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Reprintable Polymers for Digital Light Processing 3D Printing

Guangda Zhu, Yi Hou, Jian Xu,* and Ning Zhao*

3D printing is becoming a disruptive technology and shows great potential for various practical applications. Specially, digital light processing (DLP) 3D printing demonstrates advantages in high resolution and high efficiency. However, extensive production of infusible and insoluble thermosets in DLP printing causes serious resource waste and environmental problems after its disposal. Herein, a reprintable linear polymer is reported for repeatable DLP printing. Taking advantage of the dissolution of linear polymer in its monomer, printed objects can be recycled into liquid resin and reprinted via the same DLP. Polymerization kinetics and printing resolution of recycled resins and mechanical properties of reprinted polymers retain identical as the original. The thermoplastic nature of linear polymer endows 3D objects with welding and reshaping property. Recyclable composites are also successfully fabricated, and sustainable usage of high-value fillers comes true. This strategy helps to address environmental issues arising from unprocessable thermosets and may contribute to an efficient materials recycling.

1. Introduction

3D printing has become a disruptive technology across electronics, aerospace, biomedical, and automotive industries.[1–7] In particular, based on the rapid light-curing process of liquid resins, digital light processing (DLP) 3D printing shows the advantages in creating complex 3D objects with high-resolution geometry and high printing efficiency.[8–15] During DLP printing process, the rapid liquid–solid transition under light irradiation always requires dual-functional or multifunctional monomers, which cause 3D items to be constructed by thermosets crosslinked by covalent bonds.[13,16–19] Although thermosets show better durability and mechanical properties than uncrosslinked thermoplastics, their infusible and insoluble

features make them hard to be reprocessed or recycled, and will be inevitably discarded as waste at the end of their life cycle.[20–24] The gradually expanded DLP application and the complex 3D geometries of the products will result in more serious resources waste and environmental problems.

To address the above-mentioned problems, thermoplastics and dynamically crosslinked thermosets have been successfully developed for DLP printing.[19,25,26] The obtained 3D objects can be reprocessed by melting or by processing in solution. However, reprinting these materials by the same DLP has not been reported. Polymers with infinitely chemical recyclability to liquid monomers have been successfully prepared and realized a circular materials economy, but they only can be polymerized on a gram scale, and large amounts of acidic or basic solvents need to be used to recycle and purify the monomers.[27–31] Meanwhile, all the monomers lack photoactive groups and rapid liquid–solid transition ability. Therefore, developing recyclable polymers applicable for large-scale DLP repeated printing still remains a huge challenge.

Herein, we found that monofunctional isobornyl acrylate (IBOA) can be used to realize repeatable DLP printing. Different from the traditional DLP products of thermosets, the 3D objects we prepared consist of linear polymer of poly(IBOA). The linear poly(IBOA) can easily dissolve in IBOA monomer completely, and the resultant solution can be used as a new liquid resin to reprint 3D objects by the same DLP. This process is environment-friendly on industrial scales without complex procedures and using large amounts of acidic or basic solvents. The proper viscosity of liquid resin and the rapid polymerization rate to yield linear polymer with suitable solubility in its monomer contribute to the quick transition from liquid resin to solid with high-resolution geometry. The original and recycled 3D objects show almost the same printing resolution and printing efficiency, along with comparable mechanical and thermal properties. The thermoplastic nature endows the 3D objects with welding and reshaping property, which can be used to improve manufacturing efficiency and overcome the size limitation by printing area. Meanwhile, recyclable functional composites can be prepared. After usage, the polymer matrix and the high-value functional fillers can be separated and reused. This research not only expands the range of material candidates and improves the manufacturing efficiency of DLP printing but also contributes to efficient materials recycling to reuse.

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2. Results and Discussion

The DLP printing and recycling process is schematically shown in **Figure 1**. Patterned light illuminated from a laser projector stimulates the liquid resin to locally polymerize into a patterned solid layer with a thickness of 100 μm. After that, as the retracting stage moves upward, the designed 3D complex architecture will be constructed layer by layer (Figure 1a). Here, monofunctional IBOA was used as monomer, with camphorquinone (CQ) and 4-dimethylaminobenzoate (EDMAB) as the photoinitiator, and phthalocyanine Blue 15 as photoabsorber. For traditional DLP printing, bi- and/or multifunctional monomers are used to produce 3D objects constructed by thermosets crosslinked by covalent bonds. Differently, the proper viscosity of the printing resin and the rapid polymerization rate of this monofunctional IBOA contribute to the rapid transition from liquid monomer to 3D objects composed of linear poly(IBOA) (Figure 1b). The printed 3D objects can dissolve in IBOA completely, thus forming a homogenous polymer solution consisting of linear poly(IBOA) and IBOA monomer (Figure 1c). The solution can be used as a new liquid resin for the same DLP printing when photoinitiator was added. The above process can be repeated multiple times between the liquid resin and 3D objects, leading to 3D objects at the end of their life are not considered as waste but as raw materials.

Proper viscosity and rapid polymerization rate to yield a linear polymer with suitable solubility in its monomer are essential for DLP printing. During DLP printing, once a layer is cured, the retracting stage will move up for the printing of next layer. A proper viscosity of the liquid resin can ensure it flows quickly and fills the gap between the cured layer and the retracting stage for the polymerization of next layer. Rapid polymerization rate can make the liquid resin quickly transform into solid, whereas the sufficient molecular weight of obtained linear polymer can retard its dissolution in the monomer during printing.

As **Figure 2**a shows, both IBOA monomer and poly(IBOA)/IBOA solutions (9 wt%) are transparent. The similar dynamic light scattering (DLS) results of poly(IBOA) in IBOA and in THF (a good solvent for poly(IBOA)[32]) approved the good solubility of poly(IBOA) in IBOA (Figures S1 and S2, Supporting Information). IBOA has a low viscosity of 10 mPa s (=10 cps), whereas recycled solutions of poly(IBOA) in IBOA (9 wt%) show a slightly increased viscosity of about 90 mPa s (Figure 2b). The increase in viscosity results from the presence of high molecular weight poly(IBOA) in IBOA. The more poly(IBOA) added in IBOA, the higher viscosity of recycled resin. The viscosity of polymer solution at room temperature increases from 38 to 3000 mPa s with the concentration increasing from 5 to 23 wt% (Figure S3, Supporting Information). Compared with commercial photocurable resins (Table S1, Supporting Information), the recycled polymer solutions (5–17 wt%) have a relatively low viscosity, particularly suitable for DLP printing, even for other rapid printing methods.[3,33] It is worth noting that the viscosity can be decreased by increasing the temperature. Taking the recycled resin (23 wt% poly(IBOA) in IBOA) as an example, the viscosity can be decreased from 3000 mPa s at 30 °C to 160 mPa s at 110 °C (Figure S3b, Supporting Information), which is suitable for DLP printing. Thus, more thermoplastics might be recycled and reprinted if DLP printer equipped with a thermal bath was used. Figure 2c shows that both IBOA monomer and recycled resins have fast and similar polymerization rates. The double bond conversion rate can reach ≈60% within 30 s, and the recycling cycles show almost no effect on the polymerization rate.

Under light irradiation, both the original and the recycled liquid resins transform into solid films of linear poly(IBOA) with excellent transparency (Figure 2d). The transmittance in visible range can reach around 89% (Figure S4, Supporting Information). The chemical structures of virgin and recycled poly(IBOA) are consistent between rounds of recycling, as confirmed by Fourier transform infrared (FTIR) and nuclear magnetic resonance (1H-NMR) (Figure S5, Supporting Information). The gel permeation chromatography (GPC) results show that all the obtained poly(IBOA)s own a molecular weight around 38 kDa and a similar polydispersity index (PDI) (Figure 2e). The dissolution rate of poly(IBOA) in IBOA at static state (similar to the DLP printing process) is determined by the temperature (Figure 2f). The dissolution rate is very low at room temperature, and the weight loss is below 3% h⁻¹. The weight loss of film can reach 36% h⁻¹ at 110 °C. As the DLP printing was performed at ≈25 °C, the little dissolution of poly(IBOA) might not have obvious influence in DLP printing.

Figure 3a shows models of cross rings, Chinese Bird's Nest, and lattice structure printed from the pristine IBOA resin. For example, the Chinese Bird's Nest model could dissolve in IBOA monomer at 90 °C (Figure 3b). Almost the same models have been successfully fabricated by the same DLP method using the recycled polymer solution (Figure 3c). In comparison, the printed commercial thermoset models could not dissolve in dimethylformamide (DMF) even after 7 d (Figure S6, Supporting Information). Limited by the resolution
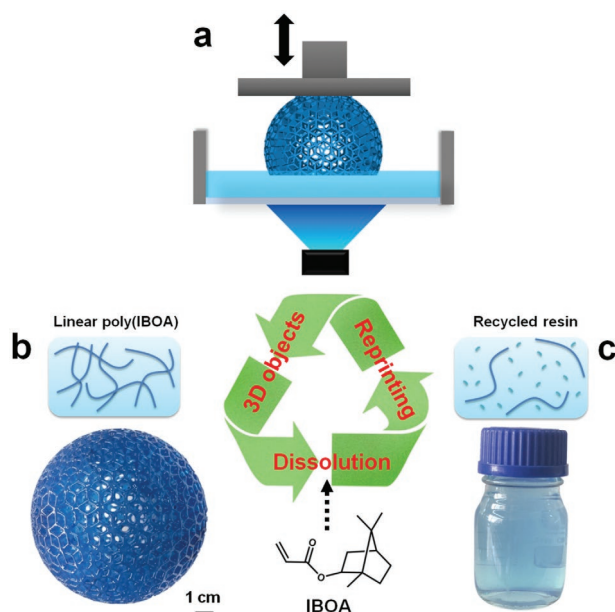

Figure 1. Repeatable DLP printing. a) Scheme of DLP printing process. b) Printed 3D objects composed of linear poly(IBOA). c) Recycled resin of poly(IBOA) in IBOA monomer.
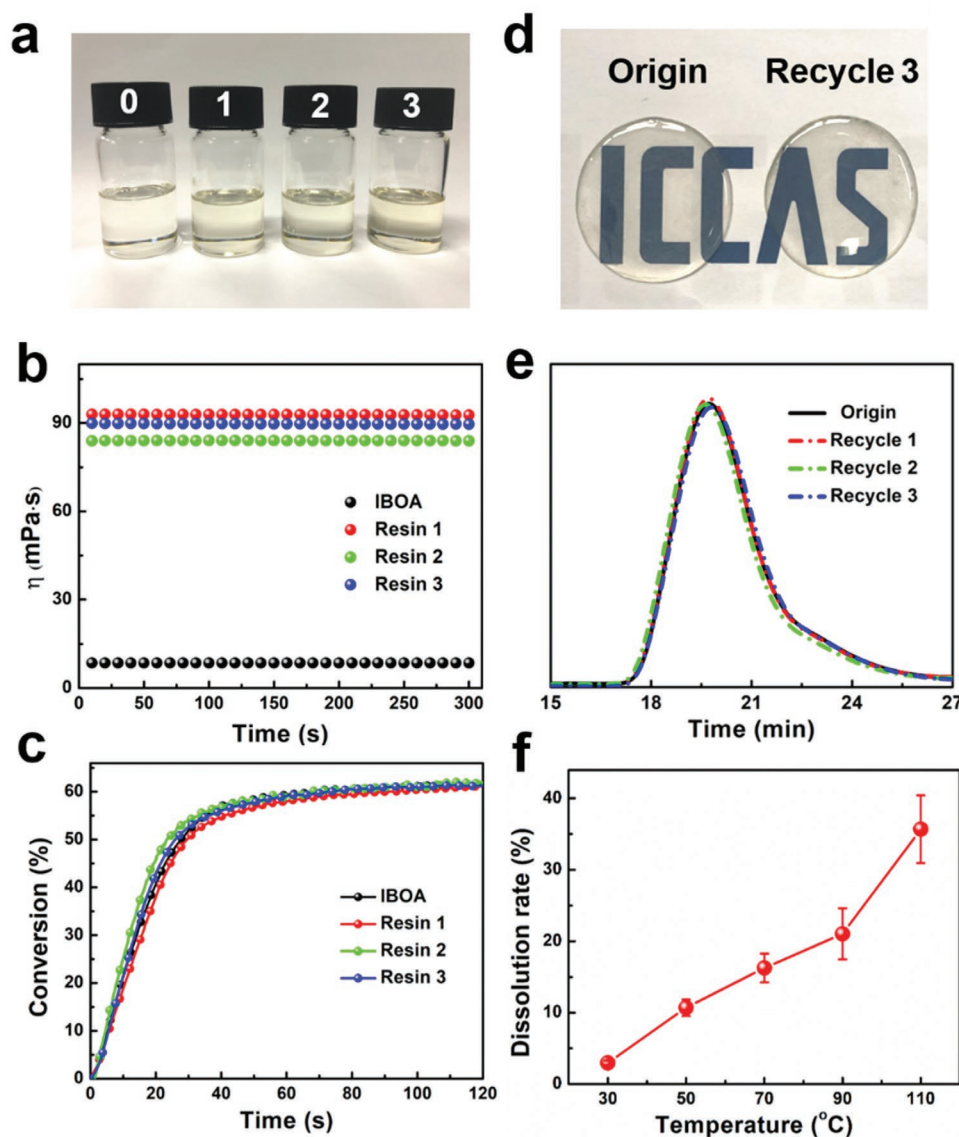
Figure 2. Printing characteristics. a) Photography, b) viscosity, and c) reaction kinetics profiles of IBOA monomer and recycled resins of poly(IBOA) in IBOA (9 wt%). d) Photography, and e) GPC curves of original and recycled poly(IBOA)s printed by 9 wt% poly(IBOA) in IBOA. f) The dissolution rate of poly(IBOA) in IBOA at different temperatures. The dissolution experiments were conducted at least five times to calculate the dissolution rate.

of the projector, the printing resolution can reach around 300–400 μm. The printing resolution of 3D objects in micrometer scale can be well retained using the same DLP printing. By recycling utilization of materials, reduction in waste and production cost can be expected.

To verify the recyclability, mechanical and thermal properties of the original and recycled poly(IBOA)s were measured. Figure 3d shows the storage modulus and tanδ versus temperature are consistent between rounds of recycling. Thermal gravimetric analysis (TGA) results also indicate the similar thermal stability for original and recycled poly(IBOA)s (Figure 3e). No obvious difference in T_g (at the peak of tanδ) and T_d (at the weight loss of 5%) can be observed, no matter the recycling rounds (Table S2, Supporting Information). Representative stress–strain curves of the linear poly(IBOA)s before and after recycling of up to three times are shown in Figure 3f. All samples show

a comparable mechanical performance, with a tensile strength around 8.0 MPa and a strain at break of ≈6.5% (Table S2, Supporting Information). The recycling efficiency, defined as the ratio of the mechanical properties of recycled samples to those of the original, is shown in Figure 3g. It can be seen that the mechanical properties are largely restored after recycling. For example, the recycling efficiency of tensile strength, strain at break, and Young's modulus for the sample after three recycling rounds are 102%, 91%, and 95%, respectively. The water contact angles of original and recycled poly(IBOA)s changed a little; meanwhile, the printed items also exhibited a good water resistance (Figure S7, Supporting Information).

Other monofunctional monomers could also be employed to realize DLP reprinting, once the requirements of proper viscosity, fast polymerization rate of the obtained linear polymer with suitable solubility in its monomer are satisfied. For
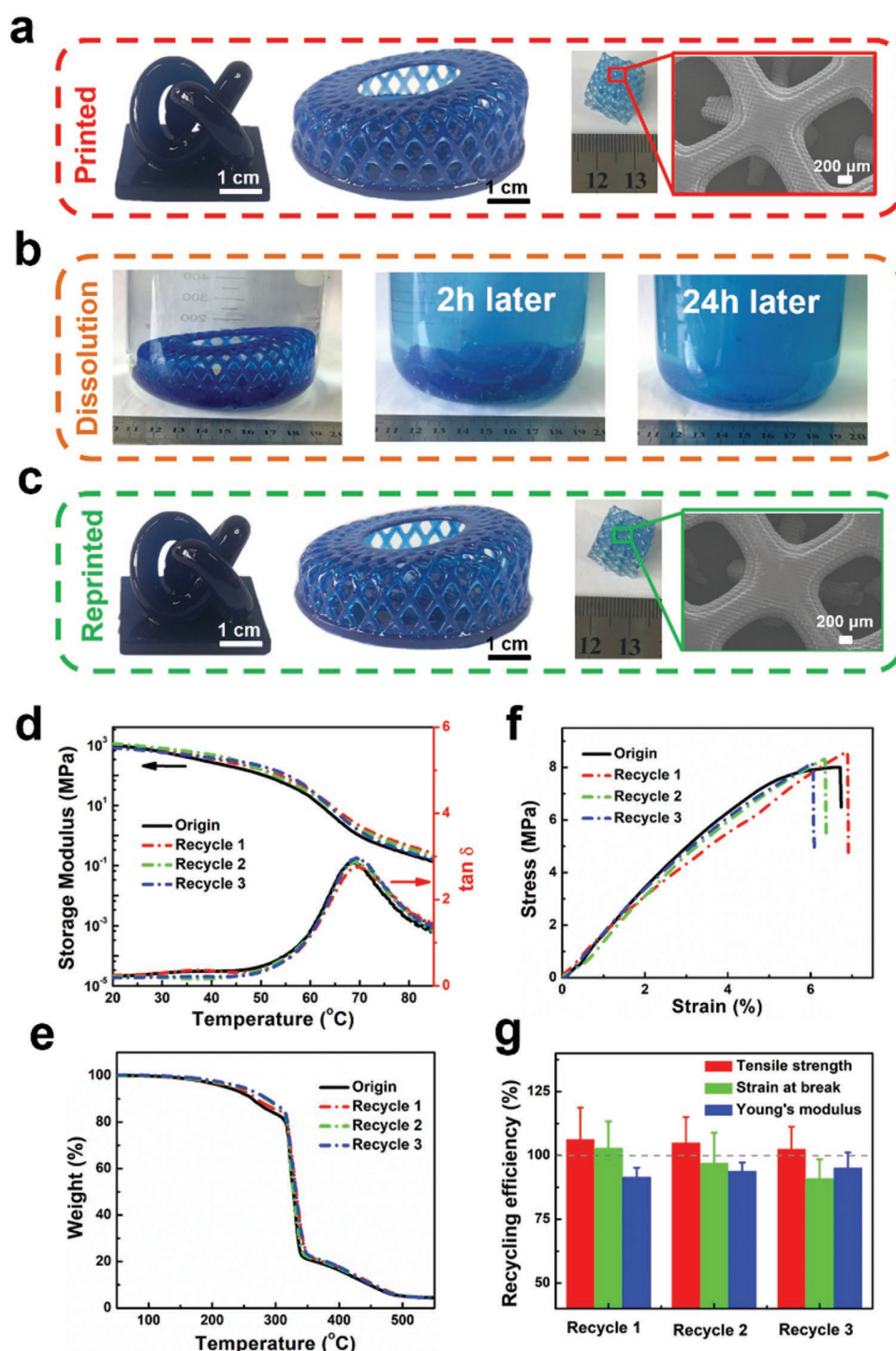
Figure 3. Reprinting performances. a) DLP printed models using IBOA. b) The dissolution process of printed model in IBOA. c) DLP reprinted models using recycled poly(IBOA)/IBOA resins (9 wt%). d) DMA, e) TGA, and f) stress–strain curves of original and recycled poly(IBOA) samples. g) Recycling efficiency of mechanical properties for recycled poly(IBOA) samples. All the recycled samples were prepared from 9 wt% poly(IBOA)s in IBOA.

example, we found that 4-acryloylmorpholine (ACMO) could be used, whereas methyl methacrylate and acrylic acid failed. Although Zhou and Xie et al. reported DLP printing of ACMO, they pointed out that the obtained thermoplastics cannot be reprinted using the same DLP method.[19] However, we find that poly(ACMO) can dissolve in ACMO completely at a temperature above its T_g, and a recycled resin can be obtained for reprinting. The viscosity and polymerization rate of ACMO and recycled solutions of poly(ACMO) in ACMO (5 wt%), and the molecular weight of original and recycled poly(ACMO) have been

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investigated (Figure S8, Supporting Information). 3D models have been successfully fabricated using ACMO resin and recycled resins by DLP printing (Figure S9, Supporting Information). Dynamic mechanical analysis (DMA) and mechanical tests confirmed the consistent material properties of the original and recycled samples (Figure S10, Supporting Information). It is worth noting that copolymers of IBOA and ACMO can also be printed, and the thermomechanical properties of the resultant copolymers can be tuned by controlling the resin composition (Figure S11a, Supporting Information). Meanwhile, the printed objects of these copolymers can also be recycled and reprinted. Taking the copolymer of IBOA/ACMO = 50:50 as an example, the printed model can be dissolved in IBOA/ACMO mixture and then reprinted into a new one (Figure S11b, Supporting Information). Poly(IBOA) can also dissolve in ACMO monomer, and the obtained polymer solution can be reprinted to form models of poly(IBOA)/poly(ACMO) blends (Figure S11c, Supporting Information). This not only suggests a more diverse way for material recycling but also provides a manner to adjust the properties of products via copolymerization or polymer blending.[34,35]

The thermoplastic nature makes printed 3D objects able to weld or reshape. The welding process of printed butterfly is schematically illustrated in **Figure 4**a. Two printed butterflies (a red one and a blue one) were both cut into half parts. The red half and the blue half can be welded together by heating or applying some IBOA resin at the cut area under light irradiation. The welded butterfly can sustain a heavy weight of 200 g (Figure 4b). Compared with the origin, both heat and IBOA welded samples can retain more than 90% mechanical properties (Figure S12, Supporting Information). The recovery of the mechanical properties is mainly because of the efficient reformation of polymer chain entanglement at the welding area. More importantly, complex structures can be prepared by a reshaping and welding manner, forgoing the time-consuming layer-by-layer printing process. Here, a thin film was printed and then transformed into a windmill at 90 °C (higher than the T_g of the linear polymer). The manufacturing efficiency increases by 20 times by printing a 1 mm thick film than directly printing the 2 cm high windmill (Figure 4c). For printing larger objects, this strategy can further improve the printing efficiency and reduce the restriction on the production size because of the limited printing area.

Fillers are usually incorporated into polymers to prepare high-performance or functional polymer composites.[9,36–40] However, once the high-value fillers were composed into thermosets, they are hard to be recycled or reused. Herein, the dissolution nature of linear polymers makes it possible to realize recycling of polymer matrix and functional fillers from printed composites. Figure 4d schematically illustrates the recycling process. Taking carbon nanotubes (CNTs) as example, an object of CNTs/poly(IBOA) composite (0.5 wt% CNTs) was printed (Figure 4e). The object was broken into pieces and decomposed in liquid resin. The obtained dispersion was then separated into polymer solution and CNTs (Figure S13a, Supporting Information). The polymer solution could be reprinted into a new 3D object of poly(IBOA) (Figure S13b, Supporting Information), whereas the recycled CNTs showed no difference in TGA results with the original CNTs (Figure S13c, Supporting Information). By adding additional CNTs, new composite resin was obtained and could be reprinted to form a new 3D object (Figure 4f). Recycled composites containing Al_2O_3 and liquid metal were also successfully fabricated (Figure S14, Supporting Information).

To the best of our knowledge, it is for the first time to report recyclable thermoplastics that can be reused for DLP reprinting. The printing resolution and efficiency of our thermoplastics are comparable to those of the traditional thermosetting resins. Although thermosets show a better solvent and heat resistance, the presently wide application of DLP in personalized product customization and model verification does not need high durability of products. On the contrary, the short service life of the products involved in these fields will result in disposal of plenty of products after use, thus wasting resources and causing great trouble in environment if thermosets were used. Therefore, developing reusable thermoplastics is of great significance for resource conservation and environmental protection. At present, we used fresh monomer to dissolve the printed objects to obtain the reprintable resins for DLP 3D printing. Although this method can be repeated multiple times, it is still far from the goal of fully recycling.[28–32,41] Photopolymerizable monomers that can be recycled from their cured polymers are desirable for DLP printing to realize a fully material recycling.
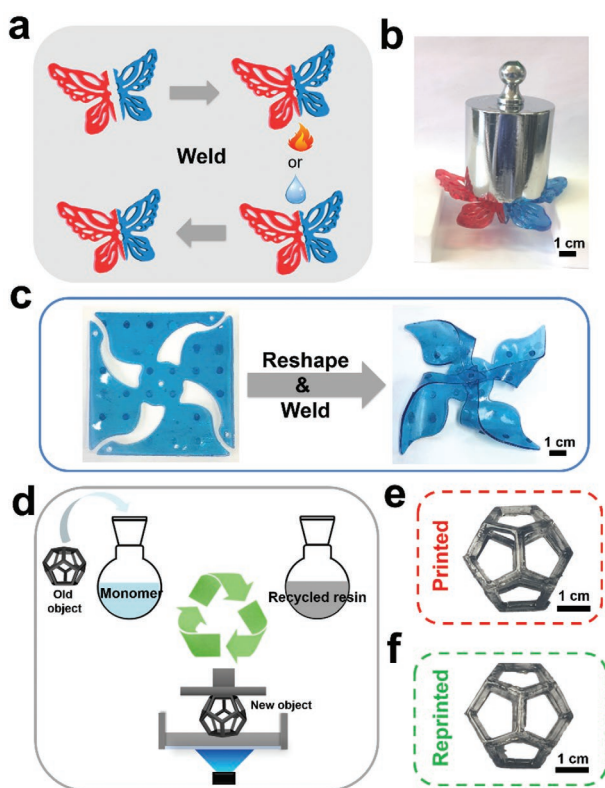

Figure 4. Welding, reshaping, and recyclable composites. a) Illustration of the welding process by heat or adding monomer. b) The weight-bearing test of printed butterfly after welding. c) Printed film was reshaped into a 3D windmill welded by heat. d) Schematic illustration of the recycling process of printed composites. e) CNTs/poly(IBOA) composite structure printed from pristine resin. f) Reprinted CNTs/poly(IBOA) composite structure from recycled resin of 9 wt% poly(IBOA) in IBOA.

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3. Conclusion

In summary, the repeatable DLP printing is realized by taking advantage of the dissolution of the linear polymer in its mono-functional monomer to form a reprintable resin. The proper viscosity and rapid polymerization rate of monomer contribute to the quick transformation from liquid to solid, enabling a layer-by-layer construction of 3D complex objects via DLP printing. The recycled resins also have appropriate viscosity and polymerization kinetics, and the reprinted objects have identical printing resolution and material properties as the original. More importantly, the thermoplastic nature of linear polymer makes printed 3D objects able to weld and reshape, offering a way to increase the manufacturing efficiency and reduce the size limit subjected to the printing area. Recyclable composites were also successfully fabricated. This study provides an effective way to address the environmental issues arising from unprocessed thermosets produced by traditional DLP printing and realize an efficient materials recycling.

4. Experimental Section

Printing Resin Preparation: Printing liquid resin was prepared by mixing the photoinitiator (1 g CQ and 1 g EDMAB) with 100 g IBOA under stirring to form a homogenous solution. Phthalocyanine Blue 15 or oil red O was added as the photoabsorber (0.02–0.5 wt%). The printing composite resins were prepared by adding carbon nanotubes (0.5 wt%), gallium (3 wt%), or Al_2O_3 (5 wt%) in the above liquid resin, respectively. Other printing resin was prepared with the same method using ACMO as monomer.

DLP 3D Printing: 3D objects were printed via a commercial DLP-based 3D printing system equipped with a blue laser projector (445 nm). The light intensity in DLP printing is 10 mW cm^{-2}. All the models were printed with a slice thickness of 100 µm. The layer curing time of IBOA is 20–30 s, whereas that of ACMO is 10–15 s. After printing, the printed objects were washed by ethanol to remove the unreacted monomers.

Recycling Process: The recycled printing resins were prepared by adding the printed objects (5, 10, 20, and 30 g) into IBOA monomer (100 g) under stirring at 90 °C until transparent solutions were obtained, with a concentration of 5, 9, 17, and 23 wt%, respectively. Then, 1 g CQ, 1 g EDMAB, and 0.02–0.5 g phthalocyanine Blue 15 were added into the solution. Printed composite objects (10 g) were added in 100 g IBOA under mixing at 90 °C until a homogeneous solution is formed, and then the obtained solution was separated via centrifugation at 8000 rpm for 10 min. The separated fillers were washed by ethanol three times and dried.

Characterizations: NMR spectra were recorded on a Bruker Fourier 400 MHz spectrometer using $CDCl_3$ as the solvent. FTIR spectra were recorded on a Perkin-Elmer 2000 FTIR spectrophotometer by 32 scans from 4000 to 400 cm^{-1}. The double bond conversion was measured using a Thermal Fisher Nicolet 5700 instrument. Light (465 nm, 10 mW cm^{-2}) was irradiated on liquid resin between two KBr plates to initiate the polymerization. The double bond conversion was calculated by the decrease of the characteristic band between 1645 and 1583 cm^{-1}. Rheology measurements were performed on a Physical MCR 302 rheometer (Anton Paar, Austria). Viscosities of the printing resins were measured at a shearing rate of 50 s^{-1} for 5 min at room temperature. GPC investigation was performed on a Waters 1515 HPLC with three Styragel columns (HT3, HT4, and HT5) and 2414 differential refractive index detector. Tetrahydrofuran was used as eluent at 1 mL min^{-1}. Polystyrene standards were used to establish a calibration curve. Poly(IBOA) films (≈1.5 g) were immersed in IBOA at different temperatures, and the weight of film was measured per hour to verify the dissolution rate. UV–vis transmittance spectra were obtained by using a UV–vis spectrometer (Lambda950, Perkin-Elmer). Scanning electron microscope (SEM) images were captured by a JSM-7500F (JEOL) at 5 V accelerating voltage. Tensile measurements were performed using a SUNS UTM4104 Instrument with a 5 mm min^{-1} strain rate at room temperature (≈26 °C). Printed dogbone shaped samples were used. Each result was the average of the data from at least three samples. DMA was conducted on a DMAQ800 apparatus (TA Instrument) in a tensile film mode. Rectangular samples (≈10 mm (L) × 5 mm (W) × 0.5 mm (T)) were tested at a frequency of 1 Hz and a strain of 0.1%. TGA was carried out on a TA instruments Q600 Simultaneous Thermal Analyzers, at a rate of 10 °C min^{-1} from 50 to 700 °C under a nitrogen atmosphere.

Conflict of Interest

The authors declare no conflict of interest.

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