

Upcycled Polyurethane Products Based Strong and Robust Inorganic/Organic Composites

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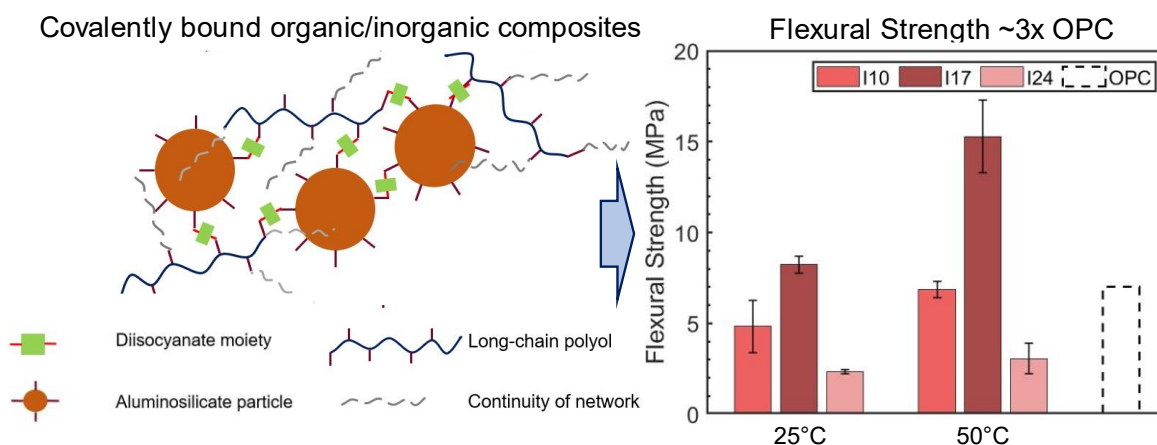
EXECUTIVE SUMMARY

In 2020, the Mattress Recycling Council California, LLC (MRC) recovered approximately 13 million pounds of flexible polyurethane foam in California. Volume in future years is expected to grow due to several factors some of which include increased popularity of all foam mattresses, improved collection and logistics processes and recycling rate improvements. MRC's research team supports new and innovative end of life solutions for post-consumer polyurethane foam. A research contract was established with UCLA to evaluate the use of upcycled polyurethane foam in structural materials.

This report summarizes the key findings of the research focusing on fabricating covalently bound organic/inorganic composites comprising aluminosilicate mineral (zeolite) microparticles and upcycled polyols (obtained from chemical depolymerization of polyurethane foam). These composites present material strength and toughness comparable to Portland cement while bearing significantly smaller energy and carbon footprints, promising to serve as eco-friendly alternatives to lightweight aggregate concrete in structural and insulation applications. The major accomplishments of this project are as follows:

- We have invented a method to fabricate strong and robust organic/inorganic composites suitable for lightweight structural applications.
- To the best of our knowledge, this is the first demonstration of highly filled microparticle composites (~60 wt%) with consistently good physical properties (uniform microstructure, high flexural strength and strain capacity).
- The invented solvent-less fabrication strategy eliminates pertinent challenges – environmental toxicity, high cost of solvent removal – associated with conventional solvent-based fabrication strategies, without compromising the flexural properties.
- The use of common inorganic materials (minerals and sand) and polyols sourced from upcycled polyurethanes, and a one-pot fabrication process with short processing times (24–48 hours) and mild reaction conditions (2–50 °C) make our fabrication approach markedly less energy intensive than OPC manufacturing while producing composites with comparable properties.
- Our highly filled composites, consisting of upcycled polyols (obtained by glycolysis of polyurethane foam), naturally occurring aluminosilicate minerals, and isocyanate linkers, possess enhanced flexural properties (strength and strain capacity) as compared to ordinary Portland cement (OPC). Optimization of the composition results in composites with significantly enhanced flexural strength (~3×) and strain capacities (~100×) as compared to OPC.

- The microstructure and flexural properties of these composites were tuned by varying the composition – inorganic and reactive isocyanate contents, type of inorganic particles, and OH value of polyol.
- Parallel fabrication approaches involving virgin polyol (PPG) resulted in highly filled composites with significantly inferior flexural strength, highlighting the advantage of employing high -OH density upcycled polyols. This was confirmed by employing polyols with varying OH values; flexural properties improved with an increase in OH value.



Summary of this work: Covalently bound inorganic-organic composites with flexural properties that substantially outperform ordinary portland cement (OPC).

INTRODUCTION

Polyurethane (PU), formed by an addition reaction between polyols and isocyanates, is processed as foams, films, and dispersions for use in mattresses, furniture and automotive cushioning, footwear, membranes, and adhesives, etc. Given its widespread applications, the global demand for PU is projected to be USD 105.2 billion by 2025.^[1–3] Consequently, a significant amount of PU waste is generated globally; 1.3 million tons of PU waste was produced in the US alone, in 2011.^[3] Attempts to valorize the PU waste and mitigate its environmental impact have led to recycling strategies including mechanical (pulverization, rebonding, hot pressing)^[2–4] and chemical (glycolysis, acidolysis, alcoholysis, aminolysis, etc.)^[2–5] processes.

However, with demand for mechanically recycled PU limited almost exclusively to carpet underlay applications, there is a growing need for identification of alternate end-of-use applications for post-consumer-use and post-industry-use PU foam. The incorporation of pulverized PU foam into ordinary Portland cement-based (OPC) concrete as a partial replacement to sand or solid aggregates represents one such avenue for utilization of mechanically recycled PU.^[6,7] These mixtures, called lightweight aggregate concrete (LWAC), are employed as thermal insulation materials, thus mitigating short and long-term energy and CO₂ costs associated with OPC production and use.^[6,7] However, due to lack of significant adhesion between OPC and pulverized PU particles, these composites de-bond under minimal strains.^[8] This results in significant reduction (>3×) in compressive and flexural strengths as compared to OPC at low loadings (~1 wt.%) of pulverized PU foam.^[9,10] Additionally, the lack of bonding between the inorganic OPC and organic PU particles in these ‘filled’ concretes do not exhibit increased resistance to crack propagation.^[11]

Here, we demonstrate an alternate strategy to fabricate structural lightweight composites that comprise naturally occurring aluminosilicate microparticles covalently bridged *in situ* by ductility-enhancing and fracture resisting organic phase composed of polyols obtained from upcycled polyurethane products and reactive isocyanates. These hybrid composites have low densities (450–1400 kg/m³; 2–5× lower than OPC), leading to lower structural weights. Most importantly, incorporation of the upcycled polyols improves the flexural strength (3× OPC) and strain capacities (~100× OPC) while also employing upcycled polyol contents up to 20 wt% without compromising the flexural properties.

We note that while the synthesis of covalently bound polymer-nanoparticle composites with high filler loadings have been previously reported,^[12,13] high solid-loadings in microparticle composites are limited by their size and aggregation tendencies.^[14,15] In this study, reactive isocyanates facilitate covalent linkages between the organic (upcycled polyol) chains and inorganic (zeolite) particles, leading to strong solid-rich composites (~60 wt% zeolite). We discuss our solvent-free strategy to develop these composites at room temperature, and the positive influence of upcycled polyol on flexural properties as compared to virgin polyol. Further, we elaborate on the influence of hydroxyl (OH) value of polyol on the flexural properties by comparing systems with different polyols. The generality of this fabrication strategy was tested by employing different inorganic particles, and strategies to tune the flexural properties are discussed. Finally, we enlist strategies to improve the workability of these solid-rich composites and provide a perspective on our future work.

RESULTS AND DISCUSSION

Solvent-less Fabrication of Organic/inorganic Composites

Organic/inorganic composites comprising polyols (upcycled or virgin), inorganic aluminosilicate particles (zeolite or sand), and a diisocyanate (isophorone diisocyanate - IPDI) were fabricated by utilizing the reactive isocyanate (NCO) groups on IPDI. Each molecule of IPDI possesses two NCO moieties that react with hydroxyl (OH) groups present on the polyol as well as on the inorganic particle surface, thereby forming a covalent, hybrid network of inorganic and organic components (**Figure 1A**). The reaction between NCO and OH leads to formation of urethane linkages and is catalyzed by organometallic or amine compounds.^[14,15]

Solvent-free composites were fabricated using upcycled polyol (Infigreen-300: IG300; hydroxyl value = 290 mg/g) or virgin polyol (poly(propylene glycol): PPG; hydroxyl value = 56 mg/g), zeolite (clinoptilolite) and isophorone diisocyanate and catalyst dibutyltin dilaurate (DBTDL). The polyol was introduced in small amounts during addition of zeolite to IPDI to maintain composite consistency and ease of mixing. The polyol aided workability of these highly filled mixtures, thereby eliminating the need for a solvent. Additionally, the mixture was repeatedly vortexed during zeolite and polyol addition. The composite paste was cured in Teflon-lined metal mold for 24 hours at 50 °C (**Figure 1B**). Alternatively, room temperature curing of the composites was carried out, aided by triethylamine (TEA) as catalyst along with DBTDL. The solid composites post curing were characterized further (**Figure 1C**).

The inorganic and reactive isocyanate in all formulations were varied between 46–60 wt% and 10–24 wt%, respectively, while the polyurethane content was maintained constant (30 wt%). The

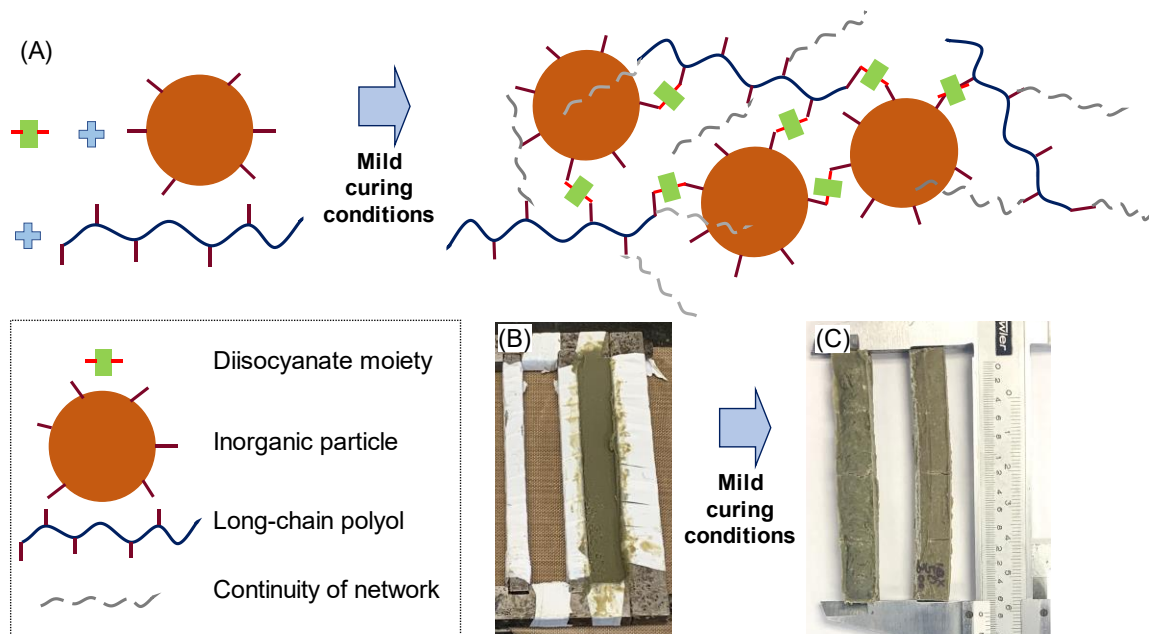


Figure 1: Schematic representing the fabrication strategy of the hybrid inorganic/organic composites based on upcycled PU products. (A) The reactive isocyanate moiety forms urethane linkages with upcycled polyol and inorganic particles via the OH groups on their surface, thereby forming a network of organic/inorganic components. The curing reaction occurs at room temperature in presence of an organometallic catalysts and an amine co-catalyst. Alternatively, the reaction can also be carried out at 50 °C in the presence of an organometallic catalysts. (B and C) Representative pictures of the reaction mixture in a mold prior to curing (B) and cured composites (C).

workability of these solid-rich composites evolved with changes in composition; an increase in the reactive isocyanate content (and a consequent decrease in the inorganic loading) resulted in more 'liquid-like' mixtures. The fabrication strategy involving no solvents eliminated the challenges associated with solvent removal – high energy requirement, cost, environmental toxicity – thereby making the process environmentally viable and industrially scalable. The absence of solvent as a viscosity modifying agent for these solid-rich composites is compensated for by the intermittent addition of polyol during zeolite addition.

Upcycled Polyols Improve the Flexural Properties of Composites

Multiple composites were fabricated by changing the reactive isocyanate (10–24 wt%) and zeolite contents (60–46 wt%) (**Table A1**). The polyurethane content (comprising upcycled or virgin polyol and isocyanate) was maintained constant at 30 wt% in all compositions. Three-point bending tests for flexural strength estimation (Instron UTM) were performed on the solid specimen obtained after 50 °C or room temperature (25 °C) curing. **Figure 2a** (upcycled polyol) and **Figure 2b** (virgin polyol) represent the evolution of flexural strength with change in composition; I10, I17 and I24 refer to reactive isocyanate contents of 10, 17 and 24 wt%, respectively. The zeolite contents in these composites were 60, 53 and 46 wt%, respectively.

The flexural strengths of no-solvent composites with upcycled (IG300) polyols ranged from 2 MPa to 16 MPa, respectively (**Figure 2a**). Amongst the composites cured at room temperature, I17 had the highest flexural strength (8 MPa), about 14% higher than OPC (**Figure 2a**). Flexural strength increased to 3× OPC by curing I17 at 50 °C (**Figure 2a**). Notably, at both curing temperatures, the optimum composition was 17 wt% reactive isocyanate, 53 wt% zeolite and 30 wt% polyurethane (I17). Additionally, composites with upcycled polyols (**Figure 2a**) performed consistently better than the no-PU composite - PU0-I34; 6 MPa (**Figure 2b**).

The flexural strengths for corresponding compositions with virgin polyols (**Figure 2b**) were mostly lower than upcycled composites (**Figure 2a**) and OPC (**Figure 2a**, dashed bar), irrespective of temperature. The highest flexural strength amongst virgin composites (13 MPa) was noted for I24-50 °C; the flexural strengths improved consistently with increasing reactive isocyanate content (10–24 wt%) (**Figure 2b**). For most of the virgin composites, however, the flexural strengths were lower than or comparable to no-PU composition (PU0-I34; 6 MPa) (**Figure 2b**).

The strain capacities of upcycled and virgin composites were significantly different (**Figure 2c, d**). Among the IG300 composites, the highest strain capacity was recorded for I17-50 °C (12%), nearly 2 orders of magnitude higher than OPC (0.2%) (**Figure 2c**). The strain capacities of upcycled composites remained consistently and significantly higher than OPC, irrespective of curing temperature. For virgin PPG composites, however, strain capacities were as high as 45% leading to highly flexible composites that buckled under very low loads (**Figure 2d**).

The superior flexural performance of the composites was corroborated by evolution of the composite morphology with composition (**Figure 3a-d**). The microstructure of I10-IG300 composite (**Figure 3a**) showed a uniform particle distribution, albeit with some aggregation. With an increase in the reactive isocyanate content (17 wt%; I17-IG300) the morphology was visibly more uniform (**Figure 3b**). Virgin compositions I10-PPG (**Figure 3c**) and I17-PPG (**Figure 3d**) showed a similar evolution in microstructure with an increase in the reactive isocyanate content.

Covalent linkages between polyol and inorganic particles are facilitated by the reactive isocyanate groups. The hybrid nature of these composites enhances their flexural properties (comparable to or greater than OPC), in contrast to conventional OPC which does not have an organic, long-chain component. The tunability of composite properties is further underscored by the notable increase in flexural strength for upcycled composites, as compared to virgin composites, ascribed to the higher OH value of IG300 (290 mg/g) as opposed to PPG (56 mg/g). A higher OH value offers more sites for covalent linkages with the reactive isocyanate, and consequently aids network formation with the inorganic particles. The OH value of IG300 can also be indicative of its branched structure, thus increasing its proclivity to form cross-linked structures, in contrast to PPG, which is linear. The high flexural strengths of upcycled composites are complimented by optimal flexural strain capacities making them good candidates for shock absorption, thermal

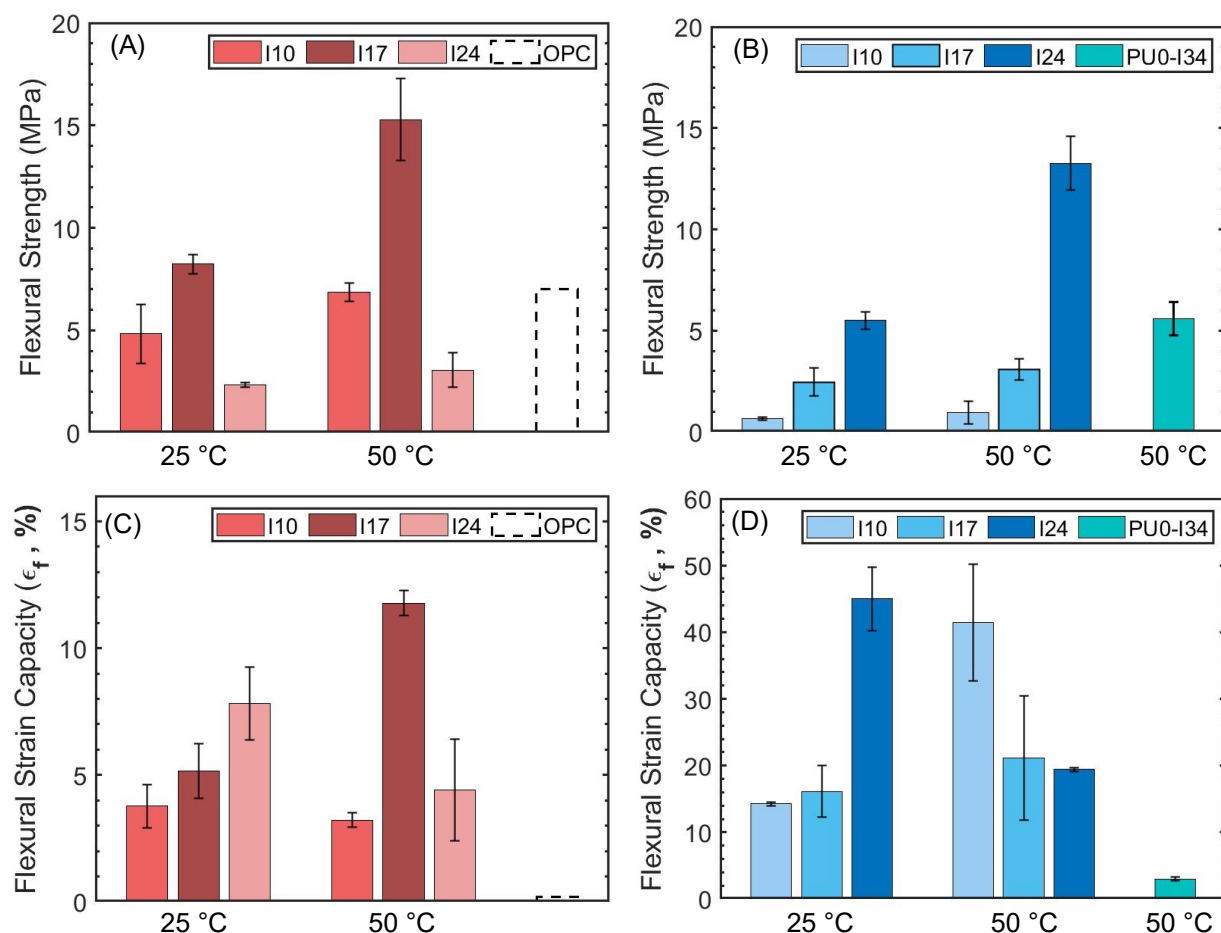


Figure 2: (A) Flexural strengths of upcycled organic/inorganic composites comprising IG300 and zeolite (zeolite 46–60 wt%, excess isocyanate 10–24 wt%, polyurethane 30 wt%) had flexural strengths between 3–16 MPa, with the highest being 3× OPC (dashed bar). I17 was the optimum composition leading to highest flexural strength, irrespective of temperature. (B) The flexural strengths of no-solvent virgin organic/inorganic composites comprising PPG and zeolite ranged from 1 MPa to 13 MPa, with changes in composition and temperature (room temperature, 50 °C). The flexural strength of PU0-I34 (0 wt% polyurethane, 34 wt% isocyanate, 66 wt% zeolite) was comparable to I17-room temperature. The flexural strengths increased with increase in isocyanate content as well as temperature. (C) Flexural strain capacities of upcycled composites peaked at 12% (I17-50 °C), about 2 orders of magnitude higher than OPC. All composites discussed here were solvent-free, except PU0-I34 (DMF). The strength and strain capacity values represent the mean from duplicate measurements. (D) The flexural strain capacities of virgin composites were as high as 15–55%, considerably higher than PU0-I34. No specific trends were observed with composition or temperature.

insulation, and sound proofing applications wherein conventional OPC would crack while virgin polyol-based composites would be too flexible.

The evolution of micromorphology of the solid-dense composites further confirm the influence of isocyanate linkers on their flexural properties. Despite high solid contents (46 – 60 wt% zeolite), the microstructure of these composites appeared uniform, likely due to the covalent linkages between the inorganic and organic component, as opposed to physical forces (van der Waals, hydrogen bonding) that lead to particle aggregation. We note that an adequate reactive isocyanate content is required to avoid aggregation, as seen from the morphology differences between I10 (**Figure 3A and 3C**) and I17 (**Figure 3B and 3D**) with inadequate and adequate isocyanate contents, respectively. Microstructural uniformity leads to a concomitant increase in the flexural strengths (**Figure 2A and 2B**) and strain capacities (**Figure 2C and 2D**) respectively, thus accentuating the influence of extent of covalent binding on physical properties.

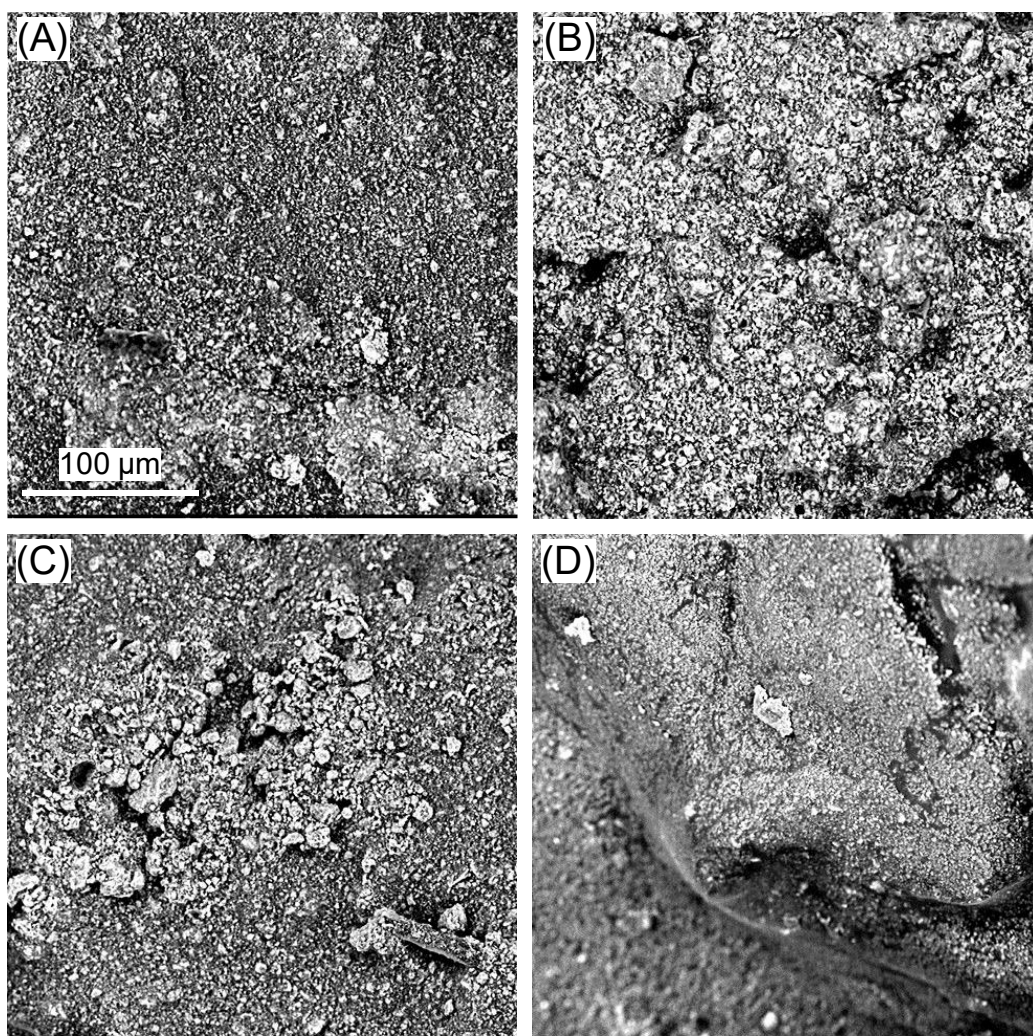


Figure 3: Microstructure of **(A)** I10-IG300 (no solvent; zeolite 60wt%, PU 30 wt%, reactive isocyanate 10 wt%) and **(B)** I17-IG300 (reactive isocyanate 17 wt%). Agglomerated regions indicated insufficient covalent binding were seen in (A) while (B) had a more uniform microstructure. A similar evolution in microstructure was seen for **(C)** I10-PPG which had some agglomerated regions, likely due to lower reactive isocyanate content (10 wt%) as compared to I17-PPG **(D)** which has a more uniform distribution of particles.

Higher OH-value Upcycled Polyols Improve Flexural Properties

The applicability of this fabrication approach for use of polyols obtained from upcycled polyurethane foam was tested with a higher OH-value polyol, Infingreen-420A (IG420A; hydroxyl value = 385 mg/g) ($\text{OH}_{\text{IG420A}} > \text{OH}_{\text{IG300}} > \text{OH}_{\text{PPG}}$). As shown in **Figure 4**, for composition with 60 wt% zeolite, 30 wt% polyurethane and 10 wt% reactive isocyanate contents, the flexural strength improved significantly ($>3.5\times$) with an increase in OH value of the polyol. Notably, the use of a higher OH value polyol (here, IG420A) compensated for the lower temperature of curing, thereby leading to higher flexural strength. The flexural strength and strain capacities (2–12%) of upcycled composites remained comparable to or significantly higher than OPC, thereby outlining the pivotal role of polyol chains in improving flexural properties. We posit that the higher availability of OH groups increase the tendency to form a robust network of inorganic and organic components, leading to enhanced properties. I10 was the optimum composition (**Figure 4**); higher reactive isocyanate contents (>10 wt%) caused significant foaming in the composite systems and were not pursued.

Composites with Sand as the Inorganic Component

The fabrication strategy is based on the principle of covalent linkages between OH (on inorganic particle surface and polyols) and NCO (from the isocyanate linkers) groups. The generality of this strategy was confirmed by the replacement of zeolite particles with sand, which is a commonly available compound with hydroxyl (OH) groups on the surface. The flexural strengths ranged from 1–7 MPa for virgin and upcycled composites, with sand and zeolite (**Figure 5**). Composites (both virgin and upcycled) comprising zeolite or sand exhibited comparable flexural strengths. However, the flexural strain capacities for sand-based upcycled composites (20–45%) were significantly higher than zeolite-based ones (4–5%) for the I10 composition. This can be ascribed to the coarse and polydisperse nature of sand leading to imperfect packing and persistent voids in the composites. Nevertheless, these encouraging results present interesting avenues for the use

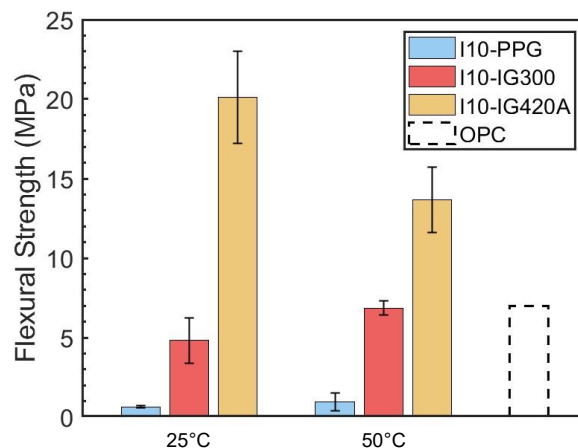


Figure 4: The change in flexural strength with increasing OH value of polyol, and temperature for Z60-PU30-I10 no solvent composition. Composites with higher OH value polyols had higher flexural strength (PPG: 56.1, IG300: 290, IG420A: 385 mg/g). The flexural strengths for both upcycled composites (red and yellow bars) remained comparable or significantly higher than OPC (dashed bar), irrespective of temperature.

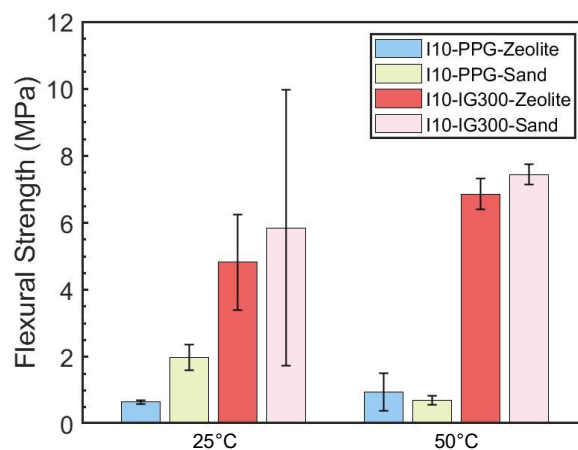


Figure 5: Flexural strength of upcycled sand and zeolite composites (pink and red) were higher than their virgin counterparts (blue and green), irrespective of temperature. The strengths remained comparable for upcycled polyols, irrespective of the nature of inorganic particle.

of commonly available OH-functionalized microparticles like silica for the fabrication of strong upcycled composites.

Optional Addition of Solvent to Enhance Workability

Solvents including acetone (Ac), dimethylformamide (DMF) and N-methyl pyrrolidone (NMP) were employed to enhance the workability of the composites involving IG300. As seen in **Figure 6**, flexural strengths of most composites remained comparable and increased with an increase in curing temperature. While this confirms that the elimination of solvent from the fabrication process does not adversely affect the flexural properties, organic solvents can be added to enhance workability of the composites and aid easy mixing. This can prove particularly useful while fabricating highly filled (>60 wt% inorganic content) specimens.

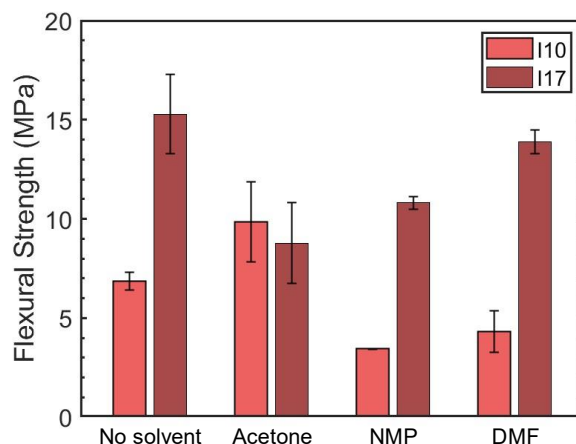


Figure 6: The change in flexural strength of polyurethane/zeolite composites without and with different organic solvents. I10 and I17 refer to composites with polyurethane content 30 wt%, zeolite content with 60 wt% and 53 wt%, and reactive isocyanate 10 and 17 wt% respectively. The highest flexural strength (15 MPa) was observed for the no solvent I17 composite. The flexural strain capacities of these composites ranged from 2–12% (not shown here).

CONCLUSIONS AND FUTURE WORK

The use of chemically upcycled polyurethane products is often limited by the lack of control over their structure and backbone. Here, we demonstrated a strategy for fabrication of solvent-less solid-rich organic/inorganic composites based on polyols obtained from upcycled PU foams. The fabrication approach is simple: formulations comprising upcycled (or virgin) polyols, mineral microparticles, isocyanate and appropriate catalyst were mixed as a one-pot mixture and then cured either at room temperature or with mild heat in casts, resulting in composites with flexural properties superior to OPC concrete (3× flexural strength, 100× flexural strain capacity).

Tunability of the microstructure and flexural properties of the composites were demonstrated by tuning the composition of the starting formulations. The fabrication process was amenable with polyols with different OH values; an increase in OH value (more reactive groups per polymer chain) led to an increase in flexural strength due to better network formation between the polyol, reactive isocyanate, and inorganic particles. The fabrication strategy was also amenable with different kinds of inorganic microparticles such as zeolites and sand; the composites derive their superior properties by utilizing the OH groups on the surface of inorganic particles to form covalent linkages with the organic phase. We further surmise that an optimum reactive isocyanate content is required for uniform distribution of the inorganic microparticles, manifesting as a significantly improved flexural strength and strain capacities. Finally, addition of an organic solvent is shown to enhance the workability of the formulations without compromising the composite properties; addition of solvents may become necessary for formulations wherein high inorganic loadings (>60 wt%) are sought.

We note that the influence of polyol structure on physical properties of the composites needs to be further mapped extensively to enable better control over the composite properties. Additionally, the nature of the backbone can play a pivotal role in determining composite properties; comparisons between branched and linear chains, chains with different alcohol functionality, and molecular weights need to be further pursued. Properties of inorganic microparticles, such as size, type of particle and content will also have an influence on the composite properties and therefore should be studied. Finally, in addition to flexural properties, thermal insulation, sound proofing and weatherability of these composites will require to be assessed to widen the horizons for the application and widespread use of these upcycled organic/inorganic composites.

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Appendix

Materials & Methods

Polypropylene glycol (PPG; virgin polyol, $M_n \sim 2000$; 56 mg KOH/g, 300 cP), Isophorone diisocyanate (IPDI), Dibutyltin dilaurate (DBTDL; organometallic catalyst), Triethylamine (TEA; room temperature organic catalyst), N-methyl-2-pyrrolidone (NMP; organic solvent), Acetone (Ac; organic solvent), N,N-Dimethyl formamide (DMF; organic solvent) were procured from Millipore Sigma and used as received. Clinoptilolite (zeolite; $< 2 \mu\text{m}$ size) and sand were purchased from Heiltropfen Store and Fisher Scientific respectively. Infigreen 300 (IG300; 290 mg KOH/g, 3000 cP) and Infigreen 420A (IG420A; 385 mg KOH/g, 1100 cP) were provided by Emery Oleochemicals.

Composite Preparation

Pre-weighed quantity of zeolite was added to a measured volume of IPDI, with continuous vortex mixing to ensure adequate wetting of zeolite particles. In solvent based systems, Ac/ NMP/ DMF was added to aid mixing, followed by addition of polyol. In solvent-free systems, polyol was added intermittently during zeolite addition, to maintain workability of the mixture. A few drops of DBTDL (and TEA for room temperature composites) were added. The slurry was transferred to a Teflon-lined metal mold and dried at 50°C (or room temperature) for 24–48 hours. Compositions ranged from 46–60 wt% zeolite, 30 wt% polymer and 10–24 wt% excess isocyanate (all basis dry weight of composite) (**Table A1**)

Assessment of Morphology and Flexural Properties

The composites were observed under a Phenom XL G2 Desktop SEM at magnifications 800x–6000x (15kV). Composite specimen of dimensions 6 mm x 8 mm x 20 mm were obtained from the molds and their flexural properties were assessed using an Instron UTM at 0.5 mm/min displacement rate. The span length was maintained between 15–20 mm depending on the available length of sample. While the measurement standards were different from the ASTM reference, the sample dimensions were accounted for in flexural strength (Eq S1) and strain capacity (Eq S2) estimation.

$$\text{Flexural Strength (MPa)} = \frac{3Fl}{2wd^2} \quad \dots(\text{Eq S1})$$

where, F : Maximum Force (N), l : Span length (m), w : Width (m), d : Depth (mm)

$$\text{Flexural Strain Capacity (\%)} = \frac{6Dd}{l^2} \times 100 \quad \dots(\text{Eq S2})$$

where, D : Maximum Deflection (m)

Sample Code	Inorganic Component	Polyol Type	Inorganic Content (wt.%)	Polyurethane Content (wt.%)	Excess Isocyanate Content (wt.%)	Solvent	Temperature (°C)
I10-PPG-25	Zeolite	PPG	60	30	10	None	25
I17-PPG-25	Zeolite	PPG	53	30	17	None	25
I24-PPG-25	Zeolite	PPG	46	30	24	None	25
I10-PPG-50	Zeolite	PPG	60	30	10	None	50
I17-PPG-50	Zeolite	PPG	53	30	17	None	50
I24-PPG-50	Zeolite	PPG	46	30	24	None	50
I10-300-25	Zeolite	Infigreen-300	60	30	10	None	25
I17-300-25	Zeolite	Infigreen-300	53	30	17	None	25
I24-300-25	Zeolite	Infigreen-300	46	30	24	None	25
I10-300-50	Zeolite	Infigreen-300	60	30	10	None	50
I17-300-50	Zeolite	Infigreen-300	53	30	17	None	50
I24-300-50	Zeolite	Infigreen-300	46	30	24	None	50
I10-420A-25	Zeolite	Infigreen-420A	60	30	10	None	25
I10-420A-50	Zeolite	Infigreen-420A	60	30	10	None	50
Sand-I10-PPG-25	Sand	PPG	60	30	10	None	25
Sand-I10-PPG-50	Sand	PPG	60	30	10	None	50
Sand-I10-300-25	Sand	Infigreen-300	60	30	10	None	25
Sand-I10-300-50	Sand	Infigreen-300	60	30	10	None	50
PU0-I34	Zeolite	-	66	0	34	DMF	50

Table A1: The sample compositions involved changes in the inorganic and excess isocyanate contents, in addition to variation in the processing temperature and types of inorganic material and polyols. In all the above samples, no solvents were used. Any use of solvent has been indicated in the figure showing related data. In the figures, Infigreen 300 and Infigreen 420A have occasionally been referred to as IG300 and IG420A. PPG stands for poly(propylene glycol). Other relevant details have been indicated in the main text and figure captions.