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Bio-inspired synthesis of multifunctional materials with self-adaptable mechanical properties and self-regeneration

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the fact that bone is a porous material with blood infused within the material so that our material system can be utilized in a non-liquid environment. We successfully demonstrated self-stiffening behaviors of the liquid-infused porous material, which showed desirable characteristics of increasing both modulus and dissipation after experiencing cyclic loadings. We envision that our findings will contribute to next generation of aerospace materials that can be utilized in a broad range of loading conditions with significantly extended lifetime and reduced fiscal and time costs associated with inspection, maintenance and downtime.

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WHITING SCHOOL
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Final Performance Report

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Bioinspired synthesis of multifunctional materials with self-adaptable mechanical properties and self-regeneration

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1. ABSRACT

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2. INTRODUCTION

The objective of the proposed research is to investigate synthetic pathways for design and synthesis of multifunctional materials with self-adaptable mechanical properties and regeneration. Nature has produced sophisticated multifunctional materials for structural applications such as bone and wood. Beyond remarkable structural properties, materials such as bone, wood, and coral reef share a unique attribute: they smartly adapt to their surrounding environment[1-4]. For instance, bone regulates mineral quantity proportional to the amount of stress. It becomes stronger in the locations subjected to the higher mechanical loads. This leads to the formation of mechanically efficient structures for optimal biomechanical and resource-efficient performance. However, it has been challenging for synthetic materials to change and adapt their structures and properties[5] to address the changes in loading conditions. While there have been pioneering works that demonstrated materials with changing stiffness upon stimuli, there is a knowledge gap to create synthetic material that can self-adapt its mechanical property depending on loading conditions. Moreover, existing materials that can enhance stiffness tend to be difficult to synthesize, expensive to create, or require additional energy to transform[6] and cannot address conditions like damages. The next generation of man-made materials for aerospace applications should resemble such adaptability leading to optimal and efficient designs. We are intrigued by the properties of bones and consider bones as model multifunctional material from nature.

We are inspired by the findings that bones are formed by the mineralization of ions from blood onto charged scaffolds[7,8] and they have signaling pathways to control the mineralization process[9,10]. **We hypothesized** that **the charges generated by applying mechanical loadings to piezoelectric materials can serve as signals for inducing mineral synthesis on the piezoelectric scaffold** from ionic solutions and **can trigger self-adaptive and repairing** behaviors similar to bones. The research aims to verify the hypothesis and to achieve the objective are summarized as below:

Aim 1 – Fundamental understanding of contributions of piezoelectric charges on mineral synthesis onto piezoelectric scaffolds

We will investigate the contributions of piezoelectric charges to the synthesis of minerals onto piezoelectric scaffolds from simulated body fluids so that we can quantitatively understand how one can tune the mineral deposition and the resulting mechanical properties.

Aim 2 – Investigation of synthetic pathways for self-adaptive material systems

We will investigate synthetic pathways for inducing mineralization processes onto piezoelectric scaffolds in proportion to mechanical loadings so that materials can adapt to the change of the loading conditions.

Aim 3 – Investigation of regeneration behaviors of the material systems

We will investigate repairing behaviors of the proposed material system by studying key parameters controlling range and rate of repairing behaviors. We will also investigate mechanisms for self-contained materials to extend the potential of the material systems.

3. SUMMARY OF ACHIVEMENTS

As we conducted studies associated with **Aims 1** and **2** in the previous reporting periods, in the final year we focused on topics related to **Aim 3**, investigating self-regeneration and damage-mitigation behaviors of our material systems. We fabricated samples with well-defined defects so that we can quantitatively study effects of stress concentration and the resulting reinforcement by mineral deposition followed by measurements of fatigue lifetime. We found that minerals were preferentially formed near cracks and significantly increased the fatigue lifetime through decreasing the crack propagation speed by ~90%. Moreover, we investigated the synthesis and characterization of liquid-infused porous piezoelectric composites for enabling the aforementioned mechanisms in non-liquid environments. We studied the effects of processing conditions such as solution concentration, curing temperature, and particle size on the resulting microstructures and piezoelectric and mechanical properties and found that the synthesized composites showed desirable characteristics of increase in both modulus and dissipation after cyclic loading in air, which will be beneficial for aerospace applications.

4. THE CONCEPT BEHIND THE DESIGN OF EXPERIMENTS

The main hypothesis of the project builds on the principle that piezoelectric materials generate charges in proportion to applied stresses. When in a mineral-rich environment such as simulated body fluid (SBF), the charges can cause minerals to form onto piezoelectric materials in proportion to the generated charges which are proportional to the applied stresses. Therefore, depending on the stress distribution, the mineral formation will change. This mechanism is potentially beneficial to mitigate the failure of materials and structures as stress concentration can potentially lead to add more reinforcing agents (i.e., minerals) to the region of a high stress so that it can result in blunting cracks and/or slowing down the propagation of damages, thus increasing the lifetime of materials and structures.

To have quantitative understanding of the underlying mechanisms, it is important to study how various parameters associated with the material system, such as loading conditions (cyclic amplitude and frequency) and environmental conditions (SBF concentration and temperature) play roles. We measured the generated charges and the resulting mineral thicknesses as we varied the loading and environmental conditions. Samples with more applied stress are expected to generate larger charges leading to higher mineral deposition rates in SBF. In addition, samples loaded at higher frequencies are expected to have larger generated charges for a given duration of time and higher temperatures are expected to increase the deposition kinetics, both leading to higher deposition rates. However, over time the mineralization is expected to decrease the generated charge at the surface of the mineralization due to an insulating nature of the minerals, leading to decreasing deposition rate.

After studying the impact of the different conditions on the mineralization process, we utilized the following four steps to verify the hypothesis of damage mitigation:

1. *Check whether piezoelectric charges are capable of inducing mineralization on the samples.*
2. *Check whether the highly stressed areas at the crack tip act as a preferential deposition site for the minerals.*
3. *Compare crack propagation speeds of samples tested in SBF with those of in DI water.*
4. *Compare the fatigue life of the samples tested in SBF with those of in DI water.*

To expand the environment that the material system can show self-stiffening and damage-mitigating behaviors, we were inspired by the fact that bone is a liquid-infused porous material that holds a liquid with minerals (i.e., blood). We investigated syntheses of open cell porous piezoelectrical composites so that the mineral solution (SBF) can be easily infused to the material and move within the material and characterized their behaviors.

5. EXPERIMENTAL SECTION

5.1 Investigation of damage-mitigation behaviors

To investigate the potential damage-mitigation behaviors of the material system, we tested various amplitudes and frequencies of cyclic loadings to find suitable conditions for damage mitigation without inducing plastic deformation of piezoelectric materials. We designed a set of experiments using commercially available piezoelectric polymer polyvinylidene difluoride (PVDF) sheets. To allow for accurate thickness measurements, these samples were taped along two edges with polyether ether ketone (PEEK) tape to locally prevent mineralization as well as not leave any residue on the PVDF sheets regardless of the loading and environmental conditions. The samples underwent loading initially in air to measure the applied stress and generated charge. Then, the samples were loaded in the same stress conditions while in SBF. After mineralization, the samples were removed from SBF and loaded with the same applied stress in air to measure the generated charge. Following this, the sample thickness was profiled and the samples were stained to visualize the mineral distribution.

The effects of load frequency, load amplitude, and SBF temperature on the generated charge, mineral deposition rate, and mineral growth thickness were studied as follows:

1) The sheet was cut into small strips (12 mm × 35 mm) and the edges were sealed with a non-residue adhesive tape (low-friction PEEK tape).
2) The sheet was then loaded at a set frequency and amplitude in air and the applied stress and generated charge were measured.
3) The sheet was then mineralized in 10× SBF for 24 hours to deposit mineral layers on both sides with the negative side developing a thicker layer. The mineralization was done at set

SBF temperature, load amplitude, and load frequency values, with the frequency and load amplitude being the same as the initial tests in air.
4) After mineralization, the sheet was loaded at the same set load frequency and amplitude in air and the charge generated by the applied stress was measured.
5) The thickness of the thicker negative side mineral layer was then measured with a laser profilometer.

The first goal of the experiment was to measure how the stress-generated charges change over time despite constant load amplitude, load frequency, and temperature conditions due to the mineral formation. In addition, the second goal was to study the ability to increase the mineralization rate and achieve a greater mineralization thickness depending on the loading and temperature conditions. It is expected that increasing load amplitude, frequency, and temperature accelerates the mineralization process.

For the fatigue experiments, PVDF samples were cut into strips (30 mm × 16 mm) and then loaded with tension-tension cyclic load on an Instron dynamic and fatigue testing machine. The experiments were all in a load-controlled mode to avoid any buckling that may occur in the thin sheets. **Fig 1** shows the testing setup.

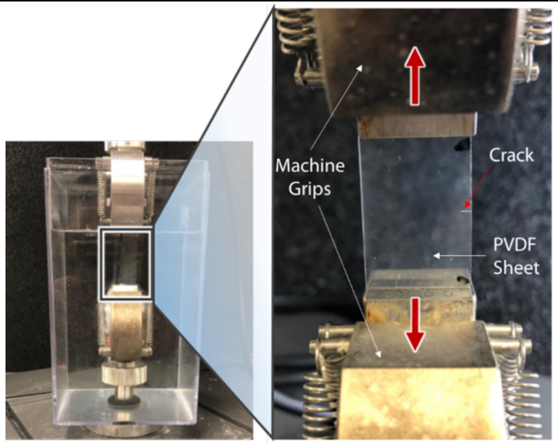


Fig 1. Fatigue testing setup.

5.1.1 Sample Fabrication

The sample geometry was selected such that the width was sufficient not to exceed the width of the shaker grips, to be sufficient to avoid tearing of the sample, and to allow room for the edges to be sealed as shown in **Fig 2**. In addition, for the sealing of the edges to create localized unmineralized regions for thickness measurements, several types of adhesive tapes were investigated. In particular, these adhesives were tested to determine suitability for continued adhesion in prolonged water and SBF exposure, suitability for adhesion under loading conditions, and suitability for adhesive in wide temperature ranges. The main challenge was in finding a suitable adhesive that remained bonded to the PVDF surface without leaving behind any residues as well as not melting under high temperature environments.

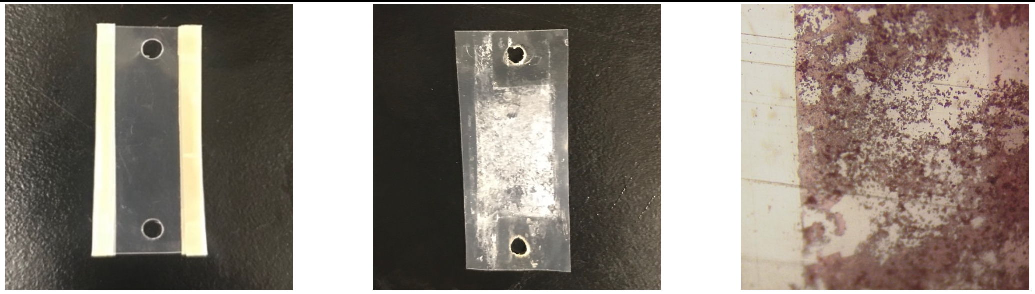


Fig 2. (Left) An unmineralized sample is shown with PEEK tapes sealing the edges. **(Middle)** A mineralized sample with lateral unmineralized regions. **(Right)** A zoomed-in image of a mineralized sample with calcium mineral deposits stained red.

For the PVDF fatigue experiments, the samples' notches were cut by Femtosecond laser to assure the consistency of the crack tip radius. Yet, due to some maintenance issues with the available Femtosecond laser equipment, the output was not as consistent as desired. Hence, a sharp board cutter was used instead as shown in **Fig 3**. After several trials, consistent results were obtained from the board cutter as well.

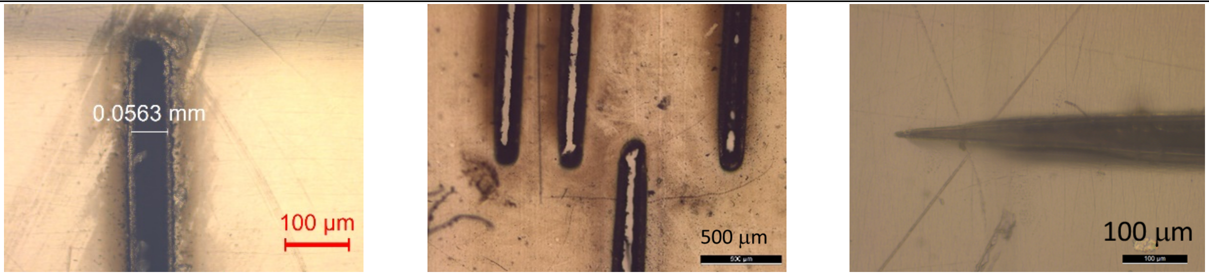


Fig 3. (Left) Good laser cut sample. **(Middle)** Defected laser cut samples. (**Right**) Board-cut sample.

5.1.2 Loading Conditions

In a previous study, mineral deposition took one week to have a well-defined mineral layer over the PVDF sheet. Therefore, the optimization was intended to accelerate this process on a shorter timescale. In addition, the loading conditions should not create plastic deformation of the PVDF that can alter the stress-strain relations on the sample, potentially greatly impacting the generated charge and deposition rate. With loads of amplitude 20 N, plastic deformation was observed, and the maximum amplitude loads were then reduced to 10 N. This load resulted in large generated charges without plastic deformation. The experiments were load-controlled to apply the same input stress. As mineral layers form, the modulus of the sample starts to increase, and thus displacement-controlled experiments may result in increasing loads over time. By fixing the applied stress, the system will always supply a consistent load even if the sample becomes less compliant.

5.1.3 SBF Preparation

The piezoelectric PVDF films were immersed in a polyacrylate container during the experiments containing ~ 400 mL of 10× simulated body fluid (SBF) solution kept at a fixed temperature during the experiment. The 10× SBF solution contained NaCl, KCl, $CaCl_2 \cdot 2H_2O$, $MgCl_2 \cdot 6H_2O$, $NaH_2PO_4 \cdot H_2O$ and $NaHCO_3$ as listed in the following table (**Table 1**). All chemicals were purchased from Sigma-Aldrich.

Table 1. Ion concentrations of simulated body fluids and human blood plasma[1,2].

	Ion concentration (mM)								
	Na^+	K^+	Ca^{2+}	Mg^{2+}	Cl^-	HCO_3^-	HPO_4^{2-}	SO_4^{2-}	Buffer*
10×SBF	1030	5.0	25	5.00	1065	10	10	-	10 Buf
1.5×SBF	213	7.5	3.8	2.30	222	6.30	1.5	0.75	1.5 Buf
SBF	142	5.0	2.5	1.50	148	4.20	1.0	0.50	Buf
Blood plasma	142	5.0	2.5	1.50	103	27.00	1.0	0.50	

SBF, simulated body fluids; *Buf: $(CH_2OH)_3CNH_2$ 50 mM and HCl 45 mM.

5.2 Investigation of liquid-infused porous piezoelectric composites

To expand the environment that the material system can be utilized, especially for aerospace applications, we investigated liquid-infused porous piezoelectric composites inspired by the fact that bone is a material that holds a liquid (i.e. blood) in a porous (piezoelectric[3,4,5]) solid. Based on the previous work by PI on a slippery liquid-infused porous surfaces (SLIPS)[6], we investigated the pathway for synthesizing open cell porous piezoelectric composites that can hold mineral solutions (i.e. SBF) and show self-stiffening behaviors.

5.2.1 Fabrication of porous piezo composite

For liquid-infused piezo composites, it is desirable to fabricate open cell porous structures for infusion and movement of minerals solutions (i.e. SBF) in composites. In addition, we also need surface properties that can facilitate liquid infusion. Based on previous studies, we utilized a sacrificial salt template to fabricate porous structures. For piezo composites, we used polydimethylsiloxane (PDMS) as a matrix material, carbon nanotubes (CNT) as conductive fillers, and $BaTiO_3$ (BTO) as piezo particles. First, we mixed CNT, BTO and PDMS together with N-heptane as a diluting solution to help the composite solution permeate into a salt template easily. Then, we dropped the composite solution on a salt template and cured the composite at 70 °C. Next, we dissolved a salt template in DI water overnight and we could get unpoled porous piezo composites, as schematically shown in **Fig. 4**. Then, we aligned the dipoles to enhance piezoelectric effects by applying a high temperature and high electric field (i.e. poling). To determine the optimum composition of the piezo composites, we investigated the effects of CNT and BTO concentration on piezoelectric properties of composites. We measured a piezoelectric coefficient (d_{33}) to quantify piezo effect of the material.

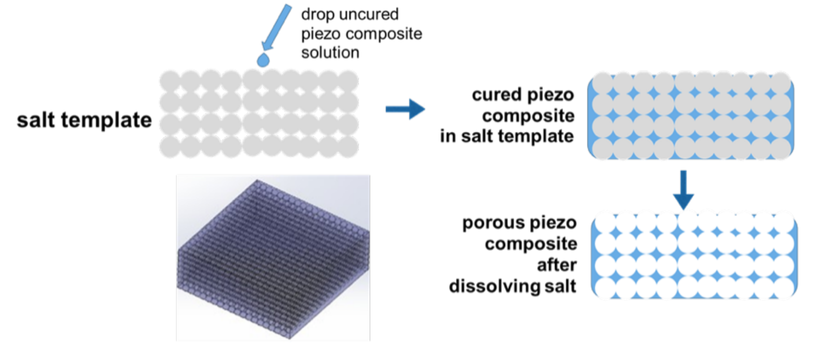


Fig 4. Schematic of fabrication process of porous piezo composites.

5.2.2 Modification of surface properties

To facilitate the liquid infusion of a composite, we investigated the modification of the surface properties of piezo composites to make the surfaces hydrophilic as the matrix material (PDMS) is hydrophobic. We used poly(acrylic acid) (PAA) to treat the composites for surface modification as it is widely used in hydrogels because it can absorb and retain water. The process of treatment includes first soaking composites in PAA aqueous solution and then curing composites at 70 °C. After treatment, the contact angle of the composites decreased from 90° to 22°, indicating that the surface was modified to be hydrophilic, as shown in **Fig. 5(a)**. With the surface treatment, the composites exhibited excellent liquid infusion ability (**Fig. 5(b)**), as liquid could occupy 91.9% of pore spaces.

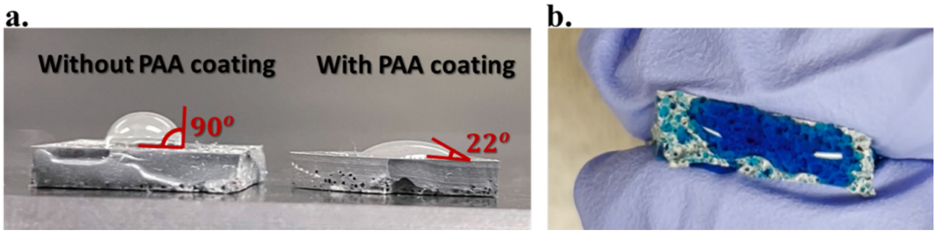


Fig 5. (a) The comparison of contact angle between the composite without and with PAA coating. **(b)** An optical image of a liquid coming out from a liquid-infused composite while squeezing to show good liquid-infusion capability of the composite.

6. RESULTS AND DISCUSSION

6.1 Damage-mitigation behaviors

6.1.1. Investigation of the effects of frequency and temperature on the mineral growth and the resulting piezo charge generation

The mineral growth rate and the stress-generated charge were measured for PVDF specimens at different loading frequencies and SBF temperatures after finding suitable loading conditions. **Table 2** shows the corresponding values for the loading frequency, loading amplitude, SBF temperature, change in generated charge and mineral growth rate over 24 hours.

Table 2. Table of change in generated charge and mineral growth rate with the same loading amplitude and different loading frequencies and SBF temperatures.

Frequency [Hz]	Mean [N]	Amplitude [N]	Temperature [°C]	Charge Change [pC]	Growth Rate [μm/day]
20	5	10	25	-2.01 (-3.99 %)	2.8
20	5	10	50	-16.13 (-35.25 %)	6.0
20	5	10	75	-26.65 (-78.96 %)	6.8
30	5	10	25	-1.74 (-22.60 %)	1.9
30	5	10	50	-6.08 (-30.46 %)	3.6
30	5	10	75	-1.27 (-5.90 %)	8.0

The mineral growth rate increased with increasing SBF temperature so that we can modulate the environmental temperature to control the growth rate. In addition, over the time, the mineral thickness increased while the measured piezoelectric charge on the mineral layer due to the applied load decreased. The results seem to indicate that the mineral layer shields the generated piezo charges to some degree so that as time goes on, while the mineral thickness increases, the effective charge "felt" by ions in the mineral solution decreases, which would result in decrease in growth rate. We will further investigate time-dependent measured charge and mineral thickness as dataset for future modeling studies. For frequency effects, we observed more detachment of minerals for 30 Hz samples while the remaining minerals seemed to be thicker than that of 20 Hz.

6.1.2. Fatigue experiments

As mentioned in section 4, the hypotheses associated with damage-mitigation were validated through 4 steps. First, PVDF samples were immersed in SBF solution with no applied load for 10 days at 37˚C. **Fig. 6** shows the sample morphology before and after immersing in SBF. The result shows that the intrinsic piezoelectric properties of the PVDF sheet can activate the mineralization process even with no applied load. Yet, in such case, the mineralization process is slow, and the minerals are evenly distributed across different areas.

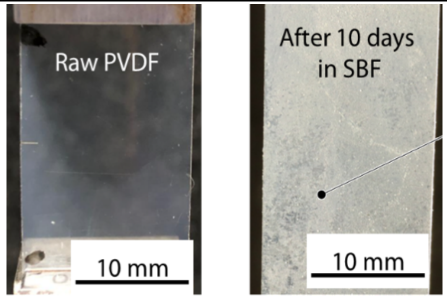


Fig 6. PVDF samples before and after mineralization

Second, alternatively, if the sample is loaded to have non-uniform stress distribution across different areas, the deposition would not be even as well. For example, if we have a notched sample and apply cyclic loading, stress is concentrated near the notch, while it will be lower further away from the crack tip. As a result, there was preferential deposition of minerals at the crack tip compared to the area far from the crack tip as shown in **Fig. 7**.

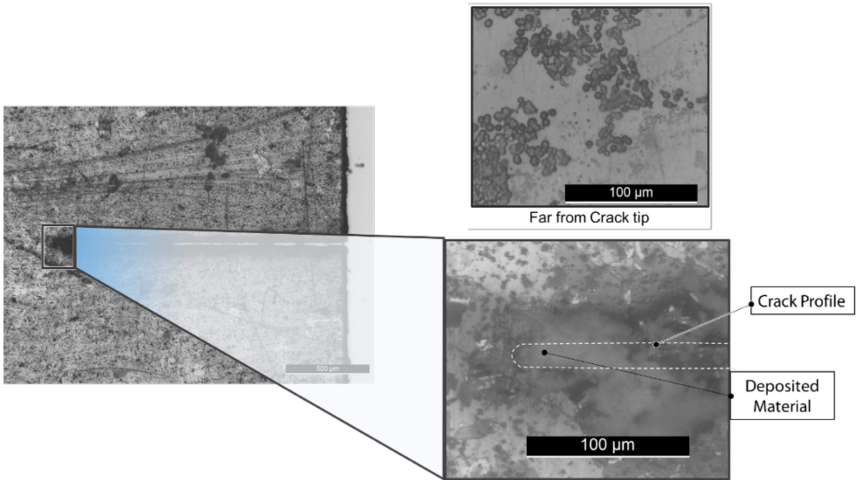


Fig 7. The mineral distribution at different areas in a notched sample with a cyclic loading in SBF.

We compared the fatigue-loaded samples in both SBF and DI water environments after 1.8 million loading cycles as shown in **Fig. 8**. The deposited minerals can clearly be seen for a PVDF sample in SBF compared with its clear counterpart tested in DI water. In addition, a longer and larger crack can be seen in the DI water sample compared to its SBF counterpart. By carefully examining the crack tip areas, as shown in **Fig 9-Left**, even if the crack propagation direction changed, the minerals still preferentially deposited at the crack tip. This observation confirms the capability of piezoelectric charge-induced mineralization to adapt autonomously to the loading conditions without any external intervention and it validates the second step of the hypothesis verification that the highly stressed areas at the crack tip act as a preferential deposition site for the minerals.

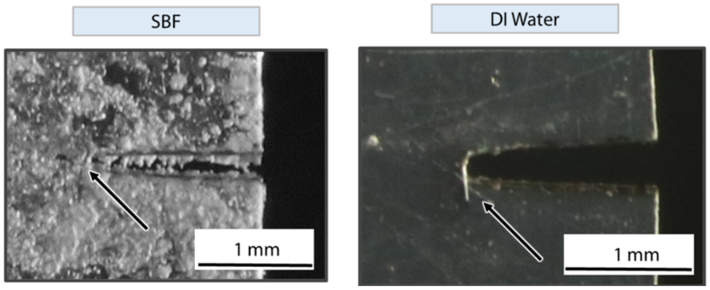


Fig 8. PVDF samples in SBF and DI water after 1.8 million cycles of tension-tension loading.

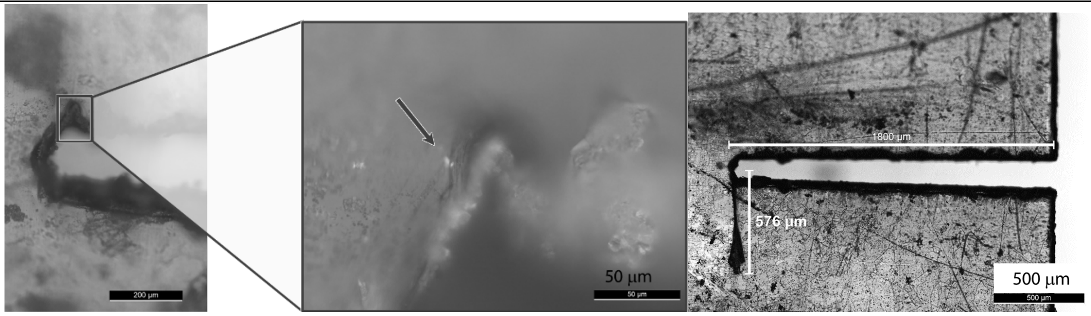


Fig 9. PVDF samples tested in SBF after 1.8 million cycles in SBF (**L**) and in DI water (**R**).

While it was expected that the crack should continue growing in the horizontal direction, it was found that the crack repeatedly deflected into the vertical direction. To study such phenomenon, the anisotropy of the PVDF sheet was characterized. **Fig. 10-Left** shows the stress-strain behavior of samples cut along different orientations. It can be clearly seen that there is a stiff direction which is perpendicular to a compliant one. Even the 45˚-cut samples followed the compliant direction behavior, indicating that the compliant direction dictates the overall behavior. The loading direction was always selected to be along the stiff direction. Hence, this vertical crack propagation can be attributed to the ease of the inter-chain bond breaking along the vertical direction compared to the covalent bond that constitutes the main backbone of the chains. **Fig 10-Right** shows the proposed mechanism for the vertical crack propagation. It should be noted that in cases of significantly high loading conditions, the crack propagated horizontally. But, in such cases, the samples failed rapidly before the mineralization effect is significant.

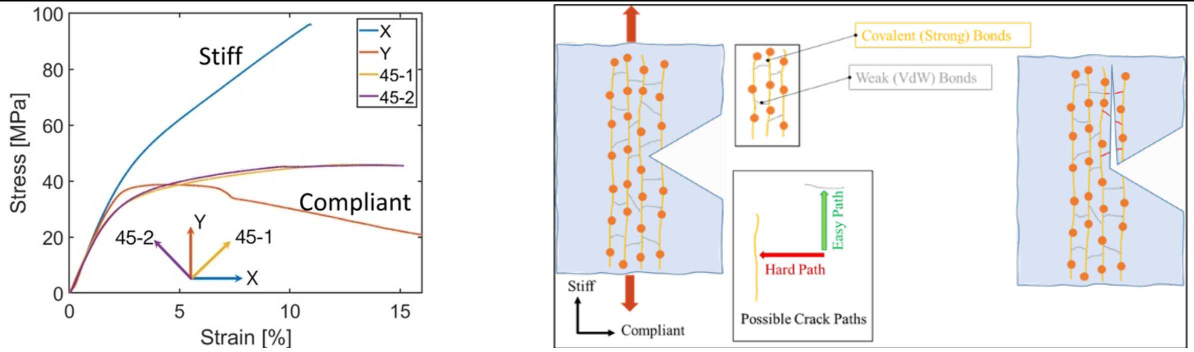


Fig 10. (**Left**) Stress-strain behavior of PVDF samples cut in different orientations. (**Right**) Proposed mechanism for vertical crack propagation.

Third, we compared the crack propagation speeds of samples tested in SBF with those of in DI water to verify the damage-mitigation capability of our material system. **Fig 11-Left** shows the measured crack lengths of samples after 1.8 million cycles in SBF and DI water. Intriguingly, the sample tested in SBF showed ~90% decrease in crack propagation speed compared with the one in DI water under the same loading condition.

Fourth, we compared the fatigue life of samples loaded under higher loading conditions to accelerate the sample failure. As shown in **Fig. 11-Right**, the sample tested in DI water failed after 1 million cycles, while the sample in SBF did not fail up to 2 million cycles (the experiment was unexpectedly interrupted, so it was assumed as a run out for the sample). It should be noted that these data should be handled as preliminary data and more experiments are ongoing to achieve the statistical significance for the quantitative data. Nevertheless, these results confirm our hypothesis of damage-mitigation capabilities of our material system with respect to the crack propagation speed and fatigue life.

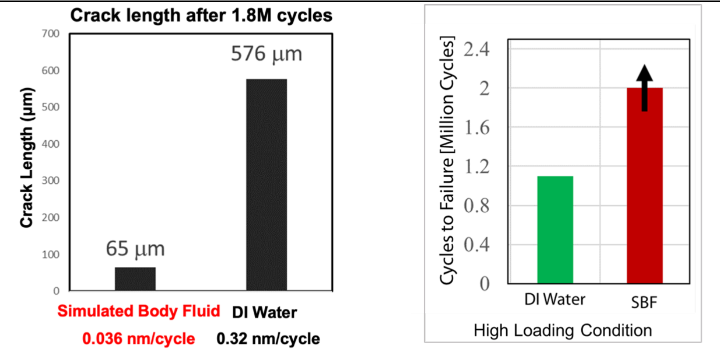


Fig 11. (**Left**) Comparison of crack lengths after 1.8 million cycles. (**Right**) Number of cycles to failure of samples tested in SBF and DI water.

6.2. Liquid-infused porous piezoelectric composites

6.2.1. Characterization of porous structure

After fabrication of porous piezo composites, we used micro-CT to characterize the porous structure. The composite exhibited open cell porous structures as shown in **Fig. 12-Left**. We analyzed a pore size distribution from scan results of micro CT using watershed algorithm. We found that the pore radius of the composite exhibited a normal distribution with a mean of 88.8 µm and standard derivation of 32.5 µm. The pore size is well below the capillary length of water (~2.7 mm) so that the surface effect will be dominant for wetting behaviors.

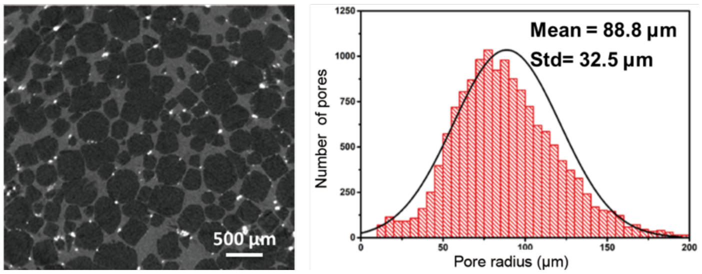
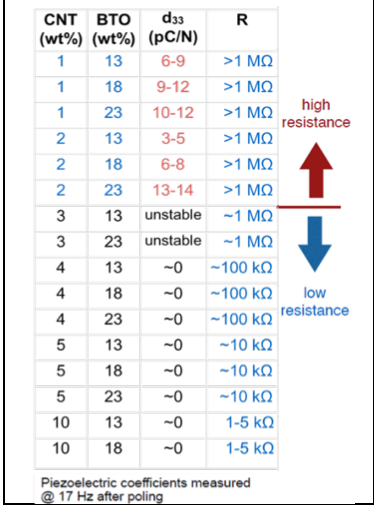


Fig 12 (Left) A micro-CT scan of porous structure of a composite. **(Right)** The pore radius distribution.

6.2.2. Investigation of piezoelectric properties of composites

We investigated the effects of CNT and BTO concentrations on piezoelectric properties of composites. We measured a piezoelectric coefficient (d_{33}) to quantify the piezo effect of the material. As shown in **Table 3**, as the BTO concentration increased between 13 wt% and 23 wt%, the d_{33} tended to increase up to 2 wt% CNT concentration. In the case of the CNT concentration, higher CNT concentration did not necessarily increase d_{33}. Rather, it tended to decrease d_{33}. Moreover, when it reached above 3 wt% CNT concentration, the resistance decreased significantly, which seems to indicate that a high concentration of conductive filler may short circuit the piezoelectric composites with more conductive path created. After investigation, we found that the composite

Table 3. Piezo coefficients with different CNT and BTO concentraitons.



CNT (wt%)	BTO (wt%)	d_{33} (pC/N)	R
1	13	6-9	>1 MΩ
1	18	9-12	>1 MΩ
1	23	10-12	>1 MΩ
2	13	3-5	>1 MΩ
2	18	6-8	>1 MΩ
2	23	13-14	>1 MΩ
3	13	unstable	~1 MΩ
3	23	unstable	~1 MΩ
4	13	~0	~100 kΩ
4	18	~0	~100 kΩ
4	23	~0	~100 kΩ
5	13	~0	~10 kΩ
5	18	~0	~10 kΩ
5	23	~0	~10 kΩ
10	13	~0	1-5 kΩ
10	18	~0	1-5 kΩ

Piezoelectric coefficients measured @ 17 Hz after poling exhibited the best piezo performance with CNT concentration of 2 wt% and BTO concentration of 23 wt%.

6.2.3. Characterization of mineralization in porous scaffold

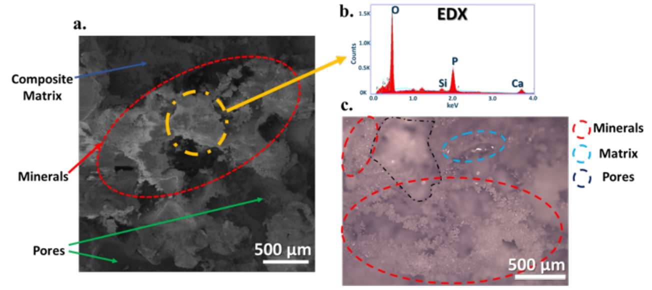


Fig 13 (a) The SEM image of minerals in a porous composite. **(b)** EDX analysis of minerals. **(c)** Optical image of minerals in a porous composite.

We used a scanning electron microscope (SEM) and an optical microscope to characterize the minerals in porous composites after mineralization under cyclic loading. As shown in **Fig. 13-a** and **c**, the minerals were accumulated on pore walls within a porous composite. Additionally, EDX analysis showed peaks of Ca, P, and O (**Fig. 13-b**), which are elements of calcium phosphates.

6.2.3 Characterization of self-stiffening behaviors

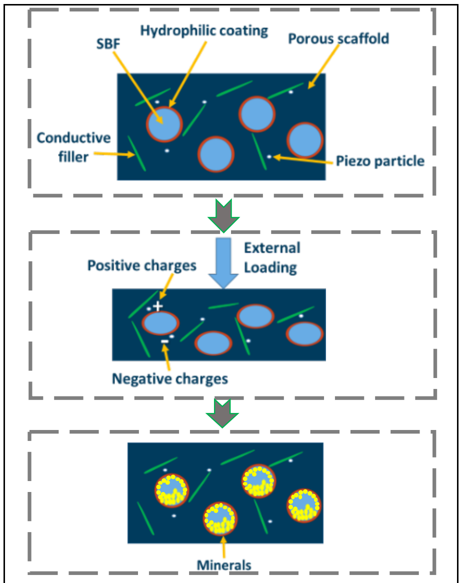


Fig 14. Schematic of mineralization in a porous piezoelectric composite.

We hypothesized that when an external loading is applied on the composite, the piezo particles within the matrix will generate charges which will be transported to pore surfaces through conductive fillers and attract mineral ions from infused SBF, resulting in mineral formation within pores as schematically shown in **Fig. 14**. With mineralization occurring inside of the composite, the modulus of the composite would increase as minerals fill the pores, enabling self-stiffening. To verify our hypothesis, we measured the modulus of the composite as a function of number of loading cycles.

As shown in **Fig. 15-a**, the modulus of the composite in SBF increased around 10% after 70,000 cyclic loadings, whereas the modulus of the composite in air without mineralization (control group) did not exhibit a significant change with cyclic loading. In addition, after 1.2 million cycles, the modulus of the composite in SBF increased around 67%, as shown in **Fig. 15-b**. We also measured stress-strain curves of porous composites before (without mineralization) and after (with mineralization) cyclic loading. As shown in **Fig. 15-c**, after cyclic loading, the stress at strain of 65% increased around 120% compared to the one before cyclic loading (without mineralization).

We observed that every time we refreshed SBF, the modulus increased faster as shown in **Fig. 15-b**. From our previous work[7], the concentrations of Calcium and Phosphate ions decreased over extended period of time in an SBF solution if SBF was not refreshed (**Fig. 15-d**). Thus, from the previous result that a higher concentration of the SBF solution led to a higher mineral deposition speed and a higher amount of mineral (**Fig. 15-e**), it is expected that every time after refreshing SBF solution, the concentrations of Calcium and Phosphate ions in SBF increase which results in a higher mineral deposition speed. With a higher mineral deposition speed, the composite will also exhibit a higher modulus. Thus, the results show that the composite modulus change is due to mineralization inside of a porous piezo material, enabling self-stiffneing of the composite.

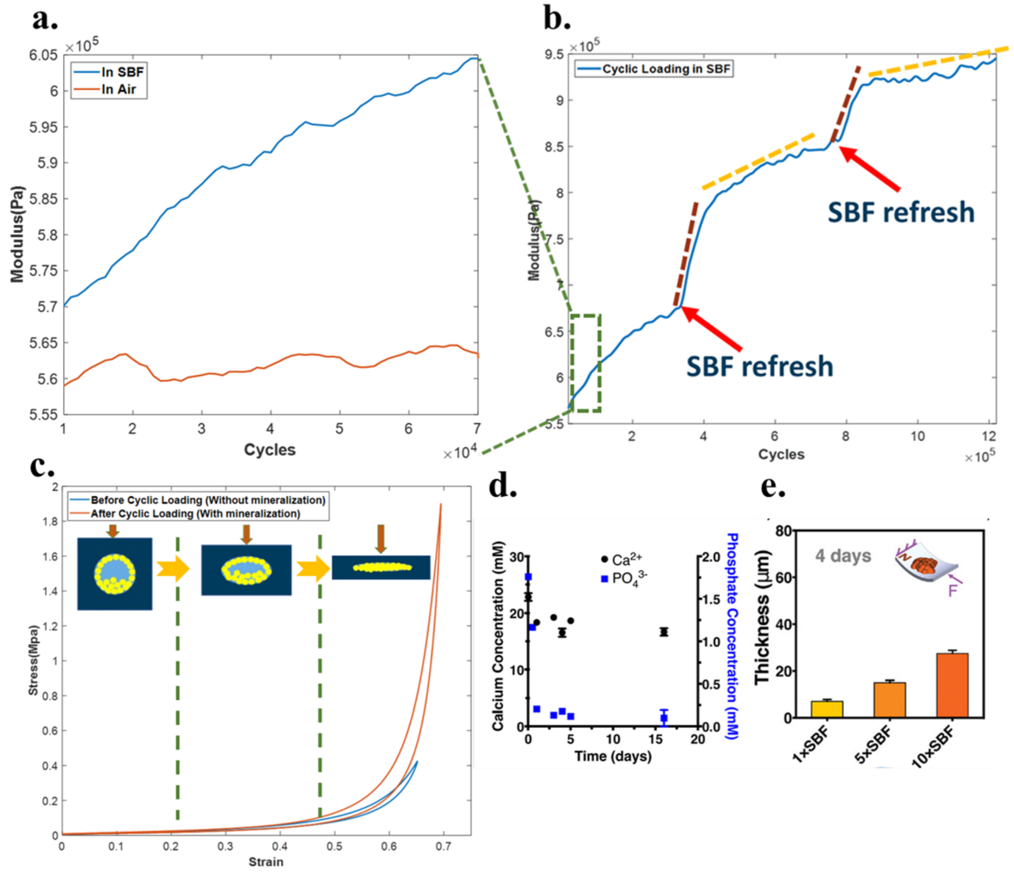


Fig 15. (**a**) Comparision of modulus changes during cyclic loading in SBF and in air, respectivly. (**b**) The increase in modulus of the composite during cyclic loading was accelerated with refreshing SBF. (**c**) Stress-strain curves of a composite before and after cyclic loading. (**d**) Change in concentrations of Calcium and Phosphate ions over extended period of time in an SBF solution without being refreshed[7]. (**e**) SBF concentration dependence test[7]. Higher concentration of the SBF solution led to higher amounts of mineral formation. The beams were subjected to static bending as represented in the schematic.

Moreover, we also observed a desirable characteristic of increase in both modulus and dissipation (hysteresis of stress-strain curve) as a result of stress-induced mineralization due to cyclic loading, while most synthetic materials show an inverse relation between modulus and dissipation[8]. The capability to enhance both modulus and dissipation will be beneficial for aerospace applications to support load and reduce unwanted vibration.

7. FUTURE WORK

In the next stage of the project, we will conduct further studies on intriguing damage-mitigation capabilities of our material systems. First, we will measure the resulting charge and mineral thickness distributions as well as the crack growth profile under a given loading as a function of time to elucidate a quantitative damage-mitigation mechanism. Second, we will investigate how the environmental factors such as temperature, pH, and concentration of mineral solutions affect the damage-mitigation so that we can accelerate the damage-mitigation process. Third, we will investigate additives to improve mineral deposition. For example, depositing a thin base mineral may help to accelerate the response of the material system which does not require nucleation of the mineral layer. In addition, the addition of collagen, inspired by bone, may help to enhance adhesion of the mineral layer and further enhance the mineralization from its piezoelectric characteristic. Fourth, we will expand the material systems for the liquid-infused porous piezoelectric composites so that we can investigate, design, and synthesize of materials for various applications.

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OUTCOMES

1. List of all conferences and presentations made for this project

1) S. Orrego, Z. Chen, U. Krekora, D. Hou, S.-Y. Jeon, M. Pittman, C. Montoya, S. H. Kang, "Bioinspired Materials with Dynamically Adaptive Mechanical Properties and Damage Mitigation," 2021 Materials Research Society Fall Meeting, Boston, MA, December 1, 2021. (contributed)

2) S. H. Kang, "Bioinspired materials with self-adaptable mechanical properties and mechanical metamaterials with adaptive energy absorption," Department of Mechanical Systems Engineering, Sookmyung Women's University, Seoul, Korea, November 2021. (invited)

3) S. H. Kang, "Bioinspired materials with self-adaptable mechanical properties and damage mitigation and metamaterials with adaptive energy absorption," Department of Advanced Materials Science and Engineering, Sungkyunkwan University, Suwon, Korea, November 2021. (invited)

4) S. H. Kang, "Bioinspired multifunctional materials with self-adaptable mechanical properties and metamaterials with adaptive energy absorption," Department of Mechanical Engineering, Korea Advanced Institute of Science and Technology, Daejeon, Korea, November 2021. (invited)

5) S. H. Kang, “Self-adaptable materials: Bio-inspired multifunctional materials with self-adaptable mechanical properties and architected materials with adaptive energy absorption,” Department of Materials Science and Engineering, Korea Advanced Institute of Science and Technology, Daejeon, Korea, November 2021. (invited)

6) S. H. Kang, “Bioinspired materials with self-adaptable mechanical properties and damage mitigation and mechanical metamaterials with adaptive energy absorption,” Korea Institute of Science and Technology, Seoul, Korea, November 2021. (invited)

7) S. H. Kang, “Bioinspired multifunctional materials with self-adaptable mechanical properties and metamaterials with adaptive energy absorption,” Department of Mechanical Engineering, Seoul National University, Seoul, Korea, November 2021. (invited)

8) S. H. Kang, “Bioinspired materials with self-adaptive mechanical properties,” Department of Materials Science and Engineering, Seoul National University, Seoul, Korea, November 2021. (invited)

9) S. Orrego, Z. Chen, U. Krekora, D. Hou, S.-Y. Jeon, M. Pittman, C. Montoya, S. H. Kang, “Bone-Inspired Adaptive Multifunctional Materials,” 2021 American Society of Mechanical Engineers International Mechanical Engineering Congress & Exposition (Virtual), November 2021. (contributed)

10) S. H. Kang, “Bioinspired multifunctional materials with self-adaptable mechanical properties and architected materials with adaptive energy absorption,” Department of Mechanical Engineering, Pohang University of Science and Technology, Pohang, November 2021. (invited)

11) S. H. Kang, “Self-adaptive materials, structures and devices,” Department of Mechanical Engineering, Johns Hopkins University, Baltimore, MD, September 2021. (invited)

12) S. H. Kang, “Bioinspired Synthesis of Multifunctional Materials with Self-Adaptable Mechanical Properties and Self-Regeneration,” ASC 36th Annual Technical Virtual Conference Tri-Agency AFOSR-ARO-ONR Symposium (virtual), September 2021. (invited)

13) S. H. Kang, “Self-adaptive materials, structures and programmable materials,” Air Force Research Laboratory, Dayton, OH, August 2021. (invited)

14) S. H. Kang, “Multi-phase Multifunctional Materials that Sense Mechanical Loading and Adapt,” 2021 Spring Materials Research Society Meeting (Virtual), April 21, 2021. (contributed)

15) S. H. Kang, “Bioinspired Materials with Self-Adaptable Mechanical Properties,” 2021 American Physical Society March Meeting (Virtual), March 2021. (contributed)

16) S. H. Kang, “Self-adaptive materials, structures and devices,” Department of Mechanical and Aerospace Engineering, Ohio State University, Columbus, OH, February 2021. (invited)

2. List of publications supported by this grant

1) M. Omar^{+}, B. Sun^{+}, S. H. Kang, “Good reactions for low-power shape-memory microactuators,” **Science Robotics**, 6, eabh1560 (2021). ($^{+}$: equal contribution)

2) B. Shen, S. H. Kang, “Designing Self-Oscillating Matter,” **Matter**, 4, 766-769 (2021).

3) M. Omar, B. Sun, G. Kitchen, S. H. Kang, “Mechanically adaptive materials”, **Journal of Composite Materials**, manuscript in preparation.

4) M. Omar, B. Sun, G. Kitchen, S. H. Kang, “Damage-mitigating materials”, manuscript in preparation.

5) B. Sun, M. Omar, M. Simmons, S. H. Kang, “Liquid-infused porous piezoelectric composites with self-stiffening and enhanced dissipation behaviors”, manuscript in preparation.

3. Honors and Awards received during this period

1) 2021 Air Force Summary Faculty Fellowship

2) Editorial Board Member – Multifunctional Materials

3) Editorial Board Member – Sensors

4) Guest Editor – Special Issue on Soft Composite-Based Sensor of journal Sensors (2021)

4. Interactions with AFRL

1) PI Kang worked at the Air Force Research Laboratory (Dayton, OH) during Summer 2021 through the support by the Air Force Summer Faculty Fellowship, working with Drs. Jeffery Baur and Philip Buskohl.

2) PI Kang gave an invited seminar at the Air Force Research Laboratory in August 2021.

3) PI Kang is collaborating with Drs. Philip Buskohl, and Nathan Hertline at AFRL in Dayton regarding reprogrammable mechanical metamaterials based on liquid crystalline elastomers and machine learning approach to modulate mechanical behaviors without changing geometries.

4) PI Kang is collaborating with Drs. Jeffery Baur and Anil Erol to validate programmable morphing aerospace structures with low energy consumption.

5. List of all students and postdocs working on this award

Students: Bohan Sun (PhD student), Mostafa Omar (PhD student), Grant Kitchen (PhD student), Mitchell Simmons (undergraduate student)