

3D Printing of Photosensitive Poly(oxime-urethane) for Network Rearrangement and Interfacial Welding

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Electronic Supplementary Information

Abstract Digital light processing (DLP) 3D printing enables high-resolution and efficient fabrication, yet achieving multimaterial printing with robust mechanical performance remains challenging due to limitations in the molecular design. Here, we report a photo-thermal dual-curing strategy to address this challenge. The photosensitive poly(oxime-urethane) resin, which forms ionic bonding between carboxylic acid and 2-(dimethylamino)ethyl methacrylate, exhibits excellent printability with low viscosity (below 5000 mPa·s), high storage moduli after gelation (exceeding 10^5 Pa), and high storage stability (over 30 days). The post-printing thermal curing between carboxylic acid and oxime-urethane bonds enables network rearrangement for mechanical enhancement and interfacial welding of modules with diverse properties. This dynamic chemical design facilitates high-performance multimaterial integration, significantly expanding the design flexibility and versatility for the fabrication of complex structures.

Keywords 3D printing; Dynamic covalent bonds; Photopolymerization; Photo-thermal dual-curing; Oxime-urethane

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INTRODUCTION

Three-dimensional (3D) printing has emerged as a revolutionary manufacturing technique by offering the design freedom to access arbitrarily complex architectures, enabling diverse applications in fields such as electronics, soft robots, and biomedicine.^[1–4] Among various options, digital light processing (DLP) 3D printing is particularly promising due to its high resolution and production efficiency. Recent advances in ultra-fast printing and resin recyclability have further enhanced the viability of DLP technology.^[5–12] A fundamental prerequisite for DLP printing is the rapid gelation of resins upon light exposure, which, however, imposes severe restrictions on the molecular design of polymer networks and often compromises the performance of printed parts.^[13]

To address the inherent conflict between printability and fi-

nal mechanical performance, a photo-thermal dual-curing strategy has recently been explored.^[14–20] Typically, the photosensitive components are first photocured to form a green part during 3D printing. Subsequently, the unreacted thermally curable component within the photocured network polymerizes into a second network for mechanical enhancement.^[14–16] However, it faces two major challenges. First, as the resin is only partially cured during printing, the amount of thermally curable components that can be incorporated is limited to maintain printability. Second, the thermal curing step tends to induce excessive crosslinking in the network, which often compromises the stretchability of the materials.

One notable example to fabricate high-performance elastomers involves the incorporation of dynamic covalent bonds. The underlying mechanism stems from the incorporation of dynamic hindered urea bonds into photocured networks. During thermal post-curing, deblocked isocyanates react with amine or carboxyl groups, which allows for post-printing network reconfiguration and thus imparts high mechanical properties. While effective, the state-of-the-art strategy has so far been largely limited to the fabrication of soft

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rubbers.^[17–20] In addition, the hindered urea bond bearing a *tert*-butyl group exhibits excessive dynamicity at room temperature,^[21,22] raising significant concerns about resin stability.

The seamless integration of diverse material properties is also essential for DLP 3D printing. However, despite significant efforts, multimaterial DLP printing remains challenging due to the need for complex resin formulations and stringent instrumentation.^[23–26] As an alternative, interfacial welding, which assembles individual 3D-printed modules with tailored properties into a multimaterial structure, offers the benefit of allowing independent control over each module's properties and functions.^[27,28] Here, we propose a photo-thermal dual-curing strategy that enables high-performance multimaterial DLP printing through synergistic network rearrangement and interfacial welding. Our approach employs a photosensitive poly(oxime-urethane) resin that incorporates dynamic oxime-urethane linkages and ionic interactions between carboxylic acid groups and 2-(dimethylamino)ethyl methacrylate. We note here that the incorporation of dynamic oxime-urethane bonds in the resin offers several benefits. First, compared with the commonly used hindered urea bearing a *tert*-butyl group, the oxime-urethane exhibits lower dynamicity at room temperature, ensuring the storage stability of the resin before printing. Second, the dissociation of oxime-urethane at high temperature allows deblocking of the isocyanate group, which facilitates the reaction of carboxylic acid groups for network rearrangement and interfacial welding. This enables the integration of multi-material structures with high mechanical properties.

EXPERIMENTAL

Materials

Poly(tetrahydrofuran) diol ($M_n=1000$ g·mol⁻¹) was purchased from B&D and dried at 110 °C under vacuum for 1 h before use. Toluene diisocyanate, dimethylolbutyric acid, dibutyltin dilaurate, 2-(dimethylamino)ethyl methacrylate (DMAEMA), trimethylolpropane triacrylate (TMPTA), tetrahydrofurfuryl methacrylate (THFMA), Sudan III, Sudan I, and Sudan Black B were obtained from Aladdin. Acetone oxime and bis(2,4,6-trimethylbenzoyl)phenylphosphine oxide (Irgacure 819) were purchased from Macklin. 2-(*tert*-Butylamino)ethyl methacrylate was provided by TCI. All chemical reagents were used as received unless otherwise noted.

Preparation of the Photosensitive Poly(oxime-urethane)

The synthesis of the photosensitive poly(oxime-urethane) was carried out in four steps. First, poly(tetrahydrofuran) diol (0.05 mol) and toluene diisocyanate (0.10 mol) were added to a three-necked flask equipped with a mechanical stirrer. The reaction was performed at 50 °C for 4 h after the introduction of dibutyltin dilaurate (0.1 wt% relative to poly(tetrahydrofuran) diol) as the catalyst. Subsequently, dimethylolbutanoic acid (0.033 mol) was added, and the reaction was continued for another 4 h. Next, acetone oxime (0.033 mol) was added to block the remaining isocyanate groups, and the mixture was reacted for an additional 4 h. Finally, 2-(dimethylamino)ethyl methacrylate was added in a 1:1 molar ratio relative to the carboxylic acid groups and allowed to react overnight. The chemical structure

of the product was characterized using nuclear magnetic resonance (¹H-NMR) and Fourier-transform infrared (FTIR) analysis. The photosensitive poly(hindered urea-urethane) was synthesized following the same procedure, except that the acetone oxime was replaced with 2-(*tert*-butylamino)ethyl methacrylate.

Digital Light 3D Printing

The DLP printing precursor for M48%-T2% was prepared by mixing the photosensitive poly(oxime-urethane) (100 g), THFMA (96 g), TMPTA (4 g), Irgacure 819 (2 g), and Sudan I (0.02 g). The DLP printing precursor for M45%-T5% was prepared by mixing the photosensitive poly(oxime-urethane) (100 g), THFMA (90 g), TMPTA (10 g), Irgacure 819 (2 g), and Sudan III (0.02 g). The DLP printing precursor for M40%-T10% was prepared by mixing the photosensitive poly(oxime-urethane) (100 g), THFMA (80 g), TMPTA (20 g), Irgacure 819 (2 g), and Sudan Black B (0.02 g). All mixtures were stored in the dark before use. Printing was performed using a bottom-up DLP printer (Moonray S, 10 mW·cm⁻²) with an exposure time of 10–25 s. The printed objects were rinsed with butyl acetate to remove uncured resin, followed by post-curing in a UV chamber (IntelliRay 600 Flood UV, Uvitron International, 955 mW·cm⁻², 265–700 nm). For thermal post-curing, the printed objects were then annealed at 120 °C for 2 h.

Characterizations

¹H-NMR spectra were collected using an Avance III spectrometer (Bruker). FTIR spectra were recorded using a Nicolet iS50 FTIR spectrometer (Thermo Fisher Scientific). DSC experiments were conducted using a TA Q200 instrument at a heating rate of 3 °C·min⁻¹. The viscosity of the printing precursors was measured using a digital viscometer (NDJ-5S), while that of poly(oxime-urethane) was measured using a rheometer (MARS 60) at a shear rate of 0.1 s⁻¹. Photo-rheology measurements were performed using an Anton Paar MCR 702e rheometer equipped with a detachable photo-illumination system (OmniCure S1500) by monitoring the evolution of storage moduli (*G'*) and loss moduli (*G''*). The gelation content was determined by extracting the samples with butyl acetate. The cross-sectional morphology of the welded interfaces was characterized by scanning electron microscopy (SEM, SU-8010, Hitachi, Japan) after the samples were fractured in liquid nitrogen and sputter-coated with platinum. The tensile tests were conducted on a testing machine (SUNS) at a constant crosshead speed of 50 mm·min⁻¹. The testing specimens were cut into dumbbell shapes (20.0 mm × 2.0 mm × 0.4 mm) according to the ISO standard 527-3:1995 before use, and at least three specimens were tested for each sample. The tensile toughness was calculated according to previous work.^[17]

RESULTS AND DISCUSSION

The photosensitive poly(oxime-urethane) comprises oxime-urethane and pendant carboxylic acid groups (Fig. 1a), synthesized via a four-step, solvent-free process (Fig. S1 in the electronic supplementary information, ESI). First, polytetrahydrofuran diol ($M_n=1000$ g·mol⁻¹) is reacted with toluene-2,4-diisocyanate to obtain an isocyanate-terminated prepolymer. Subsequently, the terminal isocyanate undergoes reaction with hydroxymethylbutyric acid, introducing two carboxylic acid groups into the side chains. The remaining isocyanate groups are then blocked

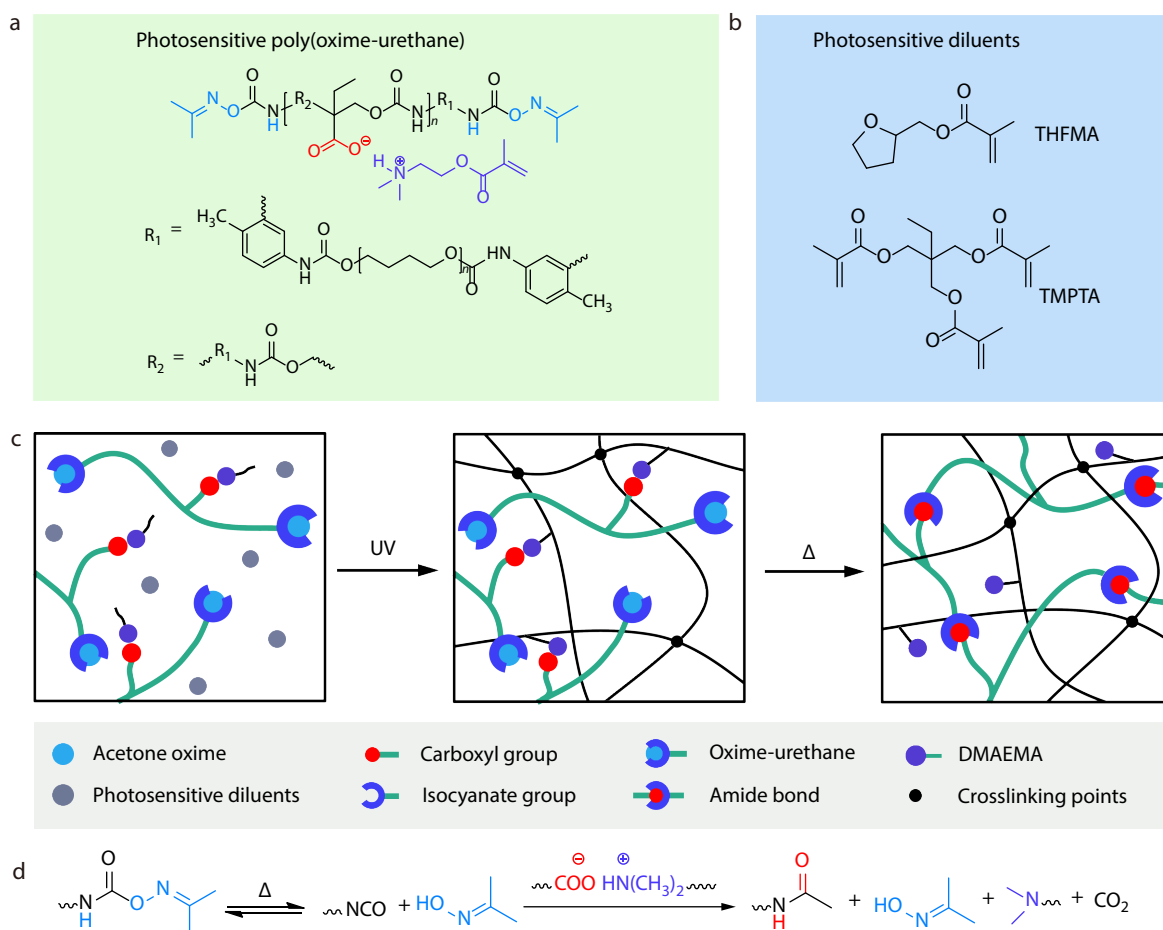


Fig. 1 Chemical design and network formation. (a) Chemical structure of the photosensitive poly(oxime-urethane); (b) Chemical structures of the photosensitive diluents; (c) Network formation via a photo-thermal dual-curing strategy; (d) The reaction between oxime-urethane and carboxylic acid groups.

with acetone oxime, forming dynamic oxime-urethane bonds. Finally, 2-(dimethylamino)ethyl methacrylate (DMAEMA) is added to form a salt with the carboxylic acids, thereby introducing UV-sensitive functional groups. The successful synthesis of the target product is verified by $^1\text{H-NMR}$ and FTIR analyses (Figs. S2 and S3 in ESI).

The resulting photosensitive poly(oxime-urethane) exhibits fast polymerization kinetics, achieving a short gelation time of 13 s (Fig. S4 in ESI). However, direct use in 3D printing is hindered by the low storage modulus after gelation (tens of kPa) (Fig. S4 in ESI) and high resin viscosity (10350 Pa·s), which stems from weak interactions involving the ionic bonds. To address this limitation, two photosensitive diluents, tetrahydrofurfuryl methacrylate (THFMA) and trimethylolpropane triacrylate (TMPTA), are incorporated (Fig. 1b). They not only reduce viscosity but also help form a robust network with tailorable mechanical properties. Here, a series of samples is prepared and denoted as Mx-Ty, where x and y represent the weight percentages of THFMA and TMPTA, respectively. The polymer networks are constructed via a photo-thermal dual-curing strategy, as illustrated in Fig. 1(c). Upon photo-illumination, the (meth)acrylate undergoes rapid free-radical polymerization to form the first network. During subsequent thermal post-curing, the oxime-urethane groups dis-

sociate to generate isocyanate groups,^[29–31] which then react with the pendant carboxylic acid groups to form the polyamide network (Fig. 1d). This process results in an interpenetrating polymer network combined with the initially photocured polyacrylate network, contributing to the high performance of the final material.

The deblocking and subsequent crosslinking behaviors of the photosensitive poly(oxime-urethane) are critical, as they significantly influence the final mechanical performance. As shown in Fig. 2(a), a distinct exothermic peak of the photosensitive poly(oxime-urethane) is observed in the differential scanning calorimetry (DSC) profile in the temperature range of 100–140 °C, which is attributed to the deblocking of dynamic oxime-urethane bonds and their subsequent reaction with the pendant carboxylic acid groups. This provides a guideline for selecting a thermal curing temperature of 120 °C. The extent of the reaction over time at this temperature (120 °C) is monitored using FTIR spectroscopy after postcuring (Fig. 2b). As time goes on, the characteristic band corresponding to the oxime-urethane bonds at 925 cm^{-1} gradually diminishes and disappears after 2 h. Quantitative analysis of the infrared spectra reveals that the conversion increases linearly, reaching approximately 100% at 2 h (Fig. 2c). The gel fraction measurements further confirm the formation of a

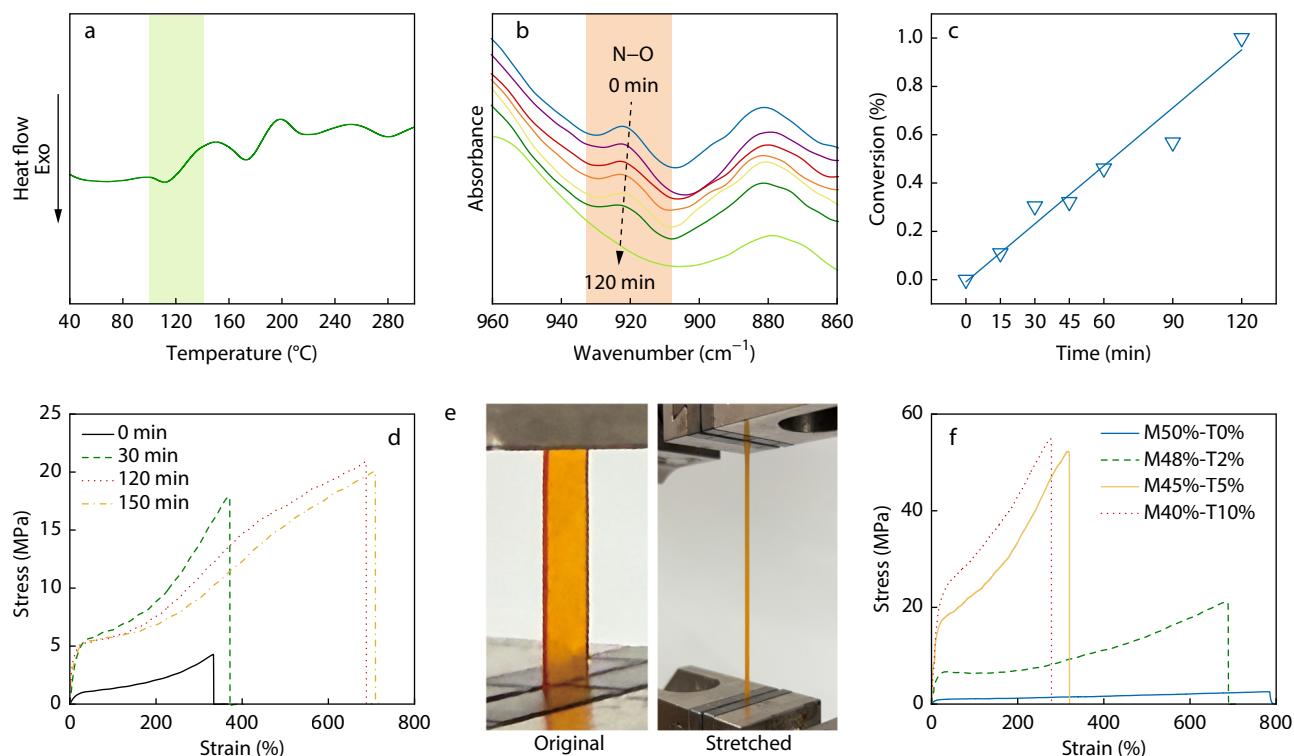


Fig. 2 Deblocking chemistry investigation and mechanical characterization. (a) DSC curves of the photosensitive poly(oxime-urethane) ranging from 40 °C to 300 °C; (b) FTIR spectroscopy with different reaction time. From top to bottom, the reaction time correspond to 0, 15, 30, 45, 60, 90, and 120 min. (c) Conversion with different reaction time; (d) Stress-strain curves of the sample M48%-T2% with different post-curing time; (e) The image of the original sample M48%-T2% and the sample after stretching to 680%; (f) Stress-strain curves of the samples with different formulations.

crosslinked network. As shown in Fig. S5 (in ESI), the gel content increases linearly and reaches 94% upon thermal annealing at 120 °C for 2 h. The stress-strain curve of the poly(oxime-urethane) after photocuring and post-curing (2 h) is presented in Fig. S6 (in ESI), showing a high breaking strain exceeding 2000%.

Having investigated the deblocking mechanism, DLP precursors are formulated by incorporating the photosensitive poly(oxime-urethane) and diluents, and the polymer networks are constructed through sequential photo- and thermal-curing processes. The influence of thermal post-curing time on mechanical performance is first evaluated using a representative formulation of M48%-T2%. As shown in Fig. 2(d), the initially photocured sample exhibits tensile strength and breaking strain of 4.3 MPa and 332%, corresponding to a toughness of 7.7 MJ·m⁻³ (Table S1 in ESI). Upon thermal post-curing, the mechanical performance is substantially enhanced. At an optimal post-curing time of 2 h, the tensile strength and breaking strain increase to 21.1 MPa and 688%, respectively, while the toughness increases nearly 10-fold to 76.8 MJ·m⁻³. Fig. 2(e) visually demonstrates the high mechanical performance of M48%-T2% during tensile testing.

Variation in the composition enables access to a broad range of material properties (Tables S2–S4 in ESI). As shown in Fig. 2(f), increasing the content of trimethylolpropane triacrylate leads to an increase in Young's modulus from 7.5 MPa for M50%-T0% to 133.8 MPa for M40%-T10% after post-curing. However, the breaking strain follows an opposite trend, decreasing from 785% to 283%. This phenomenon is

attributed to an increase in crosslinking density of the polyacrylate network by introducing a higher proportion of trifunctional crosslinker. The low tensile strength observed for M50%-T0% is primarily attributed to the uncrosslinked nature of the polyacrylate network following post-curing. In addition, formulations with different resin contents are also investigated. The results shown in Fig. S7 (in ESI) reveal that an increase in resin content leads to improved mechanical performance (Table S5 in ESI). Specifically, the tensile strength and breaking strain of M28%-T2% are 34.4 MPa and 943%, respectively. This improvement is attributed to the high proportion of the polyamide network within the final network formation. Despite variations in modulus across formulations, all materials exhibit robust mechanical performance, ensuring their use in diverse applications.

The dynamic blocking chemistry that governs the formation of interpenetrating polymer networks also facilitates interfacial welding. To evaluate this capability, we first select M48%-T2% as a representative formulation to investigate the welding performance between materials of identical composition. The welding process is conducted by bringing two photocured samples into contact and subjecting them to post-curing at 120 °C for 2 h. The resulting welded sample is sufficiently robust to undergo stretching without interfacial failure (Fig. 3a). The mechanical performance of the welded sample is assessed through tensile testing, with the welding efficiency calculated based on the change in tensile strength. The stress-strain curves in Fig. 3(b) reveal that the welded sample exhibits tensile strength and breaking strain of 16.5

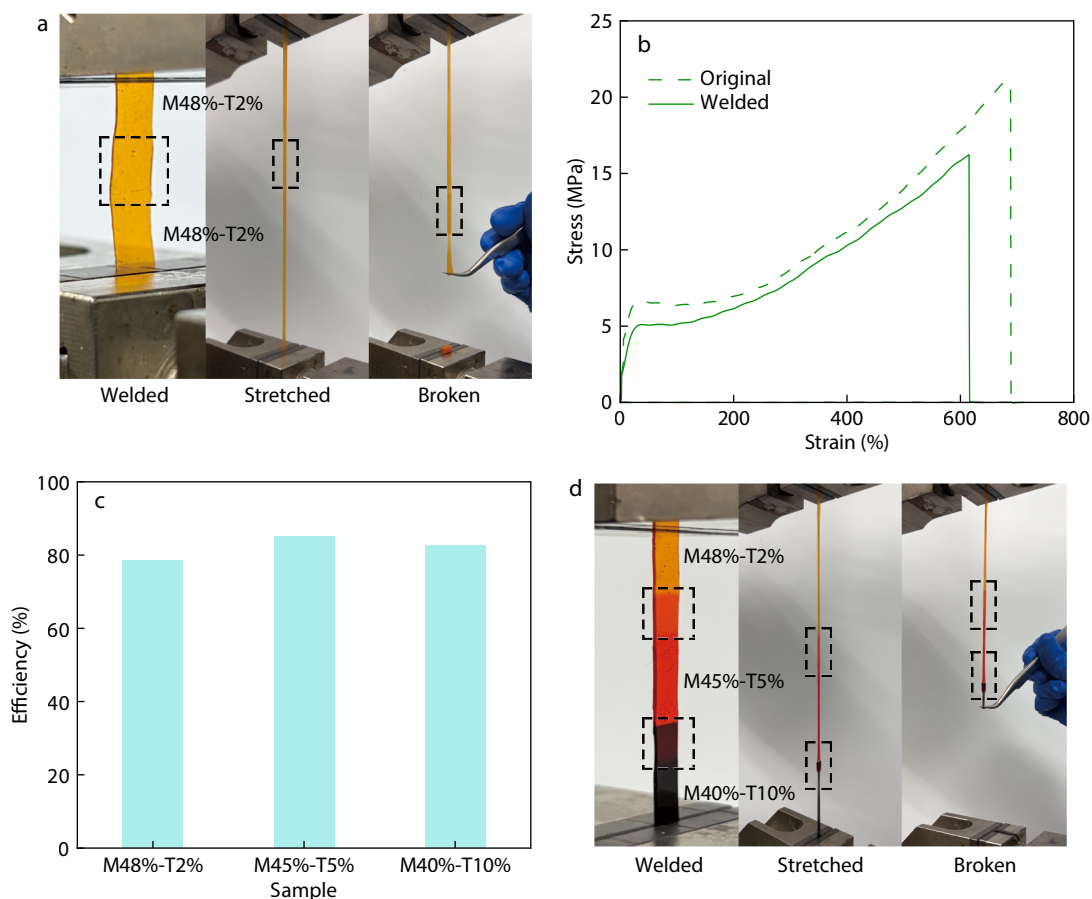


Fig. 3 Interfacial welding of dynamic polymer networks. (a) The image of the welded sample M48%-T2% before and after stretching; (b) Stress-strain curves of the original and welded sample M48%-T2%; (c) The welding efficiencies of M48%-T2%, M45%-T5%, and M40%-T10%; (d) The image of the welded sample between different formulations before and after stretching.

MPa and 610%, respectively (Table S6 in ESI). The corresponding welding efficiency is calculated as 79%. SEM images of the welded samples before and after stretching further demonstrate superior interfacial welding performance, with no significant cracks observed after stretching (Fig. S8 in ESI). Under the same welding conditions, we further examine the welding behavior of M45%-T5% and M40%-T10% (Fig. S9 and Table S6 in ESI). The results shown in Fig. 3(c) indicate that both formulations achieve high welding efficiencies, with the values achieving 91% and 87%, respectively.

We also investigate the welding performance between materials of different compositions. The formulations (M48%-T2%, M45%-T5%, and M40%-T10%) are each incorporated with different photoabsorbers for differentiation. Fig. 3(d), Figs. S8 and S10 (in ESI) show the successful welding between M48%-T2%, M45%-T10%, and M40%-T10%, with no interfacial failure observed during stretching. The above results suggest that despite differences in their macroscopic mechanical properties, the presence of the same dynamic blocking chemistry enables effective welding between different samples.

The formulation significantly influences resin viscosity and curing kinetics, both of which are critical factors in DLP 3D printing. As shown in Fig. 4(a), increasing the amount of trimethylolpropane triacrylate leads to a slight increase in vis-

cosity. However, all formulations exhibit low viscosity (below 5000 mPa·s), making them suitable for 3D printing. To investigate curing kinetics, we use photo-rheology to monitor the evolution of storage (G') and loss (G'') moduli under UV exposure. As shown in Fig. 4(b), both moduli increase rapidly for M48%-T2%, with the gelation point (defined as $G' = G''$) appearing after 20 s, indicating fast polymerization kinetics. In addition, increasing the trimethylolpropane triacrylate content reduces the gelation times (Fig. 4c and Fig. S11 in ESI), as this photosensitive diluent acts as a crosslinker that promotes network formation. In these cases, the storage modulus after gelation exceeds 10^5 Pa, making it robust for sequential DLP 3D printing. Importantly, the resin M48%-T2% exhibits negligible viscosity change even after 30 days of storage under dark conditions in open air (Fig. S12 in ESI). In contrast, under the same conditions, the viscosity of the resin prepared with hindered urea bonds bearing a tert-butyl group increases rapidly and undergoes gelation within 10 days (Fig. S12 in ESI). This comparison clearly demonstrates the high storage stability of our resin formulated with oxime urethane. Accordingly, a diversity of geometrically complex 3D structures with high fidelity are successfully printed using M48%-T2%, as demonstrated in Fig. 4(d). The 3D-printed structures exhibit superior weldability, allowing individual printed modules to be joined interfacially into an integrated one. As illustrated in Fig. 4(e), vertically sliced 3D-printed

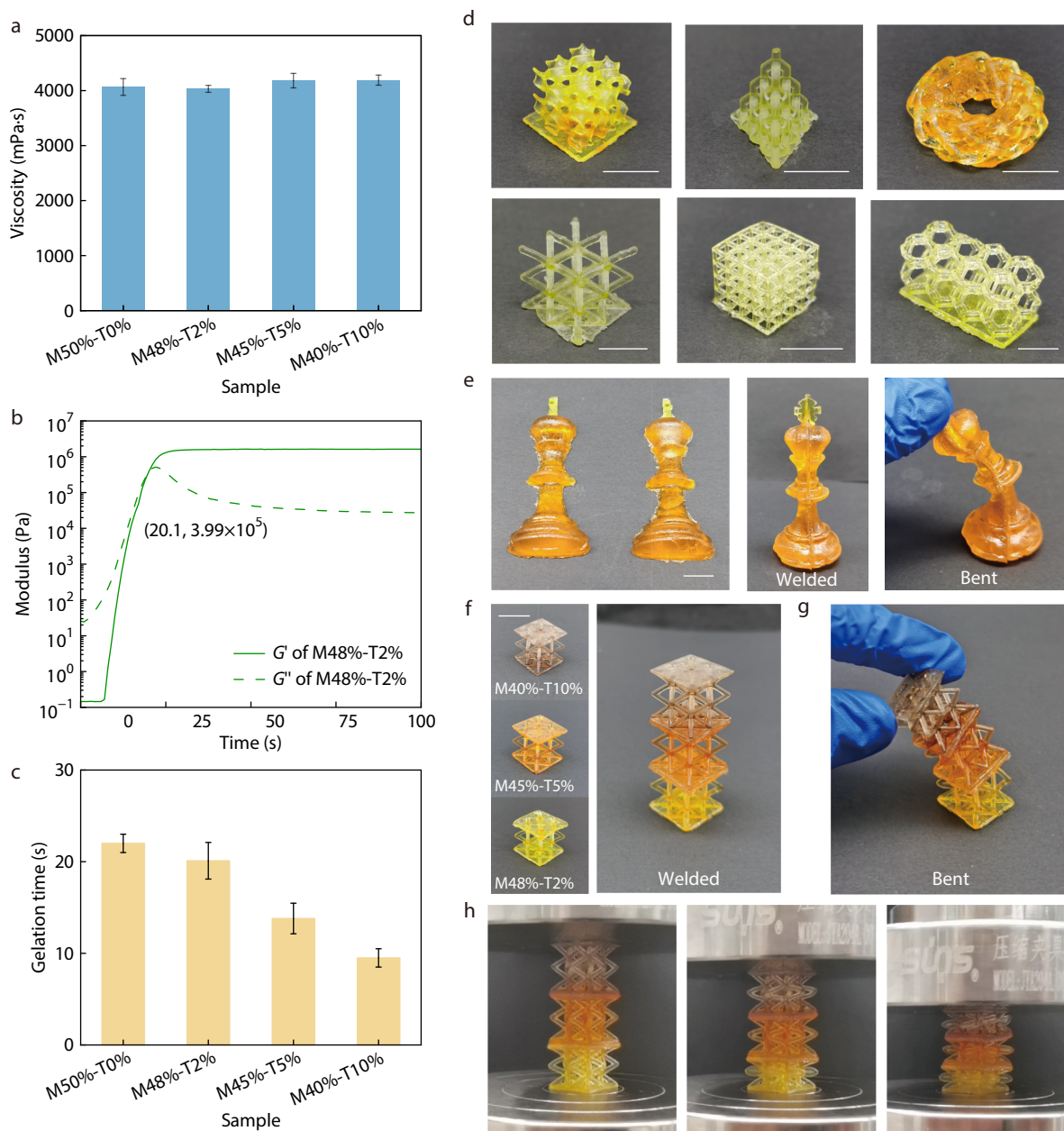


Fig. 4 DLP 3D printing and interfacial welding. (a) Viscosity of different formulations; (b) Photo-rheology of M48%-T2%; (c) Gelation times varied with different formulations; (d) Images of 3D-printed objects with complex structures for M48%-T2%; (e) The interfacial welding of 3D-printed chess modules; (f) The interfacial welding of 3D-printed modules with varying mechanical performances; (g, h) The bending and compressing behaviors of the welded multi-material objects. Scale bar, 10 mm.

chess modules are welded together (120 °C for 2 h) to obtain a complete object. In addition, 3D-printed modules with varying mechanical performance (M48%-T2%, M45%-T5%, and M40%-T10%) are also welded together to achieve multi-material integration (Fig. 4f). The resulting multi-material objects can withstand both bending and compressing (Figs. 4g and 4h), confirming the robustness of the interfacial welding.

CONCLUSIONS

In summary, we report a facile, solvent-free synthesis strategy for a photosensitive poly(oxime-urethane) tailored for DLP 3D printing. The incorporation of dynamic oxime-urethane linkage

and ionic interactions not only imparts high mechanical performance by post-printing network rearrangement, but also enables interfacial welding for multi-material integration. This approach achieves excellent printability (including low viscosity, fast gelation times, and high resin storage stability) along with tailorable high mechanical properties, establishing a versatile and scalable manufacturing route toward DLP 3D printing.

Conflict of Interests

Tao Xie is an associate editor for *Chinese Journal of Polymer Science* and was not involved in the editorial review or the deci-

sion to publish this article. All authors declare that there are no competing interests.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <http://doi.org/10.1007/s10118-026-3816-1>.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

ACKNOWLEDGMENTS

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REFERENCES

- 1 Gholami, F.; Yue, L.; Li, M.; Jain, A.; Mahmood, A.; Fratarcangeli, M.; Ramprasad, R.; Qi, H. J. Fast and efficient fabrication of functional electronic devices through grayscale digital light processing 3D printing. *Adv. Mater.* **2024**, *36*, 2408774.
- 2 Guo, Y.; Chen, S.; Sun, L.; Yang, L.; Zhang, L.; Lou, J.; You, Z. Degradable and fully recyclable dynamic thermoset elastomer for 3D-printed wearable electronics. *Adv. Funct. Mater.* **2021**, *31*, 2009799.
- 3 Zang, T.; Fu, S.; Cheng, J.; Zhang, C.; Lu, X.; Hu, J.; Xia, H.; Zhao, Y. 4D printing of shape-morphing liquid crystal elastomers. *Chem Bio Eng.* **2024**, *1*, 488–515.
- 4 Yao, K.; Lv, S.; Zhang, X.; Shen, K.; Chen, Y.; Ma, Z.; He, Y. 3D printing of multiscale biomimetic scaffold for tendon regeneration. *Adv. Funct. Mater.* **2025**, *35*, 2413970.
- 5 Sanders, S. N.; Schloemer, T. H.; Gangishetty, M. K.; Anderson, D.; Seitz, M.; Gallegos, A. O.; Stokes, R. C.; Congreve, D. N. Triplet fusion upconversion nanocapsules for volumetric 3D printing. *Nature* **2022**, *604*, 474–478.
- 6 Tumbleston, J. R.; Shirvanyants, D.; Ermoshkin, N.; Januszewicz, R.; Johnson, A. R.; Kelly, D.; Chen, K.; Pinschmidt, R.; Rolland, J. P.;

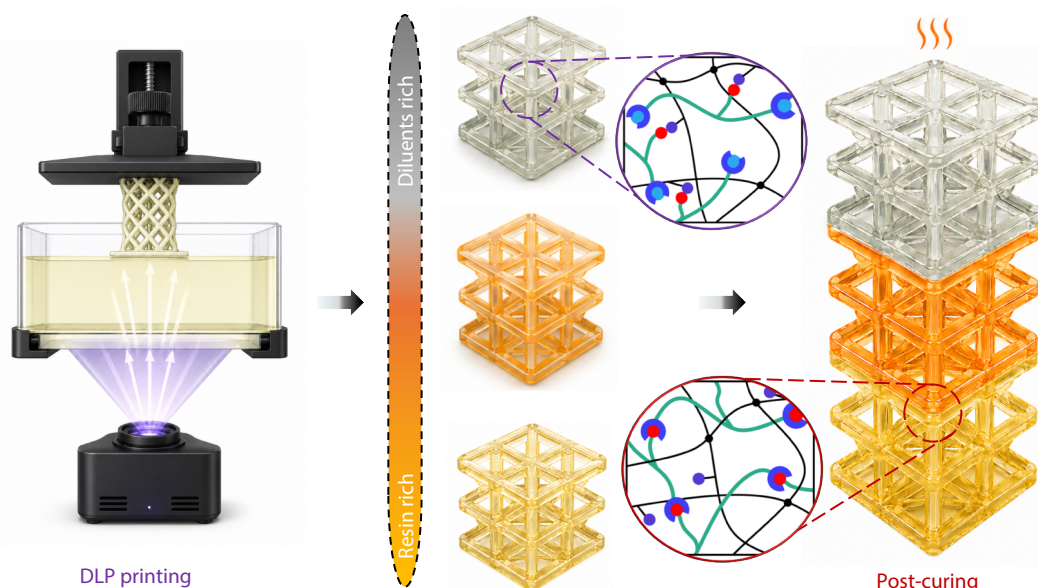
Graphical Abstract

3D Printing of Photosensitive Poly(oxime-urethane) for Network Rearrangement and Interfacial Welding

Zi-Chun Jiang, Ruo-Xuan Lv, Wen-Jun Peng, Chu-Jun Ni, Jing-Jun Wu, Qian Zhao, Zi-Zheng Fang, and Tao Xie

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This work proposed a photo-thermal dual-curing strategy that integrates dynamic oxime-urethane linkage and ionic interactions, enabling both high mechanical performance *via* post-printing network rearrangement and interfacial welding for multi-material integration.



- Ermoshkin, A.; Samulski, E. T.; DeSimone, J. M. Continuous liquid interface production of 3D objects. *Science* **2015**, *347*, 1349–1352.
- 7 Walker, D. A.; Hedrick, J. L.; Mirkin, C. A. Rapid, large-volume, thermally controlled 3D printing using a mobile liquid interface. *Science* **2019**, *366*, 360–364.
 - 8 Regehly, M.; Garmshausen, Y.; Reuter, M.; König, N. F.; Israel, E.; Kelly, D. P.; Chou, C. Y.; Koch, K.; Asfari, B.; Hecht, S. Xolography for linear volumetric 3D printing. *Nature* **2020**, *588*, 620–624.
 - 9 Yang, B.; Ni, T.; Wu, J.; Fang, Z.; Yang, K.; He, B.; Pu, X.; Chen, G.; Ni, C.; Chen, D.; Zhao, Q.; Li, W.; Li, S.; Li, H.; Zheng, N.; Xie, T. Circular 3D printing of high-performance photopolymers through dissociative network design. *Science* **2025**, *388*, 170–175.
 - 10 Machado, T. O.; Stubbs, C. J.; Chiaradia, V.; Alraddadi, M. A.; Brandolese, A.; Worch, J. C.; Dove, A. P. A renewably sourced, circular photopolymer resin for additive manufacturing. *Nature* **2024**, *629*, 1069–1074.
 - 11 Zhang, B.; Kowsari, K.; Serjouei, A.; Dunn, M. L.; Ge, Q. Reprocessable thermosets for sustainable three-dimensional printing. *Nat. Commun.* **2018**, *9*, 1831.
 - 12 Cui, J.; Liu, F.; Lu, Z.; Feng, S.; Liang, C.; Sun, Y.; Cui, J.; Zhang, B. Repeatedly recyclable 3D printing catalyst-free dynamic thermosetting photopolymers. *Adv. Mater.* **2023**, *35*, 2211417.
 - 13 Herzberger, J.; Sirrine, J. M.; Williams, C. B.; Long, T. E. Polymer design for 3D printing elastomers: recent advances in structure, properties, and printing. *Prog. Polym. Sci.* **2019**, *97*, 101144.
 - 14 Wallin, T. J.; Simonsen, L.-E.; Pan, W.; Wang, K.; Giannelis, E.; Shepherd, R. F.; Mengüç, Y. 3D printable tough silicone double networks. *Nat. Commun.* **2020**, *11*, 4000.
 - 15 Liu, J.; Miao, P.; Zhang, W.; Song, G.; Feng, J.; Leng, X.; Li, Y. Synthesis and characterization of interpenetrating polymer networks (IPNs) based on UV curable resin and blocked isocyanate/polyols. *Polymer* **2022**, *256*, 125254.
 - 16 Zhang, X.; Pu, X.; Xia, L.; Peng, W.; Ji, Y.; Xu, J.; Wu, J.; Jiang, L.; Zhao, Q.; Fang, Z.; Xie, T. Solvent- and catalyst-free bio-conversion of waste polyurethane foams into high-performance 3D printing resin. *Natl. Sci. Rev.* **2025**, *12*, nwaf501.
 - 17 Fang, Z.; Mu, H.; Sun, Z.; Zhang, K.; Zhang, A.; Chen, J.; Zheng, N.; Zhao, Q.; Yang, X.; Liu, F.; Wu, J.; Xie, T. 3D printable elastomers with exceptional strength and toughness. *Nature* **2024**, *631*, 783–788.
 - 18 Huang, X.; Peng, S.; Zheng, L.; Zhuo, D.; Wu, L.; Weng, Z. 3D printing of high viscosity UV-curable resin for highly stretchable and resilient elastomer. *Adv. Mater.* **2023**, *35*, 2304430.
 - 19 Gao, H.; Huang, X.; Arockiasamy, A. R.; Zhou, X.; Ding, X.; Zheng, L.; Liu, Y.; Ye, F.; Weng, Z.; Wu, L. Vat photopolymerization of stretchable foam with highly entangled and crosslinked structures. *Nat. Commun.* **2025**, *16*, 4756.
 - 20 Wu, T.; Zhang, Q.; Zhang, Z.; Lin, T.; Xie, Z.; Zang, Y.; Zheng, X.; Chen, L.; Hu, H.; Chen, Q.; Lai, G. Multiple hydrogen bonded 3D-printed elastomers with enhanced toughening by photothermal dual curing for customizable biomimetic flexible grippers. *Adv. Funct. Mater.* **2026**, *36*, e10489.
 - 21 Ying, H.; Zhang, Y.; Cheng, J. Dynamic urea bond for the design of reversible and self-healing polymers. *Nat. Commun.* **2014**, *5*, 3218.
 - 22 Zhang, Q.; Wang, S.; Rao, B.; Chen, X.; Ma, L.; Cui, C.; Zhong, Q.; Li, Z.; Cheng, Y.; Zhang, Y. Hindered urea bonds for dynamic polymers: an overview. *React. Funct. Polym.* **2021**, *159*, 104807.
 - 23 Ge, Q.; Chen, Z.; Cheng, J.; Zhang, B.; Zhang, Y. F.; Li, H.; He, X.; Yuan, C.; Liu, J.; Magdassi, S.; Qu, S. 3D printing of highly stretchable hydrogel with diverse UV curable polymers. *Sci. Adv.* **2021**, *7*, eaba4261.
 - 24 Kuang, X.; Wu, J.; Chen, K.; Zhao, Z.; Ding, Z.; Hu, F.; Fang, D.; Qi, H. J. Grayscale digital light processing 3D printing for highly functionally graded materials. *Sci. Adv.* **2019**, *5*, eaav5790.
 - 25 Kim, J. W.; Allen, M. J.; Recker, E. A.; Stevens, L. M.; Cater, H. L.; Uddin, A.; Gao, A.; Eckstrom, W.; Arrowood, A. J.; Sanoja, G. E.; Cullinan, M. A.; Freeman, B. D.; Page, Z. A. Hybrid epoxy-acrylate resins for wavelength-selective multimaterial 3D printing. *Nat. Mater.* **2025**, *24*, 1116–1125.
 - 26 Schwartz, J. J.; Boydston, A. J. Multimaterial actinic spatial control 3D and 4D printing. *Nat. Commun.* **2019**, *10*, 791.
 - 27 Zhu, G.; Hou, Y.; Xiang, J.; Xu, J.; Zhao, N. Digital light processing 3D printing of healable and recyclable polymers with tailorable mechanical properties. *ACS Appl. Mater. Interfaces* **2021**, *13*, 34954–34961.
 - 28 Liu, Y.; Yang, B.; Song, C.; Zhao, Q.; Xie, T.; Fang, Z.; Wu, J. Multishape programming of shape memory polymer assemblies fabricated by vat photopolymerization-based 3D printing and interfacial welding. *ACS Appl. Mater. Interfaces* **2023**, *15*, 57649–57655.
 - 29 Zhang, L.; You, Z. Dynamic oxime-urethane bonds, a versatile unit of high performance self-healing polymers for diverse applications. *Chinese J. Polym. Sci.* **2021**, *39*, 1281–1291.
 - 30 Liu, W. X.; Zhang, C.; Zhang, H.; Zhao, N.; Yu, Z.-X.; Xu, J. Oxime-based and catalyst-free dynamic covalent polyurethanes. *J. Am. Chem. Soc.* **2017**, *139*, 8678–8684.
 - 31 Zhang, L.; Zhou, X.; Xiong, X.; Cui, J. Dynamic polymers based on oxime-urethane chemistry: design, performances, and applications. *Sci. China Chem.* **2025**, *68*, 2234–2249.