Supplementary Materials for

Pressure-sensitive In-situ Underwater Adhesion

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Supplementary Methods

Materials

Acrylamide (AAm, Sigma-Aldrich A8887), ammonium persulfate (APS, Sigma-Aldrich A3678), Lithium phenyl-2,4,6-trimethylbenzoylphosphinate (LAP, Sigma-Aldrich 900889), N,N,N',N'-tetramethylethylenediamine (TEMED, Sigma-Aldrich T9281), acetic acid (Sigma-Aldrich A6283), 3-(trimethoxysilyl)propyl methacrylate (TMSPMA; Sigma-Aldrich 440159), fluorescein sodium salt (Fluorescent tracer, Sigma-Aldrich F6377) used in this work were purchased from Sigma-Aldrich and used without modification. The granular sodium polyacrylate homopolymers (Superabsorbent Polymer, Waste Lock 770) were purchased from M^2 Polymer Technologies. The acrylic sheets (8560K191, 8560K171) for mechanical testing of materials and the nylon film (8539K194) used as stiff backing for the 90-degree peeling test were purchased from McMaster-Carr. The plain microscope slides (75 mm x 38 mm x 1 mm) for peeling tests and contact area measurement used in this work were purchased from Corning. The red dye, green dye, poly bags (75 mm x 50 mm), microscope glass slides (75 mm x 25 mm) for microscopic measurements, and cover glass (50 mm x 22 mm) for confocal microscopic tests were purchased from Amazon.

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 was used as the monomer, TMSPMA in the silane solution served as the crosslinker, ammonium persulfate as the thermal initiator, and TEMED as the crosslinking accelerator. 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 the 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, 3.5 g of AAm monomer was dissolved in 5 mL of silane solution, followed by the addition of 150 μL of 0.1 wt% LAP solution and 7 μL of TEMED. For the contact area measurement and 90-degree peeling test, 50 μL of red or green dye solution was added to the mixture, while for the porosity measurements, 3 mg of fluorescent tracer was added to the mixture. 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 without interfacial water for mechanical tests and porosity measurements, we added 10 g PSIS particles into a poly bag and sealed it with its zip-type closure. To synthesize PSIS adhesive with varying amounts of interfacial water (1 mL to 10 mL) for mechanical tests, we first added different amounts of deionized water into the poly bag, then added 10 g of PSIS particles, and waited 10 seconds until the paste absorbed the water. Then, we sealed the poly bag with its zip closure. To synthesize samples for contact area measurements and peeling tests, we added one piece of the microscope slide into each poly bag, then added varying amounts of interfacial water and PSIS particles to the bag, as described previously. 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.

Osmotic pressure test and swelling test for PSIS particles

To measure the osmotic pressure of PSIS particles, we added varying masses of PSIS particles (2.4 g, 4.2 g, 6.4 g, 10.6 g) into a dry container with a diameter of 60 mm and a height of 15 mm. The dry container was covered with a porous cover (diameter is 61 mm) with approximately 100 holes (diameter is 1 mm). The container was then placed into a 500 mL beaker. Subsequently, we poured 200 mL of deionized water into the beaker and recorded the force needed to keep the cover in position using a tensile machine for about 5 minutes until the force reached a plateau.

To measure the swelling ratio and swelling speed of a single PSIS particle, we placed individual particles on a microscope slide and observed them using an Amscope T670 microscope with a 4X objective lens. For each particle, we added 500 μL of deionized water and recorded the size change over a period of 70 s (Supplementary **Figure S1**). Due to the differences in light absorption and reflection between water and the particles, we could observe the clear edges of the particles during its swelling. For the recorded images at each second, we first calculated the area of the particles and then determined the average diameter by taking the square root of the area. The swelling ratio in diameter was calculated by dividing the average diameter at each second by the average diameter at the initial time.

Contact area and porosity measurement

To measure the contact area between the substrate and PSIS adhesive, the sample with red dye was placed on a black background (Supplementary **Figure S2**). A white LED panel (color temperature 4000 K) and a camera (Nikon D800) were positioned in front of the measured sample. We adjusted the angle between the LED and the camera until the glass slides without adhesive appeared white color, while the areas with adhesive appeared red color. Next, we used image processing tools to distinguish the adhesive area from the non-adhesive area. We calculated the surface adhesive ratio by dividing the adhesive area by the total area.

To measure the porosity of the PSIS adhesive, we used a confocal laser scanning microscope (Spectral-based Olympus FluoView) with a 4X magnification objective and a 488 nm laser (10 mW) (Supplementary **Figure S3**). The porous PSIS adhesive, which was mixed with the fluorescent tracer, was positioned on the microscope stage and scanned with 0.1% laser power in the z direction at 5 μm intervals from bottom to top, covering a total distance of 200 μm. The scan area was 3600 μm x 2700 μm. Next, we counted the number of pixels with an intensity less than 0.2 and an intensity higher than 0.2 separately. We then calculated the porosity by dividing the number with intensity less than 0.2 to the total number of pixels.

Mechanical test for PSIS adhesive

All tests were conducted in ambient air at room temperature. For the uniaxial tensile test and hysteresis measurement, the samples were cut into a dog-bone-shaped with the size of 10 mm in width and 20 mm in length. For the fracture toughness test, the samples were cut into a rectangular shape with 30 mm in width, 10 mm in length. The grippers of the samples at the top and bottom were made of acrylic board. The grippers were glued with the samples using Krazy glue and the mechanical tests were performed by a universal testing machine.

To get the stress-stretch relationship of samples, the dog-bone-shaped samples were subjected to uniaxial loading monotonically until fracture. To measure the hysteresis values at different stretch

ratios, the dog-bone-shaped samples were subjected to cyclic loading-unloading tensile tests with increasing stretch ratios. To measure the fracture toughness of the sample, firstly, the rectangular unnotched sample was stretched monotonically until fracture with the force and displacement recorded. Then, a notched sample with same dimensions was monotonically loaded till critical stretch ratio λ_c. The fracture energy was calculated using equation $G = H\int_1^{\lambda c} S d\lambda$, where H is the height of original sample, S and λ is the normal stress and the stretch ratio in the pure shear test with the unnotched sample.

90-degree peeling test for interfacial toughness measurement

All tests were conducted in ambient air at room temperature. The interfacial toughness of the PSIS adhesive with the glass substrate was measured using a universal testing machine and a 90-degree peeling stage. We used a frictionless rolling wheel to construct the peeling stage, ensuring a 90-degree angle between the stage and the gripper during the peeling process. All porous PSIS adhesive samples were prepared with a width of 20 mm and a length of 45 mm. A nylon film served as a stiff backing in the peeling test and was adhered to the PSIS adhesive using superglue. All peeling tests were performed at a constant peeling speed of 0.5 mm/s. The interfacial toughness was determined by dividing the average peeling force, after the force reached a plateau, by the width of the porous material.

Customized underwater apparatus

To evaluate the practical application of PSIS particles as underwater adhesives, we designed a customized experimental setup (Supplementary **Figure S12a**) 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^{-1} and 0.25 mL s^{-1}, 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 Supplementary **Figure S12b**, the adhesive strength achieved at the higher injection rate of 0.5 mL s^{-1} was 42.7 kPa, compared to 28 kPa at the lower rate of 0.25 mL s^{-1}. Additionally, Supplementary **Figure S12c** 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^{-1}. 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.

Supplementary Note 1

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:

$$\Gamma_{\mathrm{in}} = \Gamma_0 + \Gamma_{\mathrm{D}} \tag{S1}$$

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 $\Gamma_{\mathrm{D}} \propto \Gamma_{\mathrm{in}} h_{\mathrm{m}}$, where h_m is maximum stress-stretch hysteresis ratio of the bulk PSIS under tensile loading. And combined this relationship to Supplementary **Equation S1**, we can get

$$\Gamma_{\mathrm{in}} = \frac{\Gamma_0}{1-\chi h_{\mathrm{m}}} \tag{S2}$$

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 Supplementary **Equation 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

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

Supplementary Figures

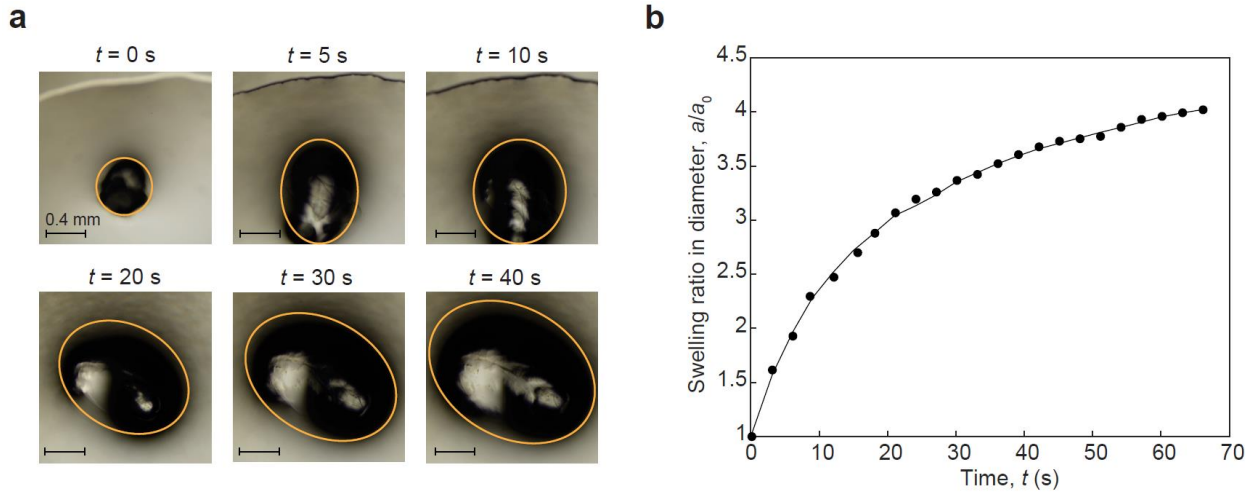

Figure S1. Swelling characterization of an individual PSIS particle. (a) Microscopic images of an individual PSIS particle during the swelling process in deionized water. The scale bars are 0.4 mm. **(b)** Swelling ratio in diameter of the PSIS particle. a represents the average diameter during swelling while a_0 represents the initial average diameter of the PSIS particle.

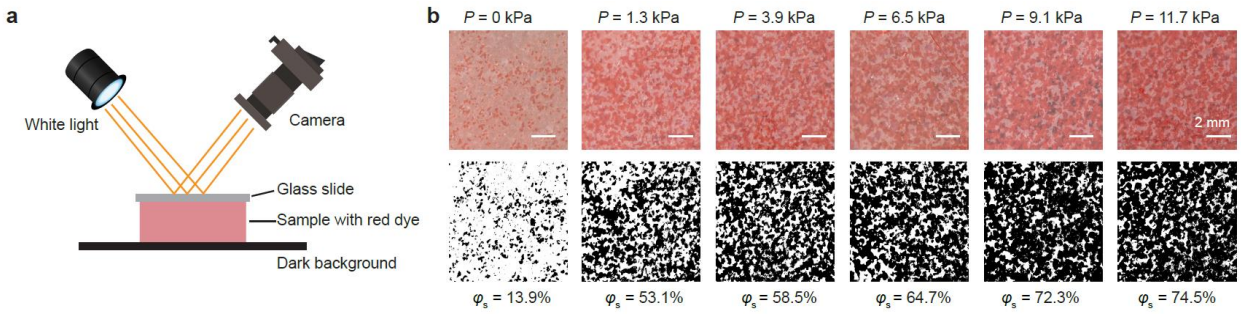

Figure S2. The contact area between glass slides and the PSIS adhesive. (a) The schematic illustrates the experimental setup for measuring the contact area. **(b)** The upper images show adhesive material in contact with glass slides, and the lower images display the processed results, where the black represents the adhesive area, and the white represents the void area. *P* represents the mechanical pressure, and ϕ_s represents the surface adhesive ratio, defined as the ratio of the back area to the total area. Scale bars are 2 mm.

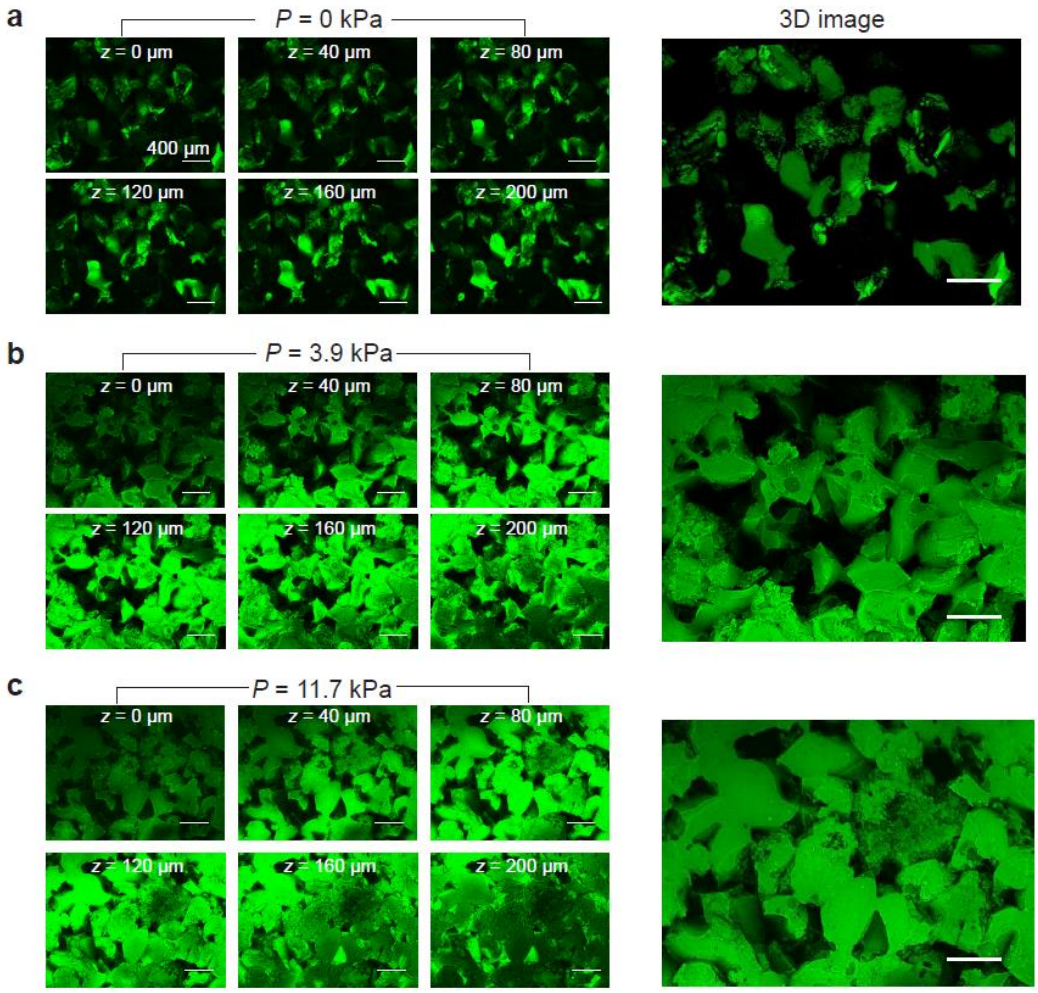

Figure S3. Confocal images of the PSIS adhesive at different focal depths and its corresponding 3D image. (a) The PSIS adhesive formed with mechanical pressure P = 0 kPa. **(b)** The PSIS adhesive formed with mechanical pressure P = 3.9 kPa. **(c)** The PSIS adhesive formed with mechanical pressure P = 11.7 kPa. Scale bars in (a-c) are 400 μm.

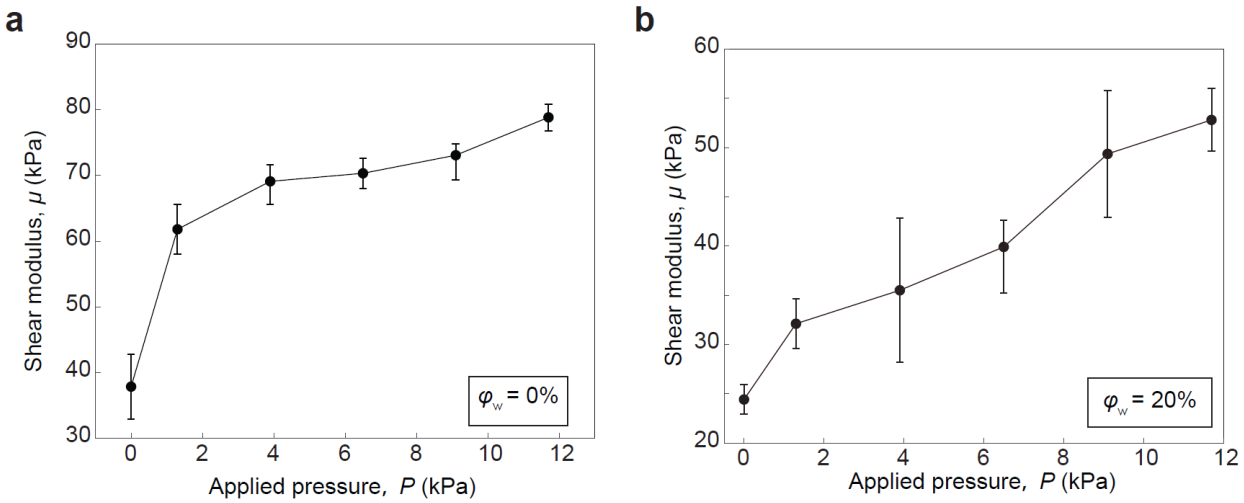

Figure S4. Shear modulus of the PSIS adhesive formed at different mechanical pressures. (a) Without absorbing interfacial water ϕ_w = 0%. **(b)** With absorbing water ratio ϕ_w = 20%.

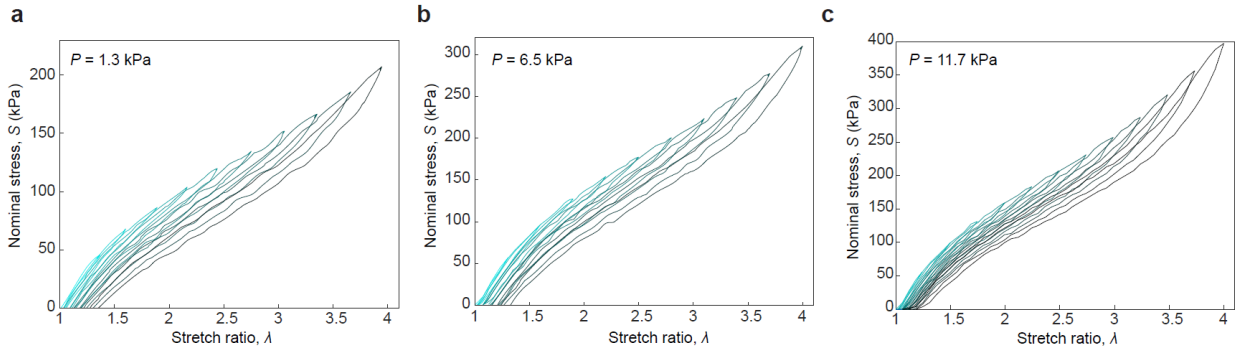

Figure S5. Cyclic loading of nominal stress versus various stretch ratios. (a) The PSIS adhesive formed with pressure P = 1.3 kPa. **(b)** The PSIS adhesive formed with pressure P = 6.5 kPa. **(c)** The PSIS adhesive formed with pressure P = 11.7 kPa.

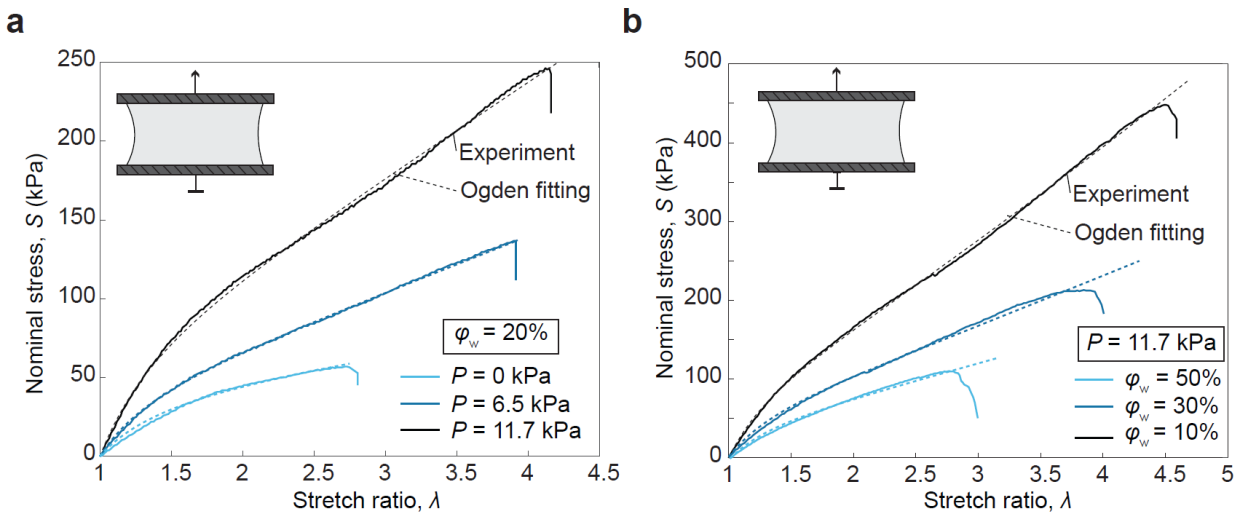

Figure S6. Nominal stress *S* versus stretch ratio λ of the PSIS adhesives under pure shear tensile loading. (a) The PSIS adhesive formed with water absorption ratio ϕ_w = 20% under various mechanical pressures *P*. **(b)** The PSIS adhesive formed with *P* = 11.7 kPa with various water absorption ratios.

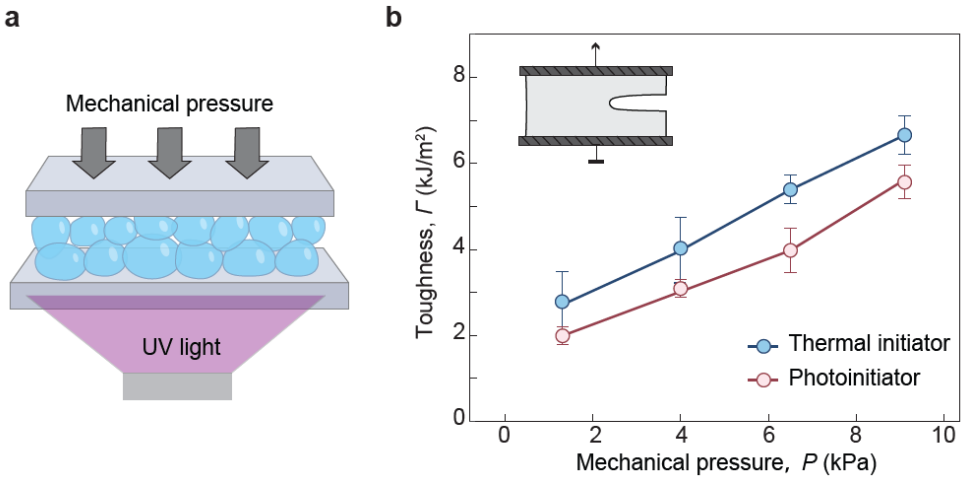

Figure S7. Demonstration of fabricating PSIS adhesives using photoinitiator. (a) Schematic illustration of the setup for fabricating PSIS adhesives via photoinitiator. **(b)** Comparison of fracture toughness between PSIS adhesives via thermal initiator and photoinitiator under varying mechanical pressures.

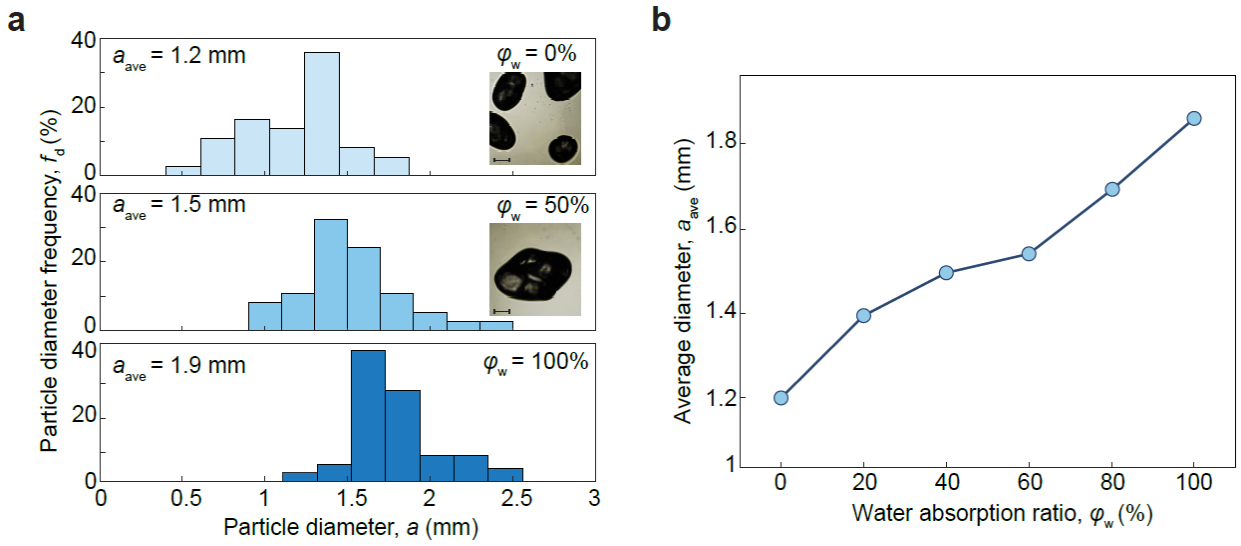

Figure S8. Particle diameter of PSIS particles after absorbing different amounts of water. (a) Histogram of particle diameter of the PSIS particles before and after water absorption. Scale bar is 0.3 mm. **(b)** The average diameter of particles versus water absorption ratio ϕ_w.

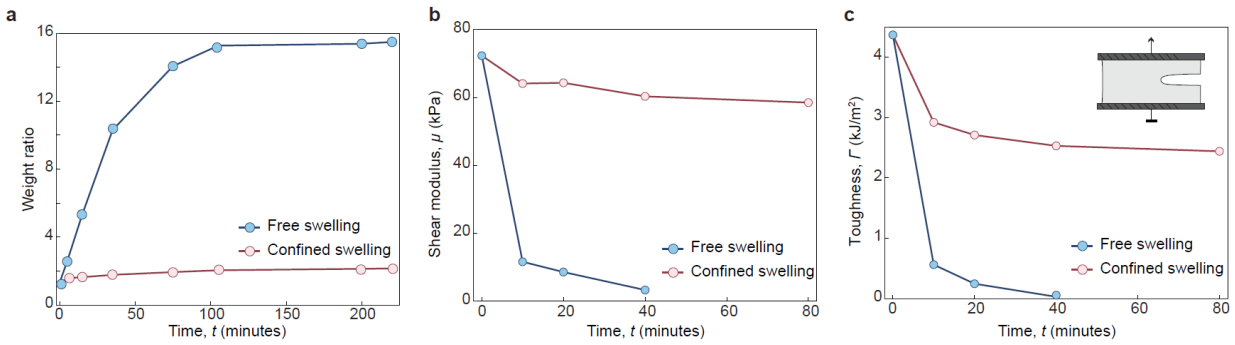

Figure S9. Stability characterizations of PSIS adhesive in an aqueous environment. (a) Weight ratio versus time t of PSIS adhesives under free and confined swelling. **(b)** Shear modulus μ versus time t of PSIS adhesives under free and confined swelling. **(c)** Fracture toughness Γ versus time t of PSIS adhesives under free and confined swelling.

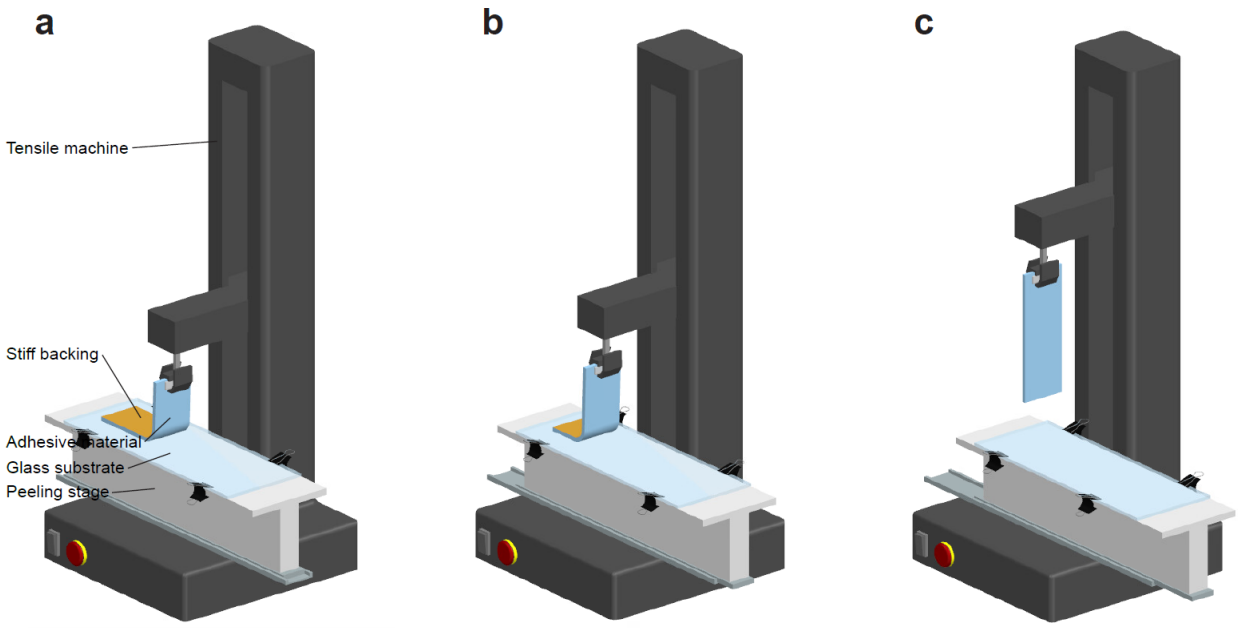

Figure S10. Schematic illustration of the 90-degree peeling experiment. (a) Steady state. **(b)** Crack propagation. **(c)** End of peeling.

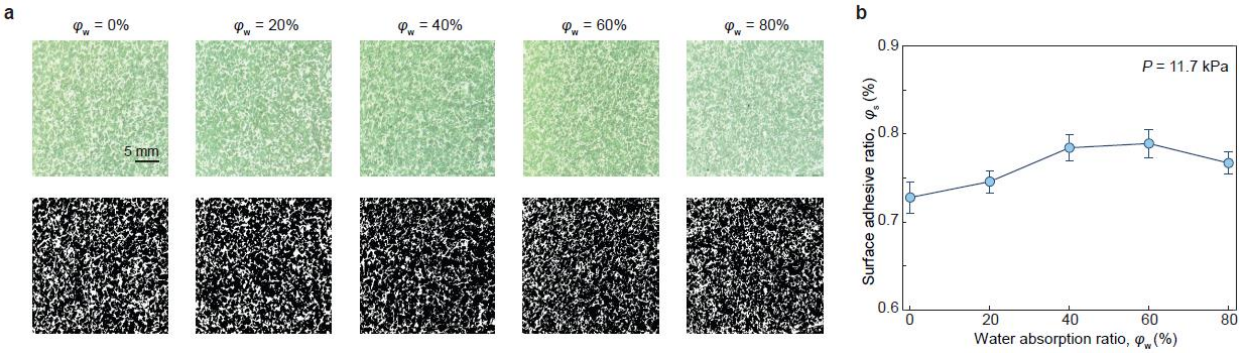

Figure S11. Measurements of surface adhesion ratio of PSIS adhesive with different water absorption ratios. (a) Measured raw images (top) and corresponding processed images (bottom) of the contact area between glass substrates and PSIS adhesive with different water absorption ratios under controlled 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.

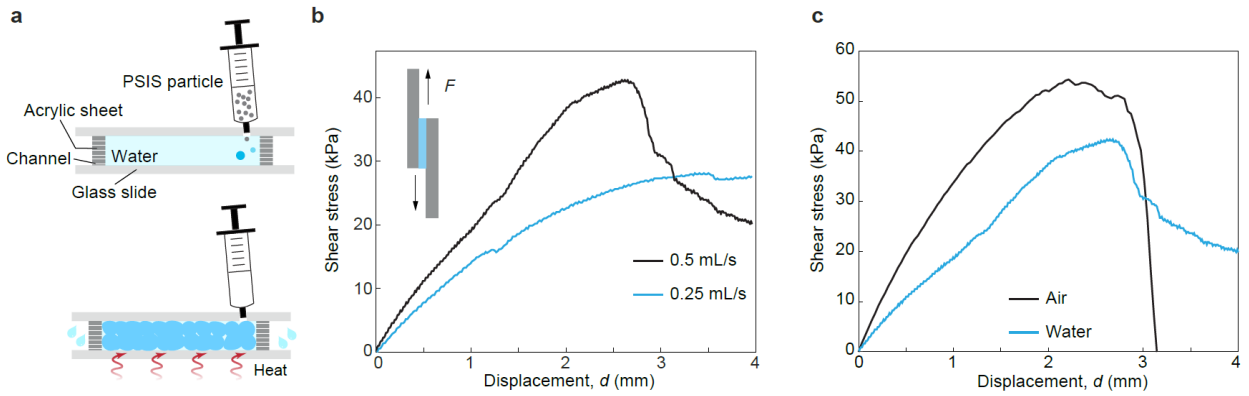

Figure S12. Demonstration of our PSIS adhesive in the real-world underwater environment. (a). Schematic illustration of the customized underwater adhesive apparatus. **(b)** Shear strength versus displacement *d* curves from lap shear experiments of PSIS adhesives cured underwater at different injection speeds. **(c)** Shear strength versus displacement *d* curves from lap shear experiments of PSIS adhesives cured in air and underwater.