nature portfolio

Peer Review File

Pressure-sensitive In-situ Underwater Adhesives

Corresponding Author: Professor Shaoting Lin

This file contains all reviewer reports in order by version, followed by all author rebuttals in order by version.

Version 0:

Reviewer comments:

Reviewer #1

(Remarks to the Author)
This manuscript reports on the development of a new class of pressure-sensitive adhesive that can form in-situ adhesion in an aqueous environment. The essential idea is to harness the synergy of mechanical pressure and osmotic pressure to enable both bulk polymerization and surface salinization by rapidly and effectively removing interfacial water molecules between adhesives and substrates. The idea is conceptually novel, supported by comprehensive structural and mechanical characterizations. Some minor comments are listed below.
1. Although this manuscript focuses on the fundamental mechanism behind the design of PSIS, it would be great to include one apple-to-apple comparison of the in-situ underwater adhesion between PSIS and traditional tough hydrogel adhesives.
2. The nonmonotonic relationship between interfacial toughness and water absorption ratio in Fig. 4f is fundamentally interesting. However, to enhance clarity, the authors can consider adding schematics to illustrate the molecular mechanisms underlying adhesive failure at low water absorption ratios and cohesive failure at higher water absorption ratios.
3. As this manuscript primarily focuses on the toughening mechanism for the development of PSIS, its fundamental insight could be further strengthened by including more qualitative theoretical analysis on how the synergy of mechanical and pressure and osmotic pressure enhances intrinsic interfacial toughness and dissipative fracture toughness through improved particle-particle and particle-substrate interactions.

Reviewer #2

(Remarks to the Author)
The manuscript entitled "Pressure-sensitive In-situ Underwater Adhesives" by Liu et al introduces a pressure-sensitive in-situ underwater adhesive composed of superabsorbent particles infused with functional silane and hydrogel precursors. The superabsorbent particles, along with the applied mechanical pressure, synergistically create extensive contact areas between the particles themselves and between the particles and the substrates, thereby achieving both high fracture toughness and interfacial toughness. The manuscript is well-written, with clear logic, and provides valuable insights into creating high performance underwater adhesives. Therefore, I recommend its publication in Communications Physics.

My main concern is as follows: I believe the primary factor contributing to the enhancement of fracture toughness and interfacial toughness in this work is the increase in polymer volume fraction. The authors present quantitative data on surface adhesion ratio and the ratio of void volume to total volume for samples fabricated under different osmotic pressures. However, the manuscript lacks quantitative data correlating the void area or volume with the mechanical performance to clarify the critical role of the high polymer volume fraction in resisting crack propagation. Or to present the polymer volume fraction directly.

Reviewer #3

(Remarks to the Author)
Comments:
Rapid and robust in-situ underwater adhesion is highly valuable for exploring and utilizing underwater resources. However, achieving fast and reliable adhesion in an aqueous environment remains a fundamental challenge due to a hydration layer, a film of water molecules that forms between the adhesive and the wet substrates. This paper develops a pressure-sensitive in-situ (PSIS) underwater adhesive featuring superabsorbent particles infused with functional silane and hydrogel precursors. When injected into an underwater crack, the PSIS adhesive quickly absorbs water, swells, and fills the crack.

Mechanical pressure is applied to synergize with the particles' osmotic pressure to improve particle-particle and particle-substrate interactions, while heat is utilized to trigger the thermal polymerization of the hydrogel precursors. This process creates a porous adhesive via bulk polymerization and covalent bonding with the substrate via surface silanization. Moreover, the mechanical pressure significantly enhances the PSIS adhesive's stretchability (from 3 to 5), stiffness (from 37 kPa to 78 kPa), fracture toughness (from 1 kJ/m2 to 7 kJ/m2), and interfacial toughness with glass substrates (from 45 J/m2 to 270 J/m2), while reducing its hysteresis ratio. Despite PSIS's questionable utility in practice, this work provides a principle for rationally designing in-situ underwater adhesives and evokes mechanisms for enhancing toughness without relying on a large hysteresis ratio. Thus, this paper could be suitable for publication in Communications Physics after several issues listed below are appropriately addressed to meet the standards expected of journal papers.
Question:
1. Some grammatical and presentation mistakes have been identified in the manuscript. The authors should double-check the documents.
e.g., "…The high osmotic pressure demonstrates that the PSIS adhesive have a large driving force for swelling..., while the driving force gradually decays as the adhesive absorb water, as manifested by...". (Page 4, The last sentence)
"…The peeling force exhibit large fluctuations due to the discontinuous connection at the adhesive area. As summarized in Fig. 4c, ...". (Page 9, The third sentence)
"…The corresponding hysteresis versus stretch ratios are summarized in Fig. 2c (should be Fig. 3c). As the stretch ratio increases, ...". (Page 7, The first sentence)
"…(e) The measured force divided by the initial width multiplied by thickness F/wt vesus stretch ratio λ of the notch…" (Page 14, Graphical notes to Fig. 3)
2. The authors demonstrate the ability of PSIS to absorb water rapidly. However, in practical applications such as underwater environments, this character may cause PSIS to swell with water at the extruded or injected end and not effectively fill between the substrates. In addition, the authors titled it "Underwater Adhesives" and should have experimented with underwater bonding tests rather than just bonding with PSIS after water absorption. For example, the authors should place two substrates underwater, inject PSIS for bonding, and measure the bonding performance.
3. Why choose a thermal initiator over a photoinitiator? In fact, in some application scenarios, such as bonding glass substrates, as shown by the authors, might it be more convenient to use UV? In addition, the 80 °C thermal initiation makes PSIS unsuitable for some low Tg polymer materials and hinders the underwater application of PSIS. Therefore, the authors need to supplement the bonding properties of PSIS with more heat-resistant or better thermally conductive substrates such as steel and Al.
4. The authors considered the large fluctuations of the peeling force due to the discontinuous connection at the adhesive area. However, Fig. 2e indicated that applied pressure significantly increases the adhesive area. Moreover, the surface adhesive ratio (φs), defined as the ratio of the adhesive area to the total area, increases from 14% to 75% as mechanical pressure increases (Fig. 2f). Even though the bonding area has increased 2 times as the author states, it seems that the bonding continuity does not improve with the increase in bonding area (Fig. 4b, nearly equal amplitude of all force/width-displacement curves)?
5. It can be observed that the toughness and the shear modulus of PSIS decrease dramatically as the φw increases (Fig. 3h and 3i). However, the difference in bonding strength between PSIS of various φw was not remarkable. Even the PSIS's bonding strength and interfacial toughness of 40% φw was greater than 10% φw of PSIS (Fig. 4f). The authors proposed that the reason lies in the balance between the adhesion strength and the cohesion strength, and the cohesion strength of PSIS with different φw was tested. Therefore, the authors should add tests (like Fig. S2) of the surface adhesive ratio (φs) of PSIS with different φw to illustrate the change in the adhesion strength.
6. How stable is PSIS in a water environment?

Version 1:

Reviewer comments:

Reviewer #1

(Remarks to the Author)
I am satisfied with their revision and the manuscript in its current state can be published in this journal.

Reviewer #2

(Remarks to the Author)
The authors have addressed all the questions, and it is now recommended for publication.

Reviewer #3

(Remarks to the Author)
My concerns have been addressed.

Response to Review Comments (Manuscript ID: COMMSPHYS-24-1082)
"Pressure-sensitive In-situ Underwater Adhesives"

Response to Reviewer 1

General comment. This manuscript reports on the development of a new class of pressure-sensitive adhesive that can form in-situ adhesion in an aqueous environment. The essential idea is to harness the synergy of mechanical pressure and osmotic pressure to enable both bulk polymerization and surface salinization by rapidly and effectively removing interfacial water molecules between adhesives and substrates. The idea is conceptually novel, supported by comprehensive structural and mechanical characterizations. Minor comments are listed below.

Response to general comment. Thank you very much for acknowledging our work in response to the initial round of reviews. We also appreciate your comments and suggestions, which further strengthen the paper. In the following sections, we address each comment point by point. Newly inserted text in the manuscript and supplementary information are marked in red.

Comment 1. Although this manuscript focuses on the fundamental mechanism behind the design of PSIS, it would be great to include one apple-to-apple comparison of the in-situ underwater adhesion between PSIS and traditional tough hydrogel adhesives.

Response to comment 1: Thank you for the reviewer's suggestion to make a direct comparison between PSIS and traditional tough hydrogel adhesives. To address this, we perform additional experiments to measure the adhesion strength of our PSIS adhesive, aligning with the standard metric used in most underwater adhesives. Specifically, we conducted lap shear experiments on the PSIS adhesive under a mechanical pressure of P = 10 kPa, with water absorption ratios ϕ_w of 0%, 20%, 40%, and 60%, respectively. As shown in **Fig. R1-1(a)**, shear force is applied until failure occurs, recording shear stress (S) as a function of displacement (d). The adhesive strength was then determined by dividing the maximum force at failure divided by the bonded area.
We first compare fracture toughness and interfacial toughness of our PSIS with several traditional tough hydrogels measured in air. As shown in **Fig. R1-1 (b)**, our PSIS adhesive exhibits higher interfacial toughness and fracture toughness than most existing tough hydrogels including PAAm-chitosan, PAAm-HA (Yuk, et al, *Nature materials*, 15, 190-196, 2016), P(AAc-co-Aa) (Yuk, et al,

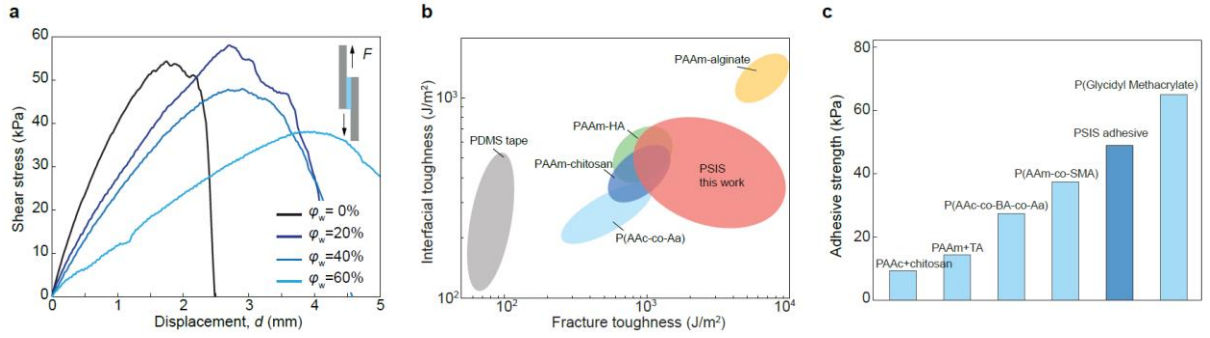

Fig. R1-1. Lap shear experiment results and comparisons with tough hydrogel adhesives. **(a)** Shear stress S versus displacement d curves of PSIS with various water absorption ratios ϕ_w from lap shear experiments. **(b)** Comparison chart in the plot of interfacial toughness and fracture toughness between our PSIS and traditional tough hydrogel adhesives. **(c)** Summarized adhesive strength between our PSIS and existing underwater hydrogel adhesives.

Nature, 575, 169-174, 2019), and PDMS tape (Zheng, et al, *Soft Matter*, 14, 5888-5897, 2018), but slightly lower than PAAm-alginate. This is likely due to the presence of cavities between adjacent particles in our PSIS adhesive.

We further compare adhesion strength of our PSIS to existing tough hydrogel adhesives used as underwater adhesives. As shown in **Fig. R1-1(c)**, our PSIS demonstrates higher adhesion strength compared to PAAc+chitosan (Yuk, et al, *Nature materials*, 15, 190-196, 2016), PAAm+TA (Qiao, et al, *ACS Applied Materials & Interfaces*, 11, 7755-7763, 2019), P(AAc-co-BA-co-Aa) (Liu, et al, *Advanced Functional Materials*, 29, 1900450, 2019), and P(AAm-co-SMA) (Han, et al, *Advanced Functional Materials*, 30, 1907064, 2020), but slightly lower than P(Glycidyl Methacrylate) (Wang, et al, *ACS Applied Materials & Interfaces*, 13, 3435-3444, 2021). Despite the higher adhesion strength of P(Glycidyl Methacrylate), it lacks the ability to effectively evacuate large interfacial water in underwater environments, and its synthesis process is highly complex, making it less economically feasible for practical applications. In future work, we will further optimize the composition of the PSIS adhesive, including the polymer fraction, crosslinker density, and superabsorbent particle fraction, to thoroughly investigate the effects of each component to enhance its interfacial toughness with solid substrates in aqueous environment.

Comment 2. The nonmonotonic relationship between interfacial toughness and water absorption ratio in Fig. 4f is fundamentally interesting. However, to enhance clarity, the authors can consider adding schematics to illustrate the molecular mechanisms underlying adhesive failure at low water absorption ratios and cohesive failure at high water absorption ratios.

Response to comment 2: Thank you very much for the reviewer's suggestion. We appreciate your recommendation to add molecular schematics to illustrate the molecular mechanisms of adhesive and cohesive failure across various water absorption ratios. As illustrated in **Fig. R2-1**, we have added the molecular schematics depicting the PSIS adhesive on solid surfaces prior to the peeling test, as well as illustrations of adhesive and cohesive failure during the peeling test. For PSIS adhesives with low water absorption ratios, the material exhibits higher bulk strength compared to adhesion strength, leading to adhesive failure at the interface. In contrast, for PSIS adhesive with high absorption ratio, the PSIS exhibits significantly reduced bulk strength, resulting in cohesive failure within the bulk material.

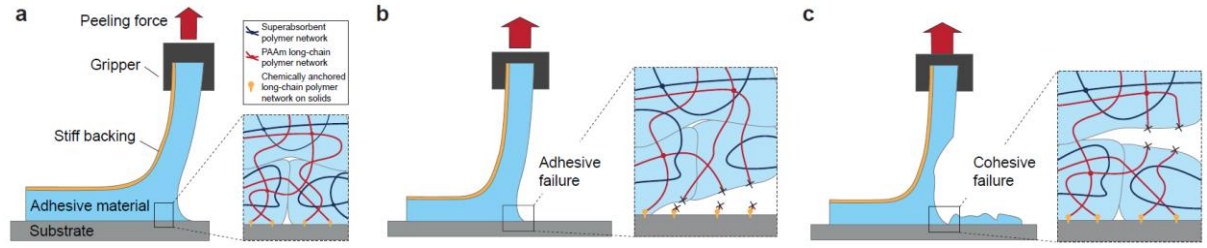

Fig. R1-2. Schematics illustrating the molecular mechanisms of adhesive and cohesive peeling failures. (a) Molecular schematics of PSIS adhesive prior to the peeling test. **(b)** Molecular schematics illustrating adhesive failure at the interface of PSIS adhesives with low water absorption ratios. **(c)** Molecular schematics illustrating cohesive failure within the bulk material of PSIS adhesives with high water absorption ratios.

Revision to comment 2: In response to the reviewer's suggestion, we have added molecular schematics in **Fig. 4a** and **Fig. 4d** to illustrate the adhesive and cohesive failure mechanisms of PSIS adhesives with different water absorption ratios. We revised paragraph "As depicted in the molecular schematics in **Fig. 4d**, for PSIS adhesive with low water absorption ratio (i.e., φ_w = 10%), the adhesive exhibits higher bulk strength compared to adhesion strength, leading to adhesive failure at the interface between PSIS adhesive and the solid substrate. During peeling test, the adhesive detaches from the solid surface, indicating a breakage of the polymer chains anchored to the solid substrate. In contrast, for PSIS adhesive with high water absorption ratio (i.e., φ_w = 80%) in **Fig. 4d**, the adhesive exhibits lower bulk strength compared to adhesion strength, leading to cohesive failure within the bulk material. As the peeling force increases, the interfacial crack starts to kink and propagate through the bulk PSIS adhesive, resulting in residual adhesive material remaining on the substrate" in Section "Adhesive performance of the PSIS adhesive". Moreover, the revised **Fig. 4** is presented below.

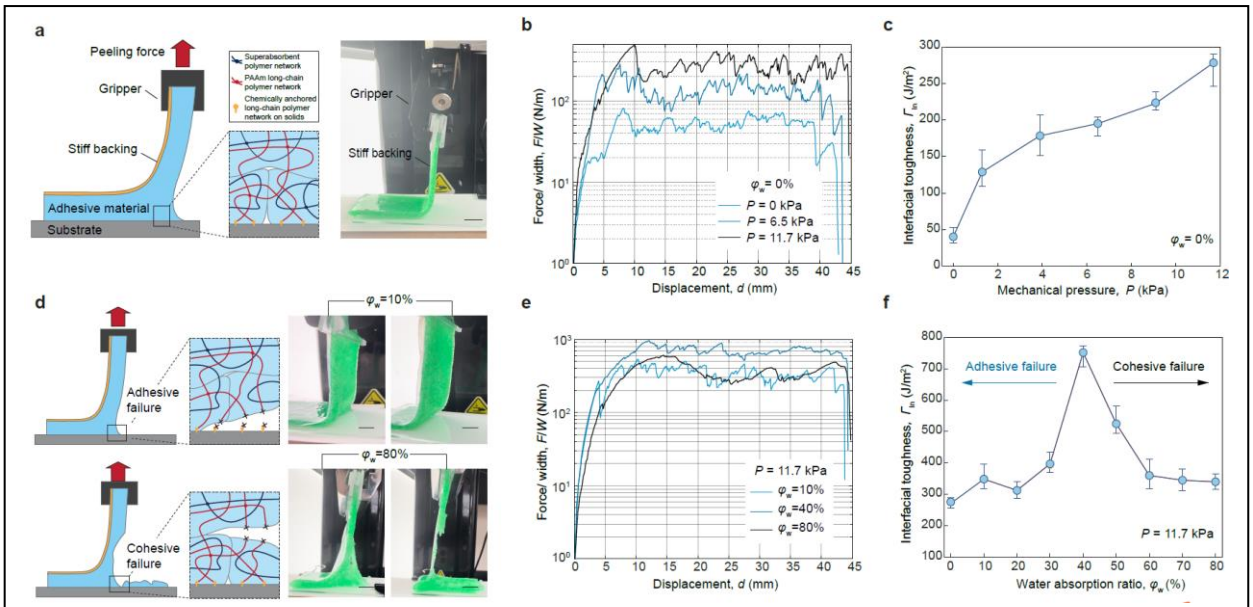

Fig. 4. Adhesion characterization of the PSIS adhesive. (a) Schematic and image of the PSIS adhesive attached to a glass substrate prior to the 90-degree peeling test. The stiff backing is adhered to the back of the bulk PSIS adhesive. Scale bar is 10 mm. **(b)** The measured peeling force over width F/W versus displacement d of the PSIS adhesive synthesized under different mechanical pressures P. **(c)** The interfacial toughness Γ_{in} increases with the applied mechanical pressure P. Values represent the mean ± s.d. (N = 3). **(d)** Schematics and images of adhesive failure and cohesive failure of the PSIS adhesives with low and high water absorption ratios φ_w. Scale bar is 10 mm. **(e)** The measured peeling force over width F/W versus displacement d of the PSIS adhesive with different water absorption ratio φ_w. **(f)** The measured interfacial toughness Γ_{in} versus water absorption ratio φ_w. As the absorbed water increases, the peeling failure mode changes from adhesive failure to cohesive failure.

Comment 3. As this manuscript primarily focuses on the toughening mechanism for the development of PSIS, its fundamental insight could be further strengthened by including more qualitative theoretical analysis on how the synergy of mechanical pressure and osmotic pressure enhances intrinsic interfacial toughness and dissipative fracture toughness through improved particle-particle and particle-substrate interactions.

Response to comment 3: Thanks for reviewer's valuable comments. As described in the working principal section, PSIS particles rapidly absorb water in an aqueous environment, leveraging both mechanical pressure and osmotic pressure to enhance particle-particle and particle-substrate interactions.

Theoretical model. Considering a PSIS adhesive adhered to solid substrate subject to a 90-degree tensile peeling, interfacial crack propagation first requires the scission of a single layer of polymer chains on the crack path. The required mechanical energy for chain scission divided by the area of crack surface at undeformed state gives the intrinsic fracture energy Γ_0, following the Lake-Thomas model (Lake, et al, *Journal of Applied Polymer Science*, 9.4, 1965). As the crack propagates, the material in a process zone around the crack path experiences a loading-unloading process, which dissipates mechanical energy due to bulk hysteresis, following the bulk dissipation model (Zhang, et al, *Extreme Mechanics Letters*, 4, 2015). The dissipated energy divided by the area of interfacial crack surface at undeformed state contributes to the interfacial fracture toughness by $\Gamma_{\mathrm{D}}^{\mathrm{bulk}}$. In addition, since the PSIS adhesive contains chain entanglements, the crack propagation also requires pulling out of chains and delocalized damage of chains adjacent to the crack path, which give the near-crack dissipation (Zheng, et al, *Extreme Mechanics Letters*, 51, 2022). The dissipated energy divided by the area of interfacial crack surface at undeformed state further contributes to the interfacial fracture toughness by $\Gamma_{\mathrm{D}}^{\mathrm{tip}}$. Therefore, the total interfacial fracture toughness of our PSIS adhesive can be expressed as

$$\Gamma_{in} = \Gamma_0 + \Gamma_{\mathrm{D}}^{\mathrm{bulk}} + \Gamma_{\mathrm{D}}^{\mathrm{tip}} \tag{R3-1}$$

$\Gamma_{\mathrm{D}}^{\mathrm{bulk}}$ can be correlated with Γ_{in} via (Zhang, et al, *Acta Mechanica Sinica*, 33, 2017)

$$\Gamma_{\mathrm{D}}^{\mathrm{bulk}} \propto \Gamma_{in} h_m \tag{R3-2}$$

where h_m is the maximum stress-stretch hysteresis ratio of the bulk PSIS under tensile loading. A combination of **Eq. (R3-1)** and **Eq. (R3-2)** further leads to

$$\frac{\Gamma_{in}}{\Gamma_0 + \Gamma_{\mathrm{D}}^{\mathrm{tip}}} = \frac{1}{1 - \chi h_m} \tag{R3-3}$$

where $0 \leq \chi \leq 1$ is a dimensionless number depending on the stretch-dependent hysteresis of the bulk PSIS. We further introduce a dimensionless parameter $\beta = \left(\Gamma_0 + \Gamma_{\mathrm{D}}^{\mathrm{tip}}\right)/\Gamma_0 \geq 1$ to account for the near-crack dissipation due to chain entanglements. Thus, we can derive a governing equation for the interfacial toughness enhancement of PSIS adhesive as

$$\Gamma_{in} = \frac{\beta \Gamma_0}{1 - \chi h_m} \tag{R3-4}$$

Material design parameters. The immersion duration determines the water absorption ratio of the as-prepared PSIS particles, denoted as ϕ_w, which affects the chemical potential difference of water molecules within PSIS. As the as-prepared PSIS is injected into a confined space between two solid substrates in an aqueous environment. Driven by the chemical potential difference of water molecules between PSIS particles and surrounding aqueous environment, the PSIS particles evacuate interfacial water, expanding their volume and filling the space. As the space between two solid substrates is confined, an osmotic pressure develops, determining both particle-substrate and

particle-particle contacts. We apply mechanical pressure P as an additional design parameter to further enhance particle-substrate and particle-particle contacts. Subsequently, we apply joule heating to facilitate thermally activated surface silanization and bulk polymerization. Surface silanization governs the performance of the adhesive layer via particle-substrate contact, characterized by intrinsic fracture energy Γ_0. Meanwhile, bulk polymerization regulates the cohesive layer via the synergy of high-hysteresis bulk dissipation and low-hysteresis near-crack dissipation, characterized by Γ_D^{bulk} and Γ_D^{tip} respectively. In summary, there are two key material design parameters, water absorption ratio ϕ_w and mechanical pressure P, governing the interfacial fracture toughness of underwater substrates adhered by our PSIS, namely $\Gamma_{in}(\phi_w, P)$.

Toughening analysis. Since this paper primarily investigates the effects of mechanical pressure on the bulk material and adhesive properties, we will specifically focus on how mechanical pressure influences fracture toughness and interfacial toughness in the following sections. The effect of osmotic pressure will be systematically investigated in our future follow-up work. Following the **Eq. (R3-4)**, the interfacial toughness Γ_{in} is governed by dimensionless parameters β and χ, intrinsic fracture energy Γ_0, and maximum stress-stretch hysteresis ratio h_m.

Notably, **Fig. 3c** demonstrates that the PSIS adhesive exhibits lower hysteresis at higher pressures compared to lower pressures, while the hysteresis values at maximum stretch ratio (λ = 4) remain similar across all pressure conditions. Additionally, the stress-stretch curves of PSIS adhesives shown in **Fig. 3b** reveal that χ slightly increases up to 1 as the mechanical pressure P increases. Since both h_m and χ exhibit minimal changes, the interfacial fracture toughness form **Eq. R3-2** is not expected to increase significantly due to pressure. However, our experimental results indicate a substantial enhancement in interfacial fracture toughness from 1 kJ/m^2 to 7 kJ/m^2, which is mainly attributed to the increase of intrinsic fracture energy Γ_0 and dimensionless parameter β. The intrinsic fracture energy Γ_0 is closely related to the surface adhesion ratio ϕ_s, which increases from 14% to 75% as the applied mechanical pressure p increases. The dimensionless parameter β characterizes the effect of molecular entanglement. Our PSIS particles were synthesized using a high monomer concentration (water-to-arylamide monomer weight ratio ~1.43) with low crosslinker density, resulting in a highly entangled, long-chain polymer network (Kim, et al, *Science*, 2021). Unlike traditional high-hysteresis toughening mechanisms, crack propagation in this PSIS polymer network stretches the entangled chains surrounding the crack tip. This process distributes chain scissions across multiple adjacent layers, enhancing energy dissipation to retard the interfacial crack propagation. In summary, the pressure-induced interfacial toughness enhancement is primary driven by the pressure-enhanced β and Γ_0,

$$\frac{\Gamma_{in}(p)}{\Gamma_{in}(p=0)} = \frac{\beta(p)}{\beta(p=0)} \frac{\Gamma_0(p)}{\Gamma_0(p=0)} \quad \text{(R3-5)}$$

Revision to comment 3: Thanks to the reviewer's suggestion to qualitative analysis on how the synergy of mechanical pressure affects the fracture toughness and interfacial toughness of PSIS adhesive material. Firstly, in the manuscript, we add sentences to discuss the entanglements in the polymer network to enhance the fracture toughness of PSIS adhesive: "The high fracture toughness achieved in the PSIS adhesive can be attributed to two factors: the molecular design within the PSIS particles and the structure alternation induced by the mechanical pressure. When we prepare the PSIS particles, a hydrogel precursor with a high monomer concentration (water-to-monomer ratio of 5.7) is used, resulting in a densely entangled long-chain polymer network within the adhesive. These long polymer chains collectively distribute the applied load by sliding through molecular entanglements without breaking, thereby enhancing crack propagation resistance and

significantly improving the material's fracture toughness." Moreover, in the supplementary information, we add a section titled "Toughening Analysis of PSIS Adhesive" to qualitatively investigate the effect of mechanical pressure on the performance of the PSIS adhesive, as follows: Considering a PSIS adhesive adhered to solid substrate subject to a 90-degree tensile peeling, the measured interfacial toughness Γ_{in} is contributed by two parts:

$$\Gamma_{in} = \Gamma_0 + \Gamma_D \tag{S1}$$

where Γ_0 is the intrinsic work of adhesion Γ_0, which results from the scission of anchored polymer chains and is calculated by dividing the mechanical energy required for chain scission by the area of the undeformed crack surface, and Γ_{D} is the dissipation energy, which results from material deformation during crack propagation. In the process zone surrounding the crack path, the material undergoes a loading-unloading cycle that dissipates mechanical energy through bulk hysteresis, as described by the bulk dissipation model. For traditional tough hydrogel adhesive on solid substrate, Γ_{D} can be correlated with Γ_{in} via $\Gamma_{\mathrm{D}} \propto \Gamma_{in} h_m$, where h_m is maximum stress-stretch hysteresis ratio of the bulk PSIS under tensile loading. And combined this relationship to Eq. S1, we can get

$$\Gamma_{in} = \frac{\Gamma_0}{1-\chi h_m} \tag{S2}$$

where $0 \leq \chi \leq 1$ is a dimensionless number depending on the stretch-dependent hysteresis of the bulk PSIS. Based on the loading-unloading tensile test of PSIS adhesive, h_m and χ exhibit minimal changes due to mechanical pressure. Unlike traditional high-hysteresis toughening mechanisms, crack propagation in the polymer network of PSIS adhesive stretches the entangled chains surrounding the crack tip. This process distributes chain scissions across multiple adjacent layers, enhancing energy dissipation to retard the interfacial crack propagation. To account for near-crack dissipation caused by molecular entanglements inside polymer network, we introduce a dimensionless parameter $\beta \geq 1$ into Eq. S2. Additionally, unlike bulk hydrogel adhesive in substrate, the intrinsic fracture energy Γ_0 of PSIS adhesive is closely related to the surface adhesion ratio ϕ_s, which increases from 14% to 75% as the applied mechanical pressure p increases. By considering both the polymer network entanglements and the effect of mechanical pressure on surface adhesion, we derive a governing equation for the interfacial toughness enhancement of PSIS adhesive as

$$\Gamma_{in} = \frac{\beta \Gamma_0(p)}{1-\chi h_m} \tag{S3}$$

Response to Reviewer 2

General comment. The manuscript entitled "Pressure-sensitive In-situ Underwater Adhesives" by Liu et al introduces a pressure-sensitive in-situ underwater adhesive composed of superabsorbent particles infused with functional silane and hydrogel precursors. The superabsorbent particles, along with the applied mechanical pressure, synergistically create extensive contact areas between the particles themselves and between the particles and the substrates, thereby achieving both high fracture toughness and interfacial toughness. The manuscript is well-written, with clear logic, and provides valuable insights into creating high performance underwater adhesives. Therefore, I recommend its publication in Communications Physics.

Response to general comment. Thank you very much for acknowledging our efforts in the initial revision and for providing valuable suggestions to improve this work. We appreciate your revision comments, which further strengthen the paper. In the following sections, we address each comment point by point. The revised text in the manuscript is marked in red.

Comment 1. I believe the primary factor contributing to the enhancement of fracture toughness and interfacial toughness in this work is the increase in polymer volume fraction. The authors present quantitative data on surface adhesion ratio and the ratio of void volume to total volume for samples fabricated under different osmotic pressures. However, the manuscript lacks quantitative data correlating the void area or volume with the mechanical performance to clarify the critical role of the high polymer volume fraction in resisting crack propagation. Or to present the polymer volume fraction directly.

Response to comment 1: Thank you very much for the reviewer's insightful comment. As discussed in the working principal section, the PSIS particle leverages both mechanical and osmotic pressure to enhance particle-particle and particle-substrate interactions in underwater environments. While in this paper, we specifically focus on the influence of mechanical pressure on the surface adhesion ratio with the substrate, the material's porosity behavior, as well as the bulk and adhesive performance of the PSIS adhesive.

We agree with the author's view that the polymer volume fraction plays a significant role in resisting crack propagation, thereby improving the fracture toughness of the PSIS adhesive. To quantitatively investigate how the polymer fraction volume affects the mechanical properties of the PSIS adhesive, we conduct new pure shear tensile tests and fracture tests on the PSIS adhesive synthesized with various concentrations of acrylamide monomer. Specifically, we prepared solutions with 0.5 g, 1.5 g, 2.5 g, and 3.5 g of acrylamide monomer in 5 mL of saline solution, yielding water-to-monomer molar ratios w of 40, 13.3, 8.1, and 5.7, respectively. A higher water-to-monomer molar ratio (i.e., w = 40) in the hydrogel precursor leads to a lower polymer volume fraction in the adhesive, while a lower water-to-monomer molar ratio (i.e., w = 5.7) corresponds to a higher polymer volume fraction in the adhesive. We keep all other conditions, such as the crosslinker density, applied mechanical pressure, constant in the experiments.

As shown in **Fig. R2-1**, the stretchability, modulus, and toughness decrease significantly as the water-to-monomer ratio w increases, corresponding to a reduction in polymer volume fraction. The fracture toughness drops from 7 kJ/m^2 to 0.3 kJ/m^2 as w increases from 5.7 to 13.3. A lower water-to-monomer ratio in the hydrogel precursor not only increases the polymer volume fraction in the hydrogel but also leads to substantial molecular entanglements within the polymer networks.

These densely entangled polymer chains can collectively withstand mechanical stress, enhancing resistance to crack propagation and thereby improving fracture toughness.

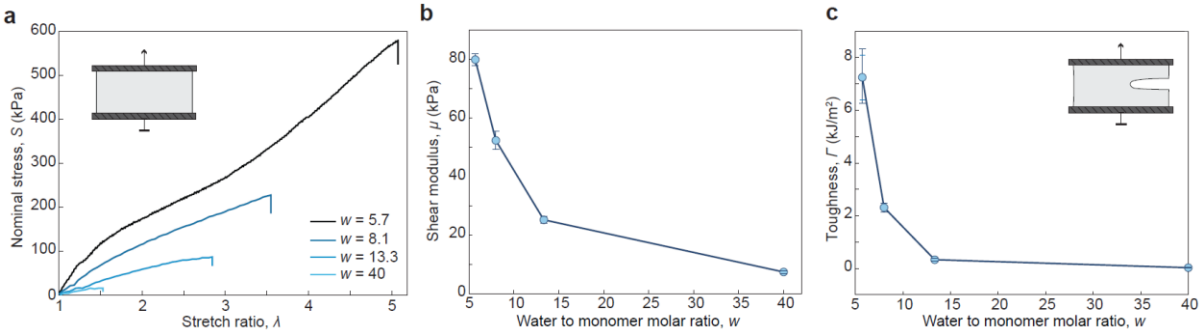

Fig. R2-1. Mechanical properties of PSIS adhesive synthesized with varying water-to-monomer ratio. (a) Stretch versus nominal stress in pure shear tensile test. **(b)** Shear modulus versus water-to-monomer ratio. **(c)** Fracture toughness versus water-to-monomer ratio.

Revision to comment 1: Following the reviewer's insightful comment, we add a discussion of the high concentration monomer contribute to the fracture toughness in Section "Bulk performance of the PSIS adhesive": "As summarized in **Fig. 3e** and **Fig. 3f**, with the increase in mechanical pressure, the critical stretch ratio is enhanced from 2.9 to 4.6, corresponding to a significantly improvement in fracture toughness from 1 kJ/m^2 to 7 kJ/m^2. The high fracture toughness achieved in the PSIS adhesive can be attributed to two factors: the molecular design within the PSIS particles and the structure alternation induced by the mechanical pressure. When we prepare the PSIS particles, a hydrogel precursor with a high monomer concentration (water-to-monomer ratio of 5.7) is used, resulting in a densely entangled long-chain polymer network within the adhesive. These long polymer chains collectively distribute the applied load by sliding through molecular entanglements without breaking, thereby enhancing crack propagation resistance and significantly improving the material's fracture toughness."

Response to Reviewer 3

General comment. Rapid and robust in-situ underwater adhesion is highly valuable for exploring and utilizing underwater resources. However, achieving fast and reliable adhesion in an aqueous environment remains a fundamental challenge due to a hydration layer, a film of water molecules that forms between the adhesive and the wet substrates. This paper develops a pressure-sensitive in-situ (PSIS) underwater adhesive featuring superabsorbent particles infused with functional silane and hydrogel precursors. When injected into an underwater crack, the PSIS adhesive quickly absorbs water, swells, and fills the crack. Mechanical pressure is applied to synergize with the particles' osmotic pressure to improve particle-particle and particle-substrate interactions, while heat is utilized to trigger the thermal polymerization of the hydrogel precursors. This process creates a porous adhesive via bulk polymerization and covalent bonding with the substrate via surface silanization. Moreover, the mechanical pressure significantly enhances the PSIS adhesive's stretchability (from 3 to 5), stiffness (from 37 kPa to 78 kPa), fracture toughness (from 1 kJ/m2 to 7 kJ/m2), and interfacial toughness with glass substrates (from 45 J/m2 to 270 J/m2), while reducing its hysteresis ratio. Despite PSIS's questionable utility in practice, this work provides a principle for rationally designing in-situ underwater adhesives and evokes mechanisms for enhancing toughness without relying on a large hysteresis ratio. Thus, this paper could be suitable for publication in Communications Physics after several issues listed below are appropriately addressed to meet the standards expected of journal papers.

Response to general comment. We sincerely appreciate your recognition of our efforts in the initial revision and for your insightful suggestions to enhance this work. Your revision comments have greatly contributed to strengthening the paper. In the sections below, we address each comment in detail. The revised text within the manuscript has been highlighted in red.

Comment 1. Some grammatical and presentation mistakes have been identified in the manuscript. The authors should double-check the documents, such as

"…The high osmotic pressure demonstrates that the PSIS adhesive have a large driving force for swelling..., while the driving force gradually decays as the adhesive absorb water, as manifested by...". (Page 4, The last sentence).

"…The peeling force exhibit large fluctuations due to the discontinuous connection at the adhesive area. As summarized in Fig. 4c, ...". (Page 9, The third sentence).

"…The corresponding hysteresis versus stretch ratios are summarized in Fig. 2c (should be Fig. 3c). As the stretch ratio increases, ...". (Page 7, The first sentence)

"…(e) The measured force divided by the initial width multiplied by thickness F/wt versus stretch ratio λ of the notch…" (Page 14, Graphical notes to Fig. 3)

Response to comment 1: Thank you very much for the reviewer's valuable comments. We have reviewed the manuscript, identified grammatical and presentation issues, and made the necessary revisions to address them.

Revision to comment 1: Following the reviewer's comment, we revised the last sentence in page 4 as "The sharp slope of the pressure Π versus time t curve at t = 0 ~ 20s of the PSIS particles with φ_v = 53% indicates a strong driving force for swelling. As the PSIS particles absorb water, the

slope of the curve gradually diminishes, suggesting a reduction in the driving force for swelling as water absorption progresses."

In response to the reviewer's 4th comment regarding the fluctuations in the peeling force, we find that the fluctuations in the peeling test are not solely caused by the discontinuous contact between adhesive substrates. They can also be attributed to other factors, including the degree of salination of the solid surface, stick-slip behavior caused by the intermittent energy dissipation in the adhesive layer. Therefore, we decided to remove the sentence "The peeling force exhibits large fluctuations due to the discontinuous connection at the adhesive area" from the manuscript.

Thank you very much to the reviewer for pointing out the inconsistency in the Figure number. We revised the first sentence in Page 7 as "The corresponding hysteresis versus stretch ratios are summarized in **Fig. 3c**. As the stretch ratio increases, the hysteresis consistently rises."

In response to the reviewer's comment, we have revised the caption of **Fig. 3e** to: "Nominal stress S versus stretch ratio λ of notched PSIS adhesive synthesized under different mechanical pressures P." The caption within the figure has also been updated accordingly.

Comment 2. The authors demonstrate the ability of PSIS to absorb water rapidly. However, in practical applications such as underwater environments, this character may cause PSIS to swell with water at the extruded or injected end and not effectively fill between the substrates. In addition, the authors titled it "Underwater Adhesives" and should have experimented with underwater bonding tests rather than just bonding with PSIS after water absorption. For example, the authors should place two substrates underwater, inject PSIS for bonding, and measure the bonding performance.

Response to comment 2: Thank you for the reviewer's insightful comment. To evaluate the practical application of our PSIS as an underwater adhesive, we newly built a customized experiment setup to demonstrate its performance in real settings. As illustrated in **Fig. R3-2(a)**, the setup consists of three main components: 1) a top glass slide with a 4 mm hole matching the nozzle diameter of the syringe for particle injection, 2) a middle acrylic sheet featuring multiple 0.05 mm diameter channels to facilitate the evacuation of water molecules during injection, and 3) a bottom glass slide. These three components form a cavity with dimensions of 25 mm × 15 mm

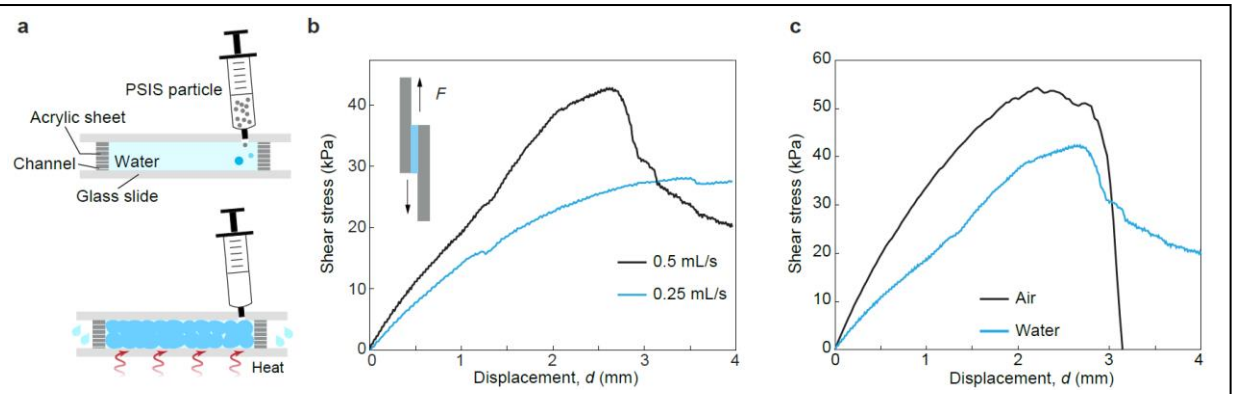

Fig. R3-2. Demonstration of our PSIS adhesive in real-world underwater environment. (a). Schematic illustration of the customized underwater adhesive apparatus. **(b)** Shear strength versus displacement d curves from lap shear experiments of PSIS adhesives cured underwater at different injection speeds. **(c)** Shear strength versus displacement d curves from lap shear experiments of PSIS adhesives cured in air and underwater.

× 3.2 mm, pre-filled with water to simulate real underwater environments. PSIS particles are injected into the cavity using a syringe at two injection rates, 0.5 mL/s and 0.25 mL/s, for an estimated total volume of 1 mL of particle suspension. After injection, heat is applied to cure the adhesive material within the cavity. Once cured, the acrylic sheet in the middle is removed, and lap shear experiments are conducted to test the adhesive strength of our PSIS adhesive.

As shown in **Fig. R3-2(b)**, the lap shear experiments show that an injection rate of 0.5 mL/s achieves a maximum force of 16 N, corresponding to an adhesive strength of 42.7 kPa. In contrast, an injection rate of 0.25 mL/s results in a maximum force of 10.5 N, yielding an adhesive strength of 28 kPa. During the injection process, the PSIS particles rapidly swell upon contact with water, filling the cavity space within the apparatus. This results in uneven adhesive and mechanical properties compared to adhesives formed under uniform mechanical pressure. Additionally, the swelling rate of the PSIS particles is affected by the injection rate, further impacting the final adhesive strength. In **Fig. R3-2(c)**, we compare the lap shear test results of a sample formed in air under a mechanical pressure of 10 kPa with a sample cured underwater formed at an injection rate of 0.5 mL/s. The adhesive strength of the underwater sample is slightly lower than that of the in-air sample, which is due to the swelling of PSIS particle by absorbing water and the uneven adhesive and mechanical performance in the underwater sample. This work primarily focuses on the design principles of the PSIS adhesive and the role of mechanical pressure in its material and adhesive properties. For future work, we plan to develop an advanced injection apparatus to achieve more efficient and uniform particle distribution, facilitating its application in real-world underwater environments.

Revision to comment 2: Thank you very much for the reviewer's comment regarding the practical application as an underwater adhesive. In this paper, we primarily focus on investigating the effects of mechanical pressure on the bulk and adhesive performance of PSIS adhesive. Accordingly, we added "To evaluate the practical application of our PSIS as an underwater adhesive, we build a customized experiment setup to demonstrate its performance in real settings. We compare the lap shear test results of a sample formed in air under a mechanical pressure of 10 kPa with a sample cured underwater formed at an injection rate of 0.5 mL/s. The adhesive strength of the underwater sample is slightly lower than that of the in-air sample, which is due to the swelling of PSIS particle by absorbing water molecules (**Fig. S12**, Supporting Information)." In the main text.

Additionally, we included the design of a customized apparatus and the corresponding experimental results in the supplementary information as a new section "customized underwater apparatus": "To evaluate the practical application of PSIS particles as underwater adhesives, we designed a customized experimental setup (**Fig. S12(a)**) that facilitates the injection of PSIS particles and their subsequent thermal gelation into adhesive material. The apparatus is constructed by three components: a top glass slide, a middle acrylic sheet with tiny channels for water leakage, and a bottom glass slide. The setup has a central cavity with dimensions of 25 mm × 15 mm × 3.2 mm, which is filled with water before particle injection. To assess the performance of PSIS particles as underwater adhesives, we conducted two experiments by injecting the particles into the cavity using a syringe at injection rates of 0.5 mL/s and 0.25 mL/s, for an estimated total volume of 1 mL of particles. After the injection, heat was applied to cure the adhesive material within the cavity. Following gelation, lap shear tests were performed to measure the adhesive strength of the formed material. As shown in **Fig. S12(b)**, the adhesive strength achieved at the higher injection rate of 0.5 mL/s was 42.7 kPa, compared to 28 kPa at the lower rate of 0.25 mL/s. Additionally, **Fig. S12(c)** compares the adhesive strength of a sample formed in air under 10 kPa

mechanical pressure to that of an underwater sample formed at an injection rate of 0.5 mL/s. The underwater sample exhibited slightly lower adhesive strength than the in-air sample. This difference is primarily attributed to the swelling of PSIS particles upon contact with water, leading to uneven cavity filling and adhesive distribution. This swelling behavior impacts the material's mechanical properties, particularly in comparison to adhesives formed under uniform mechanical pressure. In the future work, we aim to develop an advanced injection apparatus to achieve more efficient and uniform particle distribution, paving the way for the practical application of PSIS adhesives in real-world underwater environments."

Comment 3: Why choose a thermal initiator over a photoinitiator? In fact, in some application scenarios, such as bonding glass substrates, as shown by the authors, would it be more convenient to use UV? In addition, the 80 °C thermal initiation makes PSIS unsuitable for some low Tg polymer materials and hinders the underwater application of PSIS. Therefore, the authors need to supplement the bonding properties of PSIS with more heat-resistant or better thermally conductive substrates such as steel and Al.

Response to comment 3: Thank you very much for the reviewer's valuable suggestions. In this paper, we focus on the design strategy of PSIS particles, utilizing a thermal initiator (i.e., ammonium persulfate) to initiate the polymerization of the PSIS adhesive. We agree with the reviewer that UV initiation is an alternative for polymerizing the PSIS adhesive. However, the choice between thermal and UV initiation depends on the specific application requirements. For example, UV initiation is suitable for optically transparent substrates with low thermal conductivity, whereas thermal initiation is more appropriate for optically opaque substrates with high thermal conductivity.

To demonstrate the feasibility of fabricating PSIS using UV initiation, we prepared PSIS particles incorporating the photoinitiator lithium phenyl-2,4,6-trimethylbenzoylphosphinate (LAP). Specifically, we dissolved 3.5 g of AAm monomer in 5 mL of silane solution, followed by the addition of 150 μL of 0.1 wt% LAP solution and 7 μL of TEMED to prepare the pre-gel solution of PAAm-hydrogel. We fabricated the PSIS adhesive under varying mechanical pressures, including P = 1.3 kPa, 3.9 kPa, 6.5 kPa and 9.1 kPa, using the photo initiator LAP as a substitute

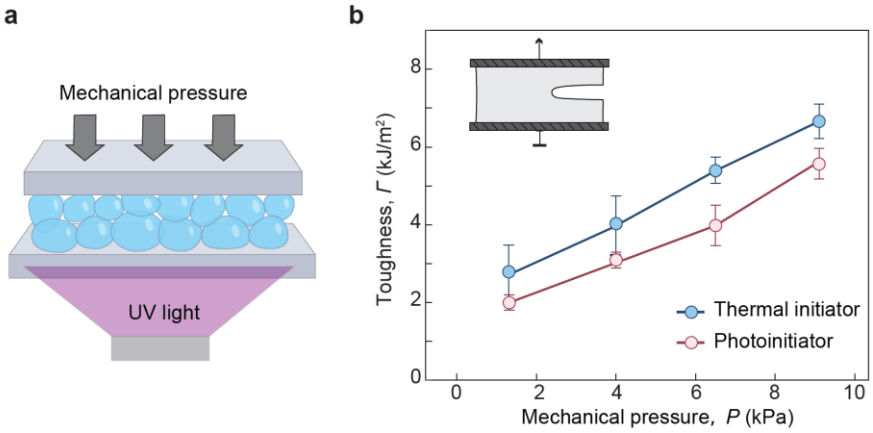

Fig. R3-3. Demonstration of fabricating PSIS adhesives using photoinitiator. (a) Schematic illustration of the setup for fabricating PSIS adhesives via photoinitiator. **(b)** Comparison of fracture toughness between PSIS adhesives via thermal initiator and photoinitiator under varying mechanical pressures.

for the thermal initiator APS. Polymerization of the PSIS adhesive was achieved using 400 nm UV light, as illustrated in **Fig. R3-3(a)**. As shown in **Fig. R3-3(b)**, the fracture toughness of the PSIS adhesive fabricated with the photoinitiator increases from 2 kJ/m^2 to 5 kJ/m^2 as the mechanical pressure increases from 1.3 kPa to 9.1 kPa. The performance is slightly lower than that of the PSIS adhesive fabricated using the thermal initiator, possibly due to the attenuation of UV light as it penetrates the substrate.

We also agree with the reviewer that thermal initiation can make the adhesion performance dependent on the thermal conduction of substrates. To examine the impact of thermal conduction of substrates, we fabricated PSIS adhesives between identical glass substrates of different thickness (i.e., 1.5 mm and 6 mm), using the same heat source (i.e., 80°C hot plate). The gelation time for the PSIS adhesive was approximately 3 minutes with the thin glass (i.e., 1.5 mm), but extended to about 10 minutes with the thick glass (i.e., 6 mm). This result indicates the thermal conduction of substrates affects the gelation time, which in turn affects the adhesion performance of the PSIS adhesive. The gelation time determines the duration available for the PSIS particles to expel water molecules in an underwater environment. These factors should be considered in real-world applications as future efforts.

We respectively disagree that the 80 °C thermal initiation renders PSIS unsuitable for polymer substrates with low glassy transition temperature T_g. A temperature of 80 °C is relatively moderate, and most polymers remain mechanically and thermally stable at this temperature. Thermal initiation becomes unsuitable for polymer substrates only if the gelation temperature exceeds the polymer's melting temperature, which is typically around 200 °C. Additionally, the fabrication of PSIS adhesive via thermal initiation can be performed at temperatures lower than 80 °C, which extends the gelation time and influences the adhesion performance of the PSIS adhesive.

Revision to comment 3: Thank you very much for the reviewer's comment regarding the use of the photoinitiator. In response to the reviewer's comment, in the Section of "Bulk performance of the PSIS adhesive", we add sentences to discuss using photoinitiator instead of thermal initiator as follows: "We also test the feasibility of fabricating PSIS adhesive using UV initiation. The fracture toughness of the PSIS adhesive fabricated with the photoinitiator increases from 2 kJ/m^2 to 5 kJ/m^2 as the mechanical pressure increases from 1.3 kPa to 9.1 kPa (**Fig. S7**, Supporting Information). The choice between thermal and UV initiation depends on the specific application requirements. For example, UV initiation is suitable for optically transparent substrates with low thermal conductivity, whereas thermal initiation is more appropriate for optically opaque substrates with high thermal conductivity."

In addition, we have added detailed information on the preparation of the pre-gel solution with the photoinitiator in section "Synthesis of the PSIS Particles" in the Supplementary Information as follows: "To prepare the pre-gel solution with thermal initiator, we dissolved 3.5 g of AAm monomer in 5 mL of the silane solution followed by addition of 170 µL of 0.1M APS solution and 7 µL of TEMED to prepare the pre-gel solution of PAAm-hydrogel. To prepare the pre-gel solution with photoinitiator, dissolved 3.5 g of AAm monomer in 5 mL of silane solution, followed by the addition of 150 µL of 0.1 wt% LAP solution and 7 µL of TEMED." Furthermore, we add **Fig. R3-3** as **Fig. S7** to Supporting Information.

Comment 4: The authors considered the large fluctuations of the peeling force due to the discontinuous connection at the adhesive area. However, Fig. 2e indicated that applied pressure significantly increases the adhesive area. Moreover, the surface adhesive ratio (φ_s), defined as the ratio of the adhesive area to the total area, increases from 14% to 75% as mechanical pressure increases (Fig. 2f). Even though the bonding area has increased 2 times as the author states, it seems that the bonding continuity does not improve with the increase in bonding area (Fig. 4b, nearly equal amplitude of all force/width-displacement curves)?

Response to comment 4: Thank you very much for reviewer's comment. We agree with the reviewer that the large fluctuations in the peeling force are not solely caused by the discontinuous connection at the adhesive area. They can be attributed to various factors, including the degree of salination of the solid surface, stick-slip behavior caused by the intermittent energy dissipation in the adhesive layer (Gandur, et al, *Journal of Adhesion Science and Technology*, 11, 11-28, 1997), nonlinear behavior of the adhesive, and measurement errors (Dalbe, et al, *Soft Matter* **12**, 4537-4548, 2016). All these factors collectively contribute to the fluctuation in the peeling force.

Revision to comment 4: Since the fluctuations in the peeling force are caused by multiple factors, we have removed the statement "The peeling force exhibits large fluctuations due to the discontinuous connection at the adhesive area" in the adhesive performance section.

Comment 5: It can be observed that the toughness and the shear modulus of PSIS decrease dramatically as the φ_w increases (Fig. 3h and 3i). However, the difference in bonding strength between PSIS of various φ_w was not remarkable. Even the PSIS's bonding strength and interfacial toughness of 40% φ_w was greater than 10% φ_w of PSIS (Fig. 4f). The authors proposed that the reason lies in the balance between the adhesion strength and the cohesion strength, and the cohesion strength of PSIS with different φ_w was tested. Therefore, the authors should add tests (like Fig. S2) of the surface adhesive ratio (φ_s) of PSIS with different φ_w to illustrate the change in the adhesion strength.

Response to comment 5: Thank you for the reviewer's insightful observations. In response to the reviewer's suggestion, we conducted additional tests to measure the surface adhesive ratio φ_s of

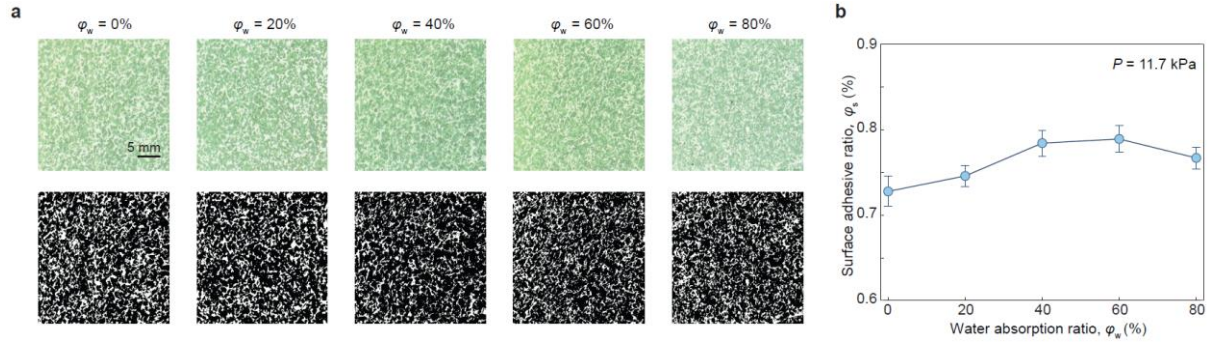

Fig. R3-5. Measurements of surface adhesion ratio of PSIS adhesive with different water absorption ratios. (a) Measured raw images (top) and corresponding processed images (bottom) of contact area between glass substrates and PSIS adhesive with different water absorption ratios under controlled mechanical pressure P = 11.7 kPa. **(b)** Measured surface adhesive ratio φ_s versus water absorption ratio φ_w of PSIS adhesives under controlled mechanical pressure P = 11.7 kPa.

PSIS with different water absorption ratio φ_w values (φ_w = 0%, 20%, 40%, 60%, 80%) at same mechanical pressure P = 11.7 kPa. The results are shown in **Fig. R3-5**.

As the water absorption ratio increases, the contact area between the glass slides and the PSIS adhesive is influenced by two factors: the modulus and size of the particles. As illustrated in **Fig. R3-5**, the contact area initially increases and then slightly decreases as the water absorption ratio increases. This behavior can be explained as follows: 1) Increase in contact area due to softening of PSIS particles. When the PSIS particles absorb water, they become softer, which enhances their ability to deform under mechanical pressure, thereby increasing the contact area; 2) Reduction in contact area due to expansion of PSIS particles. With excessive water absorption, such as at φ_w = 80%, the particles expand significantly, leading to larger cavities between adjacent particles, which ultimately causes a slight reduction in the contact area.

Revision to comment 5: Thank you for the reviewer's comment. We have added **Fig. R3-5** as Supplementary Figure **Fig. S11**, which illustrates the contact area between the glass slides and the PSIS adhesive at different water absorption ratios φ_w values. Furthermore, we add sentence "Since the intrinsic work of adhesion is correlated with the contact area between the adhesive and the substrate, we conducted experiments to measure the surface adhesion ratio ϕ_s under the same mechanical pressure (i.e. P = 11.7 kPa) but with different water absorption ratios ϕ_w, as shown in **Fig. S11**. As the water absorption ratio increases, the contact area between the glass slides and the PSIS adhesive exhibit a non-monotonic trend, which initially increases and then slightly decreases. This occurs because, as the PSIS particles absorb water, they have a stronger driving force to interact with the substrate and become softer, resulting in enhanced contact under mechanical pressure. However, when the particles absorb excessive water, such as at $\phi_w = 80\%$, their size increases significantly, creating larger cavities between them, leading to a slight reduction in the contact area. For PSIS adhesives with a low water absorption ratio, inadequate contact with the substrate results in low adhesive strength, despite the material having high toughness. This combination leads to adhesive failure" in the "Adhesive performance of PSIS adhesive" section in the manuscript.

Comment 6: How stable is PSIS in a water environment?

Response to comment 6: Thank you for the reviewer's question. While the PSIS adhesive does experience property degeneration due to swelling, this effect is mitigated when the PSIS adhesive is contrained by solid substrates, ensuring stable performance. To assess the stability of the PSIS adhesive in a water environment, we conducted two swelling experiments: 1) free swelling of the PSIS adhesive in water, and 2) confined swelling of the PSIS adhesive placed between two glass substrates in water for varying durations. During these two experiments, we recorded the weight of PSIS adhesive over time. Following the swelling experiments, we performed pure shear tensile tests and fracture tests to measure the modulus and toughness of the PSIS adhesive. As shown in **Fig. R3-6 (a)**, the adhesive swells rapidly when freely submerged in water, resulting in a significant decrease in both modulus and toughness within a short period. In contrast, when confined between two glass slides, the PSIS adhesive exhibits minimal water absorption, leading to only a slight reduction in modulus and toughness. These properties stabilize, reaching a plateau after approximately 20 minutes. In our next follow-up work, we will optimize the composition of the PSIS adhesive, including the polymer fraction, crosslinker density, and superabsorbent particle fraction, to further minimize swelling in aqueous environments. Additionally, we will focus on

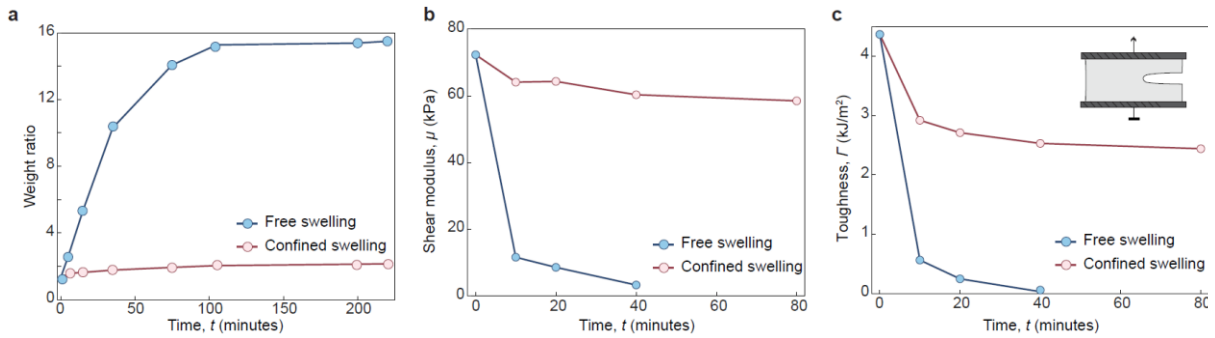

Fig. R3-6. Stability characterizations of PSIS adhesive in an aqueous environment. (a) Weight ratio versus time t of PSIS adhesives under free and confined swelling. **(b)** Shear modulus μ versus time t of PSIS adhesives under free and confined swelling. **(c)** Fracture toughness Γ versus time t of PSIS adhesives under free and confined swelling.

enhancing key material properties, including fracture toughness, interfacial fracture toughness, and adhesive strength with solid surfaces.

Revision to comment 6: In response to the reviewer's suggestion, we provided a brief discussion on the stability of our PSIS adhesive in aqueous environments in the main text "In practical applications, PSIS particles will be rapidly injected into a confined space, leading to the absorption of a limited amount of water rather than free swelling, thus preserving good mechanical performance (**Fig. S8**, Supporting Information).". In addition, we incorporated **Fig. R3-6** as Supplementary Figure **Fig. S8**, which characterizes the stability of PSIS adhesives under free and confined swellings.

Response to style and formatting guidance (Manuscript ID: COMMSPHYS-24-1082A)
"Pressure-sensitive In-situ Underwater Adhesives"

Format 1: Abstract should be 150 words or fewer. Acronyms should be avoided wherever possible.

Revision to Comment 1: Following the instructions, we remove the acronym in the second sentence. In addition, we remove the last sentence to ensure abstract less than 150 words.

Format 2: Mathematical terms should conform to the following guidelines.

Revision to Comment 2: Following the guidance of mathematical terms, we revised all mathematic terms in the manuscript and supplementary notes, such as "the surface adhesion ratio φ_s", "between intensity frequency f_{in} versus intensity I.", and "the critical stretch λ_c".

Format 3: Unit dimensions should be expressed using negative integers (e.g. kg m-1 s-2, not kg/ms2) or the word 'per'.

Revision to Comment 3: Following the guidance of dimensions, we revised dimensions in the manuscript, such as "corresponding to a significant improvement in fracture toughness from 1 kJ m^{-2} to 7 kJ m^{-2}", "the fracture toughness of the PSIS with φ_w = 20% improves significantly from 50 J m^{-2} to 4 kJ m^{-2} as the mechanical pressure increases.", and "at a peeling rate of 0.5 mm s^{-1}".

Format 4: Figures and supplementary figures should be cited in a consistent format throughout the manuscript, and in line with the labels used in the Manuscript and Supplementary Information.

Revision to Comment 4: We revised all the figure label to "Figure X" and supplementary figures label to "Supplementary Figure SX", such as "**Figure 4e** presents the curves of peeling force per unit width versus the peeling displacement of adhesive materials formed with various water absorption ratio."

Format 5: Acronyms should be defined upon first use.

Revision to Comment 5: Following this instruction, we revised the caption of Figure 1 as "Heat is applied for the thermal curing of the polyacrylamide (PAAm) polymer", the caption of Figure 2 as "φ_v is the volume ratio between the PSIS particles and the container.", and the caption of Figure 3 as "V_p represents the volume of PSIS particles, V_w represents the volume of interfacial water, and φ_w represents the water absorption ratio."

We change the symbol for particle diameter from d to a in the manuscript and supplementary to avoid confusion with displacement d used in Figure 4. The manuscript is revised as "The swelling ratio in diameter a/a_0 versus time t is plotted in **Figure 2c**, where a represents the average particle diameter and a_0 is the initial average diameter. The average diameter a is determined by calculating the square root of particle area captured in the focal plane.". The caption in Figure 2 is revised as "The swelling ratio in diameter a/a_0 of individual PSIS particles versus time. a represents the average diameter of particles anda_0 is the initial average diameter of particles.".

Format 6: The Methods and Supplementary Methods must together include sufficient detail such that the work could be reproduced. The methods section should not contain excessive use of phrases such as “as described previously”.

Revision to Comment 6: We add a section named “Methods”, including three sections named “Materials”, “Synthesis of the PSIS particles” and “Synthesis of the PSIS adhesive”. Additional experimental details are provided in the Supplementary Notes.The “Methods” section in the manuscript is shown as follows:

Materials. Unless otherwise specified, the chemicals used in this work were used without further purification. The granular sodium polyacrylate homopolymers (Superabsorbent Polymer, Waste Lock 770) were purchased from M2 Polymer Technologies. Acrylamide (AAm, Sigma-Aldrich A8887), ammonium persulfate (APS, Sigma-Aldrich A3678), N,N,N’,N’-tetramethylethylenediamine (TEMED, Sigma-Aldrich T9281), acetic acid (Sigma-Aldrich A6283), 3-(trimethoxysilyl)propyl methacrylate (TMSPMA; Sigma-Aldrich 440159) used in this work were purchased from Sigma-Aldrich. The plain microscope slides for 90-degree peeling tests and contact area measurement used in this work were purchased from Corning.

Synthesis of the PSIS particles. To synthesize the PSIS particles, we first prepared the silane solution for surface silanization. The silane solution was prepared by magnetic stirring (500 rpm) a mixture of 200 mL deionized water, 30 μL acetic acid, and 800 μL TMSPMA for 5 hours until the mixture became transparent. For the long-chain polyacrylamide (PAAm) polymer network, acrylamide (AAm) was used as the monomer, TMSPMA in the silane solution served as the crosslinker, ammonium persulfate (APS) as the thermal initiator, and TEMED as the crosslinking accelerator. To prepare the pre-gel solution, we dissolved 3.5 g of AAm monomer in 5 mL of the silane solution followed by the addition of 170 μL of 0.1M APS solution and 7 μL of TEMED to prepare the pre-gel solution of PAAm-hydrogel. The mixture was vortexed for 1 minute. Then, we added 1.5 g of granular superabsorbent particles into the pre-gel solution and vortexed for 1 minute until it evenly absorbed the AAm pre-gel solution. The PSIS particles were stored in a 5°C refrigerator before use.

Synthesis of the PSIS adhesive. To synthesize PSIS adhesive with varying amounts of interfacial water (1 mL to 10 mL) for mechanical tests, we first added varying amounts of deionized water into a poly bag (75 mm × 50 mm), followed by 10 g of PSIS particles. The poly bag was then sealed using its zip closure, and the particles were left inside the bag for 10 seconds to allow the particles to absorb the water. For each sample, we used a needle with a diameter of 0.7 mm to create approximately 100 holes evenly on the surface of each bag. These holes were used to expel excess air when applying mechanical pressure. Subsequently, we placed each sample on a hotplate at 80°C and used a universal testing machine (CellScale Testing Machine) to apply compression forces of 5N, 15N, 25N, 35N, and 45N evenly on them, respectively, for 10 minutes until thermal curing.