Supporting Information

Hydrogel Networks as Underwater Contact Adhesives for Diverse Surfaces

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Part 1. Materials

Monomer acrylamide (AM, chemical pure) and initiator ammonium peroxydisulfate (APS, analytically pure) were purchased from Sinopharm Chemical Reagent Co., crosslinker Ltd. 99% Pure N,N'-methylene acrylamide(MBA) were obtained from Energy Chemical. Ye'elimite was from sulfoaluminate cement (SAC).

Part 2. Methods

2.1 Preparation of the nanocomposite adhesives

Monomer AM and crosslinker MBA were first dissolved in two thirds of water, and the remaining water was used for dissolving initiator APS. Then dropwisely added APS solution into the solution containing AM and MBA. The mass ratio between AM and MBA and APS and water was 1: 0.0035: 0.375: 3.75. The consequent solution was mixed with SAC and manually stirred for 1.5 min at room temperature. Then the nanocomposite adhesives was ready to be applied under water. Since the solidification of the system happens within 8 minutes, the paste needs to be applied as fast as possible. Here we intentionally use excessive amount of APS to: a) ensure the complete polymerization of AM and b) accelerate the polymerization of hydrogel so that a sufficient viscidity of the adhesives can be achieved when applying under water, instead of spreading out.

2.2 Isothermal calorimetry

TAM Air 8-channel isothermal microcalorimeter was used to measure the heat evolution of pure hydrogel, ye'elimite paste and nanocomposite adhesives at 20 °C. The heat release was measured by comparison between an active (sample) and an inert (water) cell, both equipped with heat flow sensors. "Admix ampoule" with a strring motor and two syringes was used for heat release measurement inside the calorimeter. All the materials were stored inside the calorimeter for at least 24 h before test. Specifically, solid powders stored in the bottom of ampoule and APS solution and solution containing AM and MBA stored in two syringes respectively. These two solutions were first injected into the ampoule to initiate the measurement, and then all the materials were mixed by the stirring motor for 1 min.

2.3 Measurement of lap shear adhesion strength

The obtained slurry was carried by a plastic syringe and applied onto the adherent substrates directly under water with the amount of around 1 ml. Substrates made of materials of interest were first washed by DI water and ethanol, followed by oven drying. Then stored the substrates under DI water until bonded. Substrates made of Ceramic, aluminum, plastic (PPTE), and wood were tested, all of which have the same dimension, 1.0 cm * 5.0 cm with the thickness of 1 mm. Following ASTM F2255-05,

the overlap area has the dimension of 0.5 * 1.0 cm. Special care was taken to prevent the bonding outside of the overlap area. A force with approximately 1 N was applied to the bond area until each test. Adhesion strengths were determined using the tensile mode of a texture analyzer, TA-XT2i (Stable Micro System Ltd.), equipped with a 2000 N load cell. The crosshead speed was set to 5 mm/min to obtain the load-displacement curves. The adhesion strength of each specimen, in megapascals (Pa = N mm-2), was determined by dividing the peak load (N) of each load-displacement curve by and adhesion area (m2). For each type of material, at least 5 specimens were tested. The adhesion strength of each material was obtained by averaging all the replicates.

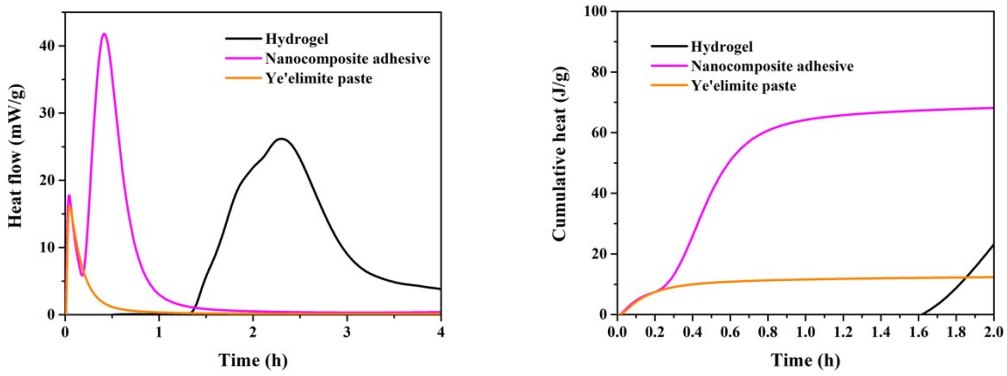
2.4 XPS measurement on the chemical interaction between ye'elimite paste and hydrogel

XPS data were collected with Thermo ESCALAB 250XI spectrometer using a monochromatic Al-Ka (1486.6 eV) X-ray source at power of 72 W. High-resolution spectra of the N1s regions were acquired with analyzer having pass energies of 20 eV. Step energies of 1 eV were used for survey spectra. The X-ray beam was focused on an area with a diameter of less than 0.5 mm.

2.5 FTIR spectra of nanocomposite adhesives

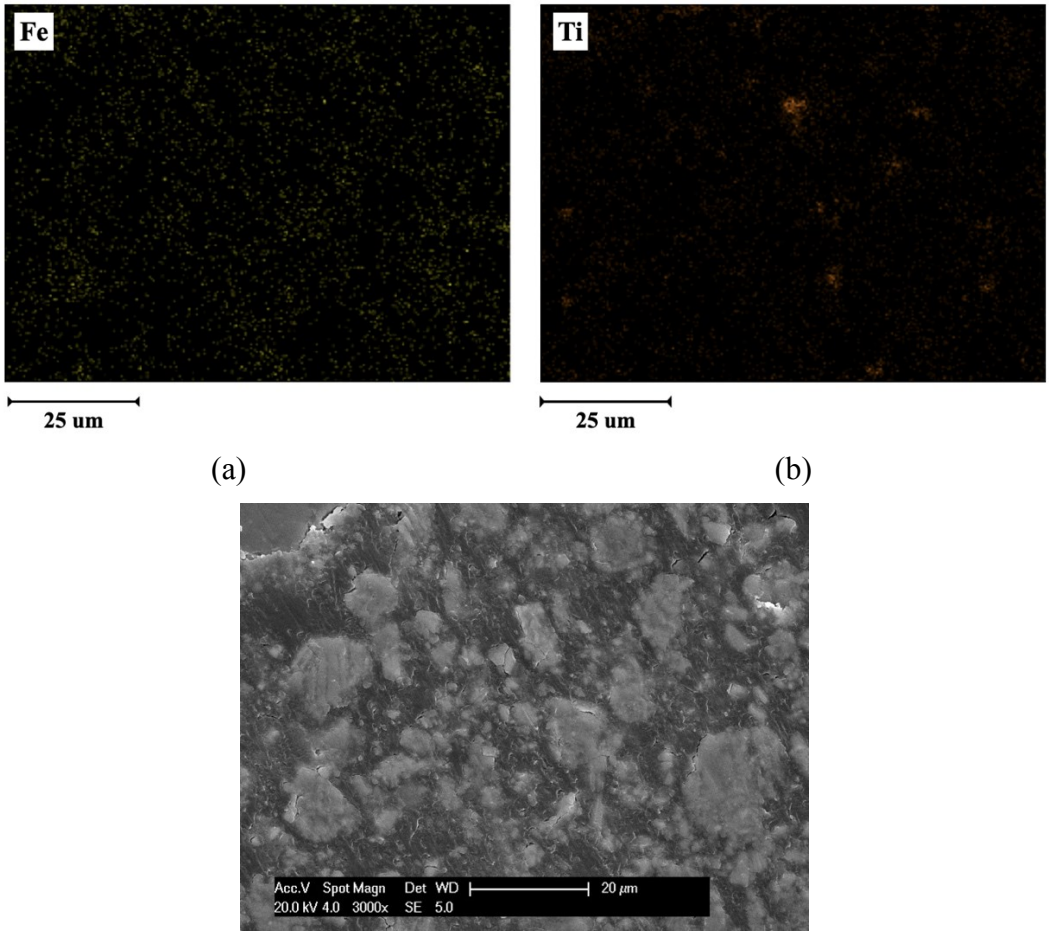
Fourier transform infrared spectroscopy (FT-IR) spectra were recorded on a Bruker Equinox 55 spectrometer with the resolution 2 cm-1 by making pellets with KBr. The nanocomposite adhesives after hydrating 1d and 2d were first immersed in ethanol to stop hydration, and then were dried in an oven at 40 ℃ till constant mass. Anhydrate SAC cement samples were directly dried in the oven till being measured.

Part 3. Figures



(a) (b)

Fig. S1 (a) Heat evolution and (b) cumulative heat of pure hydrogel, Ye'elimite paste, and nanocomposite adhesive during hydration.



(a) (b)

(c)

Fig.S2 X-ray element maps of (a) Fe and (b) Ti in Ye'elimite; (c) the SEM image of Ye'elimite.

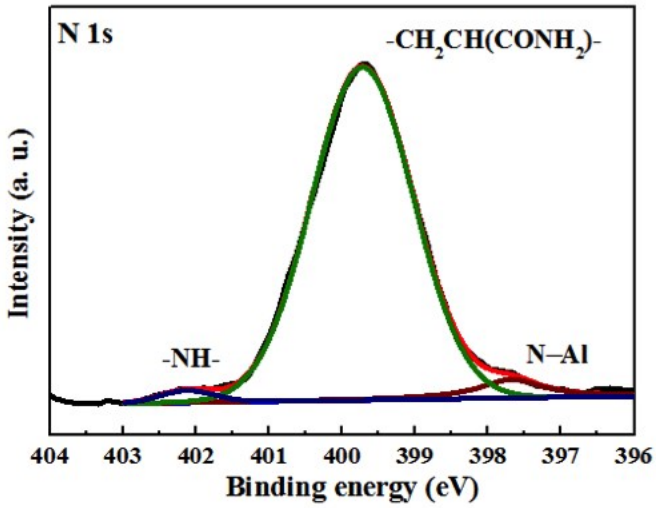


Fig. S3 XPS measurement of nanocomposite adhesives, indicating the chemical interaction between aluminum contained crystals and hydrogel.

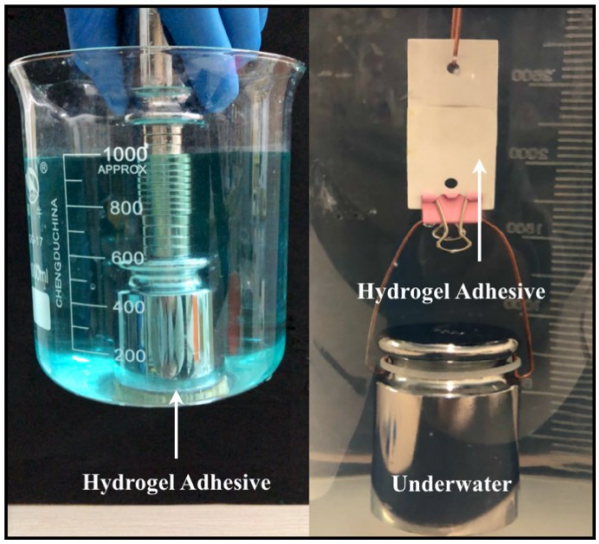


Fig. S4 Holding power of hydrogel-based adhesives underwater (a) the adhesives were applied at the bottom of a beaker, were able to lift 1000g of water plus the beaker; (b) the adhesives were applied on a small overlap area of two ceramic substrates, were able to lift one weight of 500g in water.

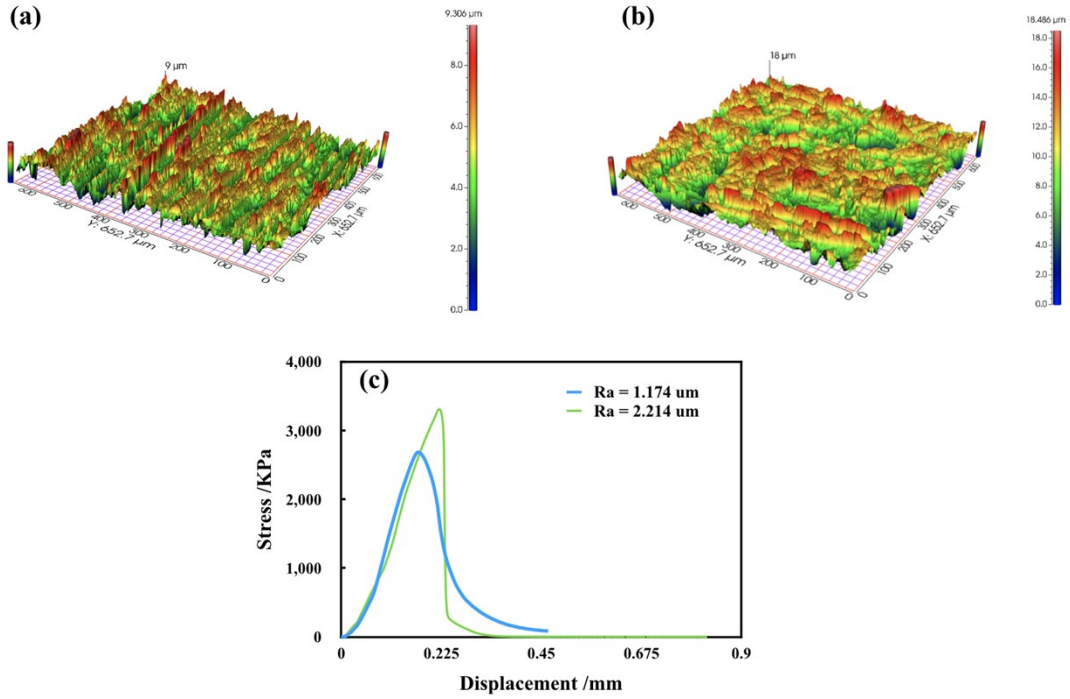


Fig S5. The 3D surface of samples with (a) Ra = $1.174 \pm 0.363\ \mu m$ and (b) Ra = $2.214 \pm 0.643\ \mu m$ measured by a nano 3D surface profilometer (CHOTEST SuperView W1). (c) Stress-displacement curves of nanocomposite adhesives on these substrates with different roughness.

Part 4. Tables

Table S1 Adhesion strength of nanocomposite adhesives on diverse substrates

Substrates	Adhesion strength (MPa)
Aluminum	3.012 ± 0.290
Ceramic	3.713 ± 0.218
Glass	1.182 ± 0.052
PTFE	0.280 ± 0.006
Wood	1.195 ± 0.151

Table S2 Underwater bonding of hydrogel adhesives compared to other systems reported in literatures.

Adhesives	Substrate	Strength (MPa)	Ref.
This work	Metal	3.012	
Biomimetic polymer	Metal	3.000	1
Biomimetic adhesives	Metal	0.762	2
Multiphase adhesive coacervates	Metal	0.973	3
This work	Ceramic	3.713	

Bioadhesive	Ceramic	0.880	4
Bioadhesive	Ceramic	0.110	4
This work	Glass	1.182	
Tough hydrogel	Glass	0.013	5
Ionically cross-linked poly(allylamine)	Glass	0.337	6
This work	Polymer	0.292	
Biomimetic polymer	Polymer	0.300	1
Ionically cross-linked poly(allylamine)	Polymer	0.361	6
Mineral-enhanced hydrogel	Polymer	0.005	7
Remote control underwater adhesives	Polymer	0.009	8
This work	Wood	1.194	
Biomimetic polymer	Wood	0.200	1
Mineral-enhanced hydrogel	Wood	0.097	7

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