ACCSCIENCE PUBLISHING

Materials Science in Additive Manufacturing

ORIGINAL RESEARCH ARTICLE

Development of a washable and antistatic waterborne polyurethane acrylate for dual photo-thermal curing vat photopolymerization three-dimensional printing

Supplementary File

1. Methods

1.1. Synthesis of hexamethylene diisocyanate–waterborne polyurethane acrylate prepolymer

The WBPUA prepolymer was synthesized via a three-step route, as illustrated in Figure S1. In the first step, hexamethylene diisocyanate (HDI; 33.6 g) and dibutyltin dilaurate (DBTDL; 0.12 g, catalyst) were added to a 500 mL four-necked flask equipped with a mechanical stirrer, reflux condenser, thermometer, and constant-pressure dropping funnel. The mixture was slowly heated to 60 °C, and pre-dried polypropylene glycol (PPG_{1000}; 100 g) was added dropwise. The reaction proceeded for two hours after the addition, yielding a polyurethane prepolymer (PPU). In the second step, 2,2-dimethylolpropionic acid (DMPA; 6.7 g, dissolved in ethyl acetate) was introduced into the system, and the temperature was raised to 70 °C for a further three-hour reaction to obtain a waterborne polyurethane prepolymer (WPPU). In the third step, the system was cooled to 60 °C, and the blocking agent 2-(tert-butylamino)ethyl methacrylate (t-BEMA, 55.5 g) was added dropwise, followed by a two-hour reaction. The temperature was then reduced to 40 °C, and excess triethylamine (TEA) was added over 0.5 hours to neutralize the mixture. Ethyl acetate was removed by rotary evaporation, affording the WBPUA. The variation of –NCO groups during the reaction was monitored via the acetone-di-n-butylamine titration method. Complete blocking was confirmed when the –NCO content remained constant.

1.2 Synthesis of 4,4′-dicyclohexylmethane diisocyanate–waterborne polyurethane acrylate prepolymer

The WBPUA prepolymer was synthesized via a three-step procedure following the synthetic route shown in Figure

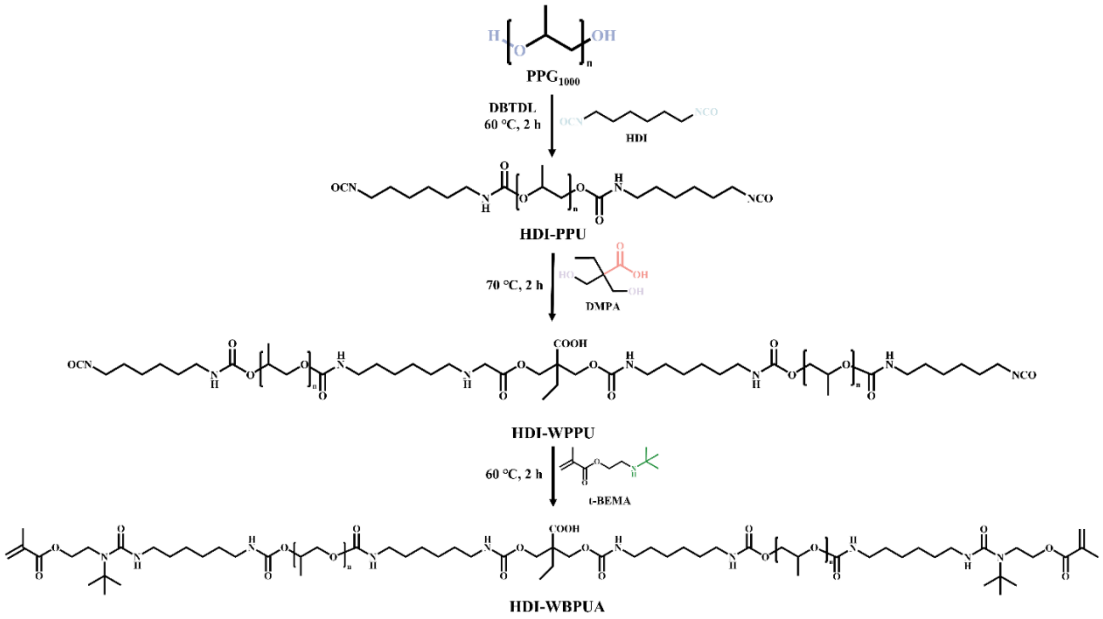

Figure S1. Preparation of hexamethylene diisocyanate–waterborne polyurethane acrylate (HDI–WBPUA)

S2. In the first step, 4,4'-dicyclohexylmethane diisocyanate (HMDI; 52.6 g) and DBTDL (0.12 g, catalyst) were placed into a 500 mL four-necked flask equipped with a mechanical stirrer, reflux condenser, thermometer, and constant-pressure dropping funnel. The mixture was gradually heated to 60 °C, and pre-dried PPG_{1000} (100 g) was added dropwise. The reaction was maintained for two hours after the addition, yielding a PPU. In the second step, DMPA (6.7 g, dissolved in ethyl acetate) was added to the reaction system, and the temperature was increased to 70 °C for an additional three hours of reaction to obtain a waterborne polyurethane prepolymer (WPPU). In the third step, the system was cooled to 60 °C, and the blocking agent 2-(tert-butylamino)ethyl methacrylate (t-BEMA; 55.5 g) was slowly added dropwise, followed by a two-hour reaction. The temperature was further reduced to 40 °C, and excess TEA was added over 0.5 hours to neutralize the mixture. Ethyl acetate was removed by rotary evaporation to afford the WBPUA. The change in –NCO group content during the reaction was monitored by the acetone-di-n-butylamine titration method. Complete blocking was confirmed when the –NCO content remained constant.

1.3. Synthesis of 4,4'-methylenediphenyl diisocyanate–waterborne polyurethane acrylate prepolymer

The WBPUA prepolymer was synthesized via a three-step route, as shown in Figure S3. In the first step, 4,4'-methylenediphenyl diisocyanate (MDI; 50.1 g) and DBTDL (0.12 g, catalyst) were added into a 500 mL four-necked flask equipped with a mechanical stirrer, reflux condenser, thermometer, and constant-pressure dropping funnel. The mixture was slowly heated to 60 °C, and pre-dried PPG_{1000} (100 g) was added dropwise. The reaction proceeded for two hours after addition to yield PPU. In the second step, DMPA (6.7 g, dissolved in ethyl acetate) was introduced, and the temperature was raised to 70 °C for a further three-hour reaction to obtain a WPPU. In the third step, the system was cooled to 60 °C, and the blocking agent t-BEMA (55.5 g) was added dropwise, followed by a two-hour reaction. The temperature was then reduced to 40 °C, and excess TEA was added over 0.5 hours to neutralize the mixture. Ethyl acetate was removed by rotary evaporation, affording the WBPUA. The variation of –NCO content during the reaction was monitored by the acetone-di-n-butylamine titration method. Complete blocking was confirmed when the –NCO content remained unchanged.

1.4. Synthesis of toluene-2,4-diisocyanate–waterborne polyurethane acrylate prepolymer

The WBPUA prepolymer was synthesized via a three-step procedure following the synthetic route shown in Figure S4. In the first step, toluene-2,4-diisocyanate (TDI; 34.8 g) and DBTDL (0.12 g, catalyst) were placed into a 500 mL four-necked flask equipped with a mechanical stirrer, reflux condenser, thermometer, and constant-pressure dropping funnel. The mixture was gradually heated to 60 °C, and pre-dried PPG_{1000} (100 g) was added dropwise. The

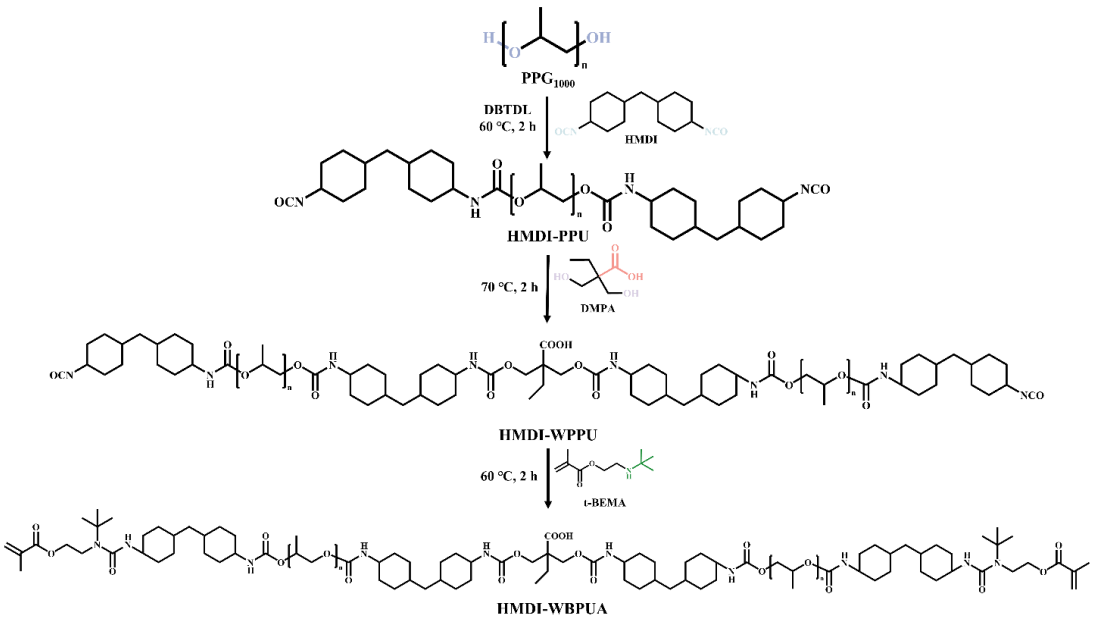

Figure S2. Preparation of 4,4'-dicyclohexylmethane diisocyanate (HMDI)–waterborne polyurethane acrylate (WBPUA)

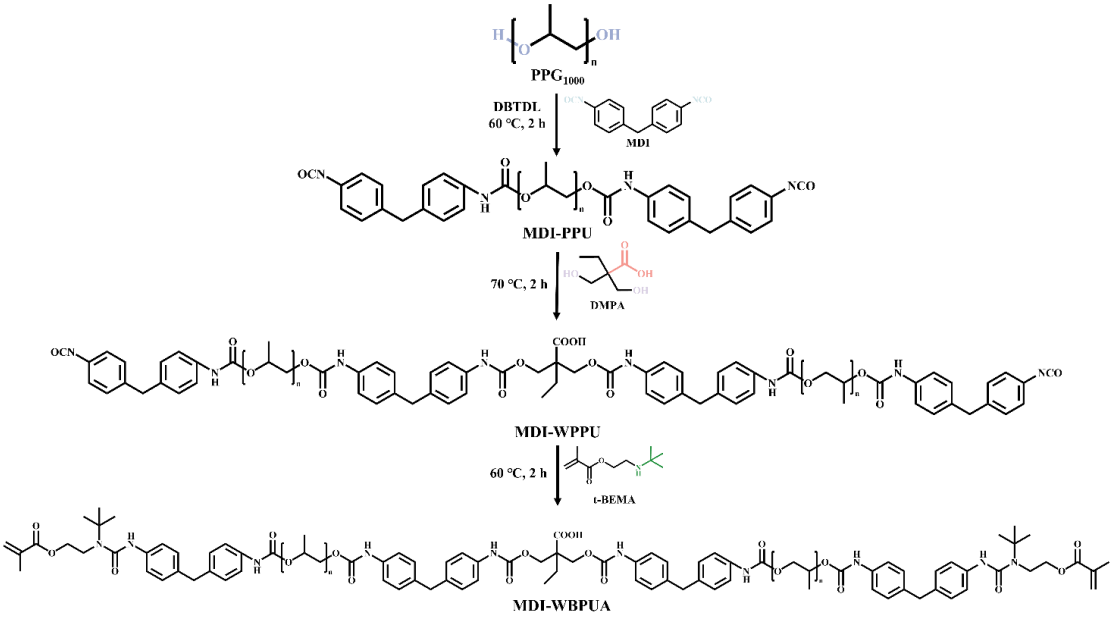

Figure S3. Preparation of 4,4'-methylenediphenyl diisocyanate (MDI)–waterborne polyurethane acrylate (WBPUA)

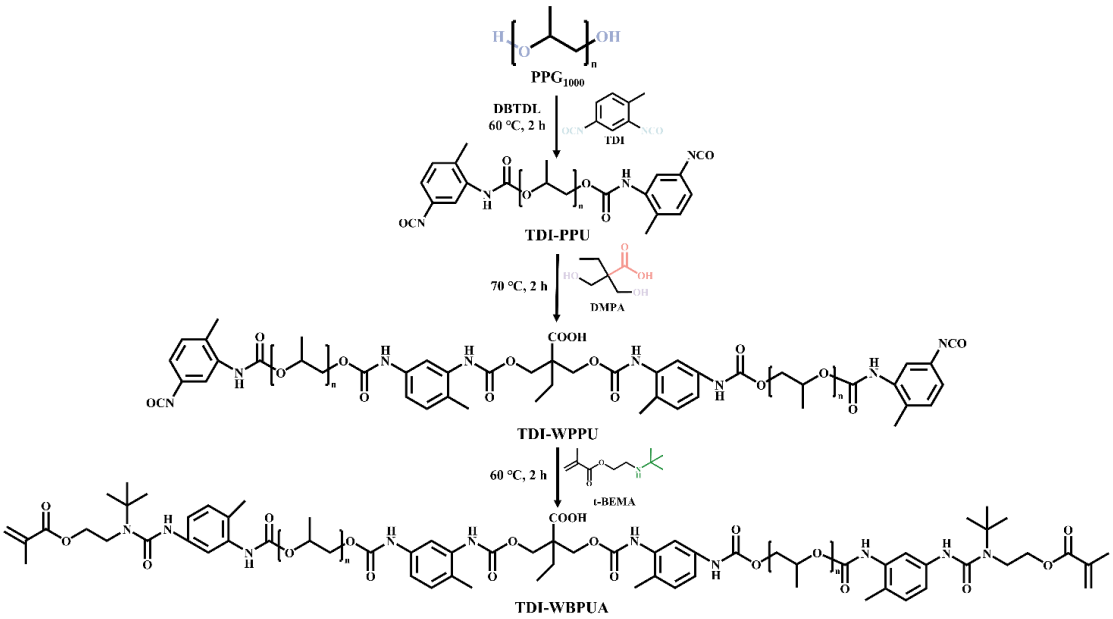

Figure S4. Preparation of toluene-2,4-diisocyanate (TDI)–waterborne polyurethane acrylate (WBPUA)

reaction was maintained for two hours after the addition, yielding a PPU. In the second step, DMPA (6.7 g, dissolved in ethyl acetate) was added to the reaction mixture, and the temperature was increased to 70 °C for an additional three hours to obtain a WPPU. In the third step, the system was cooled to 60 °C, and the blocking agent t-BEMA (55.5 g) was slowly added dropwise, followed by a two-hour reaction. The temperature was further reduced to 40 °C, and excess TEA was introduced for neutralization over 0.5 hours. Ethyl acetate was removed by rotary evaporation to afford the WBPUA. The change in –NCO group content during the reaction was monitored by the acetone-di-n-butylamine titration method. Complete blocking was confirmed when the –NCO content remained constant.

1.5. Synthesis of isophorone diisocyanate–waterborne polyurethane acrylate prepolymer

The WBPUA prepolymer was synthesized via a three-step procedure following the synthetic route shown in Figure S5. In the first step, isophorone diisocyanate (IPDI; 44.4 g) and DBTDL (0.12 g, catalyst) were inserted into a 500 mL four-necked flask equipped with a mechanical stirrer, reflux condenser, thermometer, and constant-pressure dropping funnel. The mixture was gradually heated to 60 °C, and pre-dried PPG_{1000} (100 g) was added dropwise. The reaction was maintained for two hours after the addition, yielding a PPU. In the second step, DMPA (6.7 g, dissolved in ethyl acetate) was added to the reaction mixture, and the temperature was increased to 70 °C for an additional three hours to obtain a WPPU. In the third step, the system was cooled to 60 °C, and the blocking agent t-BEMA (55.5 g) was slowly added dropwise, followed by a two-hour reaction. The temperature was further reduced to 40°C, and excess TEA was introduced for neutralization over 0.5 hours. Ethyl acetate was removed by rotary evaporation to afford the WBPUA. The change in –NCO group content during the reaction was monitored by the acetone-di-n-butylamine titration method. Complete blocking was confirmed when the –NCO content remained constant.

1.6. Characterization

1.6.1. Fourier transform infrared spectroscopy

Fourier transform infrared spectra were recorded on a Nicolet 5700 spectrometer (ThermoFisher Scientific, United States) equipped with an attenuated total reflection (ATR) accessory. Measurements were performed over 4,000–500 cm^{-1} with 32 scans and a resolution of 4 cm^{-1}.

1.6.2. Determination of isocyanate content

The isocyanate group (–NCO) content during the reaction was determined via the acetone-di-n-butylamine titration method. Briefly, 1.0 g of sample was weighed into an iodine flask containing 20 g of acetone and ultrasonically dissolved for 30 mins. Subsequently, 10 mL of di-n-butylamine-acetone solution was added accurately, followed by ultrasonic oscillation for 20 mins to ensure complete reaction. Three to four drops of 2% bromocresol green indicator were added, and the mixture was titrated with 0.1 mol/L hydrochloric acid solution until the solution turned yellow and remained unchanged for 30 seconds (titration end point). The volume of consumed hydrochloric acid was recorded as V_1. A blank test was performed under identical conditions without the sample, and the consumed hydrochloric acid volume was recorded as V_0. The –NCO content was calculated according to **Equation S1**:

$$NCO\% = \frac{(V_0 - V_1) \times C \times 0.04202}{W} \times 100\% \#\ \ 1 \qquad \text{(S1)}$$

where V_0 is the volume of hydrochloric acid solution consumed in the blank test, V_1 is the volume of hydrochloric acid solution consumed in the titration test, C is the concentration of hydrochloric acid solution, and W is the mass of the sample.

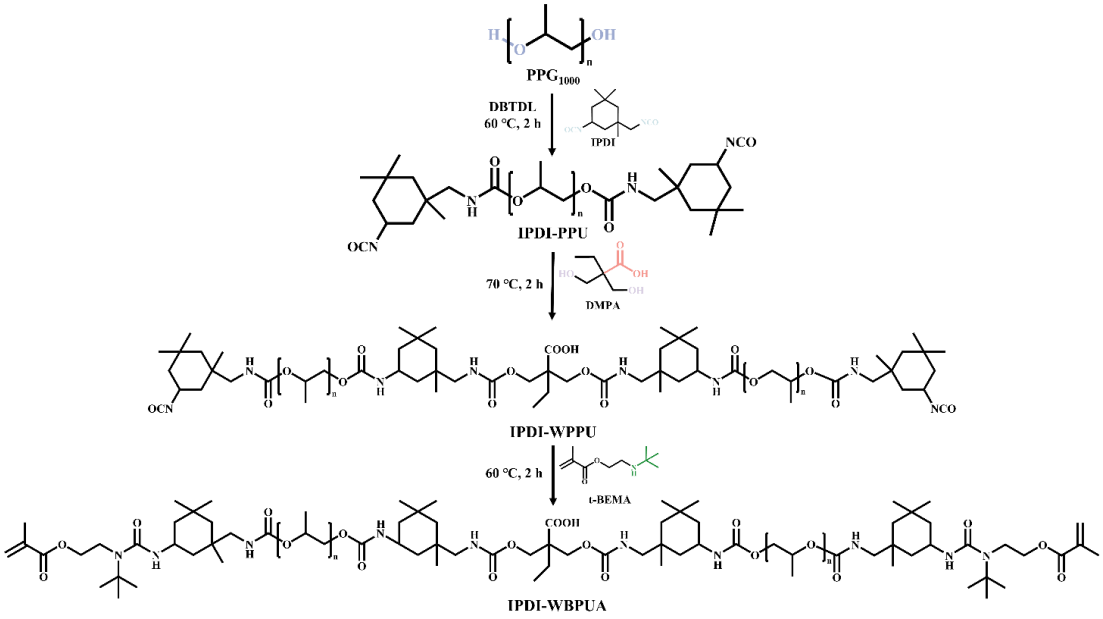

Figure S5. Preparation of isophorone diisocyanate (IPDI)–waterborne polyurethane acrylate (WBPUA)

1.6.3. Differential scanning calorimetry

Differential scanning calorimetry measurements were performed using a Q100 differential scanning calorimeter (TA Instruments, United States). The sample was heated from 20 °C to 200 °C at 10°C/min under a nitrogen atmosphere, then cooled from 200 °C to 20 °C at 10 °C/min. All data were collected during the second heating scan from 20 °C to 200 °C at 10 °C/min under nitrogen.

1.6.4. Mechanical property testing

Tensile tests were conducted on an Instron 5966 universal testing machine (Instron, United States) equipped with a 5,000 N load cell. Dumbbell-shaped specimens (20 × 4.0 × 3.0 mm) were printed for testing at a crosshead speed of 50 mm/min. True stress (σt) and true strain (εt) were calculated from the engineering stress–strain curves according to **Equations S2** and **S3**:

$$\sigma_t = \sigma\left(L + \varepsilon\right) \tag{S2}$$

$$\varepsilon_t = \ln\left(L_0 + \varepsilon\right) \tag{S3}$$

where σ is the engineering stress, L is the instantaneous length of the deformed specimen, L_0 is the original specimen length, and $\mathcal{E}$ is the engineering strain.

1.6.5. Antistatic measurement

Circular specimens (diameter: 8 cm, thickness: 3 mm) were fabricated using a digital light processing three-dimensional printer and subjected to photo-thermal dual curing. The surface resistivity was measured with a high-resistance meter (ZC-90G, Shanghai Taiou Electronic Instrument Co., Ltd., China) at 25 °C and 50% relative humidity. The specimens were stored for four weeks, and resistivity was re-measured on days 0, 7, 14, 21, and 28 under identical conditions to evaluate antistatic performance and long-term stability.

Supplementary Figures and Tables

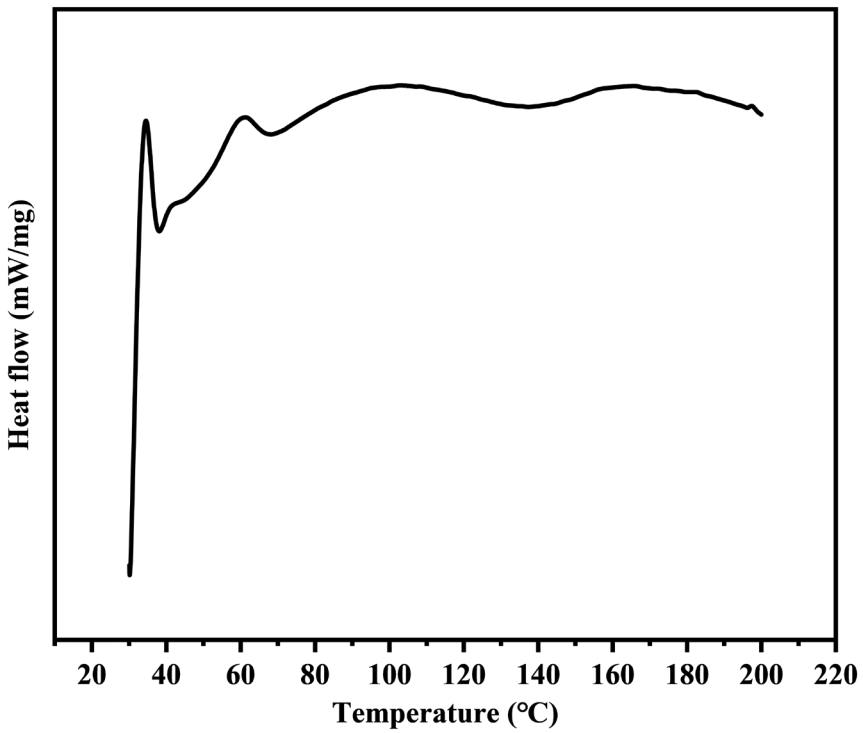

Figure S6. Differential scanning calorimetry curve of three-dimensional-printed material (4,4'-dicyclohexylmethane diisocyanate–waterborne polyurethane acrylate)

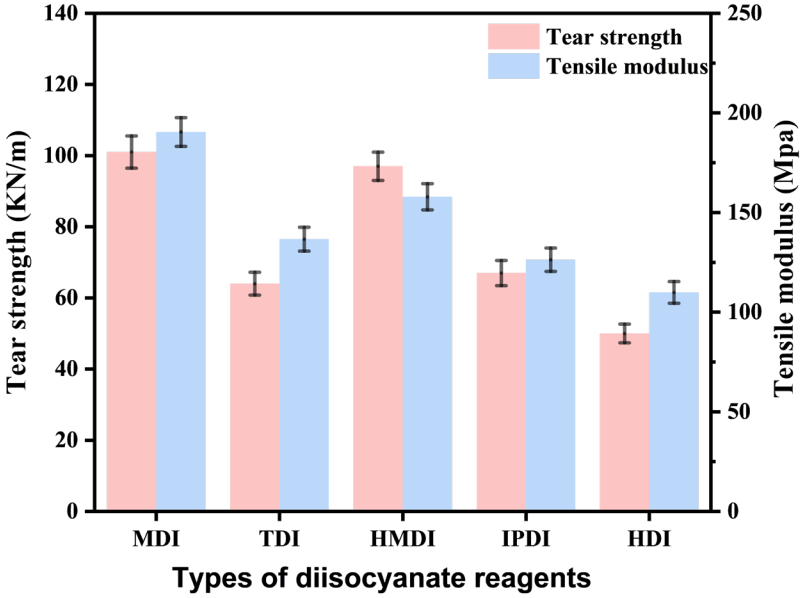

Figure S7. Comparison of tear strength and tensile modulus of waterborne polyurethane acrylate three-dimensional-printed materials synthesized with different isocyanates.
Abbreviations: HDI: Hexamethylene diisocyanate; HMDI: 4,4'-dicyclohexylmethane diisocyanate; IPDI: Isophorone diisocyanate; MDI: Methylene diphenyl diisocyanate; TDI: Toluene-2,4-diisocyanate.

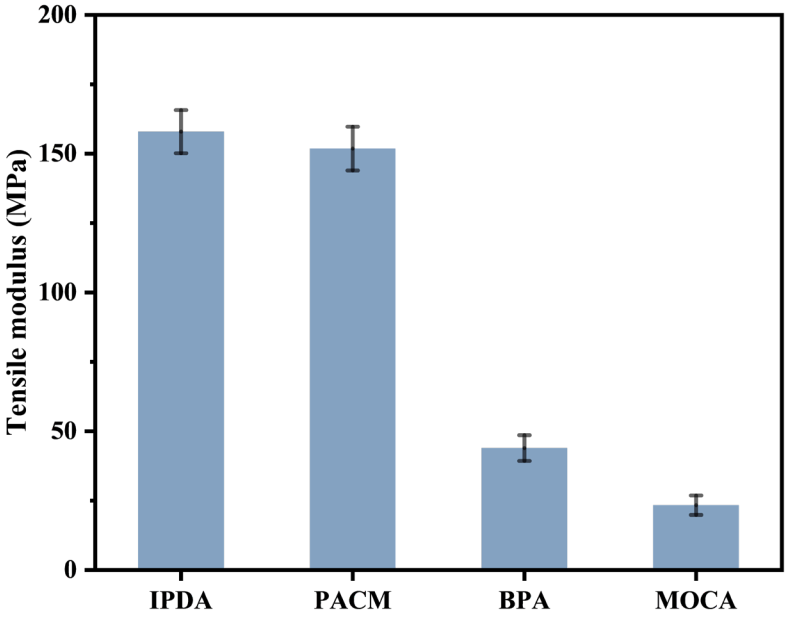

Figure S8. Comparison of tensile modulus of waterborne polyurethane acrylate three-dimensional-printed materials with different chain extenders
Abbreviations: BPA: Bisphenol A; IPDA: Isophorone diamine; MOCA: 4,4'-Methylenebis(2-chloroaniline); PACM: 4,4'-Methylenebis(cyclohexylamine).

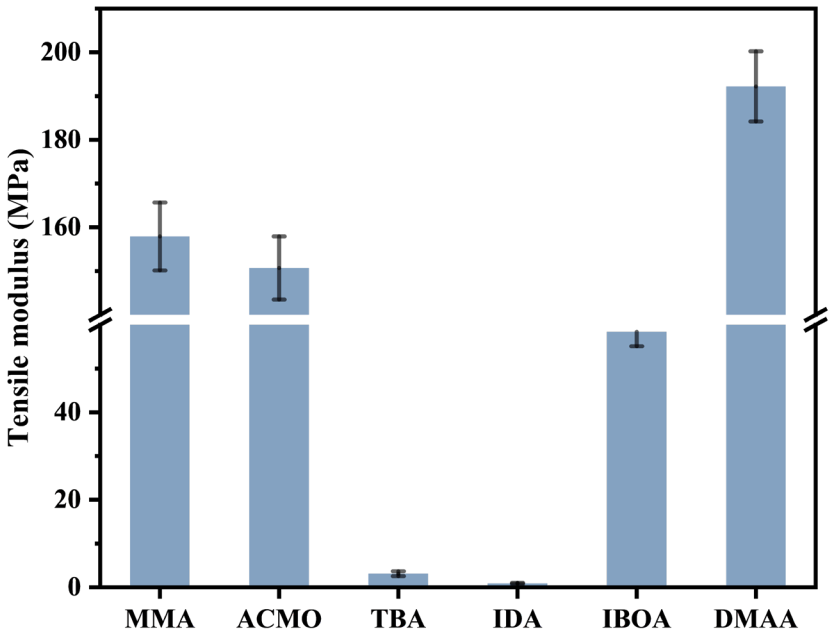

Figure S9. Comparison of tensile modulus of waterborne polyurethane acrylate three-dimensional-printed materials with different diluents
Abbreviations: ACMO: 4-acryloylmorpholine; DMAA: N,N-Dimethylacrylamide; IBOA: Isobornyl acrylate; IDA: Isodecyl acrylate; MMA: Methyl methacrylate; TBA: Tert-butyl acrylate.

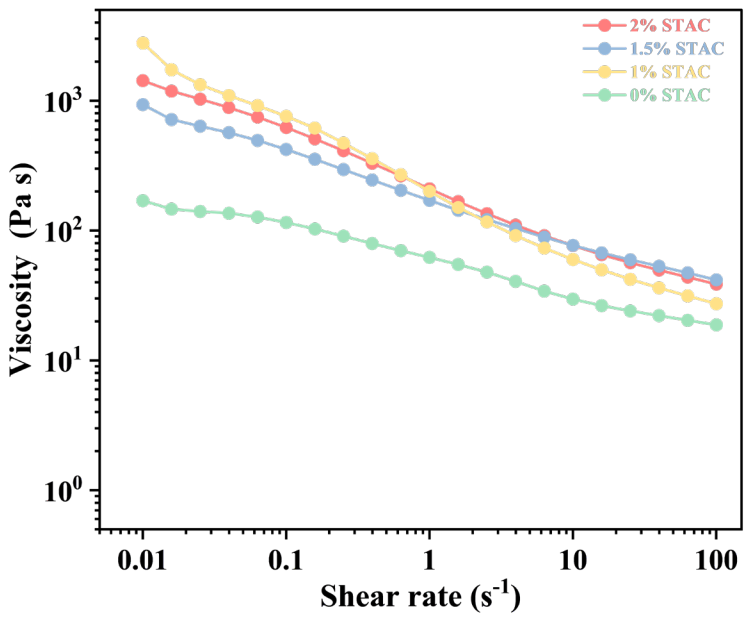

Figure S10. Steady-shear viscosity as a function of shear rate for waterborne polyurethane acrylate resins containing 0, 1, 1.5, and 2 wt% octadecyltrimethylammonium chloride

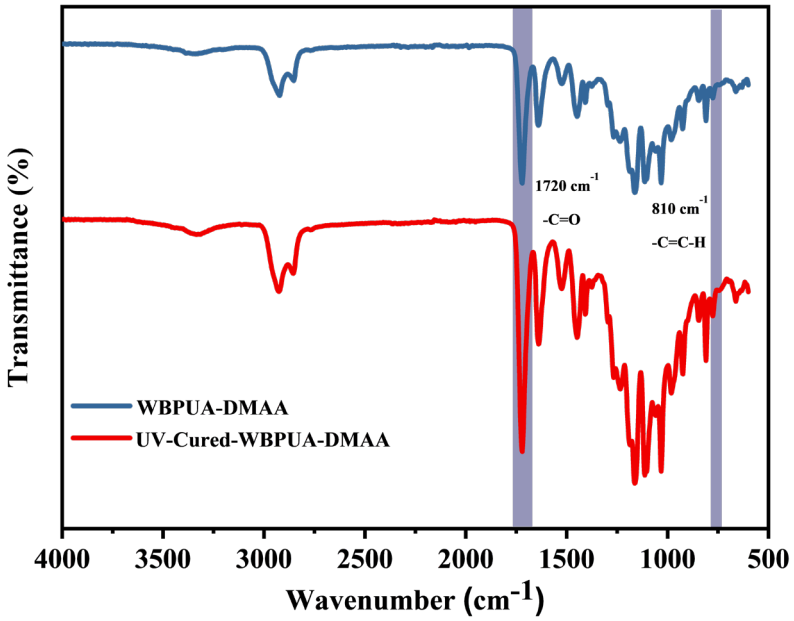

Figure S11. Fourier transform infrared spectra of pristine waterborne polyurethane acrylate–N,N-Dimethylacrylamide resin and photo-cured sample for comparison of characteristic C = C double bond absorption peaks

Table S1. Preparation of raw materials of waterborne polyurethane acrylate prepolymers containing different isocyanates

Prepolymer	Diisocyanates and dosages	PPG_{1000}	DMPA	t-BEMA
HDI–WBPUA	HDI: 33.6 g	100 g	6.7g	55.5 g
HMDI–WBPUA	HMDI: 52.6 g	100 g	6.7g	55.5 g
MDI–WBPUA	MDI: 50.1 g	100 g	6.7g	55.5 g
TDI–WBPUA	TDI: 34.8 g	100 g	6.7g	55.5 g
IPDI–WBPUA	IPDI: 44.6 g	100 g	6.7g	55.5 g

Abbreviations: DMPA: 2,2-dimethylolpropionic acid; HDI: Hexamethylene diisocyanate; HMDI: 4,4'-dicyclohexylmethane diisocyanate; IPDI: Isophorone diisocyanate; MDI: Methylene diphenyl diisocyanate; PPG: Polypropylene glycol; TDI: Toluene-2,4-diisocyanate; t-BEMA: 2-(tert-butylamino)ethyl methacrylate; WBPUA: Waterborne polyurethane acrylate.

Table S2. Formulations of photosensitive resins from waterborne polyurethane acrylate prepolymers with different isocyanates

Names of photosensitive resins	Prepolymers and dosages	Chain extender IPDA	Diluents MMA	Photoinitiators TPO
WBPUA–HDI	HDI–WBPUA: 70 wt%	2.5 wt%	26.5 wt%	1 wt%
WBPUA–HMDI	HMDI–WBPUA: 70 wt%	2.5 wt%	26.5 wt%	1 wt%
WBPUA–MDI	MDI–WBPUA: 70 wt%	2.5 wt%	26.5 wt%	1 wt%
WBPUA–TDI	TDI–WBPUA: 70 wt%	2.5 wt%	26.5 wt%	1 wt%
WBPUA–IPDI	IPDI–WBPUA: 70 wt%	2.5 wt%	26.5 wt%	1 wt%

Abbreviations: DMPA: 2,2-dimethylolpropionic acid; HDI: Hexamethylene diisocyanate; HMDI: 4,4'-dicyclohexylmethane diisocyanate; IPDA: Isophorone diamine; IPDI: Isophorone diisocyanate; MDI: Methylene diphenyl diisocyanate; MMA: Methyl methacrylate; PPG: Polypropylene glycol; TDI: Toluene-2,4-diisocyanate; TPO: Diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide; WBPUA: Waterborne polyurethane acrylate.

Table S3. Formulations of waterborne polyurethane acrylate photosensitive resins with different chain extenders

Names of photosensitive resins	Prepolymer HMDI–WBPUA	Chain extender and dosages	Diluents MMA	Photoinitiators TPO
WBPUA–IPDA	70 wt%	IPDA: 2.5 wt%	26.5 wt%	1 wt%
WBPUA–PACM	70 wt%	PACM: 2.5 wt%	26.5 wt%	1 wt%
WBPUA–BPA	70 wt%	BPA: 2.5 wt%	26.5 wt%	1 wt%
WBPUA–MOCA	70 wt%	MOCA: 2.5 wt%	26.5 wt%	1 wt%

Abbreviations: BPA: Bisphenol A; DMPA: 2,2-dimethylolpropionic acid; HDI: Hexamethylene diisocyanate; HMDI: 4,4'-dicyclohexylmethane diisocyanate; IPDA: Isophorone diamine; IPDI: Isophorone diisocyanate; MDI: Methylene diphenyl diisocyanate; MMA: Methyl methacrylate; MOCA: 4,4'-Methylenebis(2-chloroaniline); PACM: 4,4'-Methylenebis(cyclohexylamine); PPG: Polypropylene glycol; TDI: Toluene-2,4-diisocyanate; t-BEMA: 2-(tert-butylamino)ethyl methacrylate; TPO: Diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide; WBPUA: Waterborne polyurethane acrylate.

Table S4. Formulations of waterborne polyurethane acrylate photosensitive resins with different diluents

Names of photosensitive resins	Prepolymer HMDI–WBPUA	Chain extender IPDA	Diluents and dosages	Photoinitiators TPO
WBPUA–ACMO	70 wt%	2.5 wt%	ACMO: 26.5 wt%	1 wt%
WBPUA–DMAA	70 wt%	2.5 wt%	DMAA: 26.5 wt%	1 wt%
WBPUA–IBOA	70 wt%	2.5 wt%	IBOA: 26.5 wt%	1 wt%
WBPUA–IDA	70 wt%	2.5 wt%	IDA: 26.5 wt%	1 wt%
WBPUA–TBA	70 wt%	2.5 wt%	TBA: 26.5 wt%	1 wt%
WBPUA–MMA	70 wt%	2.5 wt%	MMA: 26.5 wt%	1 wt%

Abbreviations: ACMO: 4-acryloylmorpholine; DMAA: N,N-Dimethylacrylamide; HMDI: 4,4'-dicyclohexylmethane diisocyanate; IBOA: Isobornyl acrylate; IDA: Isodecyl acrylate; IPDA: Isophorone diamine; MMA: Methyl methacrylate; TBA: Tert-butyl acrylate; TPO: Diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide; WBPUA: Waterborne polyurethane acrylate.

Table S5. Formulations of waterborne polyurethane acrylate photosensitive resins with different antistatic agents and their contents

Names of photosensitive resins	Prepolymer HMDI–WBPUA	Chain extender IPDA	Diluents DMAA	Photoinitiators TPO	Antistatic agents and dosages
WBPUA–STAB-0.5	70 wt%	2.5 wt%	26 wt%	1 wt%	STAB: 0.5 wt%
WBPUA–STAB-1	70 wt%	2.5 wt%	25.5 wt%	1 wt%	STAB: 1 wt%
WBPUA–STAB-1.5	70 wt%	2.5 wt%	25 wt%	1 wt%	STAB: 1.5 wt%
WBPUA–STAB-2	70 wt%	2.5 wt%	24.5 wt%	1 wt%	STAB: 2 wt%
WBPUA–STAC-0.5	70 wt%	2.5 wt%	26 wt%	1 wt%	STAC: 0.5 wt%
WBPUA–STAC-1	70 wt%	2.5 wt%	25.5 wt%	1 wt%	STAC: 1 wt%
WBPUA–STAC-1.5	70 wt%	2.5 wt%	25 wt%	1 wt%	STAC: 1.5 wt%
WBPUA–STAC-2	70 wt%	2.5 wt%	24.5 wt%	1 wt%	STAC: 2 wt%

Abbreviations: DMAA: N,N-Dimethylacrylamide; HMDI: 4,4'-Dicyclohexylmethane diisocyanate; IPDA: Isophorone diamine; STAB: Octadecyltrimethylammonium bromide; STAC: Octadecyltrimethylammonium chloride; TPO: Diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide; WBPUA: Waterborne polyurethane acrylate.

Table S6. Optimal three-dimensional printing parameters for photosensitive resins

Parameters	Values
X/Y direction pixel resolution	50 μm
Z-axis positioning accuracy	0.01 mm
Single layer printing thickness adjustable range	25–100 μm
Single exposure time (Corresponding light intensity)	5 s (2.5 mW/cm^2)
Platform rise separation distance	5 mm
Velocity of separation	3 mm/s
Layer thickness	0.05 mm
Exposure time	2.00 s
Optical power	670 μW
Downward waiting time	2.00 s
Enhanced exposure time	2.50 s
Boost exposure power	670 μW
Lowering dwell time	2.00 s
Boost exposure power	5
Advanced exposure-layer offset calibration	0.05 mm

Table S7. Mechanical properties of three-dimensional printing materials based on waterborne polyurethane acrylate prepolymers prepared with different isocyanates

Names of photosensitive resins	Strain (MPa)	Stress (%)	Tear strength (KM/m)	Tensile modulus (MPa)
WBPUA–HDI	8.6	144.5	50	109.9
WBPUA–HMDI	14.8	231.3	97	157.9
WBPUA–MDI	19.6	134.1	101	190.4
WBPUA–TDI	17.6	154.7	64	136.6
WBPUA–IPDI	12.5	144.3	67	126.3

Abbreviations: DMPA: 2,2-dimethylolpropionic acid; HDI: Hexamethylene diisocyanate; HMDI: 4,4'-dicyclohexylmethane diisocyanate; IPDI: Isophorone diisocyanate; MDI: Methylene diphenyl diisocyanate; TDI: Toluene-2,4-diisocyanate.

Table S8. Mechanical properties of waterborne polyurethane acrylate three-dimensional printing materials with different chain extenders

Names of photosensitive resins	Strain (MPa)	Stress (%)	Tensile modulus (MPa)
WBPUA–IPDA	14.8	231.3	157.9
WBPUA–PACM	12.1	87.7	151.8
WBPUA–BPA	10.1	256.8	43.9
WBPUA–MOCA	11.3	220.4	23.3

Abbreviations: BPA: Bisphenol A; IPDA: Isophorone diamine; MOCA: 4,4'-Methylenebis(2-chloroaniline); PACM: 4,4'-Methylenebis(cyclohexylamine); WBPUA: Waterborne polyurethane acrylate.

Table S9. Mechanical properties of waterborne polyurethane acrylate three-dimensional printing materials with different diluents

Names of photosensitive resins	Strain (MPa)	Stress (%)	Tensile modulus (MPa)
WBPUA–ACMO	16.1	312.4	150.7
WBPUA–DMAA	19.2	291.3	192.2
WBPUA–IBOA	11.3	227.5	58.4
WBPUA–IDA	1.44	184.8	0.9
WBPUA–TBA	5.84	275.5	3.1
WBPUA–MMA	14.8	231.3	157.9

Abbreviations: ACMO: 4-acryloylmorpholine; DMAA: N,N-Dimethylacrylamide; IBOA: Isobornyl acrylate; IDA: Isodecyl acrylate; MMA: Methyl methacrylate; TBA: Tert-butyl acrylate; TPO: Diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide; WBPUA: Waterborne polyurethane acrylate.

Table S10. Cleaning performance of waterborne polyurethane acrylate three-dimensional printing materials

Names of photosensitive resins	Water cleaning performance	Ethanol cleaning performance
Waterborne polyurethane acrylate	Surface dry and non-sticky to paper	Surface dry and non-sticky to paper
LY6001 (Commercial)	Tacky surface, paper adhesion	Surface dry and non-sticky to paper