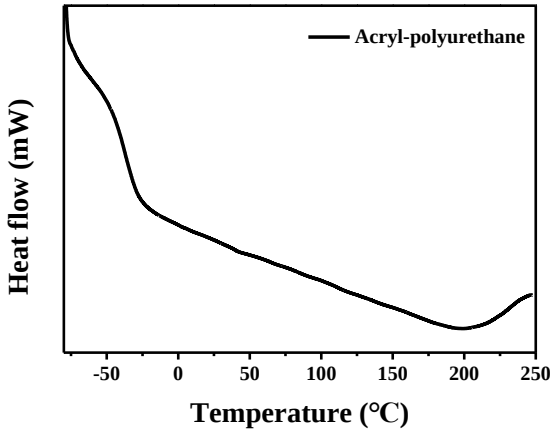
-. UV-Transmittance was increased at 550nm as the increasing amorphous parts after UV-curing

-. Increase of stress and strain after UV-curing

-. T_g was measured -52°C, T_m was measured 199°C







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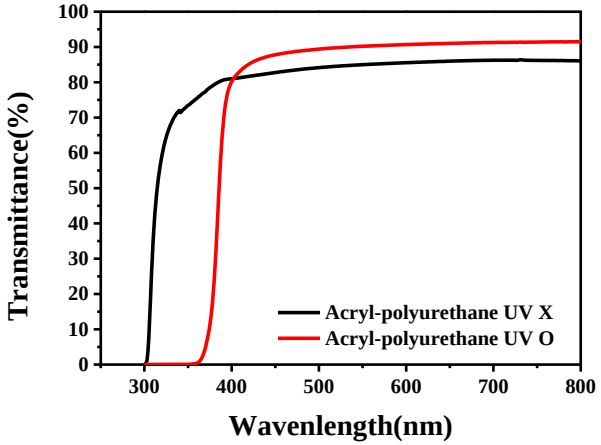
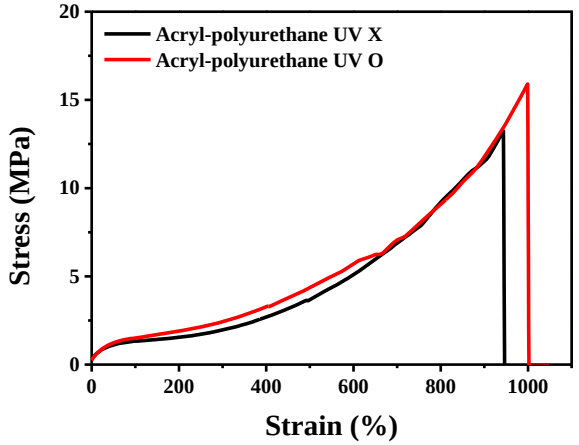
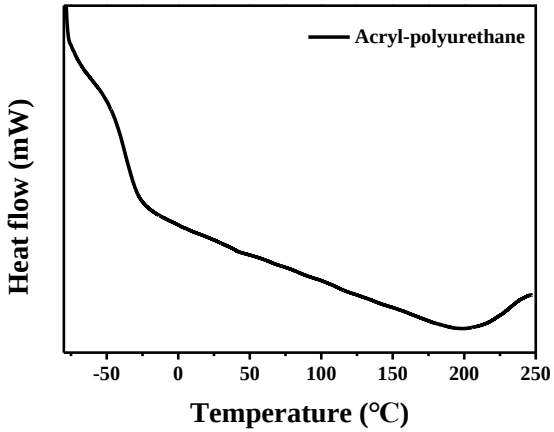
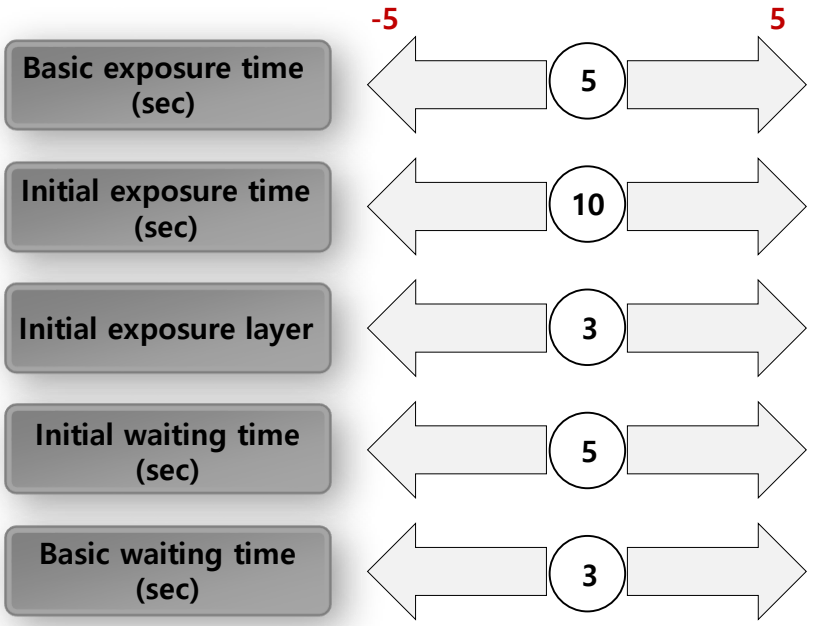
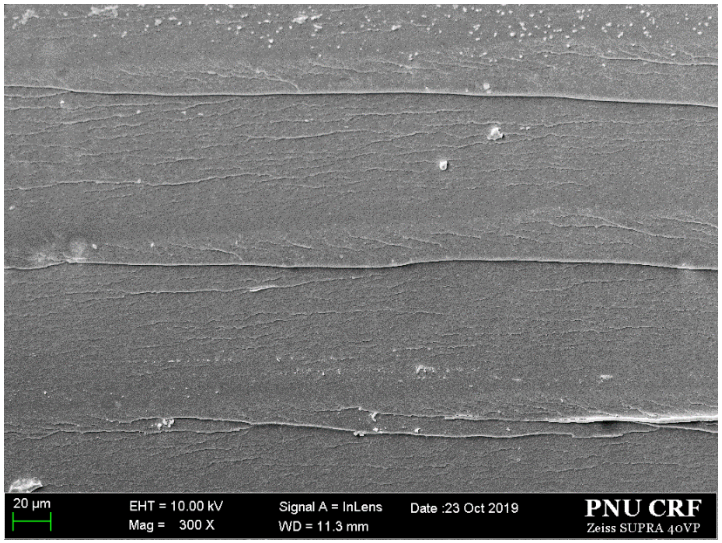






Analysis of FESEM





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

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