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Porous inorganic—organic shape memory polymers

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Abstract

Thermoresponsive shape memory polymers (SMPs) are a type of stimuli-sensitive materials that switch from a temporary shape back to their permanent shape upon exposure to heat. While the majority of SMPs have been fabricated in the solid form, porous SMP foams exhibit distinct properties and are better suited for certain applications, including some in the biomedical field. Like solid SMPs, SMP foams have been restricted to a limited group of organic polymer systems. In this study, we prepared inorganic–organic SMP foams based on the photochemical cure of a macromer comprised of inorganic polydimethylsiloxane (PDMS) segments and organic poly(ϵ -caprolactone) (PCL) segments, diacrylated PCL₄₀-*block*-PDMS₃₇-*block*-PCL₄₀. To achieve tunable pore size with high interconnectivity, the SMP foams were prepared via a refined solvent-casting/particulate-leaching (SCPL) method. By varying design parameters such as degree of salt fusion, macromer concentration in the solvent and salt particle size, the SMP foams with excellent shape memory behavior and tunable pore size, pore morphology, and modulus were obtained.

Keywords

Polymeric materials; Porous materials; Shape memory materials

1. Introduction

Thermoresponsive shape memory polymers (SMPs) are stimuli-sensitive or “smart” materials whose shape is modulated by external heat [1,2]. The “netpoints” are chemical or physical crosslinks that determine the permanent shape while the “switching segments” maintain the temporary shape and recover the permanent shape when heated above their thermal transition temperature (T_{trans}). T_{trans} may either be a glass transition temperature (T_g) or a melting transition temperature (T_m). Thus, a temporary shape formed by deformation at $T > T_{\text{trans}}$ can be fixed by cooling to $T < T_{\text{trans}}$ and subsequently recovered by heating to $T > T_{\text{trans}}$ again. For SMPs, the shape memory effect is an entropically driven process [1,3].

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Appendix A. Supplementary material

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.polymer.2012.04.053.

Solid, non-porous SMPs have been explored for various potential biomedical applications such as smart sutures [4], vascular stents [5–8], bladder sensors [9] and orthopedic fixation devices [10–12]. However, SMP porous foams exhibit distinct properties and utility. SMP foams are lightweight, highly compressible and more permeable to heat, features which contribute to their enhanced thermal actuating properties [13–19]. In the biomedical field, SMP foams have been utilized as embolic sponges to treat aneurysms [17]. They have also been proposed as self-fitting scaffolds to repair bone defects [20].

As is the case of solid SMPs, SMP foams are largely limited to those based on organic polymers, namely polyurethanes [13–15,17] and epoxies [18]. For instance, thermoplastic PU foams can exhibit significant shape change and T_{trans} values which made tuned over a wide range of temperatures ($T_{\text{trans}} = T_g = -70$ to 70 °C) [21]. Several studies have explored the utility of PU SMP foams for aneurysm occlusion [14,22,23]. Thermosetting epoxy SMP foams have also been prepared [18,24]. However, due to their high T_{trans} ($T_{\text{trans}} = T_g = \sim 90$ °C), its use in biomedical applications is limited.

To advance the utility of SMP foams, new compositions are needed which exhibit a sharp T_{trans} to modulate shape change (preferably at temperatures tolerated by tissues), high shape recovery (R_r) and shape fixity (R_f) as well as moduli tunable over a broad range. Solid poly(ϵ -caprolactone) (PCL)-based SMPs have attracted much attention due to the biocompatibility, biodegradability and elasticity of PCL [25,26]. The T_m of PCL serves as the T_{trans} which may be tailored from 43 to 60 °C with increased number average molecular weight (M_n) [27]. The thermomechanical properties of solid PCL-based SMPs have been modified by introduction of organic hard [4,28–30] or soft [31,32] segments whose T_g 's are higher and lower than that of PCL ($T_g = -60$ °C), respectively. Recently, we reported a new class of inorganic-organic solid SMPs prepared via the photochemical cure of acrylated (AcO) macromers containing inorganic polydimethylsiloxane (PDMS) soft segments and organic PCL switching segments of varying lengths (AcO-PCL_n-*block*-PDMS_m-*block*-PCL_n-OAc) [33,34]. Because the T_g of PDMS (-125 °C) [35] is much lower than that of PCL, its ability to modulate mechanical properties is quite effective. These solid PDMS-PCL SMPs exhibited excellent shape memory behavior when thermally cycled through the T_{trans} (PCL $T_m = \sim 50$ °C). Furthermore, their mechanical properties were readily tuned over a broad range by varying PCL and PDMS segment length.

In this study, inorganic-organic PDMS-PCL SMP foams were fabricated from a photosensitive AcO-PCL₄₀-*block*-PDMS₃₇-*block*-PCL₄₀-OAc macromer. Previously, the corresponding solid SMP was produced by photopolymerization of macromer solution in dichloromethane (DCM) followed by solvent evaporation [33]. The SMP exhibited excellent shape fixity ($R_f > 90\%$) and shape recovery ($R_r > 90\%$) as well as impressive mechanical properties (tensile modulus = ~ 47.4 MPa and strain at break = $\sim 800\%$). Porous PCL-based SMP foams have been limited to a single report and prepared via supercritical carbon dioxide foaming [36]. More frequently, porous PCL-based polymers have been prepared for tissue engineering scaffolds by a variety of methods including solvent-casting/particulate-leaching (SCPL) [37], phase separation [38], emulsion templating [39], electrospinning [40] and solid free-form fabrication techniques [41]. Herein, PDMS-PCL SMP foams were prepared by revising a conventional SCPL method to include salt fusion and a photosensitive macromer that forms a thermoset network. Thus, salt particles were first fused by the addition of water and the solution of AcO-PCL₄₀-*block*-PDMS₃₇-*block*-PCL₄₀-OAc macromer in DCM was photocured around the fused salt matrix which was subsequently removed via leaching to produce interconnected pores. By tuning process variables such as salt fusion (i.e. wt% water added to salt), macromer concentration and salt (porogen) particle size, the resulting inorganic-organic SMP foams demonstrated a broad

range of tunable pore sizes, degrees of interconnectivity and compressive modulus as well as excellent shape memory behavior.

2. Experimental

2.1. Materials

Poly(dimethylsiloxane)-bis(3-aminopropyl) terminated ($\text{NH}_2\text{-PDMS}_{37}\text{-NH}_2$; $M_n = 2986 \text{ g mol}^{-1}$ by $^1\text{H NMR}$), ϵ -caprolactone, triethylamine (Et_3N), acryloyl chloride, 4-dimethylaminopyridine (DMAP), stannous 2-ethylhexanoate, 2,2-dimethoxy-2-phenylacetophenone (DMP), 1-vinyl-2-pyrrolidinone (NVP), sodium chloride (NaCl) and solvents were obtained from Sigma–Aldrich. Anhydrous magnesium sulfate (MgSO_4) was obtained from Fisher. Reagent-grade CH_2Cl_2 and NMR grade CDCl_3 were dried over 4 Å molecular sieves before use.

2.2. Macromer synthesis

Photosensitive macromer $\text{AcO-PCL}_{40}\text{-block-PDMS}_{37}\text{-block-PCL}_{40}\text{-OAc}$ was prepared as previously reported [33]. In brief, the $\text{HO-PCL}_{40}\text{-block-PDMS}_{37}\text{-block-PCL}_{40}\text{-OH}$ was first prepared by ring-opening polymerization of ϵ -caprolactone in the presence of $\text{NH}_2\text{-PDMS}_{37}\text{-NH}_2$ and stannous 2-ethylhexanoate. The macromers were subsequently acrylated by reacting with acryloyl chloride to yield $\text{AcO-PCL}_{40}\text{-block-PDMS}_{37}\text{-block-PCL}_{40}\text{-OAc}$.

2.3. Fabrication of SMP foams

NaCl particles were sieved with openings of 250 μm and 425 μm to yield three salt sizes: $181 \pm 29 \mu\text{m}$, $268 \pm 35 \mu\text{m}$ and $459 \pm 69 \mu\text{m}$. The average size of each group was determined from SEM images with ImageJ® software (<http://rsb.info.nih.gov/ij/>).

To fabricate a single cylindrically shaped foam (7 mm diameter $\times$ 5 mm height), 1.8 g of NaCl salt was placed inside a 3 mL glass vial (OD = 15 mm) and a small amount of DI water (0, 2.5, 5, 7.5 or 10 wt%) was added. The mixture was sequentially mechanically stirred, centrifuged (4000 rpm for 15 min) and dried overnight at room temperature (RT). The macromer solution (0.1, 0.15, 0.2 or 0.3 g mL^{-1} in CH_2Cl_2) and 15 vol% photocatalyst solution (10 wt% DMP in NVP) were combined and added to cover the salt. The sealed vial was centrifuged at 2500 rpm for 10 min to distribute the macromer solution. The vial was subsequently exposed to UV-light (6 mW cm^{-2} , 365 nm) for 3 min. After air-drying overnight, the SMP cylinder was removed from the vial and the salt was removed by soaking in a water/ethanol (1:1 vol:vol) solution for 4 days with daily changes of solvent. Finally, the specimen was heated at 85 $^\circ\text{C}$ for 1 h, followed by cooling to RT.

Porosity: SMP foam % porosity was calculated using the following equation:

$$P(\%) = \frac{\rho_{\text{solid SMP}} - \rho_{\text{porous SMP}}}{\rho_{\text{solid SMP}}} \times 100 \quad (1)$$

The density (ρ) of the SMP foam was determined experimentally by measuring the weight of specimen of a given dimension. The density of solid non-porous SMP was determined to be 1.114 g cm^{-3} . The results are based on the average of three measurements.

2.4. Pore morphology

Pore morphology was characterized by scanning electronic microscopy (SEM). The SMP foam was freeze-fractured in liquid nitrogen. Cross-sections of the foam were then subjected

to Au–Pt coating (~4 nm) and examined by a JEOL 6400 SEM at an accelerating voltage of 15 kV.

2.5. Mechanical properties

Compression tests of cylindrical foams (7 mm diameter × 5 mm height) were performed at RT (Instron 3345). Specimens were subjected to a constant compressive strain rate (1.5 mm min⁻¹) up to 85% strain. The compressive modulus (E) was determined from the slope of the linear portion on the resulting stress-strain curve. The reported results are based on the average of three measurements.

2.6. Shape memory behavior

Shape memory properties were quantified via strain-controlled cyclic-thermal mechanical compression tests over five cycles (N) (TA Instrument, Q800 dynamic mechanical analyzer, DMA). Cylindrical foams (7 mm diameter × 5 mm height) were subjected to the following sequence: (1) after equilibrating at 60 °C (T_{high}) for 5 min, compress to a maximum strain ($\epsilon_m = -50\%$) at a rate of 50% strain min⁻¹, (2) hold at ϵ_m for 5 min and then cool to 25 °C (T_{low}) to fix the temporary shape, (3) remove the load and immediately measuring ϵ_u , (4) reheat to 60 °C (T_{high}) to recover the permanent shape, measure the recovered strain (ϵ_p) and start the next cycle. The “first cycle” ($N = 0$) is referred to as the “pre-cycle” and is followed by $N = 1-4$. After the shape recovery ($N = 0$), the sample was cooled to RT and the new dimensions of the pre-cycled sample was recorded and used for the four subsequent shape memory cycles ($N = 1-4$). Shape fixity (R_f) and shape recovery (R_r) were calculated using the equations:

$$R_f(N) = \frac{\epsilon_u(N)}{\epsilon_m} \quad (2)$$

$$R_r(N) = \frac{\epsilon_m - \epsilon_p(N)}{\epsilon_m - \epsilon_p(N-1)} \quad (3)$$

where $\epsilon_u(N)$ is the ultimate strain in the stress-free state in the fixing process. ϵ_m is the maximum compressive strain (-50%). $\epsilon_p(N-1)$ and $\epsilon_p(N)$ are the final strains of the sample in two successive cycles in the stress-free state in the recovering process. For pre-cycles ($N = 0$), $\epsilon_p(-1)$ equals “zero”. The results are based on the average of three measurements.

2.7. Differential scanning calorimetry (DSC)

DSC measurements were performed using TA Instruments Q100. PDMS-PCL SMP foams were sealed in hermetic pans and heated from -30 to 90 °C at 5 °C min⁻¹. % crystallinity was determined from the endothermic melting peak and was calculated from the equation:

$$\% \text{ Crystallinity} = \frac{\Delta H_m}{\Delta H_m^0} \times 100 \quad (4)$$

where ΔH_m^0 is 139.5 J g⁻¹ for 100% crystalline PCL [42]. The results are the average values from duplicate measurements.

3. Results and discussion

3.1. Fabrication

Porous PDMS-PCL SMP was prepared with a revised SCPL protocol (Scheme 1, Table 1). Conventional SCPL consists of casting or freeze-drying a solution comprised of a thermoplastic polymer and dispersion of sacrificial porogens (e.g. NaCl salts) which are subsequently removed via leaching. The SCPL technique is desirable as it has been used to produce foams with up to 93% porosity and does not require sophisticated equipment [43]. In addition, the pore sizes in SCPL scaffolds are easily controlled by porogen size [37]. However, there are several major disadvantages of this method. For instance, due to the nature of the dispersed NaCl particles, conventional SCPL typically generates closed-cell foams with poor interconnectivity thereby limiting heat transfer as well as mass transport [44,45]. Moreover, this method can only be used to prepare membranes less than 3 mm thick [43]. In this study, SCPL was revised in several keyways to improve and tailor the properties of the resulting SMP foams. First, to produce foams whose pores are highly interconnected, we induced “salt fusion” by the addition of a small amount of water which is known to partially dissolve isolated NaCl particles into a continuous porogen template [46,47].

After leaching out the salt template, an interconnected void space is thereby created. Past reports of SCPL utilizing fused salt is limited to thermoplastic polymers [46,47]. In this study, a photo-crosslinkable macromer was employed to form an SMP foam that is a thermoset. Its crosslinked nature is expected to contribute to enhanced shape retention and mechanical properties [48]. Because of the rapid nature of the UV-cure and the rigid nature of the crosslinked foam, porous foams may also be directly fabricated into complex geometries defined by the mold and salt volume without the need for lamination as is required for conventional SCPL [49]. In addition, unlike partially collapsed pores often observed in thermoplastic foams prepared via conventional SCPL [50], the pores of the PDMS-PCL SMPs exhibited well-defined shapes. In this study, porous SMP foams were fabricated as cylinders of 5 mm in height.

The final heat treatment step served to induce SMP foam densification by melting the PCL crystalline domains which, upon cooling, re-organized in closer proximity. This step was required prior to subjecting to shape memory tests as the first heating/cooling cycle would have likewise produced this densification and the associated dimensional change. By DSC, % crystallinity decreased slightly in the heat treated foams (Table S1). This can be explained by the higher mobility of the PCL segments which form the crystalline domains from solution (i.e. during solvent casting) versus those that do so in the bulk (i.e. during sequential heating and cooling) [51]. In addition to a slight decrease in % crystallinity, foam dimensions (volume) were observed to decrease from approximately 10 mm diameter $\times$ 7 mm height (0.55 cm³) to 7 mm diameter $\times$ 5 mm height (0.19 cm³) following heat treatment. Correspondingly, the pores of foams fabricated with, for instance, ~460 μ m salt crystals (15–5L) shrank to ~250 μ m after heat treatment but still exhibited high interconnectivity (Fig. S1).

In the following sections, three key fabrication variables - percent salt fusion, macromer concentration in DCM and salt particle size - were systematically altered to produce PDMS-PCL SMP foams with controlled pore size, pore interconnectivity, % porosity and modulus values as well as excellent shape memory behavior.

3.2. Pore size and interconnectivity

Pore morphology, including shape and interconnectivity, of PDMS-PCL foams was tuned by the extent of salt fusion which was controlled by varying the weight % (wt%) water added to the NaCl salts (Fig. 1, Table 1). During fabrication, 2.5–10 wt% of water was mechanically

mixed via spatula with 1.8 g of salt contained in the glass vials (15 mm diameter). Vortexing and subsequent centrifugation was used to uniformly distribute the water within the salt and to compact the salt particles, respectively. After drying overnight, the fused salt template was obtained. At “zero” salt fusion (i.e. 0 wt% water added), cubic pores with poor interconnectivity was produced (Fig. 1a). Addition of 2.5–7.5 wt% water resulted in progressively more interconnected pores due to enhanced salt fusion (Fig. 1b–d). With 5 and 7.5 wt% water, the pores were highly interconnected and spherical. With the addition of 10 wt% water, interconnectivity continued to increase but the shapes and sizes of the pores were no longer defined by the salt particles (Fig. S2) and the resulting foam was very fragile. This upper limit was previously noted for a porous thermoplastic PCL scaffold prepared by SCPL in which the addition of 10 wt% water to fuse the salt produced a loose and fragmented structure [47].

Previous studies of foams prepared via SCPL employing thermoplastic polymers demonstrated that the polymer concentration in solvent has a significant impact on the resulting pore morphology [37,47]. As the polymer concentration increases, more space between adjacent salt particles is occupied by polymer which results in thicker pore walls. A series of PDMS-PCL SMP foams similarly produced with large salt particles (~460 μm) and fused with 5 wt% water but with varying the macromer concentration (0.1–0.3 g mL^{-1}) produced considerable change to pore morphology (Fig. 2). While pore size was not substantially changed, increased macromer concentration produced thicker pore walls in the foams prior to heat treatment (Fig. S3). Thus, while pore size decreased for all foams after heating, pore interconnectivity remained the highest for those prepared with low macromer concentration.

To produce SMP foams with different pore sizes, NaCl salts were hand-sieved into three different average sizes and fused with 5 wt% water (Table 1). The macromer concentration was maintained at 0.15 g mL^{-1} . As shown in Fig. 3a–c, the pores shrank to ~250, ~150 and ~100 μm after heat treatment for the SMPs foams prepared with large (~460 μm), medium (~270 μm) and small (~180 μm) salt particles, respectively. The foams prepared with either medium or large salts exhibited spherical, highly interconnected pores. However, when small salts were used, pores became more cubic and pore interconnectivity was reduced. For small salts, the surface to volume ratio of a fixed quantity of salts (1.8 g) was much higher versus that of medium and large salts. Thus, 5 wt% of water inadequately wet the small salts, causing only partial salt fusion. We also prepared PDMS-PCL SMP foams using a 50/50 wt ratio mixture of large and small salts. This produced a particularly high level of pore interconnectivity due to a more efficient packing of mixed salts (Fig. 3d).

On the basis of these results, this SCPL protocol involving salt fusion with water represents an effective method to fabricate PDMS-PCL SMP foams with interconnected pores. Other strategies may also be explored to achieve potentially greater pore interconnectivity. For example, heat treated spherical sugar particles fused via heat treatment could be substituted for salts as the sacrificial porogen [52]. Polymerization of the continuous phase of high internal phase emulsions (PolyHIPEs) is capable of producing highly interconnected pore morphology and had been proposed for porous SMPs [53]. However, pore sizes in polyHIPEs generally exhibit a wide distribution and pore sizes of only 1–100 μm [54,55].

3.3. Compressive modulus and % porosity

The compressive modulus (E) of PDMS-PCL SMP foams were assessed via uniaxial compression tests. As is observed for other porous materials [41,56], an inverse relationship was observed for E versus % porosity (Fig. 4). For all SMP foams, the % porosity ranged from ~72 to ~86% (Table 1).

Increased levels of wt% of water used to enhance pore interconnectivity produced an increase in % porosity and corresponding decrease in E (Fig. 4a). Increasing the macromer concentration produced the most significant change in foam E and % porosity (Fig. 4b). As observed in Fig. 2, increased macromer concentration produced thicker solid struts between pores and reduced interconnectivity, thereby reducing % porosity but substantially increasing E . Finally, while salt size considerably impacted pore size and interconnectivity, it did not produce substantial changes in % porosity and E (Fig. 4c).

Compared to conventional SCPL which employs thermoplastic polymers [57], our use of a thermosetting macromer and the densification (i.e. shrinkage) of the foam after heat treatment enhanced the mechanical rigidity. Certain PDMS-PCL foams exhibited compressive E values comparable to that achieved via melt molding/particulate-leaching. For example, thermoplastic PCL was melt-extruded in the presence of poly(ethylene glycol) (PEG) and NaCl as leachable porogens [58]. The resulted porous scaffolds exhibited porosity-dependent compressive modulus from 1 to 5.2 MPa and porosities from 75 to 88% but pores had limited interconnectivity. PDMS-PCL foams with lower moduli values may be achieved by increasing the PDMS segment length. Alternatively, substantially more rigid foams may be produced as composites by the incorporation of rigid fillers.

3.4. Shape memory properties

Shape memory properties of the SMP foams were determined via strain-controlled cyclic-thermomechanical compression tests and were quantified in terms of strain fixity (R_f) and strain recovery (R_r) over a total of five cycles, $N = 0-4$ (Table 2 and S2-S4). For the pre-cycle ($N = 0$), R_f was somewhat low for foams prepared with no salt fusion (e.g. ~76% for 15-0L), the lowest macromer concentration (e.g. ~70% for 10-5L) or with the smallest salt size (e.g. ~77% for 15-5S). For 15-0L and 15-5S, this can be explained by their reduced pore interconnectivity which diminished heat diffusion [19,59]. While the pores of 10-5L were highly interconnected, its low density as indicated by its high % porosity led to a particular low $R_f(0)$. However, for all foams, R_f values reached $> \sim 93\%$ during the subsequent cycle ($N = 1$) and $> \sim 97\%$ ($N = 2$). An increase in R_f after the first shape memory cycle has been previously observed for non-porous [31,60] and porous [36] SMPs (including the solid analogues of these PDMS-PCL foams [33]). It is hypothesized that the first shape memory cycle removes the residual strain that originates from processing such that subsequent shape recovery is improved [1]. For the PDMS-PCL SMP foams, the pre-cycle produced minor decreases in % porosity (Table S5) but pores remained highly interconnected (Fig. S4).

For all compositions and all cycles, R_f was actually slightly higher than 100% due to an additional compression of up to 0.7% strain (ϵ). An R_f value greater than 100% was previously observed for PCL-based SMP foams and was attributed to the rapid crystallization of PCL segments to form more compact structure in the cooling process [36]. It may also be a result of a compression-induced crystallization of PCL.

4. Conclusion

Inorganic-organic SMP foams comprised of inorganic PDMS soft segments and organic PCL switching segments were prepared. A traditional SCPL strategy was revised to include fusion of salt porogens and formation of a thermoset foam. Highly interconnected pores were obtained by the addition of variable amounts of water to fuse the salt particles into a continuous template. A photocrosslinkable macromer (AcO-PCL₄₀-*block*-PDMS₃₇-*block*-PCL₄₀-OAc) dissolved in DCM and distributed throughout the fused salt template was subjected to rapid photocuring to produce crosslinked SMP foam. Thus, the degree of salt fusion (i.e. wt% water added), macromer concentration in solvent as well as salt particle size

were systematically altered. This produced PDMS-PCL SMP foams with tunable pore interconnectivity, shape, size and % porosity as well as modulus. In addition, these foams exhibited excellent shape recovery and fixity when cycled through the T_{trans} ($T_m = \sim 52^\circ\text{C}$).

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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Fig. 1. SEM images showing effect of salt fusion on pore morphology. a) 15–0L [0 wt% water]; b) 15–2L [2.5 wt% water]; c) 15–5L [5 wt% water]; and d) 15–7L [7.5 wt% water]. Scale bars = 200 μm .

Fig. 2. SEM images showing effect of macromer concentration on pore morphology. a) 10–5L [0.1 g mL^{-1}]; b) 15–5L [0.15 g mL^{-1}]; c) 20–5L [0.2 g mL^{-1}]; and d) 30–5L [0.3 g mL^{-1}]. Scale bars = $200 \text{ }\mu\text{m}$.

Fig. 3. SEM images showing effect of salt particle size on pore morphology. a) 15–5L [large salts]; b) 15–5M [medium salts]; c) 15–5S [small salts]; and d) 15–5X [50:50 small:large salts]. Scale bars = 200 μm .

Fig. 4. Effect of a) salt fusion (i.e. wt% water added); b) macromer concentration; and c) salt particle size on compressive modulus (E) and % porosity of PDMS-PCL SMP foams. Figs. a, b and c correspond to foam series depicted in Figs. 1, 2 and 3, respectively.

Scheme 1.

Inorganic–organic SMP foams were fabricated via a revised solvent-casting/particulate leaching (SCPL) protocol. Salt fusion was used to increase pore interconnectivity. A photocrosslinkable macromonomer (AcO-PCL₄₀-*block*-PDMS₃₇-*block*-PCL₄₀-OAc) produced a thermoset foam. Finally, heat treatment above T_m of PCL induced foam densification.

Table 1

SMP foams notations and formulations.

Sample ^a	Macromer (g)	DCM (mL)	NaCl (g)	Water (wt%)	Avg. salt size (μm)	Porosity (%)
15-0L	0.15	1	1.8	0	459	76.8 ± 0.4
15-2L	0.15	1	1.8	2.5	459	77.7 ± 0.3
15-5L	0.15	1	1.8	5	459	79.5 ± 0.4
15-7L	0.15	1	1.8	7.5	459	82.3 ± 0.2
10-5L	0.1	1	1.8	5	459	85.5 ± 0.4
15-5L	0.15	1	1.8	5	459	79.5 ± 0.4
20-5L	0.2	1	1.8	5	459	74.1 ± 0.6
30-5L	0.3	1	1.8	5	459	72.1 ± 0.5
15-5S	0.15	1	1.8	5	181	79.9 ± 0.5
15-5M	0.15	1	1.8	5	268	80.7 ± 0.2
15-5L	0.15	1	1.8	5	459	79.5 ± 0.4
15-5X	0.15	1	1.8	5	<i>b</i>	79.7 ± 0.2

Amounts are used to fabricate one cylindrical foam (7 mm diameter × 5 mm height).

^a“xx-yyZ”: “xx” indicates the amount of macromer in 1 mL DCM (e.g. “15” is 0.15 g). “yy” indicates the weight percent of water added per 1.8 g NaCl (e.g. “5” is 5 wt%). “Z” indicates the particle size of NaCl (e.g. “L” indicates large salt ~459 μm).

^b A 50/50 weight ratio mixture of large (~459 μm) and small (~181 μm) salts.

Table 2Shape recovery (R_r) for pre-cycle ($N=0$) and $N=1$.

Sample	$R_r(0)$ (%)	$R_r(1)$ (%)
<i>Effect of salt fusion</i>		
15-0L	76.3 ± 1.0	95.3 ± 2.6
15-2L	84.4 ± 1.1	96.0 ± 2.3
15-5L	86.5 ± 2.7	94.7 ± 2.7
15-7L	89.5 ± 1.5	95.7 ± 2.4
<i>Effect of macromer concentration</i>		
10-5L	69.5 ± 2.9	92.4 ± 2.7
15-5L	86.5 ± 2.7	94.7 ± 2.7
20-5L	90.5 ± 1.8	97.4 ± 0.2
30-5L	96.8 ± 1.3	97.9 ± 0.7
<i>Effect of salt size</i>		
15-5S	77.2 ± 1.1	94.9 ± 1.2
15-5M	87.9 ± 1.1	96.2 ± 2.2
15-5L	86.5 ± 2.7	94.7 ± 2.7
15-5X	90.8 ± 0.7	96.2 ± 1.6