

ORIGINAL RESEARCH ARTICLE

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

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Abstract

Traditional photocurable three-dimensional (3D) printing materials rely on organic solvent cleaning, emit high volatile organic compounds, have insufficient mechanical properties, and easily generate static charge. Herein, we developed a water-washable, antistatic, photo-thermal dual-curable waterborne polyurethane acrylate for digital light processing-based vat photopolymerization 3D printing. A waterborne polyurethane skeleton was constructed using polypropylene glycol, isocyanate, and 2,2-dimethylolpropionic acid, and a tertiary amine blocking agent with photosensitive groups was introduced to synthesize prepolymers containing thermally reversible urea bonds. An ionic antistatic agent was compounded to prepare a photosensitive resin, which was then molded via photo-thermal dual curing. The effects of isocyanate type and content, chain extender, diluent, and antistatic agent on material properties were systematically investigated. Results showed that the material exhibited optimal overall performance with 4,4'-dicyclohexylmethane diisocyanate as the isocyanate, isophorone diamine as the chain extender, N,N-dimethylacrylamide as the diluent, and 1.0 wt% octadecyltrimethylammonium chloride as the antistatic agent. After thermal curing at 110 °C for six hours, the material achieved a tensile strength of 26.8 MPa and an elongation at break of 110%, maintaining stable antistatic performance (surface resistivity $< 1 \times 10^{10} \Omega$) within 28 days. The material is fully water-washable with zero volatile organic compound emissions, integrating high strength-toughness, long-term antistatic property, and environmental friendliness. This work provides a new strategy for developing eco-friendly functional 3D printing materials.

Keywords: Waterborne polyurethane acrylate; Photo-thermal dual curing; Vat photopolymerization; Digital light processing; Water washability; Antistatic property; Mechanical properties

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1. Introduction

Three-dimensional (3D) printing technology has developed rapidly in precision manufacturing,¹ electronic devices,² aerospace,³ and the medical model field.⁴ Vat photopolymerization, represented by digital light processing (DLP) and stereolithography,

has become a mainstream additive manufacturing technology due to its high molding accuracy,⁵ fast processing efficiency,⁶ and excellent surface quality.⁷ As the core photocurable resin, polyurethane acrylate (PUA) combines the high toughness and wear resistance of polyurethane with the fast curing characteristic of acrylate, thus finding wide applications.⁸ However, single ultraviolet curing has inherent limitations, such as excessively fast curing, inhomogeneous crosslinking, and low polymerization degree, leading to insufficient strength, poor toughness, high brittleness, and weak dimensional stability of molded parts, which restricts their application in industrial structural components.⁹ Critically, conventional photocurable 3D printing materials generally require cleaning with organic solvents such as ethanol and isopropanol after molding. This process incurs high costs, causes volatile organic compound (VOC) emissions, environmental pollution, and safety hazards, and easily leads to surface swelling and accuracy degradation of materials, conflicting with the concept of green manufacturing.¹⁰⁻¹²

Waterborne PUA (WPUA), with water as the dispersion medium, exhibits low VOC, low toxicity, environmental friendliness, and easy processability, making it a key research direction for green photocurable materials.¹³ Nevertheless, existing waterborne photocurable resins still have significant drawbacks, including insufficient crosslinking density from single photocuring, which limits mechanical performance improvement; and being prone to static electricity generation, which adsorbs dust, interferes with the normal operation of electronic components, and triggers sparks and safety accidents.¹⁴ Although most waterborne resins are water-washable, they often suffer from low strength and poor toughness, failing to simultaneously satisfy the core requirements of water washability, high strength-toughness, and antistatic property, thus restricting their application in functional and structural 3D-printed parts.¹⁵

Antistatic performance is a critical indicator for applications in electronics, precision instruments, automotive interiors, and packaging materials.¹⁶ Traditional antistatic modification relies on physical blending of conductive fillers or small-molecule antistatic agents, which deliver short-term effectiveness but suffer from poor compatibility, easy migration, insufficient durability, and impaired mechanical properties.¹⁷ Notably, the polar carboxyl groups ($-\text{COOH}$) in WPUA molecular chains can form hydrogen bonds and electrostatic interactions with ionic antistatic agents, significantly improving the dispersion uniformity of antistatic agents and system stability, inhibiting migration and loss, and achieving

long-term stable antistatic performance, which provides a promising solution to address electrostatic issues.^{18,19}

The photo-thermal dual curing strategy is a vital approach to overcome the performance bottleneck of single photocuring.²⁰ This technology adopts a two-step mechanism: rapid molding via photocuring followed by secondary crosslinking via thermal curing. Specifically, ultraviolet light enables rapid curing for precise DLP-based vat photopolymerization molding; subsequent heating triggers the cleavage of thermally reversible urea bonds, releasing highly active isocyanate groups ($-\text{NCO}$) to undergo secondary crosslinking with active groups ($-\text{NH}_2$, $-\text{OH}$, $-\text{COOH}$), significantly increasing the polymerization degree and crosslinking density, and simultaneously enhancing strength and toughness. This strategy effectively resolves the trade-off between strength and toughness in single-photocured materials, offering a new direction for developing high-performance 3D printing resins.²¹

Against this background, this study designed and synthesized a photo-thermal dual-curable, water-washable, antistatic waterborne PUA for 3D printing. A waterborne polyurethane skeleton was constructed from polypropylene glycol (PPG_{1000}), isocyanate, and 2,2-dimethylolpropionic acid (DMPA). A tertiary amine blocking agent with photosensitive groups (2-(tert-butylamino)ethyl methacrylate [t-BEMA]) was introduced to incorporate photocurable groups and thermally reversible urea bonds (hindered urea bonds [HUBs]); and an ionic antistatic agent was compounded to form a stable antistatic system. This work systematically investigated the effects of the type and content of isocyanate, chain extender, diluent, and antistatic agent on the mechanical properties, antistatic stability, and water washability of 3D printing materials. The aim is to develop a green 3D printing resin that eliminates organic solvent cleaning, has low VOC, high strength-toughness, and long-term antistatic performance, providing a theoretical basis and technical support for industrial applications of eco-friendly functional additive manufacturing materials.

2. Materials and methodology

2.1. Materials

Isophorone diisocyanate (IPDI), hexamethylene diisocyanate (HDI), 4,4'-dicyclohexylmethane diisocyanate (HMDI), toluene-2,4-diisocyanate (TDI), and methylene diphenyl diisocyanate (MDI) were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd (China). PPG_{1000} was obtained from Jilin Ruiji Special Chemicals Co., Ltd (China). Dibutyltin dilaurate (DBTDL), t-BEMA, 4-acryloylmorpholine (ACMO),

methyl methacrylate (MMA), bisphenol A (BPA), DMPA, isobornyl acrylate (IBOA), isophorone diamine (IPDA), diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide (TPO), octadecyltrimethylammonium chloride (STAC), and octadecyltrimethylammonium bromide (STAB) were supplied by Sinopharm Chemical Reagent Co., Ltd (China).

2.2. Synthesis of blocked waterborne polyurethane acrylate prepolymer

Waterborne PUA prepolymer was synthesized via a three-step method (Figure 1). Briefly, a certain amount of diisocyanate and DBTDL 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 PPG₁₀₀₀ was added dropwise, followed by a two-hour reaction to obtain polyurethane prepolymer (PPU). In the second step, DMPA (dissolved in ethyl acetate) was added to the system, the temperature was raised to 70 °C, and the mixture was allowed to react for three hours to yield waterborne PPU (WPPU). In the third step, the system was cooled to 60 °C, and the t-BEMA blocking agent was added dropwise, followed by allowing the mixture to react

for two hours. The temperature was further reduced to 40 °C, triethylamine (TEA) was added for neutralization for 0.5 h, and ethyl acetate was removed by rotary evaporation to obtain the final blocked WBPUA prepolymer.

Five diisocyanates (MDI, TDI, HMDI, IPDI, HDI) were separately reacted with PPG₁₀₀₀ to synthesize WBPUA prepolymers. The molar ratio of isocyanate groups (R value) was set to 2, with the molar ratio of diisocyanate:PPG₁₀₀₀:DMPA:t-BEMA fixed at 2:1:0.5:1.5. Detailed feed ratios and synthesis routes are provided in Table S1 and Figures S1–S5.

2.3. Preparation of waterborne polyurethane acrylate-based photosensitive resin for digital light processing-based vat photopolymerization

Waterborne PUA oligomer, diluent, and TPO photoinitiator were sequentially added to an opaque container according to different feed ratios. The mixture was mechanically stirred for two hours to ensure homogeneity, then a chain extender was added and stirred for another 20 mins. Ultrasonic degassing was performed to remove bubbles prior to DLP-based vat photopolymerization.

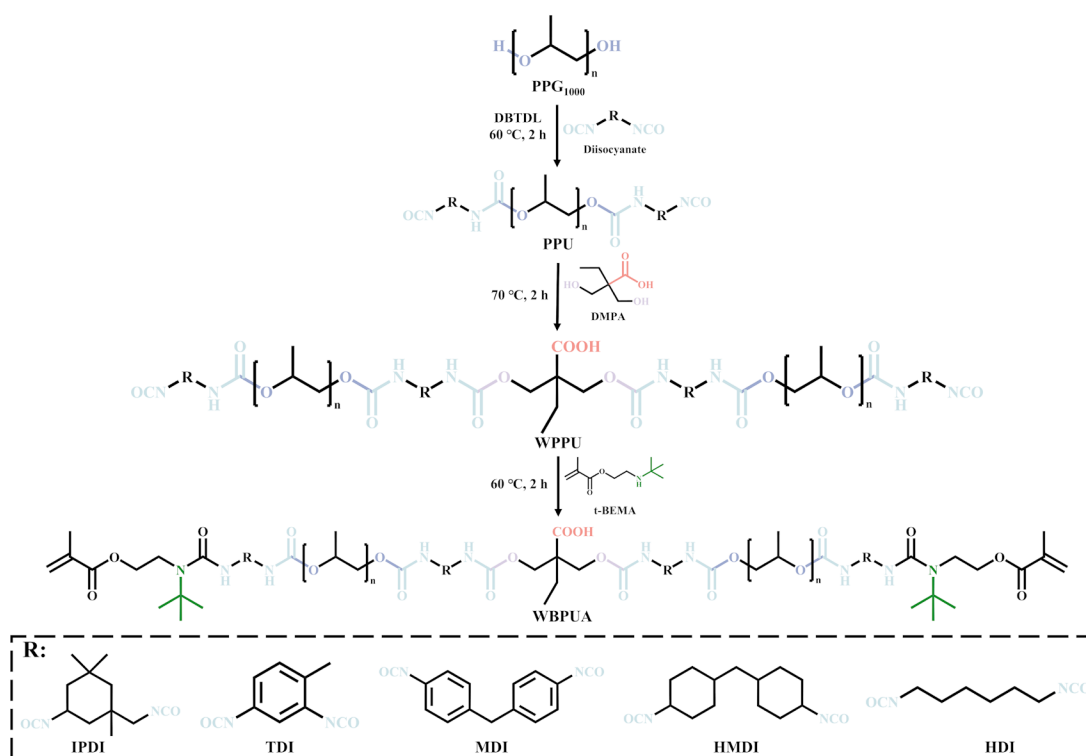


Figure 1. Synthesis of blocked waterborne polyurethane acrylate (WBPUA) prepolymer

Abbreviations: DBTDL: Dibutyltin dilaurate; DMPA: 2,2-dimethylolpropionic acid; HDI: Hexamethylene diisocyanate; HMDI: 4,4'-dicyclohexylmethane diisocyanate; IPDI: Isophorone diisocyanate; MDI: Methylene diphenyl diisocyanate; PPG: Polypropylene glycol; PPU: Polyurethane prepolymer; TDI: Toluene-2,4-diisocyanate; t-BEMA: 2-(tert-butylamino)ethyl methacrylate.

Detailed compositions of the WBPUA-based photosensitive resins are listed in Tables S2–S5.

2.4. Fabrication of digital light processing-based vat photopolymerization materials

Based on the photo-thermal dual curing principle, the formulated photosensitive resins were poured into the resin tank of a heated DLP 3D printer (ANYCUBIC PHOTON P1, Shenzhen Anycubic Technology Co., Ltd., China). The resin was preheated to 35 °C and maintained at this temperature throughout printing to ensure stable rheological and curing properties. After optimizing the printing parameters, photocuring 3D printing was performed. The printed samples were carefully removed from the substrate, ultrasonically cleaned in water for 120 s (repeated three times) to remove uncured resin residues, dried, and post-cured for 2.5 mins on each side in a post-curing chamber. Finally, the printed parts were thermally treated at 110 °C for six hours to complete thermal curing. Detailed printing parameters are summarized in Table S6.

2.5. Characterization

The characterization methods of all materials are provided in the Supplementary File.

2.6. Antistatic test

Circular specimens (diameter: 8 cm, thickness: 3 mm)

were fabricated via DLP-based vat photopolymerization and subjected to photo-thermal dual curing. Surface resistivity was measured using 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 surface resistivity was re-measured on days 0, 7, 14, 21, and 28 under identical conditions to evaluate antistatic performance and long-term stability.

3. Results and discussion

3.1. Synthesis and characterization of blocked waterborne polyurethane acrylate prepolymer

As the photosensitive resin matrix, the blocking efficiency and chemical structure of WBPUA determine the photocuring behavior, crosslinked network structure, and final properties of 3D printed materials. The reaction progress during synthesis was monitored via Fourier transform infrared spectroscopy. Figure 2a shows the Fourier transform infrared spectroscopy spectra of PPU (first step product), WPPU (second step product), and WBPUA (final product). A strong characteristic peak at 2,262 cm^{-1} in the PPU spectrum corresponds to the –NCO group, confirming the retention of terminal active –NCO groups. The absorption peak at 3,327 cm^{-1} is attributed to N–H stretching vibration from the reaction between

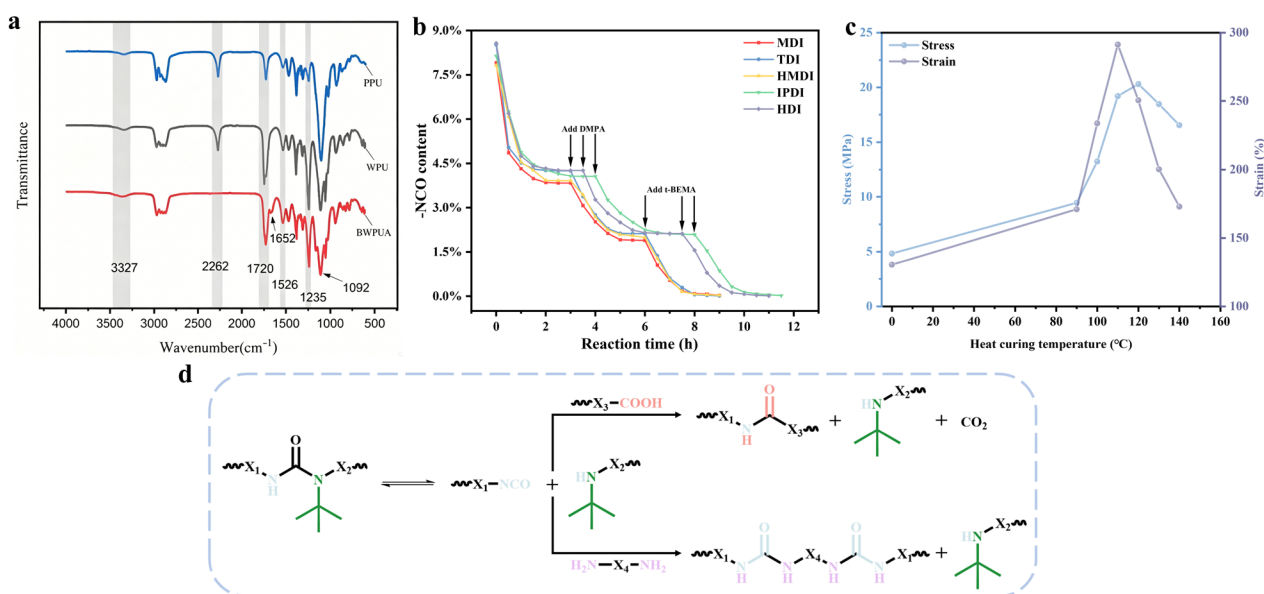


Figure 2. Synthesis monitoring and thermal curing optimization of waterborne polyurethane acrylate (WBPUA). (a) Fourier transform infrared spectroscopy spectra during the synthesis of WBPUA prepolymer. (b) Variation of NCO group content during the synthesis of WBPUA prepolymers with different isocyanates. (c) Stress–strain curves of 3D-printed materials (WBPUA–HMDI) cured at different thermal temperatures. (d) Schematic mechanism of hindered urea bond thermal dissociation and chain extension reaction with carboxyl groups and diamines.

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; t-BEMA: 2-(tert-butylamino)ethyl methacrylate.

–NCO and –OH, verifying the reaction between PPG₁₀₀₀ and diisocyanate. In the WPPU spectrum, the enhanced absorption intensities at 3,327 cm⁻¹ (N–H stretching), 1,720 cm⁻¹ (C = O stretching), and 1,526 cm⁻¹ (N–H bending), accompanied by the weakened –NCO peak, indicate the reaction between DMPA and PPU, reducing NCO content and forming NCO-terminated WPPU. In the WBPUA spectrum, a new peak at 1,652 cm⁻¹ (C = C stretching) was observed, and the –NCO peak completely disappeared, confirming the successful blocking of –NCO by t-BEMA and the introduction of acrylate groups, yielding a WBPUA prepolymer with blocked urea bonds.

The variation of –NCO content during WBPUA synthesis was determined via the acetone-di-n-butylamine titration method²² to monitor reaction progress (Figure 2b). The –NCO content decreased sharply within the first hour because of the high initial diisocyanate concentration and rapid reaction with hydroxyl groups in PPG₁₀₀₀. The reaction rate reduced after two hours as hydroxyl groups were depleted, marking the completion of the first step. Adding DMPA increased hydroxyl concentration, accelerating the reaction and further reducing –NCO content in the second step. The addition of t-BEMA caused a continuous decrease in –NCO content, with complete consumption within 1.5 hours, confirming full blocking of –NCO groups.

3.2. Optimal thermal curing conditions for digital light processing-based vat photopolymerization materials

Thermal curing temperature significantly affects the dissociation and rearrangement of dynamic HUBs and the crosslinked structure, thereby altering the mechanical properties of 3D-printed materials (Figure 2d). Differential scanning calorimetry was performed on WBPUA-HMDI specimens to determine the optimal thermal curing temperature and verify the effect of HUB dissociation/rearrangement on mechanical properties (Figure S6). The endothermic peak in the 90 °C–140 °C range indicates HUB dissociation, an endothermic reaction.²³ Specimens were thermally cured at 90 °C, 100 °C, 110 °C, 120 °C, 130 °C, and 140 °C for six hours, and mechanical properties were characterized to identify the optimal condition (Figure 2c). Thermal curing enhances tensile performance, with tensile strength and elongation at break increasing and then decreasing with temperature. The optimal temperatures for elongation at break and tensile strength differed: elongation at break reached a maximum of 291.3% at 110 °C (tensile strength: 19.2 MPa), while tensile strength peaked at 20.3 MPa at 120 °C (elongation at break: 250.5%). Below the optimum, insufficient HUB dissociation led to poor crosslinking and limited mechanical improvement. At 110

°C–120 °C, optimal HUB dissociation/rearrangement and synergistic interaction with small-molecule diamines form a dual network, achieving superior mechanical properties. Temperatures ≥ 130 °C cleave urea and urethane bonds, embrittle the material, and promote excessive crosslinking and blending of soft/hard segments, weakening hard-segment reinforcement and degrading mechanical properties.²⁴ Thus, the optimal thermal curing condition is 110 °C for six hours.

3.3. Effect of isocyanate type on mechanical properties of waterborne polyurethane acrylate three-dimensional-printed materials

Tensile tests were conducted on DLP-printed and photo-thermal dual-cured materials prepared with different isocyanates (Table S2). Isocyanate molecular structure significantly influences crosslinking density, microphase separation, and chain mobility, leading to distinct mechanical performance. As shown in Figure 3a and 3b, tensile strength followed the order: WBPUA-MDI (19.6 MPa) > WBPUA-TDI (17.6 MPa) > WBPUA-HMDI (14.8 MPa) > WBPUA-IPDI (12.5 MPa) > WBPUA-HDI (8.6 MPa). This trend correlates with isocyanate rigidity, reactivity, and symmetry. Aromatic MDI and TDI contain rigid benzene rings: conjugation between benzene rings and –NCO reduces electron density at C atoms in –NCO, enhancing reactivity with nucleophiles and increasing polymerization/crosslinking density; rigid benzene rings as hard segments restrict chain motion, improving tensile strength and modulus.²⁵ MDI, with dual benzene rings and higher symmetry, forms more ordered hard segment aggregates and better microphase separation.²⁶ Alicyclic HMDI and IPDI have cyclohexyl rigid structures with intermediate rigidity between benzene rings and aliphatic chains, resulting in lower strength than aromatic systems but higher than aliphatic HDI. HMDI's symmetric dicyclohexyl structure imparts better chain regularity and hard-segment aggregation than asymmetric IPDI, leading to higher tensile strength.²⁷ Aliphatic HDI has a linear chain structure with no rigid rings, high chain flexibility, poor hard segment aggregation, and weak microphase separation, resulting in the lowest tensile strength.

Elongation at break exhibited an opposite trend: WBPUA-HMDI (231.3%) > WBPUA-TDI (154.7%) > WBPUA-HDI (144.5%) > WBPUA-IPDI (144.3%) > WBPUA-MDI (134.1%), reflecting the inverse effect of hard segment rigidity/content on toughness. The MDI system had the highest strength, but excessive hard segment rigidity restricted chain motion/slippage, increasing brittleness and reducing elongation at break. The HMDI system balances rigidity and flexibility: the symmetric dicyclohexyl structure provides sufficient hard segment

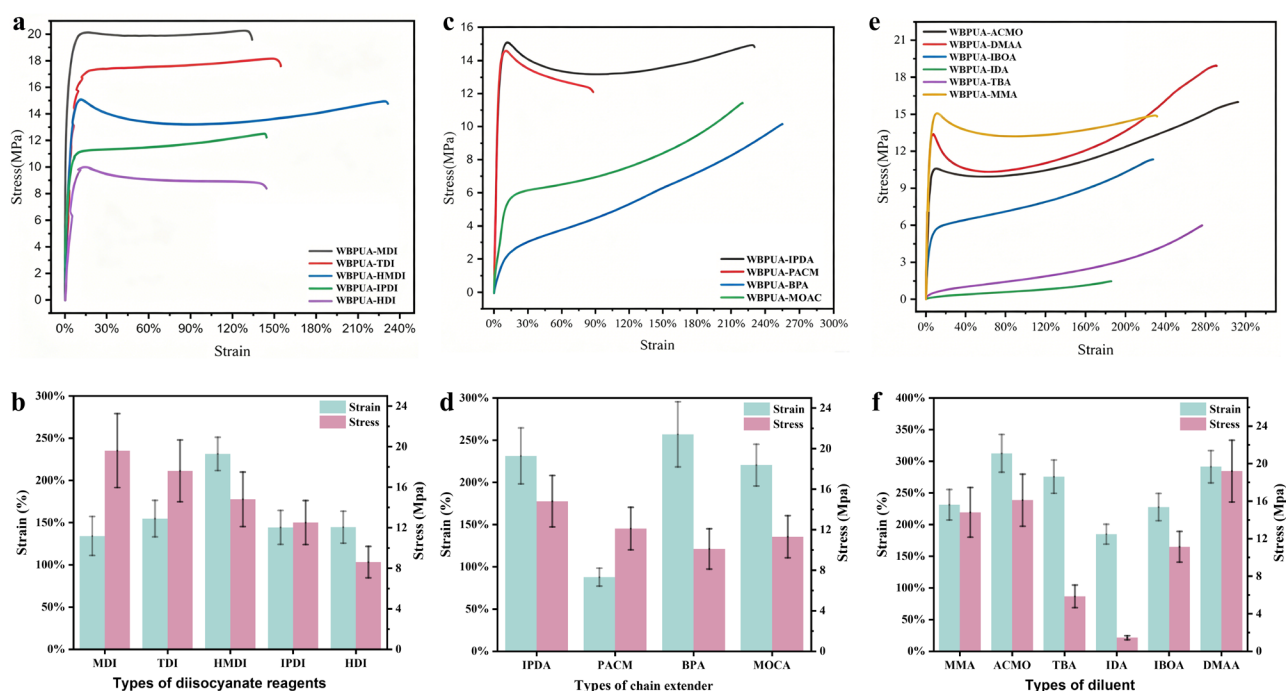


Figure 3. Effects of formulation components on the mechanical properties of photo-thermal dual-cured waterborne polyurethane acrylate (WBP UA) three-dimensional (3D)-printed materials. (a) Stress-strain curves of WBP UA 3D-printed materials synthesized with different isocyanates. (b) Comparison of stress-strain curves for WBP UA 3D-printed materials synthesized with different isocyanates. (c) Stress-strain curves of WBP UA 3D-printed materials with different chain extenders. (d) Comparison of stress-strain curves for WBP UA 3D-printed materials with different chain extenders. (e) Stress-strain curves of WBP UA 3D-printed materials with different diluents. (f) Comparison of stress-strain curves for WBP UA 3D-printed materials with different diluents.

Abbreviations: ACMO: 4-acryloylmorpholine; BPA: Bisphenol A; DMAA: N,N-Dimethylacrylamide; HDI: Hexamethylene diisocyanate; HMDI: 4,4'-dicyclohexylmethane diisocyanate; IBOA: Isobornyl acrylate; IDA: Isodecyl acrylate; IPDA: Isophorone diamine; IPDI: Isophorone diisocyanate; MDI: Methylene diphenyl diisocyanate; MMA: Methyl methacrylate; MOCA: 4,4'-Methylenebis(2-chloroaniline); PACM: 4,4'-Methylenebis(cyclohexylamine); TBA: Tert-butyl acrylate; TDI: Toluene-2,4-diisocyanate.

rigidity and crosslinking strength without excessive rigidity-induced brittleness, enabling soft segment elastic recovery.²⁸ Thus, it achieved a high tensile strength of 14.8 MPa and a high elongation at break of 231.3%, optimizing the strength-toughness trade-off (Table S7).

Tear strength followed the order: WBP UA-MDI (101 kN/m) > WBP UA-HMDI (97 kN/m) > WBP UA-IPDI (67 kN/m) > WBP UA-TDI (64 kN/m) > WBP UA-HDI (50 kN/m). The MDI system's dense crosslinked network and hard segment aggregation effectively dispersed stress and inhibited crack propagation, resulting in the highest tear strength; the HMDI system's symmetric structure and moderate crosslinking density delivered excellent tear resistance; the HDI system's low crosslinking density and weak interchain interactions allowed rapid crack propagation, leading to the lowest tear strength (Figure S7).

Comprehensive analysis of tensile strength, elongation at break, tear strength, and modulus confirms that the

HMDI system exhibits optimal mechanical performance, balancing strength and toughness for subsequent water-washable and antistatic modification.

3.4. Effect of chain extender type on mechanical properties of waterborne polyurethane acrylate three-dimensional-printed materials

Tensile tests were performed on photo-thermal dual-cured materials prepared with different chain extenders (Table S3). Chain extender molecular structure, reactivity, and rigidity significantly influence polymerization degree, crosslinked network structure, and microphase separation. As shown in Figure 3c and 3d, tensile strength followed the order WBP UA-IPDA (14.8 MPa) > WBP UA-4,4'-diaminodicyclohexylmethane (PACM) (12.1 MPa) > WBP UA-4,4'-Methylenebis(2-chloroaniline) (MOCA; 11.3 MPa) > WBP UA-BPA (10.1 MPa), correlating with chain-extender reactivity, symmetry, and rigidity. The IPDA system delivered the highest tensile strength (14.8 MPa) and modulus (157.9 MPa). The two amino groups in

IPDA exhibited different reactivities (α -amino < β -amino), enabling controllable chain extension, uniform molecular weight distribution, and well-defined soft/hard segment microphase separation, enhancing mechanical strength and modulus.²⁹ PACM's two amino groups have identical reactivity, leading to uncontrolled chain extension, uneven molecular weight distribution, and crosslinked network defects, resulting in lower tensile strength (12.1 MPa).³⁰ BPA and MOCA contain benzene rings that conjugate with N/O atoms, reducing nucleophilic reactivity of active hydrogens and limiting chain extension/polymerization, leading to low tensile strength (10.1 MPa for BPA, 11.3 MPa for MOCA).³¹

Elongation at break followed the order: WBPUA-BPA (256.8%) > WBPUA-MOCA (220.4%) > WBPUA-IPDA (231.3%) > WBPUA-PACM (87.7%), determined by chain extender-induced chain flexibility and crosslinked network structure. The PACM system had the lowest elongation at break (87.7%) due to uniform reactivity-induced inhomogeneous crosslinking, localized high crosslinking restricting chain motion, and rigid alicyclic structure limiting chain slippage.³² The IPDA system balanced high tensile strength and elongation at break (231.3%) via controllable chain extension-induced ordered microphase separation, providing hard-segment strength support and soft-segment elastic recovery space (Table S8 and Figure S8).

Comprehensive mechanical analysis confirms IPDA as the optimal chain extender for WBPUA systems.

3.5. Effect of diluent type on mechanical properties of waterborne polyurethane acrylate three-dimensional-printed materials

Tensile tests were conducted on photo-thermal dual-cured materials prepared with different diluents (Table S4). Diluent molecular structure, polarity, and reactivity directly affect crosslinking density, intermolecular forces, and chain mobility. As shown in Figure 3e and 3f, N,N-Dimethylacrylamide (DMAA) and ACOMO exhibited optimal comprehensive performance: DMAA (19.2 MPa, 291.3%), ACOMO (16.1 MPa, 312.4%), followed by MMA (14.8 MPa, 231.3%); IBOA and tert-butyl acrylate (TBA) showed significantly reduced strength, while isodecyl acrylate (IDA) delivered the weakest performance (1.44 MPa, 184.8%). DMAA and ACOMO contain polar N/O groups that form strong hydrogen bonds with -COOH in WBPUA chains, enhancing intermolecular cohesion and crosslinked network stability, thus achieving simultaneous high strength and toughness. MMA is a highly reactive rigid monomer with high crosslinking density and good comprehensive performance. IBOA and TBA have

bulky side groups that create steric hindrance, reducing photocuring rate and crosslinking density, degrading mechanical properties. IDA has a long flexible chain with no rigid units, weak intermolecular forces, and low crosslinking density, resulting in poor strength and toughness (Table S9 and Figure S9). Thus, DMAA was selected as the optimal diluent for WBPUA systems.

Subsequent experiments used HMDI as the WBPUA prepolymer raw material, DMAA as the diluent, and IPDA as the chain extender for the photosensitive resin formulation.

3.6 Mechanical performance comparison of waterborne polyurethane acrylate prepolymers with different structures and multiple crosslinked network mechanism analysis

To elucidate the superior mechanical performance of the WBPUA resin containing HUBs, carboxyl groups, and diamine chain extenders, a series of structurally progressive model prepolymers (Oligomer A-D) were compared with the target system (Oligomer) (Figure 4). Differences in crosslinking mechanism, functional group distribution, and curing mode determine crosslinked network density, microphase separation, and mechanical performance.

Oligomer A is a conventional single-photocured PUA without carboxyl or HUBs, forming a single crosslinked network via acrylate double bond polymerization, with the lowest tensile strength (~2.71 MPa) and elongation at break (~97.6%). Oligomer B incorporates carboxyl groups (-COOH), with hydrogen bonding enhancing intermolecular forces, improving strength (~4.36 MPa) and elongation at break (~122.8%), but still relying on single photocuring with low crosslinking density and network defects.

Oligomers C and D introduce HUBs for photo-thermal dual curing, enabling secondary crosslinking with potential reactive sites. Oligomer C (no carboxyl groups) undergoes limited post-crosslinking during thermal curing, achieving a tensile strength of ~10.42 MPa and elongation at break of ~160.7%. Oligomer D (with carboxyl groups) benefits from hydrogen bonding-enhanced intermolecular interactions and additional polar reactive sites, further improving performance (strength: ~13.89 MPa, elongation at break: ~203.4%).³³ However, the absence of diamine chain extenders in C and D limits full chain extension during thermal curing, resulting in incomplete crosslinked networks.

The target material (Oligomer) incorporates carboxyl groups, HUBs, and diamine chain extenders, creating a synergistic, multi-crosslinked network: photocuring crosslinking, thermal-curing chain extension, and

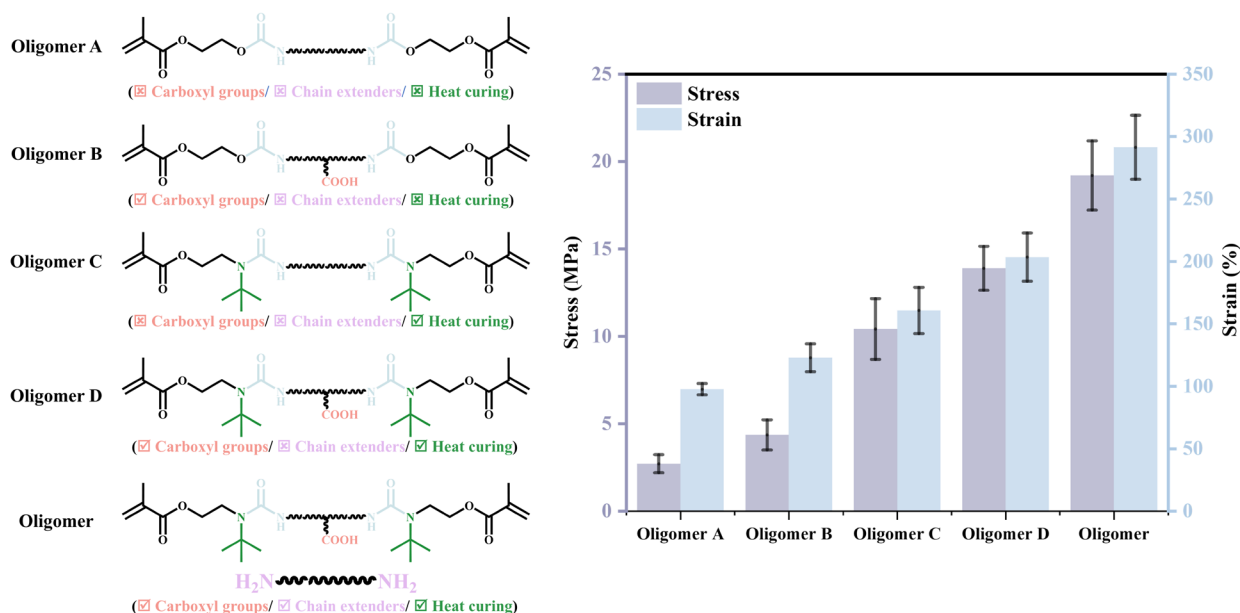


Figure 4. Comparison of molecular structures and cured mechanical properties of waterborne polyurethane acrylate prepolymers with different structures

carboxyl hydrogen bonding. Photocuring forms an initial crosslinked skeleton for molding stability; thermal curing triggers HUB dissociation to release $-NCO$, reacting with diamines to increase chain length and crosslinking density, forming a dense 3D crosslinked network; carboxyl groups form hydrogen bonds with polar groups, further enhancing intermolecular forces and network stability. This synergistic effect results in a tensile strength of ~ 19.2 MPa and elongation at break of $\sim 291.3\%$, significantly outperforming all control systems.

In summary, the synergistic combination of carboxyl groups, HUBs, and diamine chain extenders enables the WBPUA resin to form a highly crosslinked network with strong intermolecular forces and ordered microphase separation, maximizing the advantages of photo-thermal dual curing and achieving simultaneous improvements in strength and toughness.

3.7. Photocuring conversion verified by Fourier transform infrared spectroscopy

Fourier transform infrared spectroscopy was performed to characterize the consumption of acrylate $C=C$ double bonds before and after photopolymerization, eliminating the impact of residual photopolymerization (Figure S11). The characteristic absorption peak corresponding to the $C=C$ stretching vibration was clearly observed in the pristine WBPUA-DMAA resin, while this signal nearly disappeared upon photocuring. This spectroscopic evidence shows that

photopolymerization proceeds sufficiently, with barely any residual acrylate double bonds remaining in the photocured network, excluding confounding effects from unreacted vinyl groups.

3.8. Effect of antistatic agent type on antistatic performance of waterborne polyurethane acrylate three-dimensional-printed materials

Antistatic tests were performed on photo-thermal dual-cured materials prepared with different antistatic agents (Table S5). STAC and STAB were added at varying contents to investigate their effects on surface resistivity and long-term stability. A surface resistivity $< 1 \times 10^{10} \Omega$ is defined as effective antistatic performance. Surface resistivity decreases significantly with increasing antistatic agent content for both systems, with the STAC system exhibiting superior antistatic performance and long-term stability (Figure 5a and 5b).

At the same loading, the STAC system has lower surface resistivity and slower attenuation: at 1.0 wt%, STAC maintained surface resistivity $< 1 \times 10^{10} \Omega$ for 28 days with no obvious decay; the STAB system approached the critical value at 21 days and exceeded it at 28 days. This difference arises from stronger interactions between Cl^- in STAC and $-COOH$ in WBPUA chains, forming stable ion-conducting channels and inhibiting antistatic agent migration. Br^- in STAB exhibits weaker interactions, facilitating migration and loss, leading to rapid antistatic performance decay.³⁴

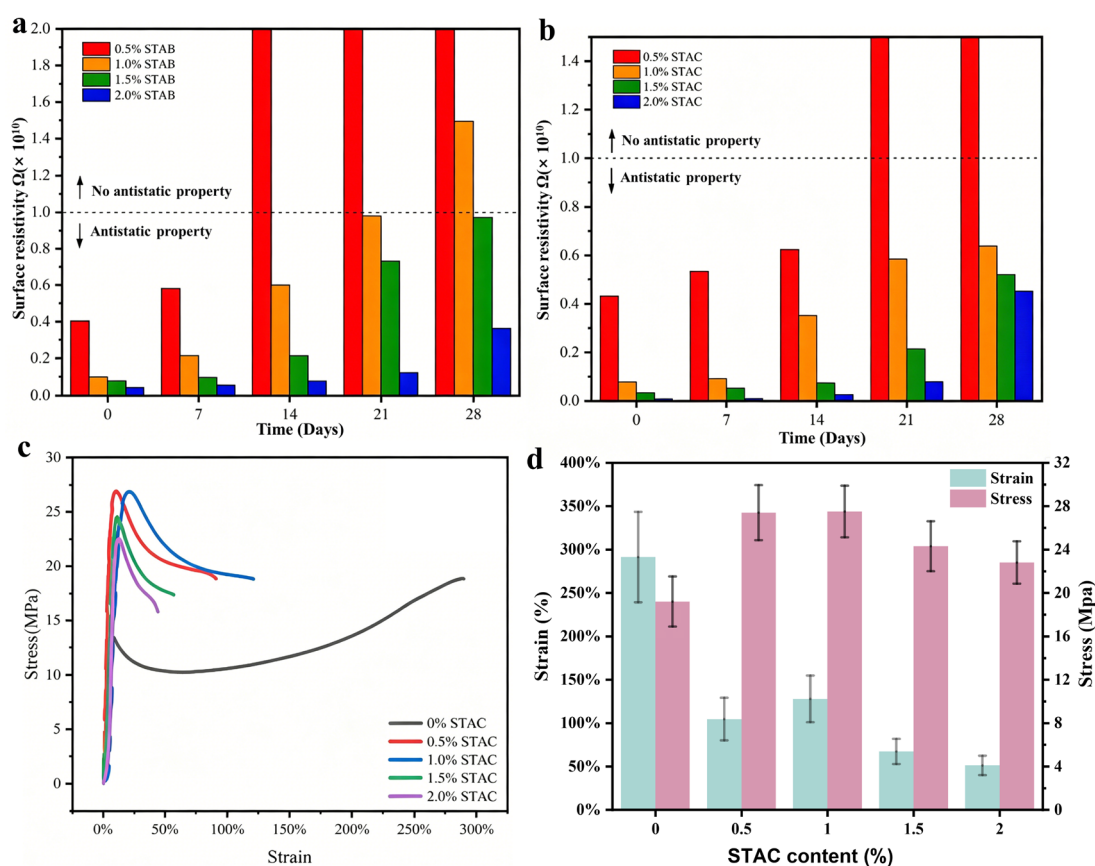


Figure 5. Antistatic performance, long-term durability, and mechanical properties of photo-thermal dual-cured waterborne polyurethane acrylate (WBPUA) three-dimensional (3D)-printed materials with ionic antistatic agents. (a) Antistatic performance and durability (0–28 days) of WBPUA 3D-printed materials with octadecyltrimethylammonium bromide (STAB) as an antistatic agent. (b) Antistatic performance and durability (0–28 days) of WBPUA 3D-printed materials with octadecyltrimethylammonium chloride (STAC) as an antistatic agent. (c) Stress–strain curves of WBPUA 3D-printed materials with different STAC contents. (d) Comparison of stress–strain curves for WBPUA 3D-printed materials with different STAC contents.

At loadings > 1.5 wt%, the reduction rate of surface resistivity decreased for both systems, as excess antistatic agents aggregate and settle in the aqueous system, impairing mechanical properties without further improving antistatic performance. Comprehensive analysis of antistatic performance, long-term stability, and system compatibility confirms 1.0 wt% STAC as the optimal loading, enabling long-term stable antistatic performance with minimal impact on mechanical properties.

3.9. Effect of octadecyltrimethylammonium chloride content on mechanical properties of waterborne polyurethane acrylate three-dimensional-printed materials

The effect of STAC loading on mechanical properties of photo-thermal dual-cured WBPUA materials was investigated using the HMDI–WBPUA–IPDA–DMAA base resin. As shown in Figure 5c and 5d, STAC addition

significantly altered mechanical behavior, with performance closely correlated with the loading. Compared with the blank sample, all STAC-loaded systems exhibited increased tensile strength, peaking at 26.8 MPa with 1.0 wt% STAC (0.5 wt%: ~ 26.5 MPa). Strength gradually decreased at loadings of 1.5 wt% (~ 24.8 MPa) and 2.0 wt% (~ 22.8 MPa) but remained higher than the blank sample (~ 19.2 MPa). Elongation at break decreased with increasing STAC loading: blank sample ($\sim 291.3\%$), 1.0 wt% STAC ($\sim 110\%$), 2.0 wt% STAC ($\sim 40\%$).

This performance change stems from interactions between STAC and the WBPUA matrix, as well as its dispersion state. Polar quaternary ammonium groups in STAC form hydrogen bonds or ionic interactions with $-\text{COOH}$ and urethane groups in resin chains, enhancing intermolecular forces and increasing tensile strength at low loadings (≤ 1.0 wt%). Excess STAC aggregates form defect sites in the matrix and disrupt crosslinked

network continuity, reducing strength. As a non-reactive additive, STAC physically disperses in the matrix without participating in crosslinking, restricting chain slippage/motion and reducing toughness/elongation at break. Comprehensive analysis of strength and toughness confirms 1.0 wt% STAC as the optimal loading, balancing antistatic and mechanical performance.

The superior long-term antistatic durability of WBPUA–STAC systems is rationalized by electrostatic and hydrogen-bond interactions between cationic quaternary ammonium groups from STAC and pendant anionic carboxyl ($-\text{COOH}$) groups along the WBPUA molecular backbone. This intermolecular anchoring suppresses STAC migration and leaching and stabilizes continuous ion-conducting channels within the polymer matrix, consistent with previously reported carboxyl-rich water-borne polyurethane/quaternary ammonium composite systems.^{33,34}

3.10. Water washability of waterborne polyurethane acrylate three-dimensional-printed-materials

The eco-friendly processability of WBPUA materials was evaluated by comparing cleaning efficiency with commercial LY6001 resin (Table S10). WBPUA specimens cleaned with 10% aqueous detergent were dry, residue-free, and non-sticky, comparable to ethanol cleaning; LY6001 specimens remained sticky with uncured resin residues after water cleaning, requiring ethanol for thorough cleaning. This difference arises from abundant polar carboxyl groups ($-\text{COOH}$) in WBPUA chains, which impart excellent water dispersibility to uncured resin, allowing it to emulsify, dissolve, and be removed by

aqueous detergent. Commercial LY6001 is a solvent-based resin with low polarity and poor water solubility, requiring organic solvents to remove uncured resin. Results confirm that WBPUA eliminates organic solvent cleaning, reduces VOC emissions, and meets green manufacturing requirements. Few existing commercial water-washable DLP resins can simultaneously achieve the combination of water washability, high strength-toughness, and long-term antistatic properties demonstrated in this work.

3.11. Digital light processing printing of complex structures/machinability

The steady-shear rheological properties of WBPUA resins with different STAC loadings were characterized to assess their processability for DLP-based vat photopolymerization (Figure S10). All formulations displayed typical shear-thinning behavior, with viscosity decreasing progressively with increasing shear rate—a feature favorable for DLP recoating and layer spreading. Compared with the STAC-free resin, viscosity increased upon STAC incorporation at identical shear rates due to enhanced intermolecular interactions. Importantly, all systems remained within the applicable range for DLP printing, providing a reliable rheological basis for formulation design and printing parameter optimization.

To demonstrate the practical manufacturability of the WBPUA resin via DLP-based vat photopolymerization, a series of complex planar structures—spider web, hexagonal honeycomb lattice, and perforated plate—were fabricated (Figure 6). The as-printed samples exhibited well-defined edges, continuous layered morphology, and negligible macroscopic defects, confirming that the resin satisfies

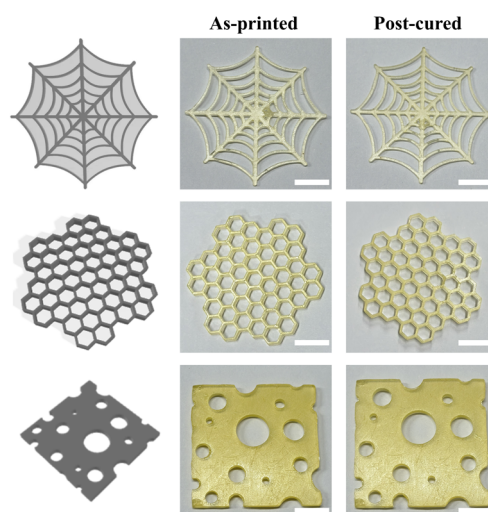


Figure 6. Digital models and optical photographs of digital light processing three-dimensional-printed complex structures (spider web, hexagonal honeycomb lattice, and perforated plate) in the as-printed and post-cured states. Scale bar: 10 mm

the fundamental requirements for DLP processing. Upon photo-thermal post-curing, the printed parts retained structural integrity and dimensional accuracy with no detectable warping or fracture, validating the compatibility of the dual-curing route with DLP-printed objects.

To assess the dimensional stability and computer-aided design-to-part accuracy of DLP-based vat photopolymerization fabricated parts upon photo-thermal post-curing, dumbbell specimens were measured along the X, Y, and Z axes (Figure 7). The optical photographs and

vernier-caliper measurement data are displayed in Figure 7a, and the calculated dimensional retention rate for each direction is plotted in Figure 7b. Values close to 100 % represent very small dimensional variation. All three axes showed high dimensional retention after post-curing, and no visible warpage or distortion was observed on the printed samples. This high dimensional retention confirms the excellent dimensional fidelity of the WBPUA resin system, supporting its use for fabricating high-precision vat-photopolymerization parts.

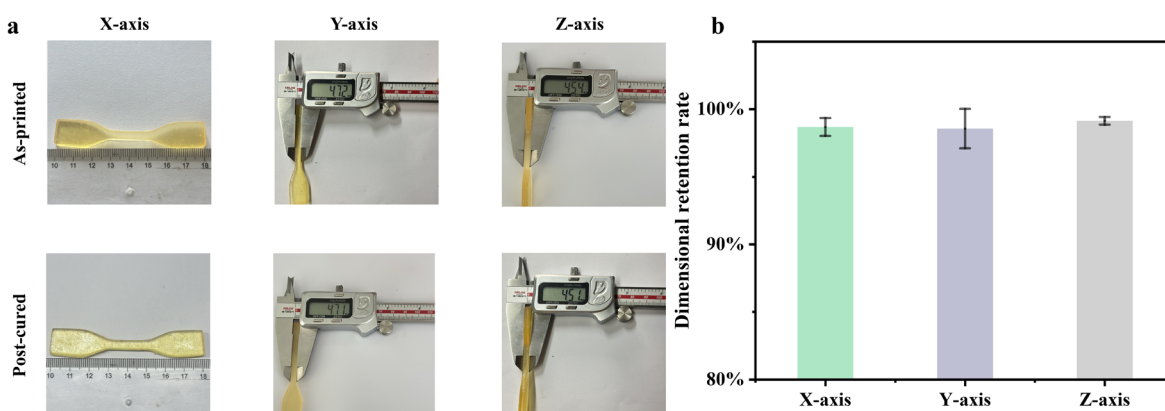


Figure 7. Dimensional characterization of DLP-printed dumbbell specimens before and after photo-thermal post-curing. (a) Optical photographs and caliper measurements of as-printed and post-cured samples along the X, Y, and Z axes. (b) Statistical dimensional retention rates of printed parts in three orthogonal directions after post-curing.

4. Conclusion

A blocked WBPUA prepolymer containing thermally reversible urea bonds and carboxyl groups was successfully synthesized, verifying complete introduction and reaction of acrylate groups for photo-thermal dual curing. Systematic optimization of raw material composition and the curing process identified the optimal preparation conditions: HMDI as the isocyanate, IPDA as the chain extender, DMAA as the diluent, 1.0 wt% STAC as the antistatic agent, and thermal curing at 110 °C for six hours. This approach constructed a synergistic, multi-crosslinked network (photocuring crosslinking, thermal-curing chain extension, carboxyl hydrogen bonding) that balances material strength and toughness. The optimized material integrates excellent mechanical properties, long-term antistatic performance, and water washability, achieving a tensile strength of 26.8 MPa, elongation at break of 110%, stable antistatic performance for 28 days, and zero VOC emissions via water-only cleaning. This WBPUA-based DLPbased vat photopolymerization material addresses the critical trade-off between environmental friendliness, mechanical performance, and antistatic property in

traditional materials, enabling applications in functional and structural components for electronics and precision instruments, and providing a theoretical basis and technical support for the industrial application of eco-friendly additive manufacturing materials.

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Conflict of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Availability of data

The data and materials of the study can be obtained from the corresponding author upon request.

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