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Supporting information for
Soft hydrogel-embedded ceramic skeleton mimicking bone structure via sacrificial bond concept

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Fabrication of porous ceramic skeleton

Porous ceramic skeletons were fabricated using the sponge template method. Two commercial sponge templates with different porous structures (S1 and S2) were cut using a laser cutter (ULR-60, Universal Laser Systems, US) into dimensions of 40 mm in length, 9 mm in width, and 5 mm in thickness. The sponge templates were then washed with distilled water and ethanol to remove carbon residue from the cutting process. The sponges were dried at room temperature for 3 hours.

A ceramic precursor slurry was prepared by mixing a 10% w/v PVA solution, 5% v/v POIZ 520 dispersant solution, and distilled water. The mixture was stirred using a labolution machine (Primix Corporation, Japan) at 3000 rpm for 3 hours. In the initial stage of slurry preparation, the PVA, POIZ 520, and water solutions were stirred simultaneously, followed by the addition of HAp powder at 15-minute intervals. During this stage, condition optimization was conducted by varying the weight ratio of the PVA binder (5, 10, 15, 20 wt%) and the HAp powder (50, 55, 60 wt%). Each weight percentage of PVA binder and HAp powder was relative to the total weight of the ceramic precursor slurry components.

The ceramic precursor slurry was then centrifugally defoamed using a planetary vacuum at 1000 rpm and 1000 Pa for 2 minutes to eliminate air bubbles. The S1 and S2 sponges were then homogeneously dipped in the ceramic precursor slurry and placed in a vacuum oven (Yamato ADP 300, Japan) for 5 minutes to remove air bubbles. To remove excess slurry from the dipped sponges, the coated sponges were placed in a 3 mm thick silicone spacer, covered with clean lab tissue, and pressed using a glass mold. The coated sponges were then dried in a vacuum oven at 100 °C for 24 hours (Yamato ADP 300, Japan).

The dried, coated sponges were then sintered using the following temperature program: First, the temperature was raised from room temperature to 80 °C and held for 1 hour. Next, the temperature increased to 400 °C and held for 3 hours. The sponges were then heated to 800 °C and maintained at that temperature for an additional 8 hours. Finally, the temperature increased to 1000 °C and held for 12 hours. This sintering process was carried out using an electric furnace (KDF 1500-Plus, Denken High Dental Co., Ltd., Japan). The skeletons obtained from the sintering process were used for further experiments and labeled as ceramic skeletons with the same names as the urethane sponges, S1 and S2.

Characterization of crystal structure

The crystal structures of the HAp raw powder and the sintered porous ceramic skeleton were analyzed using an X-ray diffractometer (XRD, MiniFlex, Rigaku, Japan) with Cu K α radiation ($\lambda = 0.154$ nm, 30 kV, 15 mA) at room temperature. The scanning was performed at a rate of 4°/min in the 2 θ range of 10° to 60°.

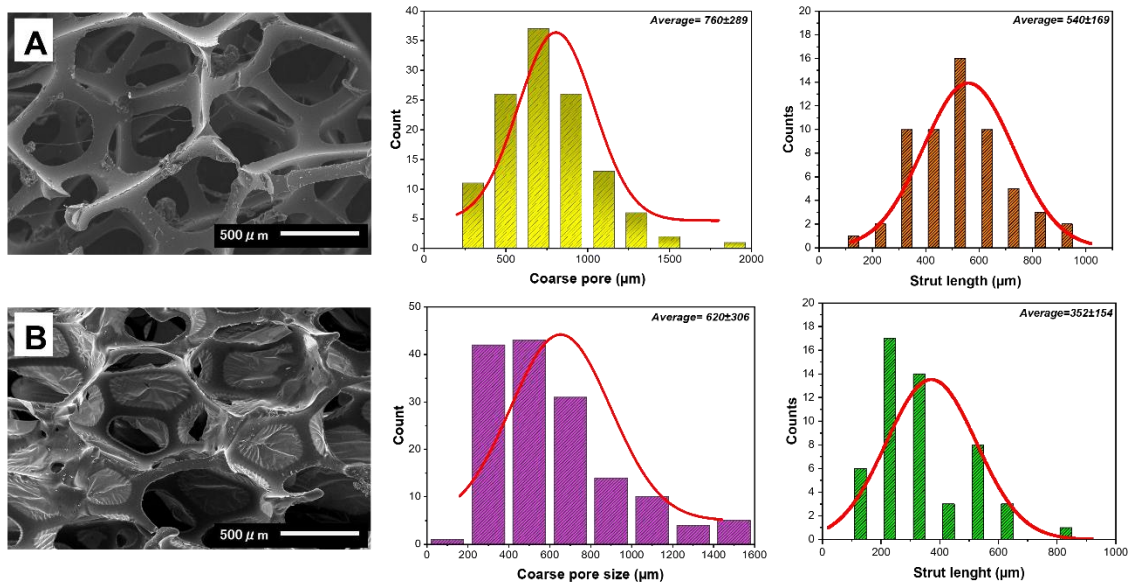


Fig.S1. Geometry of sponge templates of (A) S1 and (B) S2.

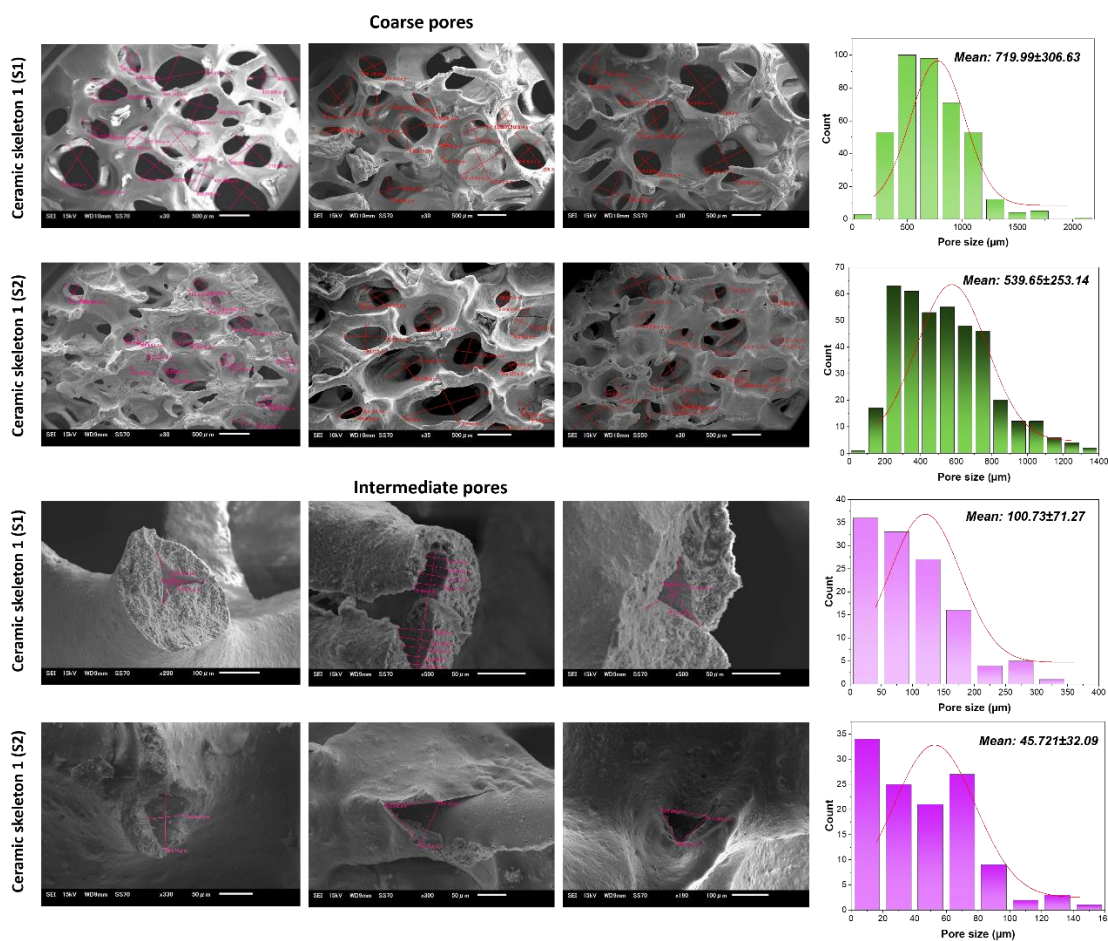


Fig. S2 Coarse and intermediate pore measurements of S1 and S2 ceramic skeletons.

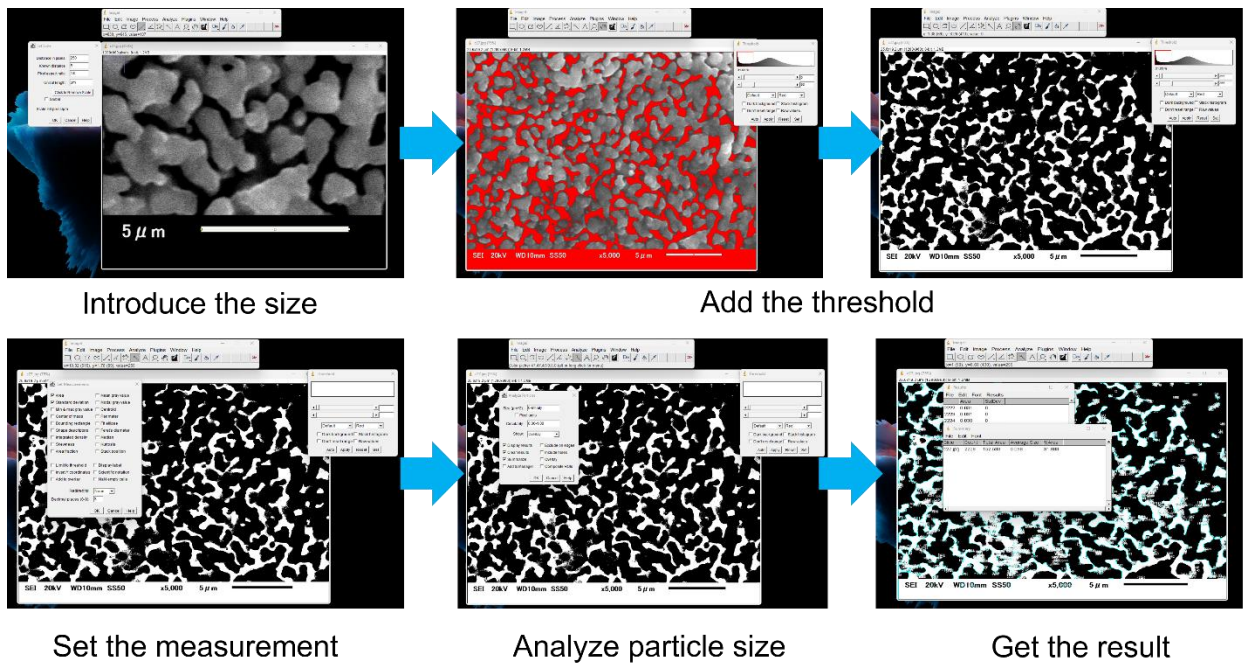


Fig S3. Fine pore measurement of S1 ceramic skeleton using ImageJ software.

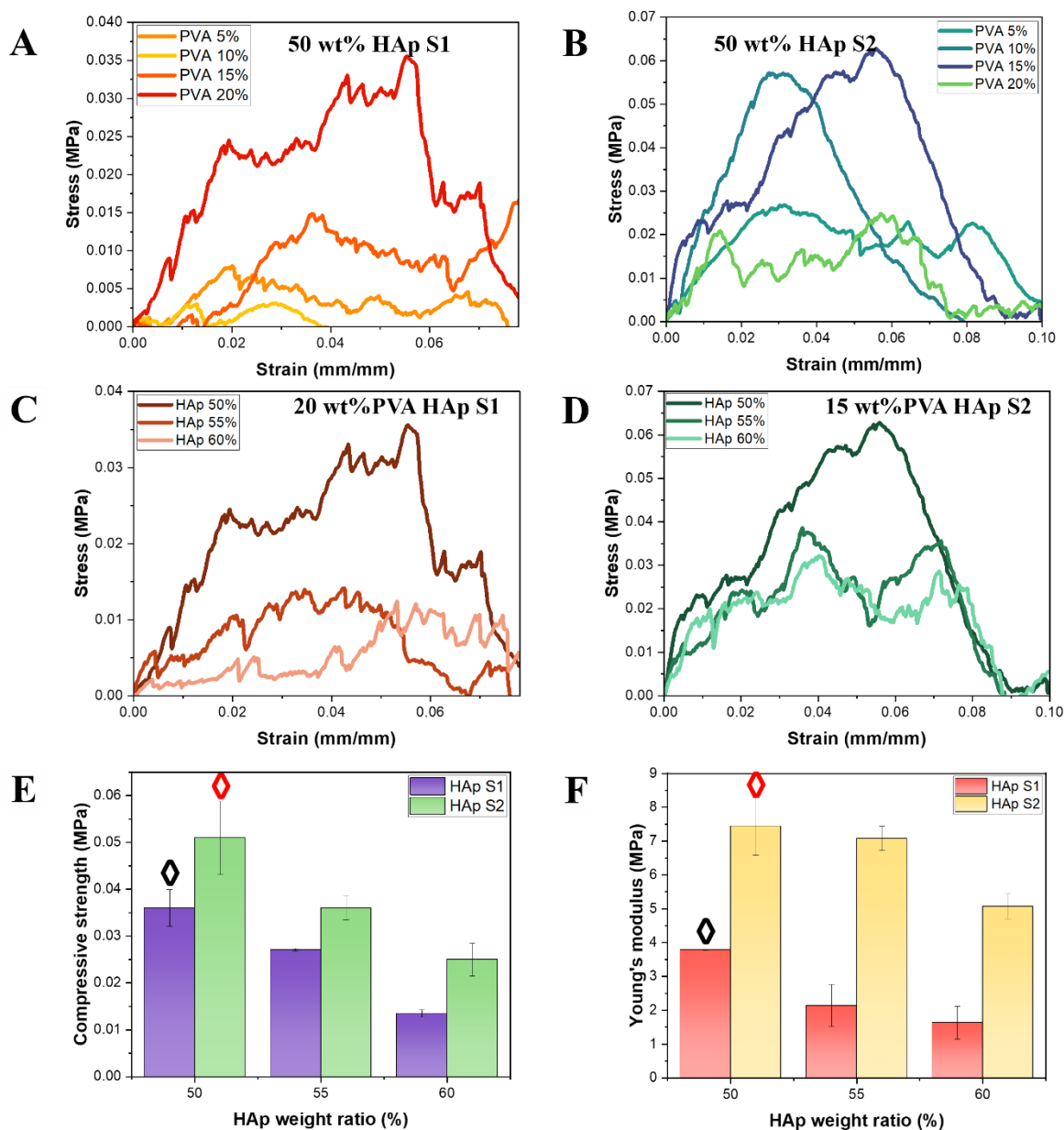


Fig.S4. Compressive profile and mechanical properties of ceramic sponge skeleton. Strain-stress curve of (A) S1 at different PVA ratio at 50wt% HAp powder and (B) S2 at different PVA ratio at 50wt% HAp powder. (C) S1 at different HAp powder ratio at 20 wt% PVA. (D) S2 at different HAp powder ratio at 15 wt% PVA. (E) Compressive strength of S1 and S2 at different HAp powder ratio at 20 and 15 wt% PVA. (F) Young's modulus of S1 and S2 at different HAp powder ratio at 20 and 15 wt% PVA. $\diamond$ Indicating the optimum weight percentage of HAp powder on the optimum PVA binder condition.

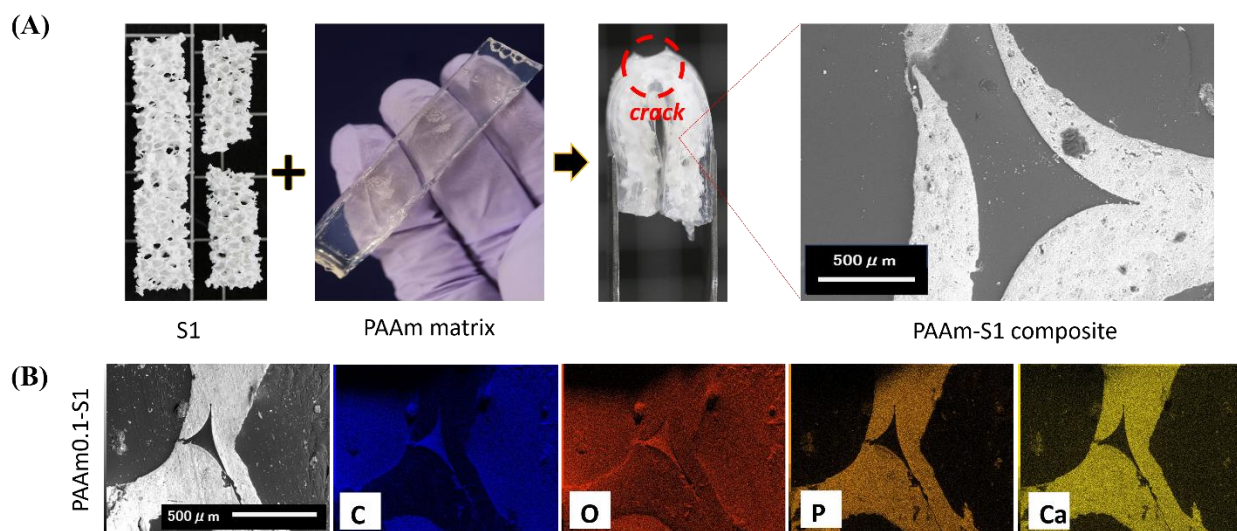


Fig. S5 Morphology of PAAm-S1 composite (A). Elemental analysis of PAAm-S1 composite (B).

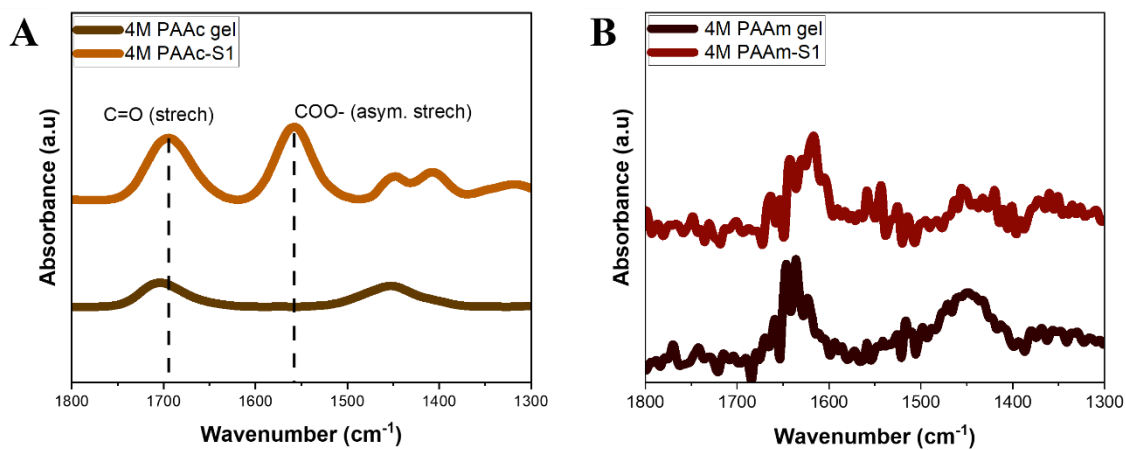


Fig. S6 FTIR spectra of soft composite and matrix. (A) 4M PAAc-S1 composite and gel matrix and (B) 4M PAAm-S1 composite and gel matrix.

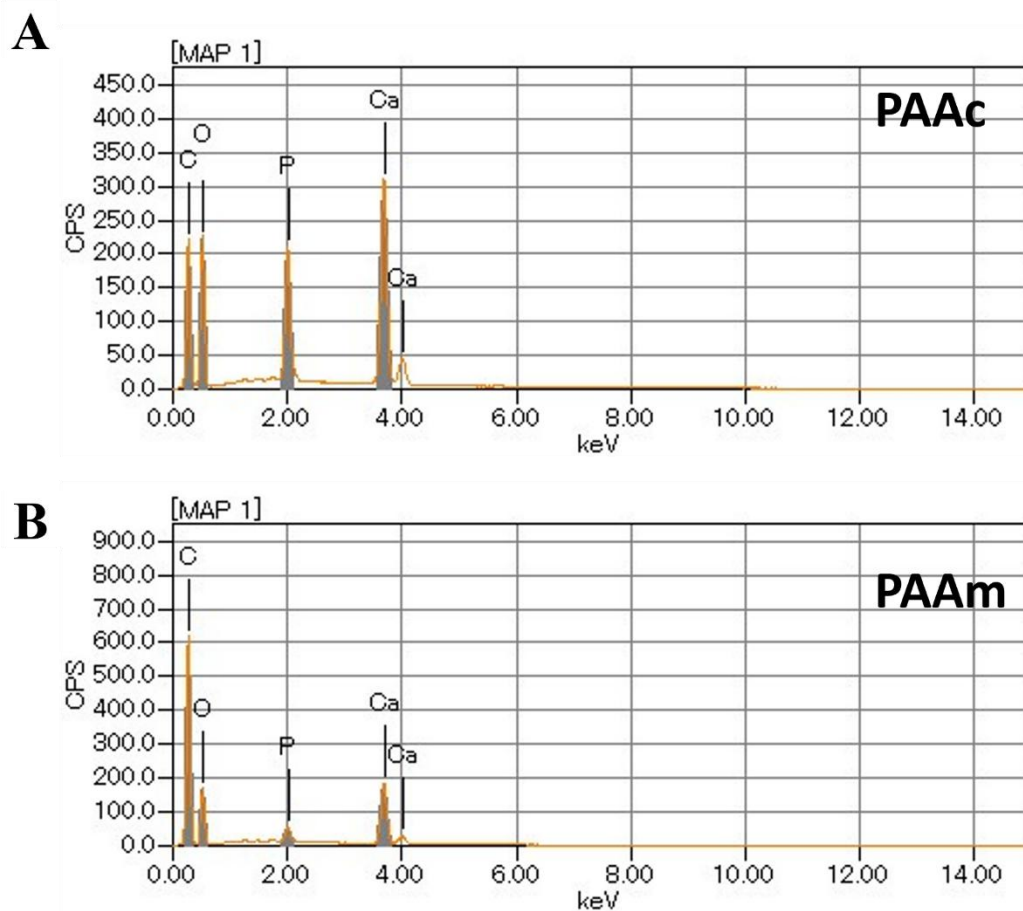


Fig.S7 EDX profiles of the hydrogel-filled coarse pore region of (A) PAAc-S1 composite and (B) PAAm-S1 composite.

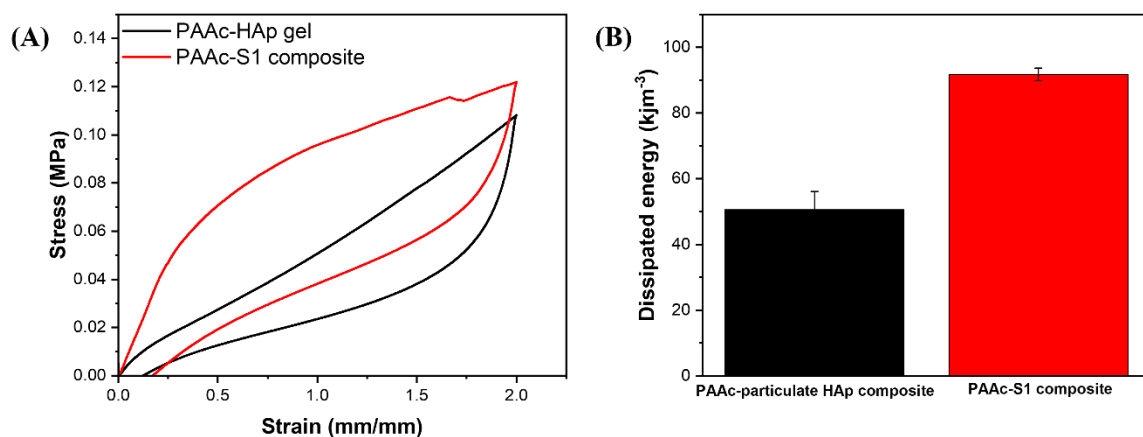


Fig. S8 (A) Cyclic tensile test and (B) dissipated energy of HAp-particulate PAAc composite and PAAc-S1 soft/hard composite.

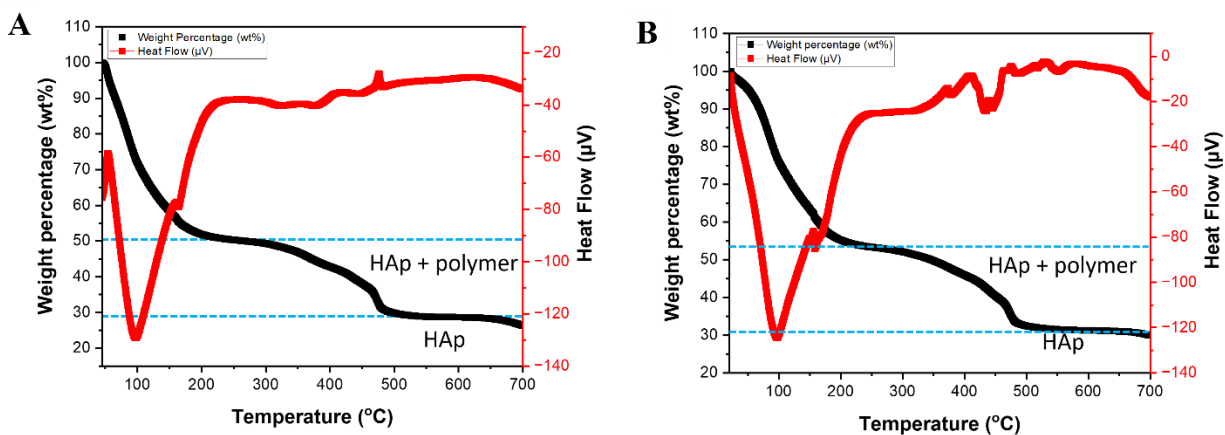


Fig. S9 TG-DTA profile of soft/hard composite. (A) PAAc0.1-S1 and (B) PAAc0.1-S2.