Supplementary Materials for

Closed-loop additive manufacturing of upcycled commodity plastic through dynamic cross-linking

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Supplementary Text

Extended background of FFF-printable ABS-vitrimer design

The current environmental and socio-economic situation calls for more sustainable, logistics-independent, and on-demand polymer material manufacturing technology (2-4, 9-11, 57-59). Now, the production and incineration of 1 ton of plastics emit 5.2 tons of CO$_2$ and the resulting annual CO$_2$ emission is forecasted to grow from 750 Mt/yr, 2.5 % of total emission in 2013, to 2.1 Gt/yr by 2050, occupying 16% of the total 2050 global emissions based on the growth of demands on plastics and its net incineration (1-5, 57, 60). In addition, the plastic particles are ending up in soils, water, or air at a vastly accelerating pace, now becoming a geochemical tracer for the earth system (1). Therefore, a transformative approach is desperately needed on the manufacturing methodologies and materials towards a circular economy of plastics, by on-demand, user-driven, carbon-efficient manufacturing process with re-/upcyclable materials in simple manners (9, 59).

Additive manufacturing (AM) or 3D printing technologies can transform traditional subtractive manufacturing into customized bottom-up material production to construct desired 3D structures in an energy/resource-efficient way (10, 11, 13, 14, 58, 61). The simplicity, accessibility, and performance of AM method determine how broadly and effectively the AM can be adopted in manufacturing. Fused Filament Fabrication (FFF), alias Fused Deposition Modeling (FDM), is a strong candidate to satisfy such widespread deployment. FFF directly extrudes and deposits fused polymer filaments layer-by-layer to build up complex 3D structures pre-rendered by computer-aided design (CAD). Owing to such simple printing principles compared with other AM techniques, FFF printers are available in compact desktop scales with printing feedstocks commercialized as filament spool forms, that also provide convenient handling. Consequently, the in-house usage has been surveyed to cover 71 % of FFF uses (2021), while FFF occupies ~69 % of the 3D printing market share (2018) and the sales of FFF polymer feedstocks alone took up ~$200M in $5B+ global market revenue (2016) (13-15, 62-64). In addition, the scalability of the FFF is demonstrated by the Big Area Additive Manufacturing system that can build large-scale vehicles, buildings, or aircraft parts (16, 65).

Polymers for FFF filaments have been thermoplastics since the FFF mechanism requires deformation and flow of the filaments upon heating and quick solidification upon cooling. Acrylonitrile butadiene styrene (ABS) is one of the most broadly used copolymer thermoplastics for FFF due to its cost-effectiveness and great mechanical properties such as impact resistance, toughness, and rigidity (17). ABS is produced 11.17 Mt in 2018, expected to increase to 12.59 Mt by 2023 (66), and serves as an excellent engineering thermoplastic in many applications including electronic housings, auto parts, pipes, table tennis balls, and LEGO blocks, dominating the engineering plastics market (17, 67). In ABS, the polar acrylonitrile blocks are known to impart good strength, hardness, and thermochemical resistance, while the polystyrene blocks contribute to the hardness, rigidity, processability, and shiny impervious surface (17). Meanwhile, the rubbery butadiene blocks provide ductility and toughness to the material.

We hypothesized that ABS can be upcycled to an ABS vitrimer and it can be designed to be printable in regular thermoplastic FFF processing conditions and methodologies that satisfy the convoluted thermomechanical-chemical-environmental requirements for sustainable
manufacturing. Vitrimer, the covalent adaptable network polymer, behaves as a crosslinked thermoset at room temperature with mechanical robustness and chemical resistance superior to thermoplastics, but it can be malleable, reprocessable, and recyclable by the reconfiguration of reversible dynamic crosslinking bond exchange at high temperature (18-20, 27, 68). The recyclability (reprocessability) therefore clearly distinguishes vitrimers from traditional thermosets with irreversible crosslinks, making vitrimer an exciting material to be used in AM. Vitrimers exhibit “associative” bond exchange wherein bond breaking and forming occur almost simultaneously, maintaining the crosslink density (35, 36). Thus, in non-reactive solvents, vitrimers are solvent-resistant, unlike networks with “dissociative” covalent or noncovalent crosslinks that disintegrate upon the initial bond dissociation (35, 36, 48, 55). Therefore, we projected that the fast associative bond exchange between the vitrimer layers upon printing could improve both solvent-stability and the inter-filament strength of the printed part, the fundamental weaknesses of FFF due to the physicochemical and geometrical constraints of the methodology and the feedstock material (Fig. 1B) (13, 37).

There have been efforts to 3D-print thermosets using diverse AM techniques. AM of thermosets usually mandates in-situ or post-crosslinking processes. In stereolithography (SLA) and digital light processing (DLP), a photocurable resin is crosslinked by laser, LED, or UV light (69, 70), while direct ink writing (DIW) (27, 71-73) and FFF involve post-extrusion curing often with multi-hour annealing or repolymerization upon cooling (23, 74). These printed thermoset materials by these AM techniques typically cannot be reprocessed or reprint and are limited to a single-use without significant modifications of the original AM protocols, which compromises the procedural simplicity, user-friendliness, and wide-ranging deployment of AM. Hence, upcycling commodity thermoplastics into robust crosslinked polymers with full recyclability for direct FFF printing provides a strategy to transform manufacturing towards a carbon-neutral, sustainable society.
# Medical usage of small molecules used in chemical upcycling pathway

| Chemicals     | Description                                                                 | Enlisted in                                                                                     | Usage                                                                                     | Commercial Brands    | Sources   |
|---------------|-----------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------|----------------------|-----------|
| Cysteamine    | Amino thiol with the chemical formula HSC\(\text{H}_2\text{H}_4\text{NH}_2\). Derived from coenzyme A degradation, endogenously. | WHO (ATC code A16AA04, S01XA21); FDA (for human uses); EMA (for human uses)                     | Treatment of radiation sickness, neurological disorders, cancer, cystinosis                | Procysbi, Cystagon, Cystaran | (75-77)   |
| Glutaraldehyde| Homobifunctional crosslinker with aldehyde groups at both ends of a 5-carbon chain with chemical formula C\(\text{H}_6\text{(CHO)}_2\). Primary reactivity is toward amine groups. | WHO (World Health Organization's List of Essential Medicines); FDA (as disinfectants/sterilant for medical devices) | Disinfectant, sterilant, preservative, wart treatments, biochemical fixatives              | Cidex, Glutaral      | (78, 79)  |

Table S1. The medical usage of cysteamine and glutaraldehyde that are used in our synthetic pathway to form ABS-vitrimer, where the former was used for thiol-ene reaction, the latter for dynamic transimination. WHO: World Health Organization, FDA: Food and Drug Administration (USA), EMA: European Medicines Agency
Upcycling ABS waste into transimination precursor via thiol-ene click reaction

Fig. S1. The upcycling of used ABS waste via thiol-ene functionalization to attach amines to form vitrimers that can go through dynamic transimination. The failed printed parts of Neat-ABS were dissolved in THF and went through a thiol-ene reaction with cysteamine initiated by AIBN as described in the Methods. The reacted solution became a pale lime yellow color well-consistent with our observation in Fig. 2A.
**1H-NMR before and after the thiol-ene reaction**

Fig. S2. **1H NMR spectra** of before (upper panel) and after (lower panel) the thiol-ene reaction of ethylene (ethene) in the butadiene block of ABS with cysteamine to attach the amine groups. THF-d₈ was used as the solvent (peak at 1.73, 3.58 ppm). The inset shows the assignment of Hs in the backbone structure to the signals in the spectra (80). The peaks observed at a chemical shift of 5.9-4.7 ppm (H2) correspond to the ethylene unit (highlighted red). The signals in the range of 7.4-6.3 ppm (H1) correspond to Hs of the aromatic ring in the styrene unit. The residual H (H3-7) signals in the wide region of 1.0-3.0 ppm indicate the CH₂- and CH-groups of the polymer chain, including the acrylonitrile unit. After the thiol-ene reaction, the two CH₂-groups in the attached cysteamine branch show peaks at 2.8, 2.9 ppm (highlighted green). The calculation via integration gives [residual ethylene unit]:[attached cysteamine branch] = 2:7 after the thiol-ene reaction, which reveals that the original 18 mol% of the molar quantity of the ethylene units in the ABS backbone has been reduced to 4 mol%, indicating that 14 mol% has been functionalized with amine groups.
FTIR spectra of Neat-ABS, ALD-0, ALD-33

**Fig. S3.** FTIR spectra of Neat-ABS, ABS after the thiol-ene reaction (ALD-0), and that after the imine formation (ALD-33). (A) All three samples show the characteristic FTIR bands of ABS polymers (81). For example, C-H stretching in the aromatics at 3025 cm⁻¹, C=C stretching in the aromatics at 1600 cm⁻¹ and C-H bending in the benzene rings at 759 and 700 cm⁻¹ indicating the styrene groups. The band at 2238 cm⁻¹ corresponds to the C≡N stretching from nitrile. The band at 966 cm⁻¹ is indicative of the butadiene region. The characteristic signal of imine bonds (1640-1690 cm⁻¹) in the 1600-1700 cm⁻¹ region is highlighted and magnified in (B). (B) The signals from C=N stretching in the imine at 1640-1690 cm⁻¹ show up in the ALD-33 (30, 82). Note that the ALD-XX indicates the -CHO/-NH2 = XX%.
Solid-state $^{13}\text{C}$-NMR of ALD-33

**Fig. S4.** Solid-state $^{13}\text{C}$-NMR spectra from duplicate runs of ALD-33 show carbon peaks from C=N imine bonds at ~160-170 ppm as highlighted in green (83).
**T<sub>g</sub> upon crosslinking**

| Method        | Neat   | ALD-0  | ALD-33 |
|---------------|--------|--------|--------|
| DMA tan δ peak| 117.5 °C | 116.5 °C | 118.5 °C |
| DSC ΔH peak   | 113.3 °C | NA     | 112.9 °C |

**Table S2.** T<sub>g</sub> is estimated by loss factor (tan δ) and enthalpy transition (ΔH) peak of Neat-ABS, ALD-0, and ALD-33 by DMA (Dynamic Mechanical Analysis) and DSC (Differential Scanning Calorimetry) measurement, respectively. The measured T<sub>g</sub> values did not show significant change by chemical reactions.
Thermal decomposition test

Figure S5. TGA was performed to test the thermal decomposition of the Neat and ALD-33. Both systems showed very similar decomposition trends where there was no significant decomposition below 250 °C as seen from the derivative weight change trends.
Solvent-resistance test

![Solvent-resistance test results](image)

**Fig. S6. The solvent-resistance test** on Neat-ABS (left), ALD-33 (middle) and AcAc-33 (right, i.e., system crosslinked with an alternative aliphatic acetylacetate crosslinker, please see fig. S23 to fig. S28 for more details on this system) in acetone, tetrahydrofuran (THF), chloroform, dichloromethane (DCM), and dimethylformamide (DMF). The solvent-resistance of a vitrimer system is known to be a trait of associative crosslinking (35, 36). The 3 mg disc-shaped samples were immersed in 3 mL of solvents. White arrows indicate the undissolved samples for better clarification. These solvents, except DMF, were reported to have good solubility for ABS (41). The Neat-ABS dissolved in all solvents within 24 hours while some debris was still observed in acetone. The Neat-ABS showed the fastest dissolution in chloroform, where it was completely dissolved within 1 hour. The Neat-ABS was reported to be moderately stable in DMF (41), which it was until 1 hour, but it also dissolved after 24 hours. In contrast, both ALD-33 and AcAc-33 stayed intact while swelled within the displayed time range. Note that there was no significant dissolution even after 4 months. We also note that there was no meaningful change observable for all samples in water.
Tensile mechanical properties

| Specimens | Toughness (MPa) | UTS (MPa)   |
|-----------|----------------|-------------|
| Neat      | 3.86 ± 1.17    | 24.90 ± 2.39|
| ALD-0     | 1.95 ± 0.34    | 28.83 ± 9.18|
| ALD-08    | 3.75 ± 1.06    | 28.02 ± 2.66|
| ALD-17    | 5.55 ± 0.75    | 29.25 ± 2.84|
| ALD-33    | 7.18 ± 1.29    | 38.38 ± 3.71|
| ALD-66    | 3.83 ± 0.74    | 43.99 ± 3.46|
| ALD-124   | 1.41 ± 0.33    | 35.34 ± 0.74|

Table S3. Tensile mechanical properties including toughness and UTS in Figure 2D, 2E, respectively.
Apparent crazing

Fig. S7. Apparent crazes of ALD-0, ALD-33, and ALD-124 that went through tensile fracture by Instron. The ALD-33 shows the most eminent crazing upon tension, indicating the most plastic deformation among the three samples. ALD-124 apparently shows the least crazing. These observations are in good correspondence with the plasticity trends displayed in stress-strain profiles of each sample.
Generation of rheological master curves

| Temperature °C | aT (x variable) ALD-33 | aT (x variable) Neat |
|----------------|------------------------|----------------------|
| 130            | 136.845                | 43.714               |
| 140            | 8.087                  | 5.012                |
| 150            | 1.000                  | 1.000                |
| 160            | 0.393                  | 3.590                |
| 170            | 0.159                  | 0.505                |

Table S4. Shift factors aT used for time-temperature superposition from frequency sweep measurements (frequency range from 100 to 0.1 rad/s at 1 % strain) on ALD-33 and Neat-ABS at 130, 140, 150, 160, 170 °C to generate master curves at 150 °C (Fig. 3B).

The master curves were constructed using TA Instrument TRIOS software using shift factors derived from the Williams, Landel, Ferry (WLF) equation according to:

\[
\log aT = \frac{-c_1 (T - T_o)}{c_2 + (T - T_o)}
\]

where aT is the temperature shift factor, T is the temperature of shifted data, To is an arbitrary reference temperature, c1 and c2 are constants derived from curve fitting and are generally accepted at 17.44 and 51.60 respectively when To=Tg.
Stress-relaxation of ABS-vitrimer
(Fig. S8, Table S5)

![Graphs showing stress-relaxation of ALD-33](image)

**Fig. S8.** Stress-relaxation of ALD-33 (at 1% strain) over 1000 s at the temperatures at 130 - 170 °C with 10 °C intervals shown in logarithmic scale (left) and linear scale (right) showing typical stress-relaxation profiles of viscoelastic materials. The τ was determined at 37% (1/e) of the normalized relaxation modulus from the Maxwell model of viscoelasticity (See Materials and Methods for details). The τ was selected as the median of the recorded time values close to $G(t)/G_i = 1/e$. The complete relaxation at high temperature (170 °C) was observed proving that there are no non-exchangeable permanent crosslinks.
Table S5. The relaxation times ($\tau$) of ABS-vitrimer obtained from the stress-relaxation test (fig. S8) to construct the Arrhenius plot (Fig. 3C). The $\tau$ was selected as the median of the recorded time values close to $G(t)/G_i = 1/e$. The apparent activation energy of $E_a \approx 151$ kJ/mol calculated from the linear fitting is consistent with reported values ($48–157$ kJ/mol) for polyimine vitrimers (28-30, 33-35).

| T (°C) | T (K) | 1/T (K$^{-1}$) | 1000/T (K$^{-1}$) | $\tau$ (s) | ln (τ) |
|--------|-------|----------------|-------------------|-----------|--------|
| 130    | 403   | 0.00248        | 2.48              | 20.00     | 3.00   |
| 140    | 413   | 0.00242        | 2.42              | 7.20      | 1.97   |
| 150    | 423   | 0.00236        | 2.36              | 2.33      | 0.85   |
| 160    | 433   | 0.00231        | 2.31              | 0.79      | -0.24  |
| 170    | 443   | 0.00226        | 2.26              | 0.32      | -1.14  |
Stress-relaxation of Neat-ABS
(Fig. S9, Table S6)

Fig. S9. Stress-relaxation of Neat-ABS (at 1 % strain) over 1000 s at the temperatures at 130 - 170 °C with 10 °C intervals. (A) Stress-relaxation profile of Neat-ABS. Compared to ALD-33, the relaxation of Neat-ABS is up to 5 times faster and completely relaxed at all temperatures within 200 s (see table S6 for more details.). (B) The derived relaxation times by the Maxwell model show poor Arrhenius relation in contrast to ALD-33 where the dynamic imine crosslinks were present (Fig. 3C).
Table S6. The relaxation times ($\tau$) of Neat-ABS obtained from the stress-relaxation test (fig. S9B) which poorly followed the Arrhenius behavior. The $\tau$ was selected as the median of the time values that reached $G(t)/G_i = 1/e$.

| $T$ (°C) | $T$ (K) | $1/T$ (K$^{-1}$) | $1000/T$ (K$^{-1}$) | $\tau$ (s) | $\ln (\tau)$ |
|-----------|---------|------------------|---------------------|-----------|--------------|
| 130       | 403     | 0.00248          | 2.48                | 4.00      | 1.39         |
| 140       | 413     | 0.00242          | 2.42                | 3.33      | 1.20         |
| 150       | 423     | 0.00236          | 2.36                | 0.75      | -0.29        |
| 160       | 433     | 0.00231          | 2.31                | 0.64      | -0.45        |
| 170       | 443     | 0.00226          | 2.26                | 0.22      | -1.51        |
Creep and Arrhenius behaviors of ABS-vitrimer (Fig. S10 and S11, Table S7)

\[
\dot{\gamma}^{-1} = \dot{\gamma}_0^{-1} \exp \left( \frac{E_a}{RT} \right)
\]

**Fig. S10. Creep tests on ABS-vitrimer.** (A) The creep test on ALD-33 at 130, 140, 150, 160 °C at a constant stress of 50000 Pa. The strain rate after the initial elastic regime (i.e., creep rate \(\dot{\gamma}\)) can be deduced by linear fitting (see fig. S11 and table S7 for more details). The creep behavior of ALD-33 well followed that of a viscoelastic liquid showing the initial elastic response followed by a slow-down of the creep rate to reach a steady rate. (B) The reciprocal of \(\dot{\gamma}\) follows Arrhenius relation (30) as relaxation time (\(\tau\)) in fig. S8. The deduced apparent \(E_a\) from the Arrhenius plot was \(\sim 112\) kJ/mol, which agrees well with the values reported for polyimine vitrimers (28-31) as did the apparent \(E_a\) obtained from the stress-relaxation test (fig. S8). We note that the Neat-ABS was unable to withstand the stress of 50000 Pa to record the creep behavior reliably in the same experimental conditions due to sample failures.
**Fig. S11. Arrhenius fitting from creep tests on ABS-vitrimer.** Linear fitting of elastically unrecoverable, linear deformation regime (selected time range from 1000 to 1500 s) in the creep test (fig. S10) to deduce creep rate ($\dot{\gamma}$) by the slope of the fitted lines in strain versus time curve. The $\dot{\gamma}$ values were obtained as 0.0108, 0.0217, 0.045, 0.1116 %/s at 130, 140, 150, and 160 °C, respectively. The viscosity at 160 °C calculated from the strain rate is $4.48 \cdot 10^7$ Pa·s.
| T (°C) | T (K) | 1/T (K⁻¹) | 1000/T (K⁻¹) | ˙γ (s⁻¹) | - ln (˙γ) |
|--------|------|----------|-------------|---------|---------|
| 130    | 403  | 0.00248  | 2.48        | 0.01    | 9.13    |
| 140    | 413  | 0.00242  | 2.42        | 0.02    | 8.44    |
| 150    | 423  | 0.00236  | 2.36        | 0.05    | 7.71    |
| 160    | 433  | 0.00231  | 2.31        | 0.11    | 6.80    |

Table S7. The temperature, creep rate ˙γ obtained from the creep test on ABS-vitrimer to construct the Arrhenius plot (fig. S10B).
Table S8. The parameters to find the topology freezing temperature ($T_v$) of our system using the Arrhenius fitting from the stress-relaxation test (fig. S8, table S5). The equation of the fitted Arrhenius plot is as follows:

$$\ln (\tau) = 18.713 \left(\frac{1000}{T}\right) - 43.401$$

The $T_v$ is conventionally defined as the temperature where the viscosity $\eta$ reaches $\sim 10^{12}$ Pa·s (43). Above $T_v$, the exchange reaction can occur fast and the vitrimer can be reprocessed and recycled; below $T_v$, the exchangeable reaction is limited and the vitrimer is similar to the traditional permanently crosslinked thermoset (44). We can compute the corresponding $\tau$ at the given viscosity from $\eta \approx G\tau$, where $G$ is the elastic shear modulus. From the rheological frequency sweep (Fig. 3B), the $G$ can be regarded as the $G' \sim 1$ MPa in the rubbery plateau region. Plugging in these values gives the $T_v$ of 327.06 K or 54.06 °C. We note that the $T_v$ deduced by the Arrhenius relation from creep tests (fig. S10, S11) is 81°C, which is consistently below the $T_g$ of our ABS systems, indicating the transimine exchange readily takes place in the temperature range we tested. Note that the transition from elastomer to viscoelastic liquid by dynamic covalent exchange at such low $T_v$ below $T_g$ is only hypothetical, not practically observable since any segmental motion to enable any bond rearrangement of the network is frozen below $T_g$ (55).
DMA on ABS samples

Fig. S12. DMA spectra comparing the Neat-ABS and the ALD-33. Both samples followed very similar trends and thermal deformation. The deformation of both samples at high temperature eventually going over the stretching limit of the apparatus resulted in the characterization above 130 °C unsuitable by DMA.
Tensile mechanical properties upon recycling

| Recycled #, Label | Elongation at Break (%) | UTS (MPa) |
|-------------------|-------------------------|-----------|
| 0, Pristine       | 21.60 ± 7.94            | 38.38 ± 3.71 |
| 1, Re 1           | 20.50 ± 7.10            | 35.83 ± 1.87 |
| 2, Re 2           | 18.23 ± 5.62            | 36.89 ± 5.08 |
| 3, Re 3           | 17.17 ± 3.30            | 36.22 ± 2.28 |

Table S9. Tensile properties of recycled ALD-33 specimens up to 3 cycles (pristine, Re 1, Re 2, Re 3). The tensile strength stayed above 30 MPa through all cycles, which is higher than the Neat-ABS. There was no significant difference in the strength, suggesting successful recovery of elastic mechanical properties upon reprocessing consistent with the DMA results (Fig. 3D, 3E). We note that the total ductility (elongation) in the plastic regime tends to be reduced by 3-4% upon 2nd and 3rd recycles, which is consistent with phenomena observed in previous reports on recycled dynamic thermosets (27, 84). We ascribe this minor loss in plastic elongation at later cycles to possible impurity inclusion through repeated inevitable contacts in sample handling, breakage, and hot-pressing. The data is shown as the average ± standard deviation.
Printer feedstock filament processing

**Fig. S13. Fabrication of polymer filaments for 3D printing.** (A) The polymer pellets or powder were inserted into the hopper and extruded at 230 °C. The filament was extruded through a 1.75 mm die nozzle. The extrusion and winding rates were adjusted accordingly to produce the filament of diameter 1.75 mm stably. (B) The spools of filaments produced from ALD-33 (left), Neat-ABS (middle), and commercial ABS filament spools (right). Note that there was no meaningful mechanical difference between the house-made filament of Neat-ABS and the commercial ABS filament spool.
FFF-printed dogbone specimens

Fig. S14. Tensile specimens of Neat-ABS (left) and ALD-33 (right) in (A) transverse and (B) longitudinal printing paths. The tensile test on the transverse specimen measures the interlayer bond strength. The dimensions of printed specimens followed the 0.2× size of the ASTM D638 Type I model (i.e., full length 33 mm, gauge width 3.0 mm, grip width 4 mm, thickness 0.5 mm).
Cross-sectional observation on interlayer structures

Fig. S15. Cross-sectional view on the interlayer joints of the Neat-ABS (left) and the ALD-33 (right). The ALD-33 visually shows better integration between the layers. However, the curvatures and topological valleys created by the extrusion of cylindrical filaments through the circular nozzle are still present, although smoother. These topological valleys are where stress concentrates and result in the lower UTS in the transverse direction than in the longitudinal direction. We speculate that the fast bond rearrangement time of our vitrimer system provides the system with insufficient time to flow like a liquid to form completely isotropic structural properties. The scale bar indicates 100 μm.
Post-annealing effect

**Fig. S16. Annealing effect on the ABS-vitrimer systems.** The annealing was performed by placing the free-standing samples in the vacuum oven at 150 °C for over 3 hours. (A) The tensile stress-strain profiles of transverse-printed dogbone specimens of Neat, ALD-33, and ALD-33 that underwent further annealing as above. (B) The UTS of the samples in (A). The post-annealing appears to further enhance the interlayer strength. (C) The reduction of surficial scratches on the Neat, ALD-17, and ALD-33 films. All three samples exhibited decreased visible scratches after the heat treatment. These observations further support the thermally activated chain and bond rearrangements in the ABS-vitrimer systems.
Preservation of the layered structure of printout in solvents

Fig. S17. Solvent-resistance observation for layered printout structures from the top-front view of the Neat-ABS and ALD-33 (0.3 g) immersed in THF over 24 hours at ambient condition (Fig. 4H). The layered structure of the oak leaf printed from ALD-33 was kept intact whereas that from Neat-ABS completely disintegrated. We also compared the sample mass after 24 h swelling followed by the vacuum-drying for 24 h and could not determine significant changes in the mass by the dissolution of ALD-33 after the tests. We note that the apparent change in the mass was within ±5% and we consider this error can come from any possible contamination or the mechanical breakage of the swollen softened sample during the handling process rather than the dissolution of the sample.
Solvent reprocessing via chemical decrosslinking of ABS-vitrimer

Fig. S18. The chemical decrosslinking of ABS-vitrimer waste for solvent reprocessing. First, the ALD-33 wastes (0.2 g) were put into the THF solution (8 mL). Then the excess amount of octylamine (2 mL) was used for transimination to decrosslink the imine bonds formed between the ABS-amine and glutaraldehyde. After 1 hour, the ALD-33 was completely dissolved in the THF-octylamine solution. To retrieve the decrosslinked ABS-vitrimer, the solution was dropped into ethanol to precipitate the decrosslinked polymer, then centrifuged to facilitate further precipitation. The precipitation process can be repeated multiple times to enhance the yield and purity, followed by decanting and drying in a vacuum (over 24 hours). Thus-obtained decrosslinked ABS-vitrimer can be completely dissolved in THF for further solvent reprocessing for further transimination. These results suggest another possible extraction-separation path of ABS-vitrimer from other polymer waste mixtures insoluble to monofunctional amines or solvents.
Upcycling ABS-vitrimer/Neat-ABS waste mixtures into useful 3D-printed structures

**Fig. S19.** The upcycling of ABS-vitrimer waste through the same filament fabrication and FFF printing protocols. First, the used vitrimers were broken down into small sizes feedable into the extruder, then the recycled filament is produced through the extrusion. This vitrimer reprocessing could be easily blended with Neat-ABS to control the production amount and color of the filaments and printouts. The reusability and compatibility of ABS-vitrimer with Neat-ABS may save resources and energy by upcycling the used/failed printing parts or mixtures of vitrimer and Neat-ABS produced during changing the resins, purging, or unsorted ABS waste disposal process.
Example parameters to design FFF-(re)printable vitrimer
(Table S10 and S11)

| Parameters* | Major Relevant FFF Process | Preference | Possible Effects in Extreme (too low | too high)* |
|-------------|-----------------------------|------------|---------------------------------------|
| Bond Rearrangement Time (τ) ** | Extrusion, Deposition | Short: for faster bond exchange for extrusion, interlayer integration, and reprocessing | system relaxes too fast | relaxes too slow for stable extrusion-deposition |
| Apparent Activation Energy ($E_a$) | Extrusion, Thermal Processing Controllability | High: for structural- thermochemical stability at low T near $T_g$ and faster bond exchange upon heating | system too reactive at low T near $T_g$ and dynamic behavior too insusceptible to T change*** | dynamic behavior too susceptible to T change**** |
| Deformability | Filament Winding, Loading, Feeding, Post-print Handling | High: for fracture-free pre- or post-extrusion steps (e.g., printout detachment from hotbed stage) | system too brittle | too malleable for stable pre-extrusion or post-printing steps involving mechanical stress***** |

* Proper numerical value range will correspond to the particular hardware settings.
** Relevant to viscosity (table S5, S7, S8) – if the viscosity is too low, the system flows too fast, if too high, the system flows too slow for stable extrusion.
*** The dynamic behavior should enter the printable regime upon T change before polymer degradation temperature.
**** The system should be tolerant for stable printing upon operational T fluctuation.
***** In the case of the material has good ductility but poor elasticity.

Table S10. Example viscoelastic and mechanical properties to consider for implementing the direct FFF-(re)printability to a vitrimer. Note that if a vitrimer has an extrudable viscosity but too long τ, the interlayer integration upon printing and reprocessing through FFF protocols (fig. S19) will be limited due to the long time required to re-establish crosslinks. In such case, one-time direct extrusion from the ingredients via DIW instead of the continuous FFF, post-treatment such as annealing for interlayer bonding, and depolymerization steps before reuse may be preferable.
| System           | $E_a$ (kJ/mol) | $\tau$ at 150 °C (s) | $\tau$ at 170 °C (s) | $\tau$ at 230 °C (s)* | Ductility (%) |
|------------------|----------------|---------------------|----------------------|----------------------|---------------|
| Neat-ABS         | NA             | 0.75                | 0.22                 | NA                   | 18            |
| ABS-vitrimer     | 155            | 2.33                | 0.32                 | 0.002                | 21            |
| Epoxy-vitrimer (45) | 55            | 480                 | 120                  | 8.680                | 7             |

Table S11. **Example comparison of design parameters** between Neat-ABS, ABS-vitrimer, and a disulfide epoxy-vitrimer from a previous report (45). The bond recombination is 200 times faster at 150 °C and becomes 3 orders of magnitude faster as the temperature increases to 230 °C (i.e., typical extrusion temperature of ABS) in ABS-vitrimer compared to the epoxy-vitrimer, thanks to the high $E_a$ of the transimination. The comparison indicates that significantly longer time or higher temperature, thus more energy, would be required for epoxy-vitrimer for possible FFF processing and interlayer bonding compared with the ABS-vitrimer, using the same printing hardware. Thus, the rationale of selecting the dynamic exchange chemistry with the suitable $E_a$ as well as evaluating the viscoelastic dynamic behavior of the network would be important for designing FFF-(re)printable vitrimers. The asterisk (*) indicates the value has been extrapolated from the Arrhenius relation.
Compression test on 3D-printed beetle-forewing-inspired structures (Fig. S20 to S22)

The intricate structures such as bioinspired honeycomb structures of beetles’ forewings known for their exceptional mechanical resistance against compression (46, 56) are difficult to be manufactured by conventional casting or molding methods. Here, the beetle’s forewing-inspired structures were facilely printed through FFF (Fig. 4K). The SEA measured by the compression test of the beetle-inspired ABS-vitrimer printout was similar to that of chopped carbon fiber-reinforced epoxy composites (47), which is three times greater SEA than those of filled structures of unmodified ABS (85, 86).

**Fig. S20.** Experimental setup used for the mechanical evaluation in compression of printed specimens. Visible in the picture are the test specimen, the 3-post die set, and a spring-loaded linear variable differential transformer (LVDT) to monitor test specimen axial deformation.
Fig. S21. Bioinspired structures before and after the compression test of ALD-33 (upper panel) and Neat-ABS (lower panel). We note that the dimensions after the compression vary according to each sample.
Fig. S22. An example of determining the onset of the densification by taking the first derivative of the load vs displacement curves of each sample. The shown curve is the value trends of the derivative of the load-displacement curve corresponding to the ALD-33 sample in Fig. 4M. A clear transition can be observed at displacements greater than 2.5 mm when the derivative exhibits oscillatory behavior. The specific energy absorption (SEA) was calculated up to that point.
Generalization of ABS-vitrimer design pathway using different dynamic crosslinks
(Fig. S23 to S28)

To test the generality of our chemical upcycling pathway of producing ABS-vitrimer, we synthesized two alternative crosslinkers with acetylacetate (AcAc) functional groups for imine formation and dynamic exchange via transamination of vinylogous urethanes (48, 49) (i.e., aliphatic-AcAc, bisphenol-AcAc; fig. S23 to S26). We could also obtain the successful imine formation as seen from the FTIR result showing the C=N stretching signals (fig. S27). The UTS of AcAc samples could also be enhanced to the similar level reached by ALD-33 (fig. S28), proving our synthetic path indeed can versatilley work with different crosslinkers to strengthen the ABS. We further tested the stability of the AcAc system in the solvents we tested for the ALD system (fig. S6) and confirmed that AcAc systems likewise showed solvent-resistance. These results further supplement the thermoset features achieved by our general “vitrimerization” strategy using different crosslinkers.

Synthesis and Characterization of AcAc-crosslinkers

Bisphenol Acetoacetate (Bisphenol-AcAc). Bisphenol A (22.8 g, 0.10 mol) and tert-butyl acetoacetate (79.0 g, 0.50 mol) were added to a 500 mL flask attached with a pressure tube. The mixture was heated for 4 hours at 150 °C, and the tert-butanol product was continuously removed by distillation throughout the reaction. After the reaction was finished, the product was purified by column chromatography over silica gel using 2:0.1 methylene chloride/methanol as the eluent to afford a yellowish liquid (25 g, 63 %).<sup>1</sup>HNMR (400 MHz, CDCl<sub>3</sub>, δ): 7.25 (d, J = 7.2 Hz, 4H), 7.03 (d, J = 7.2 Hz, 4H), 3.70 (s, 4H), 2.37 (s, 6H), 1.69 (s, 6H).<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, δ): 201, 166, 149, 129, 121, 50.6, 43.0, 31.4, 30.6.

![Fig. S23. <sup>1</sup>H NMR of Bisphenol Acetoacetate](image-url)
Propyl Acetoacetate (Aliphatic-AcAc). 1,3-Propanediol (10.0 g, 0.13 mol) and tert-butyl acetoacetate (103 g, 0.65 mol) were added to a 500 mL flask attached with a pressure tube. The mixture was heated for 4 hours at 150 °C, and the tert-butanol product was continuously removed by distillation throughout the reaction. After the reaction was finished according to thin-layer chromatography (TLC), the excess of tert-butyl acetoacetate was removed by washing with hexane (3 ×50 mL), yielding pure propyl acetoacetate (27 g, 85 %). $^1$H NMR (400 MHz, CDCl$_3$, δ): 4.02 (t, J = 6.5 Hz, 4H), 3.30 (s, 4H), 2.07 (s, 6H), 1.81 (m, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$, δ): 201, 163, 61.9, 49.9, 30.2, 28.1.

Fig. S24. $^{13}$C NMR of Bisphenol Acetoacetate

Propyl Acetoacetate (Aliphatic-AcAc). 1,3-Propanediol (10.0 g, 0.13 mol) and tert-butyl acetoacetate (103 g, 0.65 mol) were added to a 500 mL flask attached with a pressure tube. The mixture was heated for 4 hours at 150 °C, and the tert-butanol product was continuously removed by distillation throughout the reaction. After the reaction was finished according to thin-layer chromatography (TLC), the excess of tert-butyl acetoacetate was removed by washing with hexane (3 ×50 mL), yielding pure propyl acetoacetate (27 g, 85 %). $^1$H NMR (400 MHz, CDCl$_3$, δ): 4.02 (t, J = 6.5 Hz, 4H), 3.30 (s, 4H), 2.07 (s, 6H), 1.81 (m, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$, δ): 201, 163, 61.9, 49.9, 30.2, 28.1.

Fig. S25. $^1$H NMR of Propyl Acetoacetate
Fig. S26. $^{13}$C NMR of *Propyl Acetoacetate*
Fig. S27. Generalization of ABS-vitrimerization pathway using different crosslinker units containing acetylacetate (AcAc) functional groups that undergo imine-enamine formation and dynamic exchange via transamination of vinylogous urethanes (48, 49). The same processing to prepare ALD specimens has been performed to prepare the AcAc specimens. (A) The bisphenol-AcAc and aliphatic-AcAc were synthesized as alternative crosslinkers for glutaraldehyde, then reacted with ALD-0. (B) The full FTIR spectra of bisphenol-AcAc and aliphatic-AcAc ABS systems. (C) The focused spectra in the 1600–1750 cm⁻¹ region. The C=N stretching from imine groups in 1640–1690 cm⁻¹ was found in both systems, indicating successful imine formation. The -AcAc/-NH₂ was 0.33 similar to ALD-33 where -CHO/-NH₂ was 0.33.
Fig. S28. Tensile stress-strain tests on AcAc systems. The -AcAc/-NH$_2$ was 0.33 corresponding to ALD-33 where -CHO/-NH$_2$ was 0.33. The enhancement in tensile strength from the Neat-ABS by dynamic vinylogous urethane crosslinking was obtained for both bisphenol- and aliphatic-AcAc systems similar to ALD-33 systems. We note that the ductility of the bisphenol-AcAc system was depreciated ascribed to the less flexible, rigid aromatic structure as the crosslinking chain, which also could cause phase separation by π-π stacking. The aliphatic-AcAc crosslinker is more flexible than bisphenol-AcAc, but still reduced the ductility of the bulk network compared to the ALD-33 crosslinker which produces the subchain with only linear sp$^3$ carbon chains between the imine bonds. These results support that the mechanical property of the network is dominantly controlled by the imine crosslinking rather than the backbone chain of ABS.
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