

Water-insensitive Self-adhesive Elastomers Derived from Hydrophobic Deep Eutectic Polymers

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Experimental Section

Materials

1-Naphthol (Nap, AR,99%), L-menthol (Men, 99%), ethylene glycol phenyl ether acrylate (EGPEA, 90%), diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide (TPO, 97%), 1,3-diisopropenylbenzene (97%), benzyl acrylate (97%), benzyl methacrylate (98%), 2,2,2-trifluoroethyl methacrylate (98%) and n-Butyl acrylate (AR, 99%) were purchased from Shanghai Macklin Biochemical Co., Ltd and used as received.

Preparation of the hydrophobic DESs

The preparation of hydrophobic DESs was by mixing two solid components at a molar ratio of 1:2. Typically, 2.88g of 1-Nap and 6.25g of Men was heated and stirred at 80°C in Blue Cap Bottles until a homogenous colorless solution was formed. The prepared DESs were then kept in a vacuum desiccator for further use.

Preparation of the prepolymer solution

Monomers with different mole ratios and photoinitiator TPO (0.1 mol% to monomer) were added to the as-prepared 1-Nap/Men DES and stirred until clear and transparent mixture was formed. The prepared prepolymer solution was then kept in a vacuum desiccator for further use.

Preparation of hydrophobic deep eutectic polymer (HDEP)

The 1-Nap/Men/EGPEA DES-based prepolymer solution was injected into a mold from two glass plates and a silica gel pad. Then, the reactions were initiated by a UV light source (RW-UVA-Φ200U, Shenzhen Runwing Company, China) with a dominant wavelength of 365 nm for 5 min. The light intensity was 20 mW·cm⁻² measured by a UV radiometer (type UV-A, Photoelectric Instrument Factory, Beijing Normal University).

Characterization

Differential scanning calorimeter (DSC) was employed a 214 polyme NETZSCH tester. The mixture was placed into aluminum pans and heated at $10\text{ }^{\circ}\text{C min}^{-1}$ from -80 to $80\text{ }^{\circ}\text{C}$ under a nitrogen atmosphere. Fourier transform infrared (FTIR) spectra were recorded on a Bruker Vertex 33 spectrometer. Temperature-dependent FTIR spectra were recorded on a Magna 360 (Nicolet) with a resolution of 4 cm^{-1} . The heating rate was $5^{\circ}/\text{min}$. ^1H NMR spectra (400 MHz) were tested using a Bruker spectrometer AVANCE III HD 400. Chloroform was used as an external reference.

The lap-shear test was conducted using a tensile machine (INSTRON 5565, 100N load cell) with a rate of 10 mm/min. The shear strength is determined as the maximum force per unit area. For 180° peeling-off tests, the HDEP film was fixed on the testing machine (INSTRON 5565, 100N load cell). The initial adhesion area was fixed at $10 \times 2\text{ cm}^2$. Before testing, a 2 cm length was prepeeled from the substrate and clamped to the testing machine. The peel rate was set to 10 mm/min. The thickness of the test samples is ~ 0.1 mm.

The tensile testing was performed using a tensile machine (INSTRON 5565, 100 N load cell). The strain rate was set to 10 mm/min. The samples were cut into $50\text{ mm} \times 10\text{ mm} \times 0.1\text{ mm}$. Visual images were taken by a Canon EOS 60D camera. The testing conditions were at room temperature 25°C , and the relative humidity was 50%.

Molecular Dynamics Simulation :

The partial charge of EGPEA, 1-Naphthol and Menthol molecules were calculated using Gaussian 16 code^[1] and the 6-31+g(d,p) basis functions were applied^[2]. The OPLSS-AA force field^[3] and MKTOP ^[4]were used to parametrize all atoms, such as the bond parameters, angle parameters and the dihedral angles, and so on.

Firstly, the simulation model under the vacuum system was build. Details were as follows. We set the monomer ratio of EGPEA/1-Naphthol/Menthol

molecules to 2:1:2 and 40 1-Naphthol molecules, 80 Menthol molecules and 80 EGPEA molecules were randomly inserted into a cube box with a side length of 6.5 nm. And then, filled the simulation box under the vacuum with 259 water molecules in order to construct the model under the water system. The model of water molecule is TIP3P ^[14].

The molecular dynamics (MD) simulations were performed in the GROMACS 2019 software package ^[5-9] and the simulation time is 20 ns. The steepest descent method was applied to minimize the initial energy for each system with a force tolerance of 1 kJ/(mol⁻¹ nm⁻¹) and a maximum step size of 0.002 ps before MD calculations^[10]. In all the three directions, periodic boundary conditions were imposed. Leapfrog algorithm was used to integrate the Newtonian equation of motion ^[10]. The MD simulation was calculated in NPT ensemble, the pressure was maintained at 1 bar by the Berendsen barostat in an isotropic manner ^[11] and the temperature was maintained by the V-rescale thermostat at 298.15 K. The LINCS algorithm ^[12] was performed for constrain bond lengths of hydrogen atoms. The Particle-Mesh-Ewald (PME) with a fourth-order interpolation was used to evaluate the electrostatic interactions and the grid spacing is 1.0 Å ^[13], whereas a cutoff of 1.0 Å was employed to calculate the short-range van der Waals interactions. Based on the MD simulations, the intermolecular interaction and number of hydrogen bonding in this polymer materials were calculated.

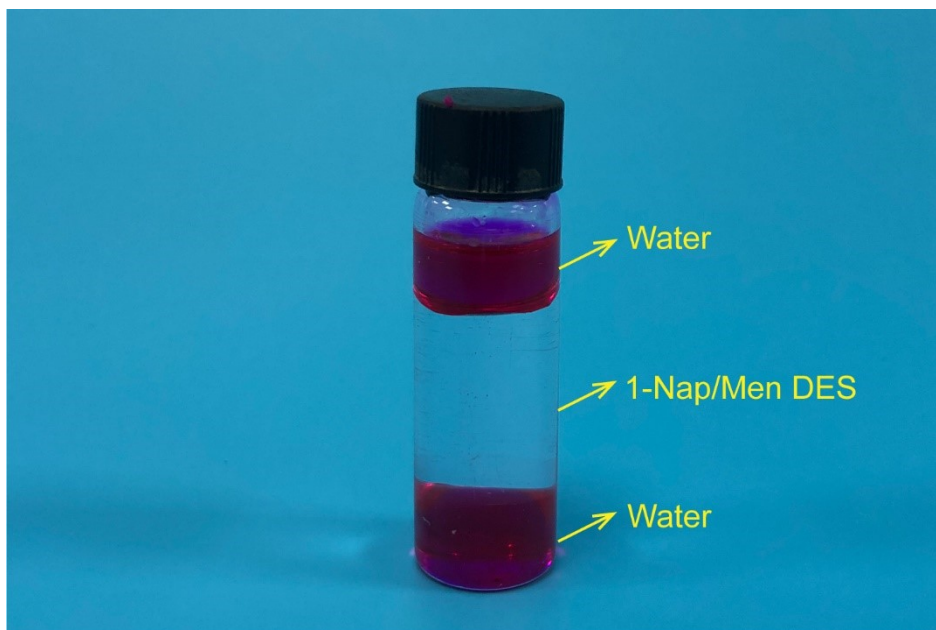


Figure S1. Optical photograph of 1-Nap/Men DES mixed with water, showing a clear phase separation interface.

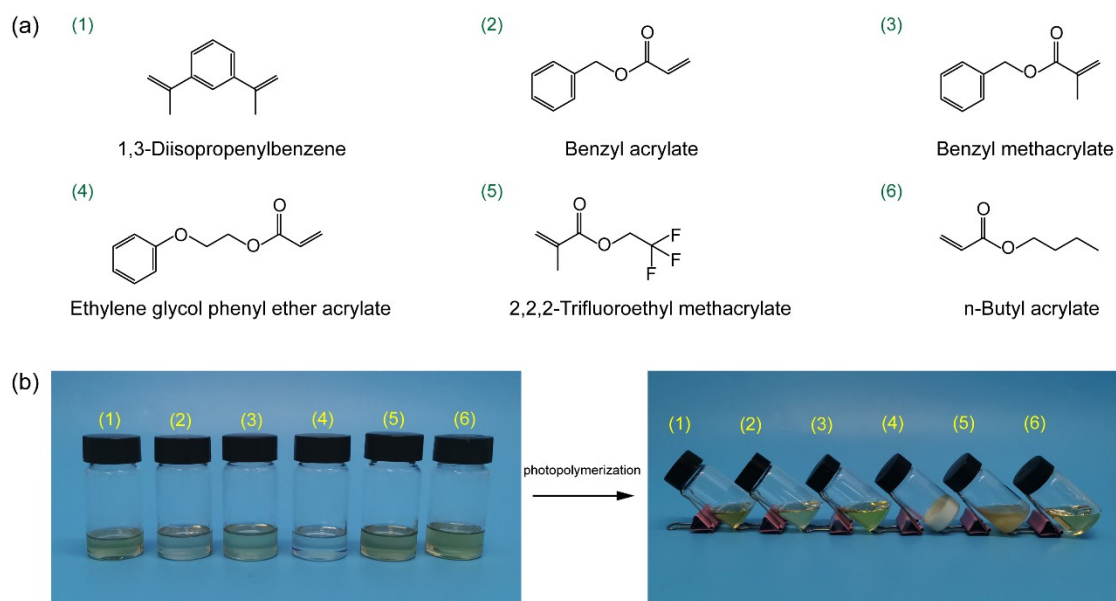


Figure S2. (a) The different types of monomers selected in the experiment. (b) Variation of different types of monomers after UV radiation for 5min in 1-Nap/Men DES.

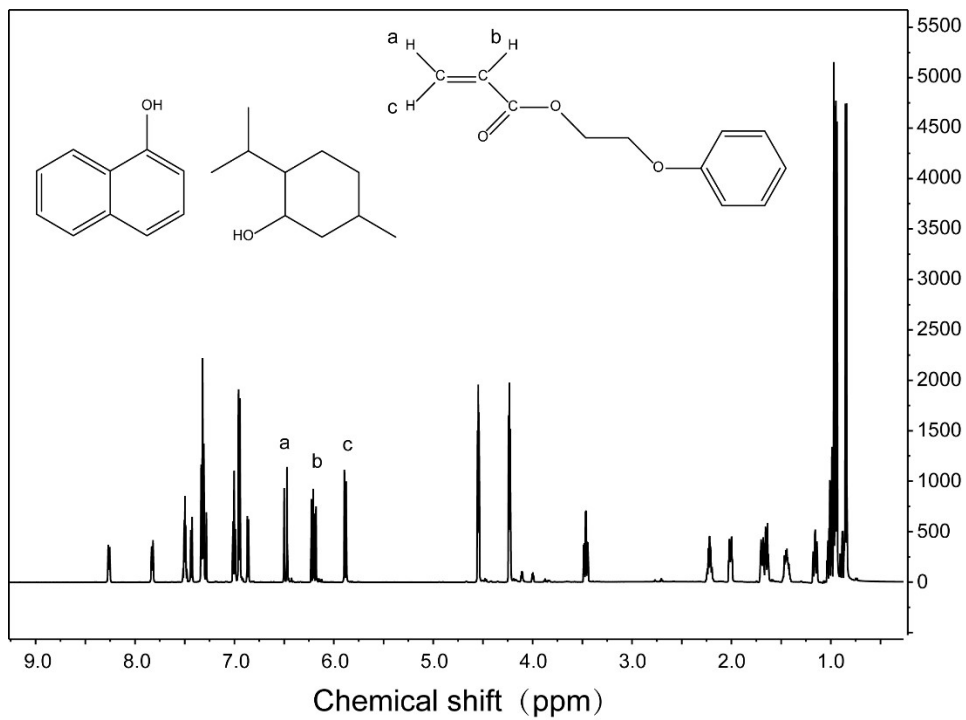


Figure S3. ^1H NMR spectra of 1-Nap/Men/EGPEA DES.

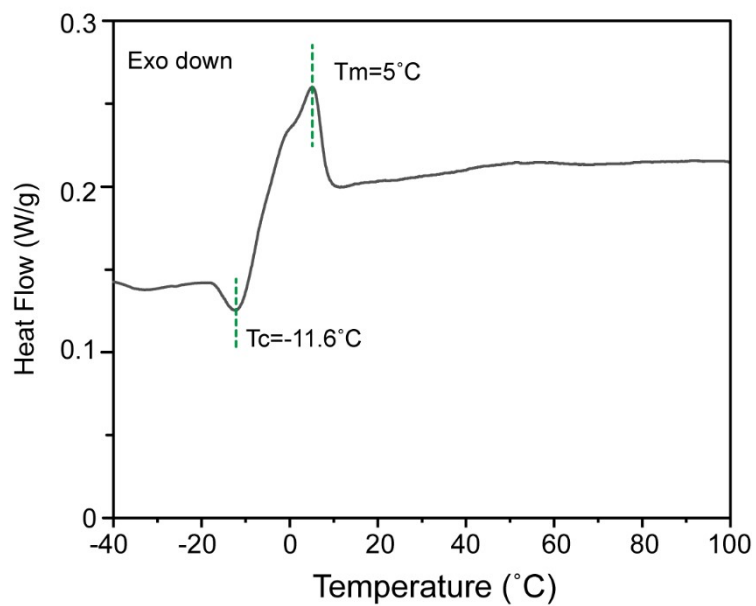


Figure S4. DSC trace of 1-Nap/Men/EGPEA DES (scan rate was $10^{\circ}\text{C min}^{-1}$).

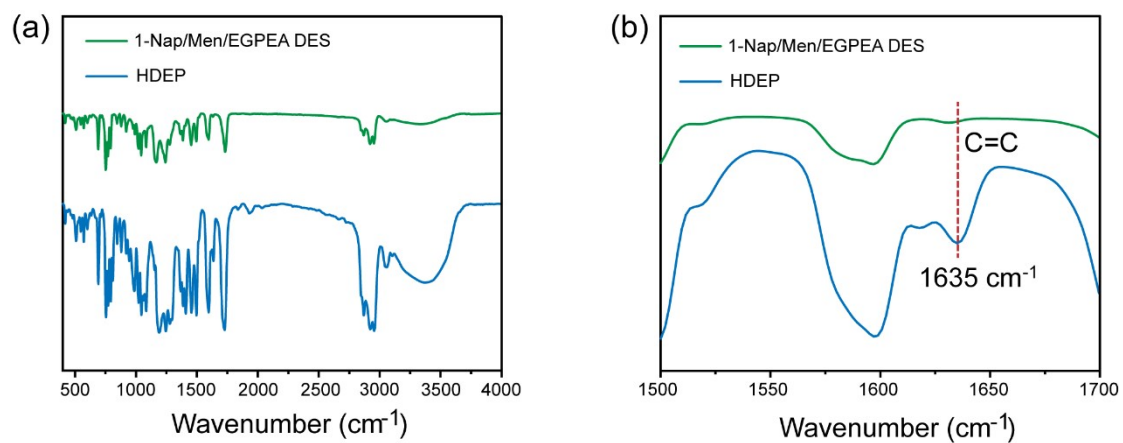


Figure S5. (a-b) FTIR spectra of 1-Nap/Men/EGPEA DES before and after photopolymerization.

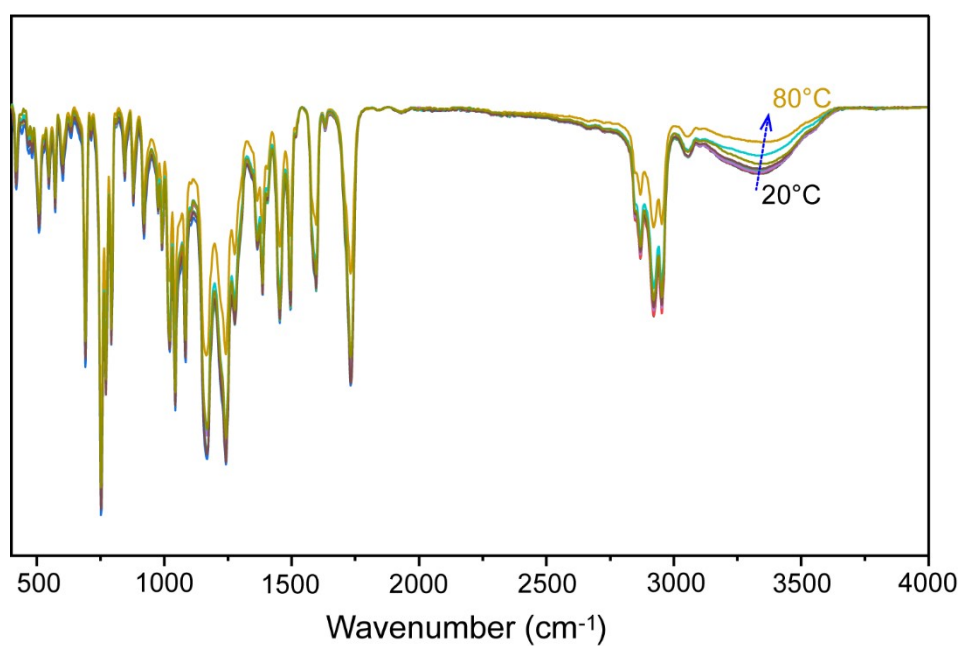


Figure S6. Temperature-dependent Fourier transform infrared (FTIR) spectrum of HDEP heating from 20°C to 80 °C.



Figure S7. HDEPs exhibit rapid response characteristics when exposed to dichloromethane solvent, i.e., a change from opaque to transparent state.



Figure S8. Optical photograph of HDEPs adhering to the surface of a nitrile glove and following the motion of the finger.

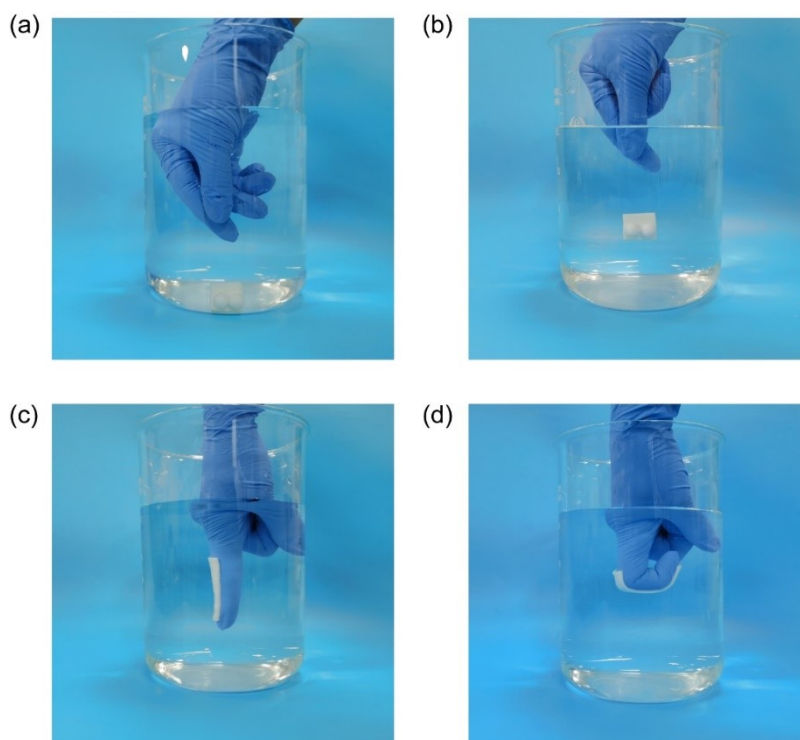


Figure S9. (a-b) HDEPs can act as underwater adhesives to adhere ceramic beads and lift them out of the water. (c-d) HDEPs adhere to the surface of nitrile glove and can follow finger bending and straightening underwater.

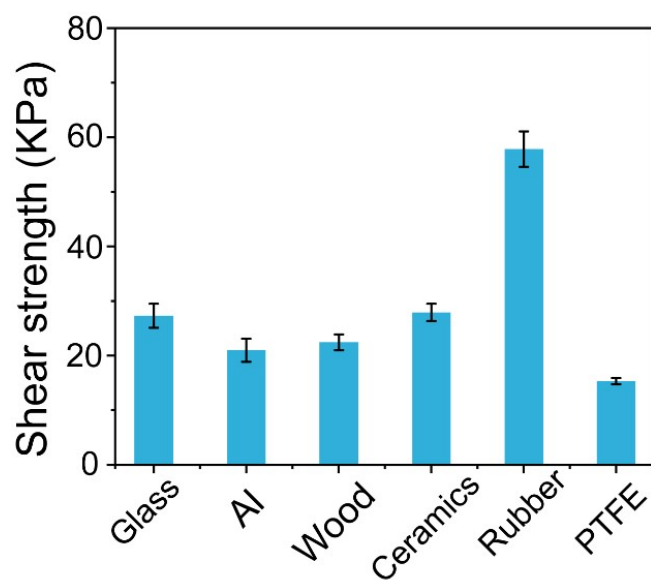


Figure S10. Shear strength of HDEP-2 adhering to PTFE, Al, foam, glass, PET and rubber after 7 days of soaking in water.

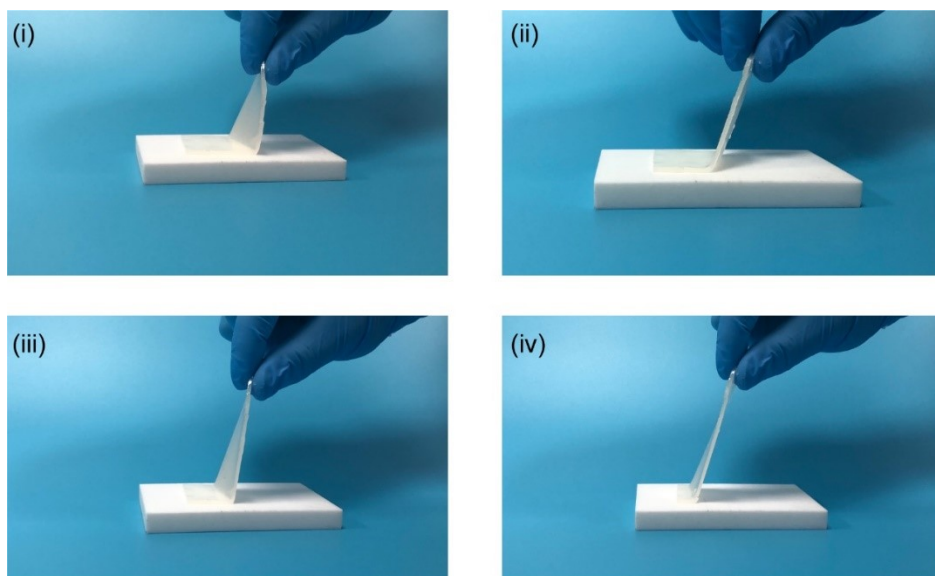


Figure S11. HDEPs can still adhere tightly to the PTFE surface after 7 days of soaking in water.



Figure S12. Comparison of the adhesion properties of HDEP-2 in water and in TOL.

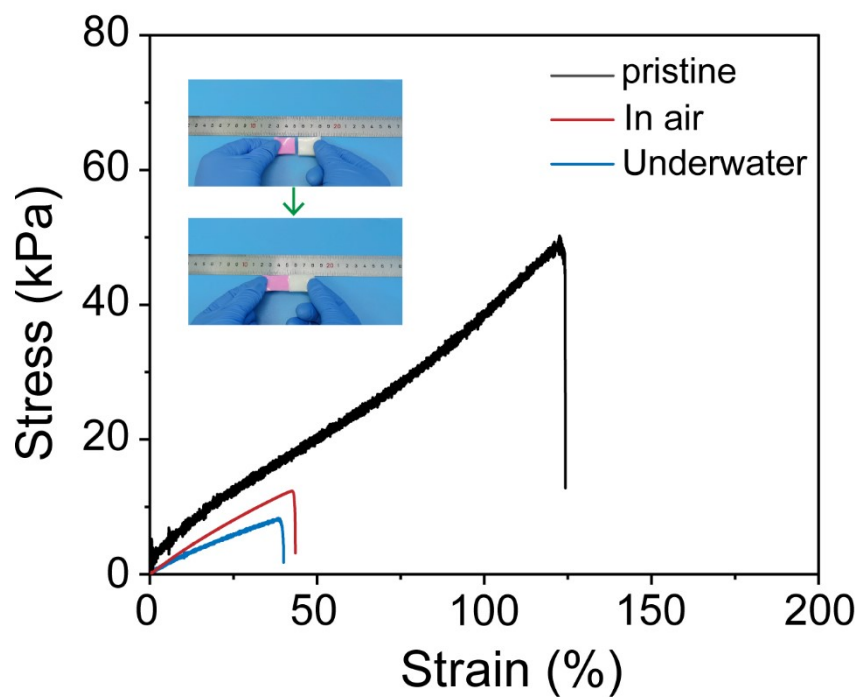


Figure S13. The stress–strain curves of the HDEPs self-healed in air and underwater for 24 hours. The inset pictures showed the self-healing process of HDEP in air.

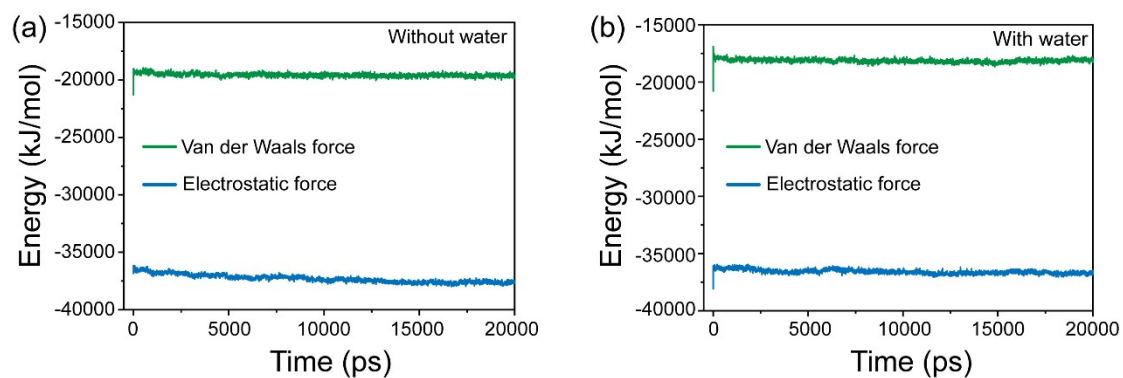


Figure S14. The interaction energy changes (a) in the absence and (b) presence of water.

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