Supporting Information

Exploiting Valuable Supramolecular Materials from Waste Plastics

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Materials

E-51 epoxy resin and curing agent, 4, 4-diaminodiphenyl methane (DDM) were provided by Bluestar Chemistry Company and Aladdin Chemistry Company, respectively. Hydrogen peroxide (H_2O_2, ⩾30 wt%), hydrochloric acid (HCl, 36 wt%), tertiary butanol, n-hexane, petroleum ether, dichloromethane, chloroform, and ethanol were purchased from Chengdu Kelong Chemical Reagent Company (China). All chemicals were directly used as received without further purification. Ethylene vinyl acetate (EVA) copolymer and amorphous poly-alpha-olefin (APAO) were purchased from Haosheng New Material Co., Ltd.

Degradation of EP

Firstly, EP was prepared as below: E-51 was pre-cured with DDM in weight ratio of 4:1 at 80^{o}C for 2 h and followed by a post-cure at 120^{o}C for 2 h. Then, the crushed EP particles (CEPs) with size ranging from 0.075 to 0.2 mm were fabricated using a pulverizer. Next, 1 g CEPs and 10 mL H_2O_2 were simultaneously added in a round-bottom flask. The mixture was kept in the oil bath at 85^{o}C with stirring. After reaction for 5 h, resin particles stuck together to form solid blocks and collected by filtration, and then washed with deionized water to remove residual H_2O_2. Finally, the solid was dried in an oven at 80^{o}C for 12 h to obtain DEP.

Characterization

Fourier transform infrared spectroscopy (FTIR) was collected at ambient temperature on a Nicolet 6700 (USA). Solid-state nuclear magnetic resonance (NMR) spectra were recorded on a Bruker advance III spectrometer (400 MHz). Liquid-state NMR spectra were obtained on a Bruker Avance Ⅲ spectrometer (400 MHz) with dimethyl sulfoxide-d6, deuterated chloroform

($CDCl_3$) or deuterium oxide (D_2O) as solvent. X-ray photoelectron spectroscopy (XPS) spectra were analyzed by a XSAM800 spectrometer (KRATOS, U.K.). The relative molecular weight was measured using gel permeation chromatograph (GPC). Standards of narrow polystyrene were used for calibration and tetrahydrofuran as eluent. The flow rate was 1 mL/min. Identification of DEP was detected by a mass spectrometry (MS, TSQ quantum ultra) in electrospray negative ion mode (ESI^-). The glass transition temperature (T_g) and melting point were measured using a differential scanning calorimeter (Q200, USA). Thermal stability was characterized using a thermo-gravimetric analyzer (TGA 5500, USA). The oscillatory rheological measurements were performed on a dynamic rheometer (Discovery HR-2, USA) equipped with a parallel-plate made of stainless steel with a diameter of 25 mm.

Adhesion Strength Test

The substrates (80 mm × 20 mm × 2 mm) were cleaned by ultrasonic with acetone, ethanol and water successively, and then dried for the later use. Appropriate dosage of DEP was spread onto one aluminum slide with a coverage area of 20 mm × 10 mm. Then, the DEP powders without any additive were heated directly to their melting temperature. Or viscous flowing DEP was obtained by adding ethanol with just a few minutes of infrared irradiation. Before DEP transformed into solid, another aluminum sheet was covered and some pressure was applied. Adhesion strength was tested using an Instron 3345 instrument with a load cell of 2 kN and a cross-head speed of 2 mm min^{-1}. After the test, DEP was collected from separated substrates to performed cycling tests.

Underwater Adhesion Test

First, two aluminum slides used as the base substrates were immersed in a water bath at 60°C. DEP-C_2H_5OH (20:1) was then added into one aluminum slide. When it softened, another piece of aluminum slide covered on it with a coverage area of 20 mm × 10 mm, followed by clamping these two aluminum slides with long tail clips. Next, the water was heated to 80°C and held for 15 min. After the water was cooled to room temperature, adhesion strength of samples was tested using an Instron 3345 instrument with a load cell of 2 kN and a cross-head speed of 2 mm min^{-1}.

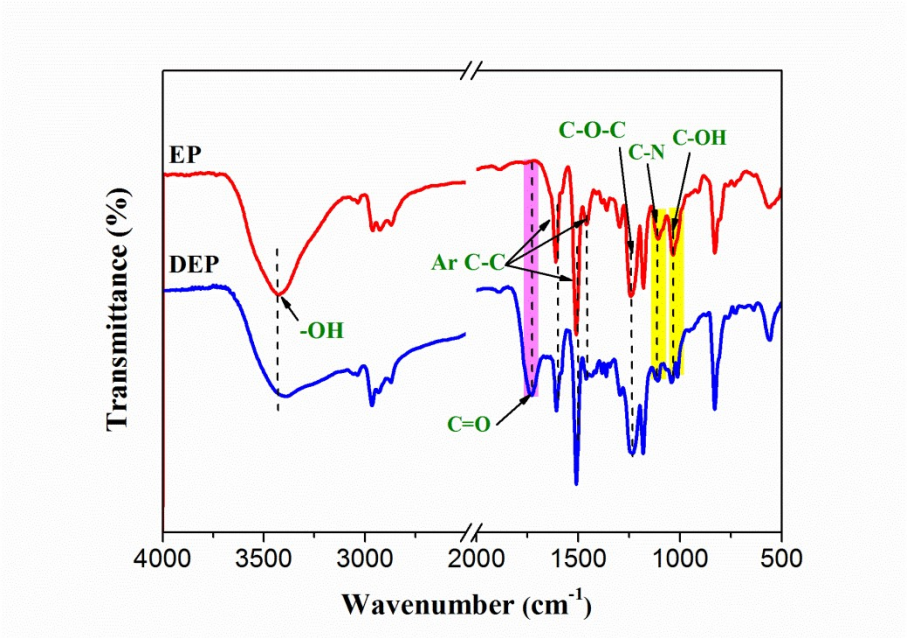

Figure S1. FTIR spectra of EP and DEP.

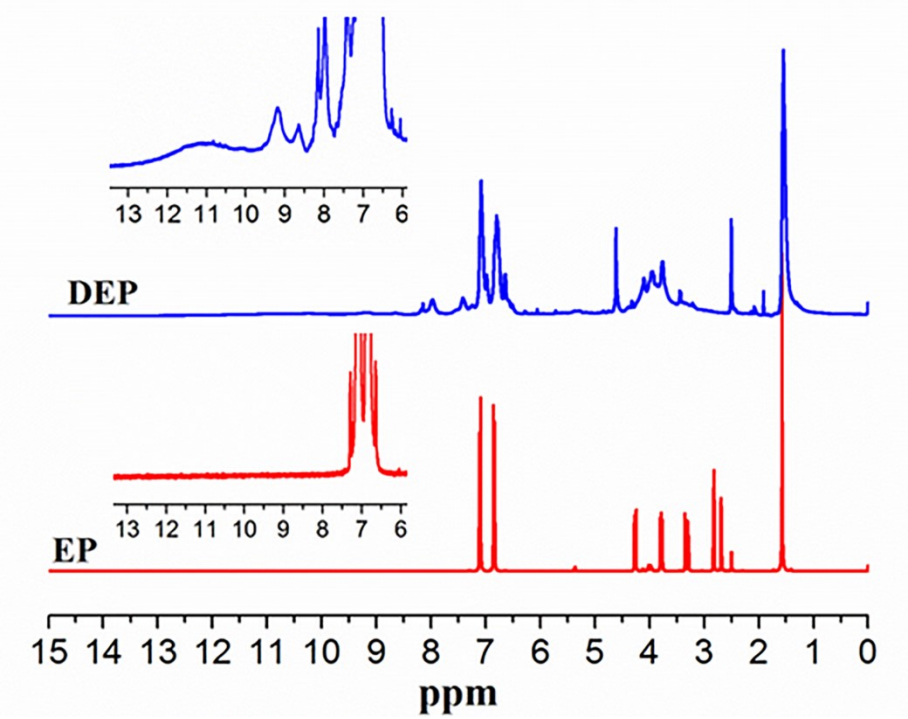

Figure S2. ^{1}H-NMR spectra of EP and DEP.

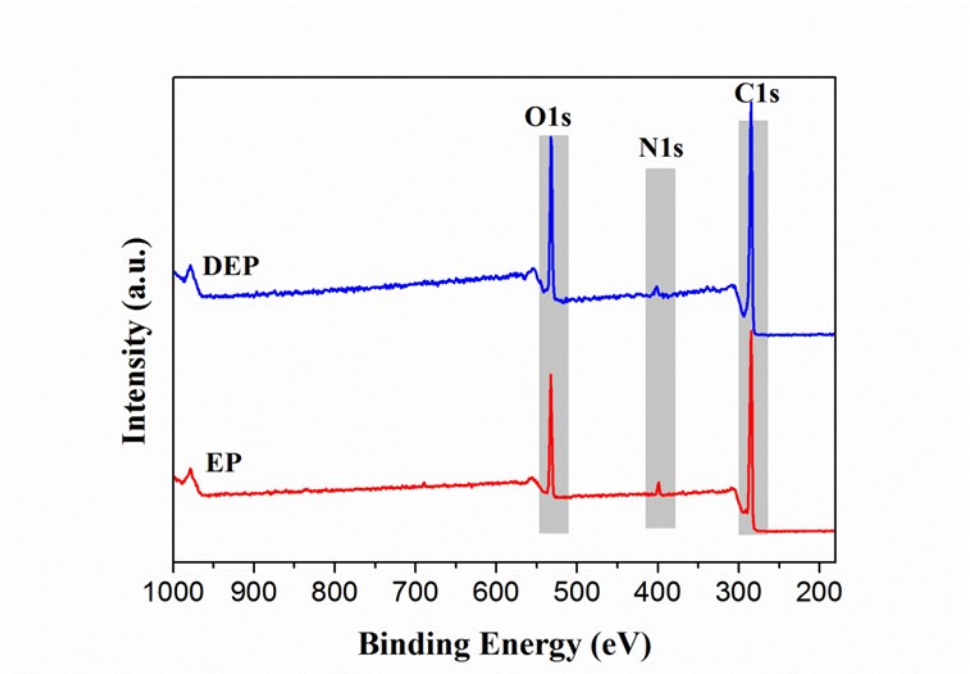

Figure S3. XPS survey spectra of EP and DEP.

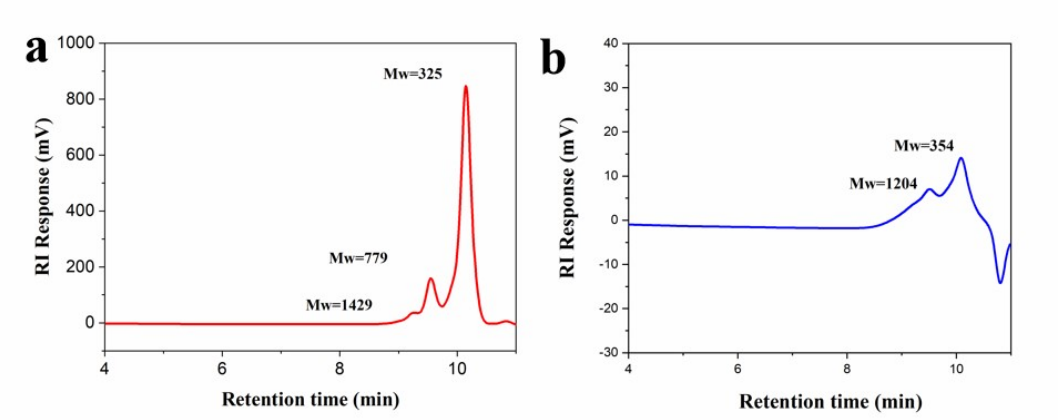

Figure S4. GPC curves of (a) DGEBA and (b) DEP.

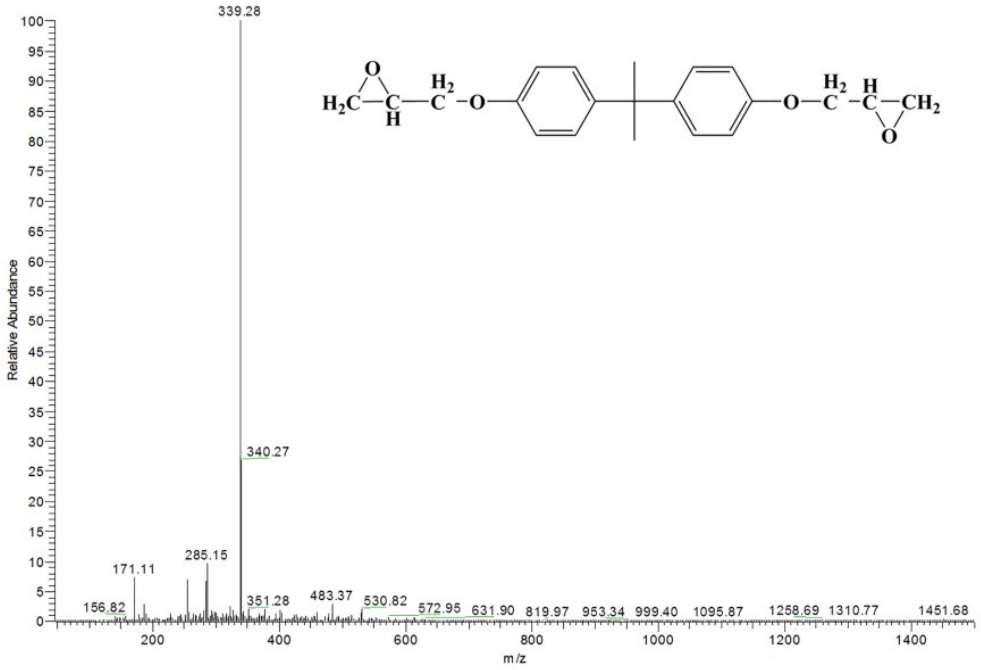

Figure S5. ESI Mass spectrum of DGEBA.

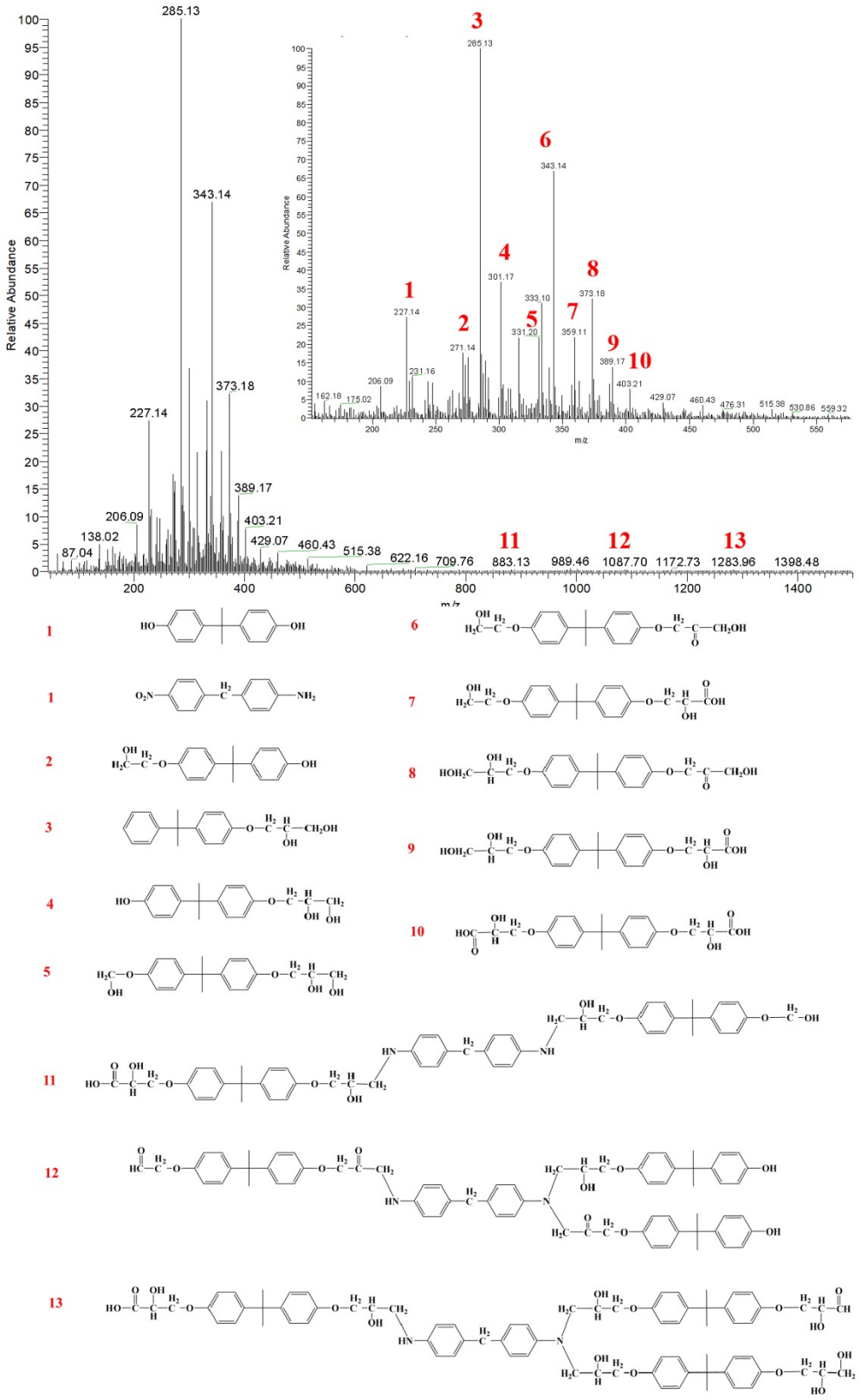

Figure S6. ESI Mass spectrum of DEP and the possible molecular structures.

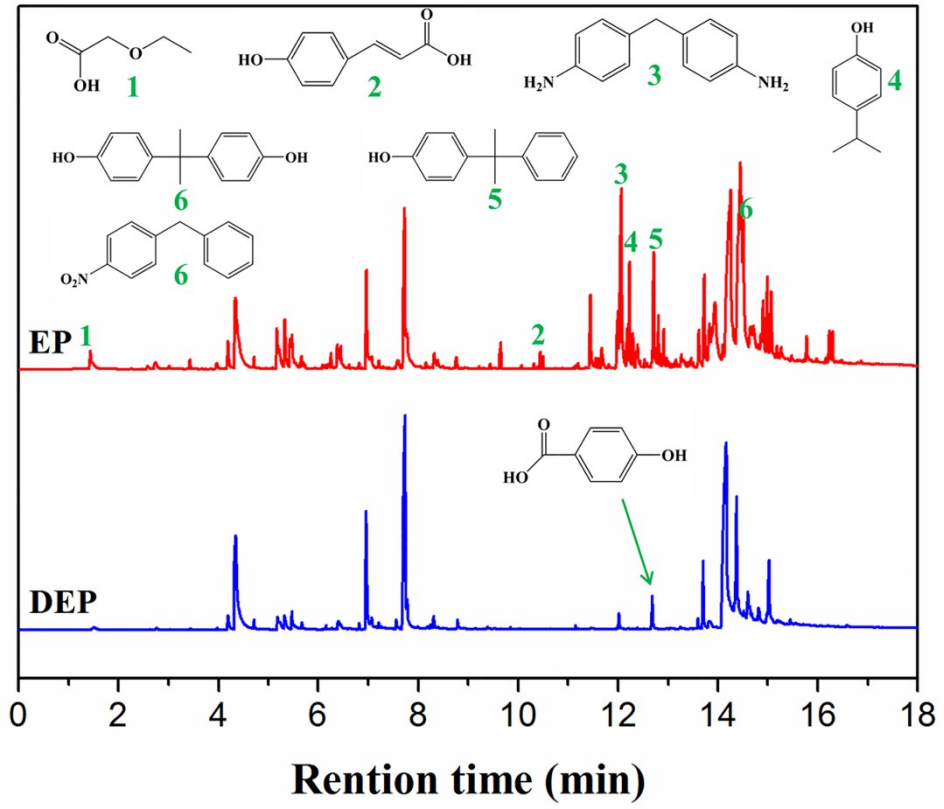

Figure S7. The total ion chromatogram and pyrolysates of EP and DEP at 700°C.

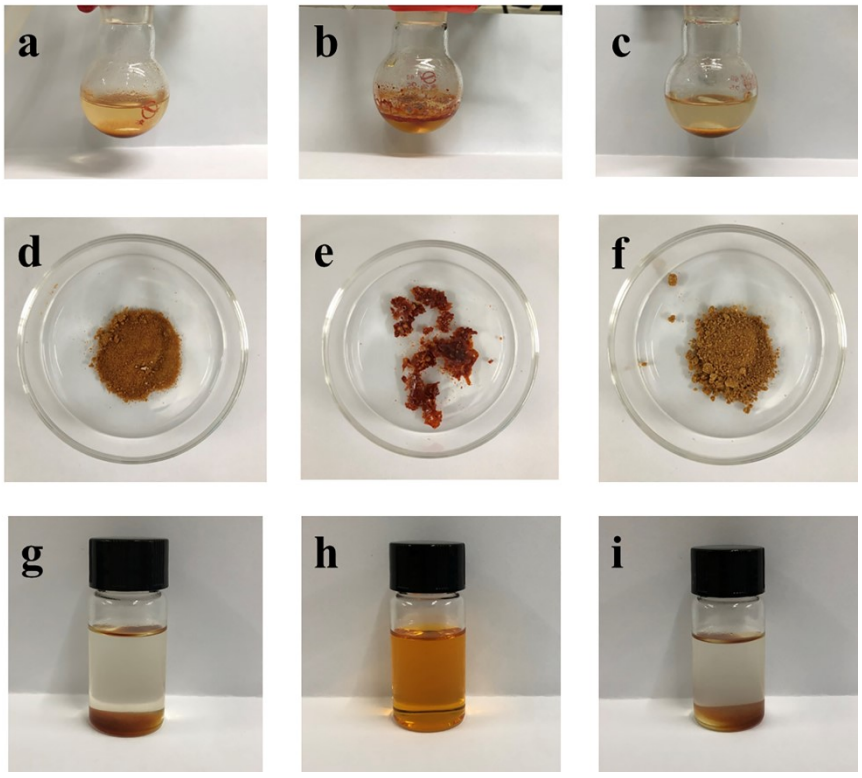

Figure S8. Photographs of EP after degraded in H_2O_2 for 4 h, obtained DEP and its solubility in DMF, (a, d and g) tert-butanol, (b, e and h) nothing and (c, f and i) ethanol was added in the reaction, respectively.

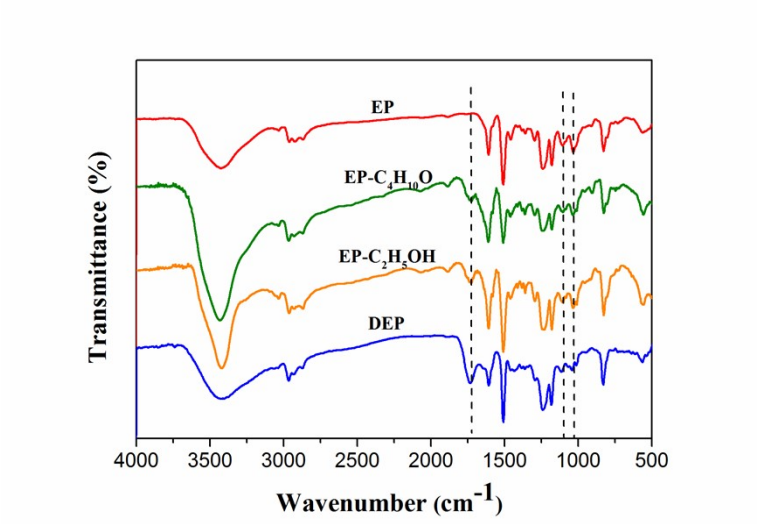

Figure S9. FTIR spectra of EP, EP-$C_4H_{10}O$, EP-C_2H_5OH and DEP.

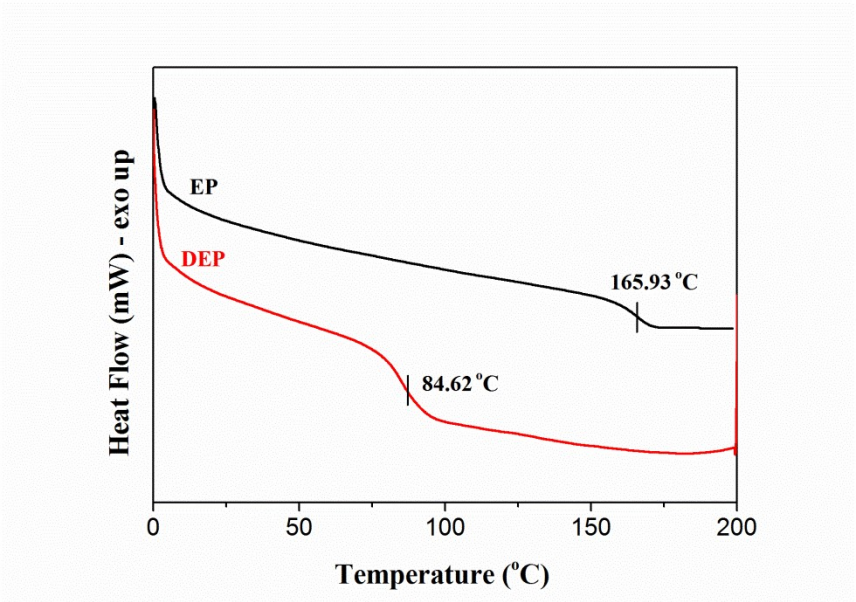

Figure S10. The DSC curve of EP and DEP in the second heating.

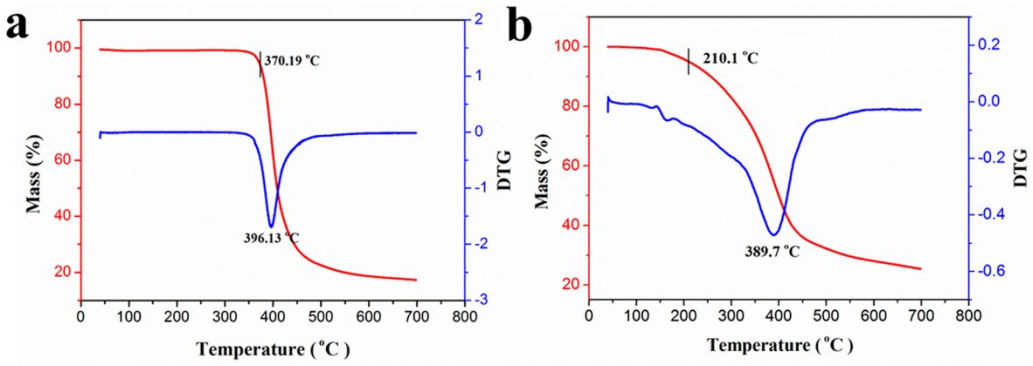

Figure S11. a, b, Thermal decomposition behavior of (a) EP and (b) DEP.

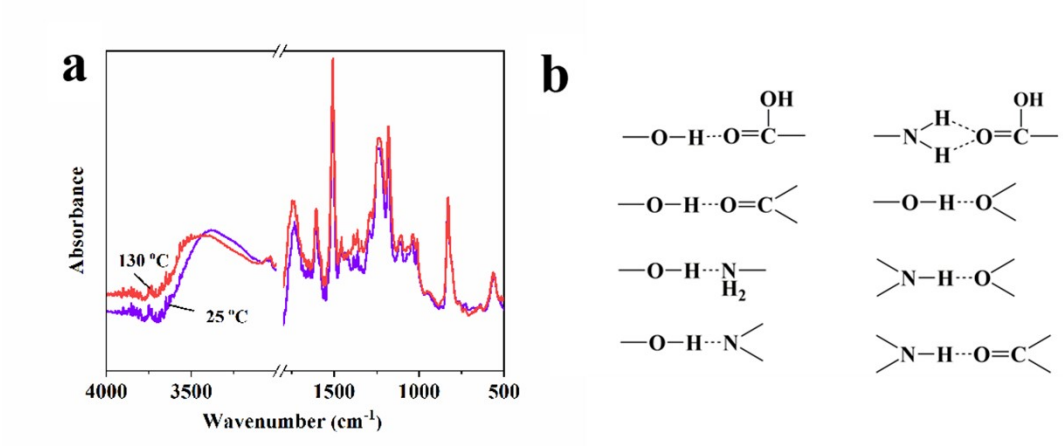

Figure S12. (a) FTIR spectra of DEP at 25 and 130°C. (b) Multiple hydrogen-bond network in DEP.

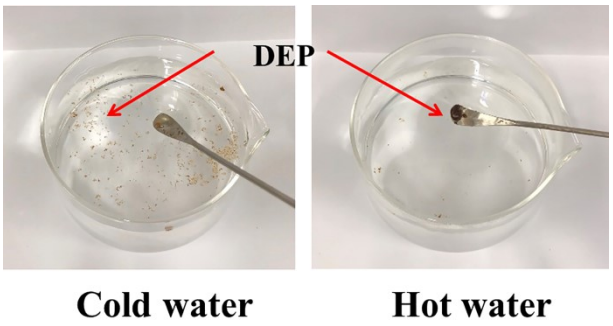

Figure S13. Photographs of DEP when immersed in cold and hot water. The powdered DEP exhibited viscosity and stuck together after immersed in hot water for a few minutes.

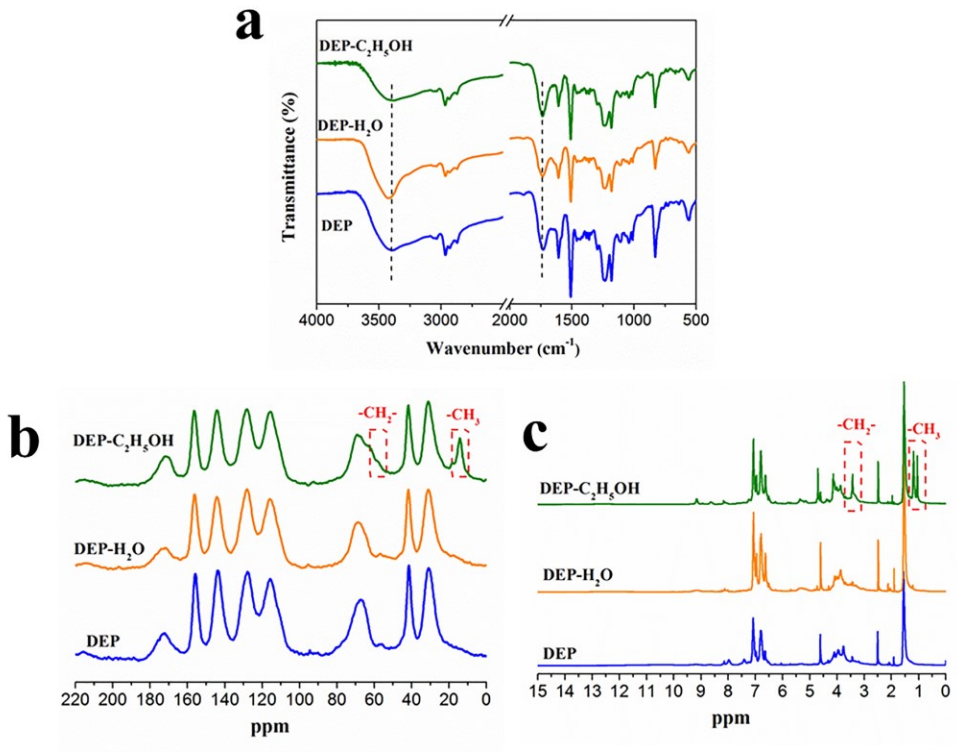

Figure S14. FTIR, ^{13}C-NMR, ^{1}H-NMR spectrum of DEP, DEP-C_2H_5OH and DEP-H_2O.

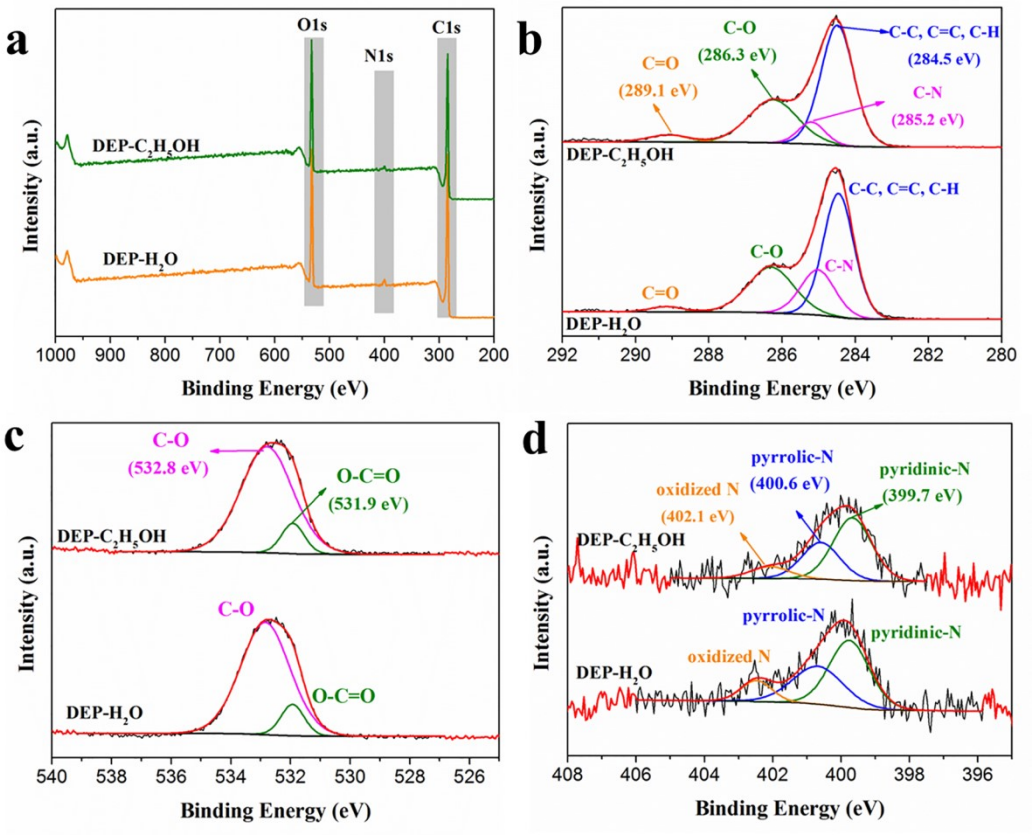

Figure S15. a-d, XPS spectra of DEP-C_2H_5OH and DEP-H_2O, (a) survey scan spectra, (b) C 1s, (c) O 1s and (d) N 1s narrow scans.

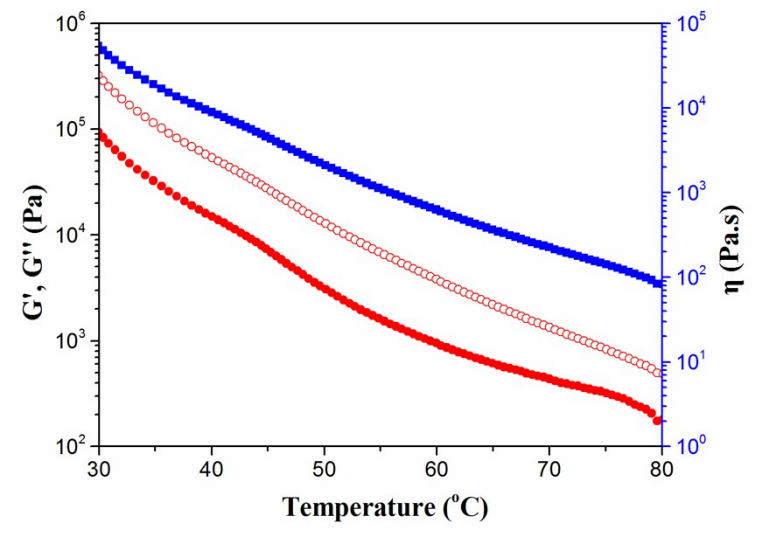

Figure S16. Temperature sweep of the storage (G'), loss (G'') modulus and complex viscosity of DEP-C_2H_5OH (20:3).

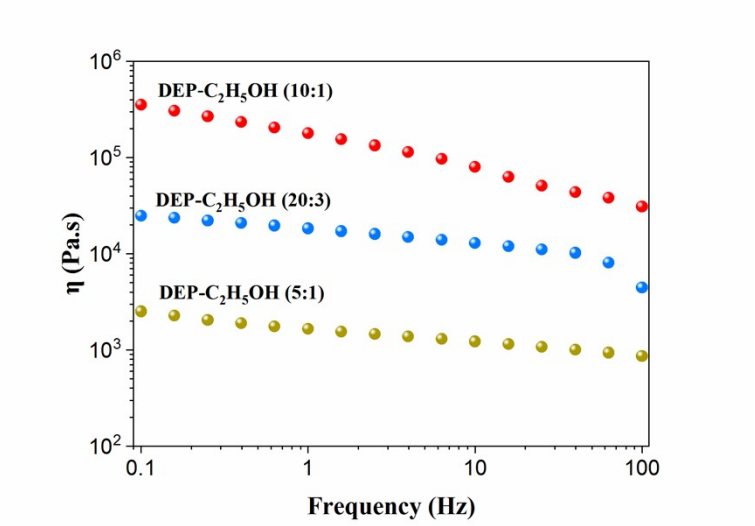

Figure S17. Frequency sweep of the complex viscosity of DEP-C_2H_5OH at 30°C.

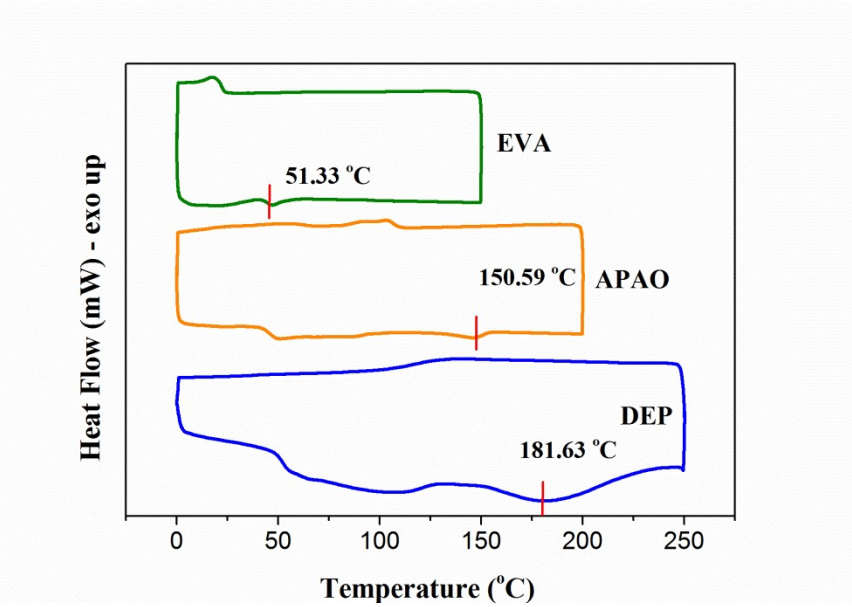

Figure S18. DSC traces of EVA, APAO and DEP in the first heating-cooling cycle.

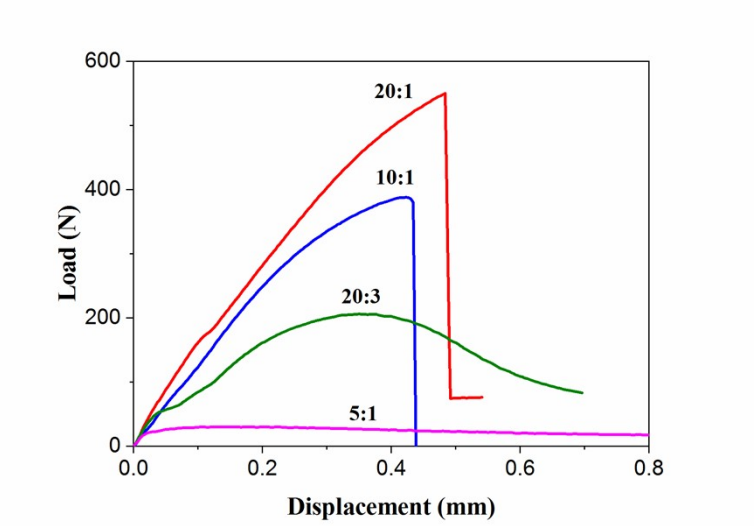

Figure S19. Lap shear strength curve of DEP with different ethanol content (DEP layer size: 2×1 cm^2).

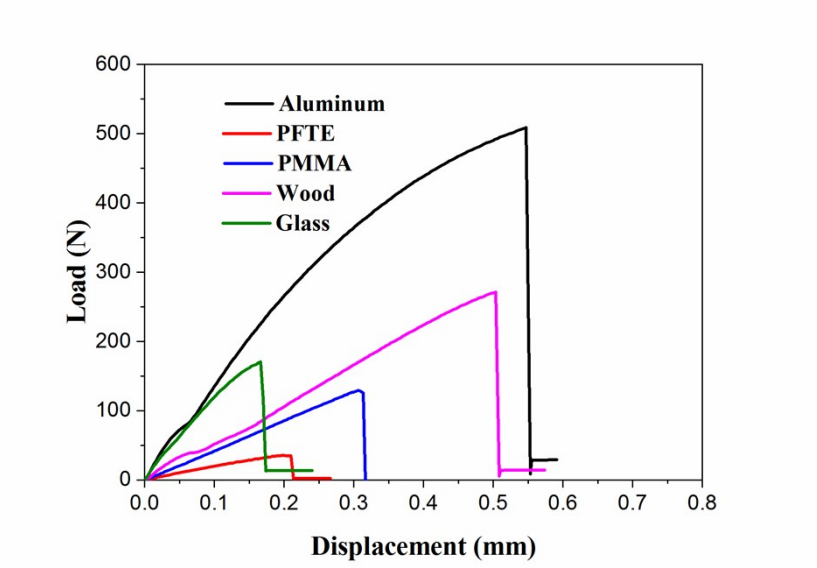

Figure S20. Lap shear strength curve of DEP on different substrate surfaces (DEP layer size: 2×1 cm^2).

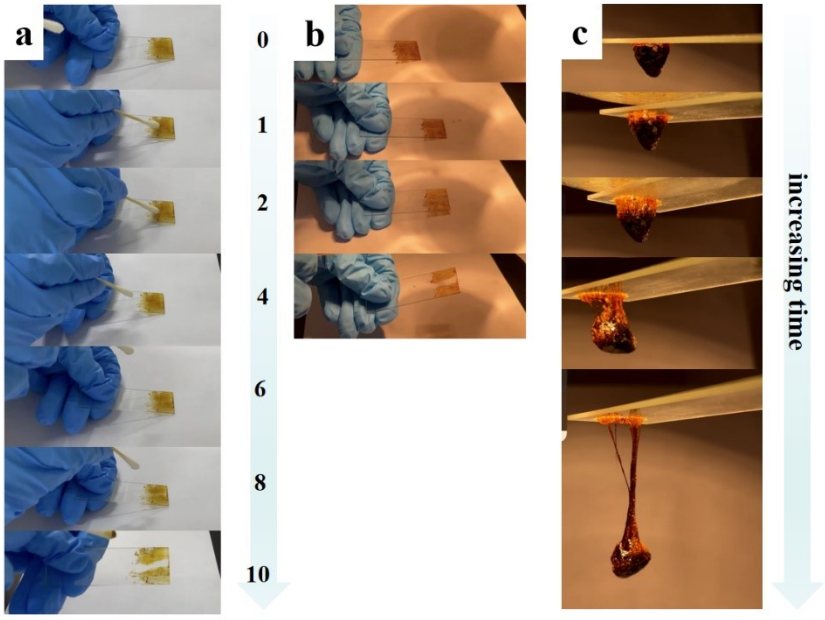

Figure S21. Pictures of cleaning of DEP coating (a) at room temperature and (b) under infrared irradiation. (c) DEP falls down from glass substrate with increasing the exposure time of infrared irradiation.

DEP exhibits excellent adhesive performances to various substrates due to the abundant functional groups which tend to form hydrogen bonds with substrate surfaces for binding together. Here, thin layer of DEP was applied to glass surfaces. At room temperature, it took 10 swipes with ethanol to remove DEP from glass surface (Figure S21a), whereas it took only 4 swipes after heating (Figure S21b). What's more, DEP gradually detached from the glass substrate with increasing temperatures (Figure S21c). Owning to the presence of heat-labile hydrogen bonds, a decrease in adhesive force between DEP and substrate was detected with increasing temperatures, supporting the above hypothesis.

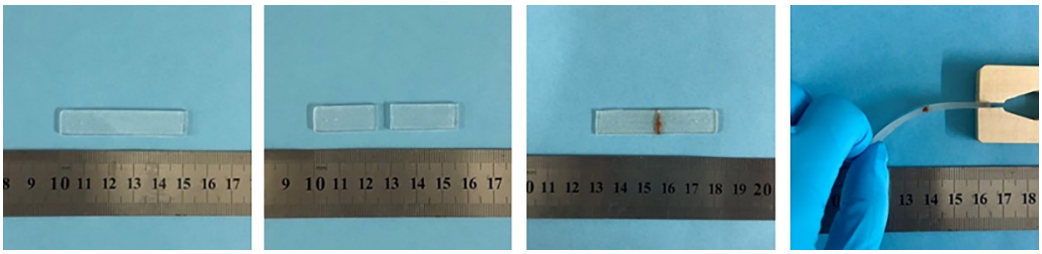

Figure S22. Pictures of DEP bonded flexible PDMS, when the PDMS was bent to a certain extent, there was no breakage occurred at the cutting point.

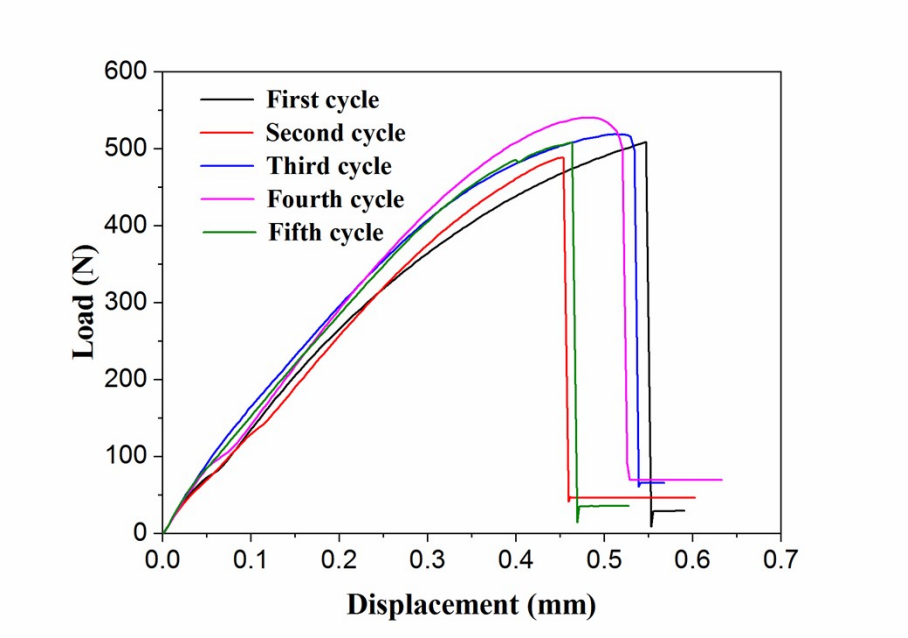

Figure S23. Reversible adhesion of DEP on Al slides (DEP layer size: 2×1 cm^2).

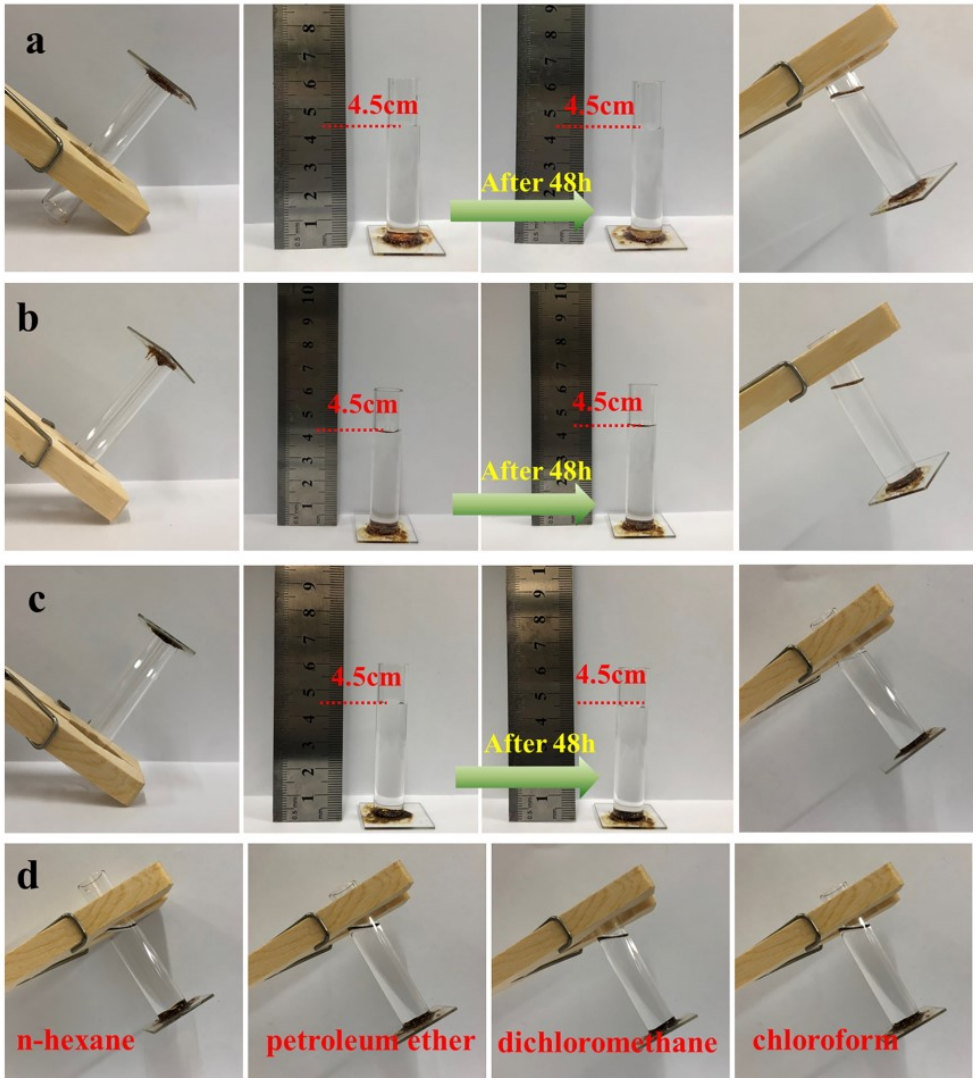

Figure S24. Corrosion resistance test of DEP. a-c, The separated glass tube and glass sheet were bonded DEP, then appropriate (a) H_2O, (b) 1mol/L HCl, and (c) 1mol/L NaCl were added up to the liquid level of 4.5 cm. After 48 h, the height of the liquid was constant and the bonded container was complete without separation. d, The container was also stable with various organic solvents.

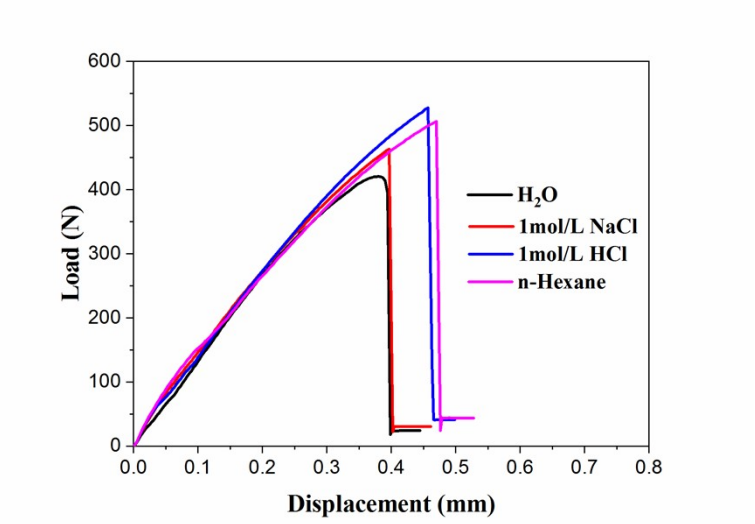

Figure S25. Lap shear strength curve of DEP after immersed in various solutions for 48 h.

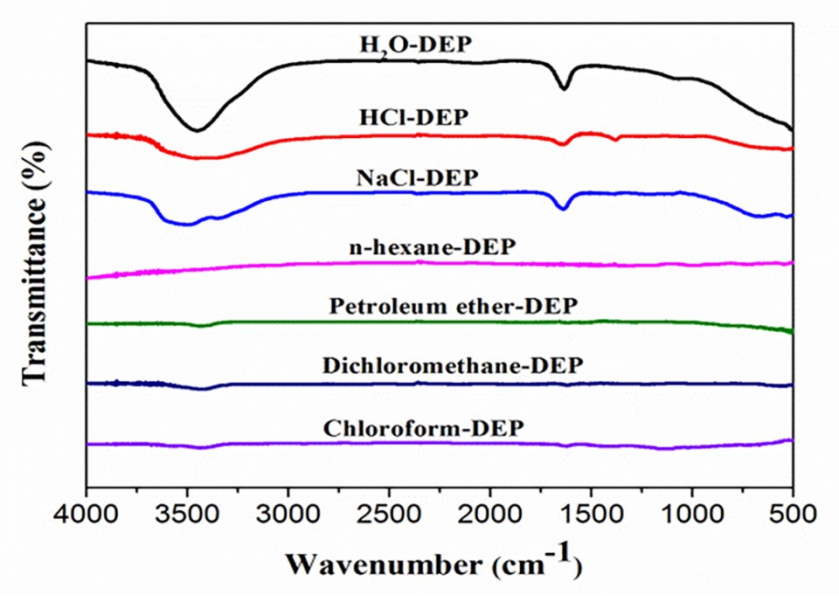

Figure S26. FTIR spectra of H_2O, HCl, NaCl, n-hexane, petroleum, dichloromethane and chloroform solutions after DEP soaked in them for 48 h.

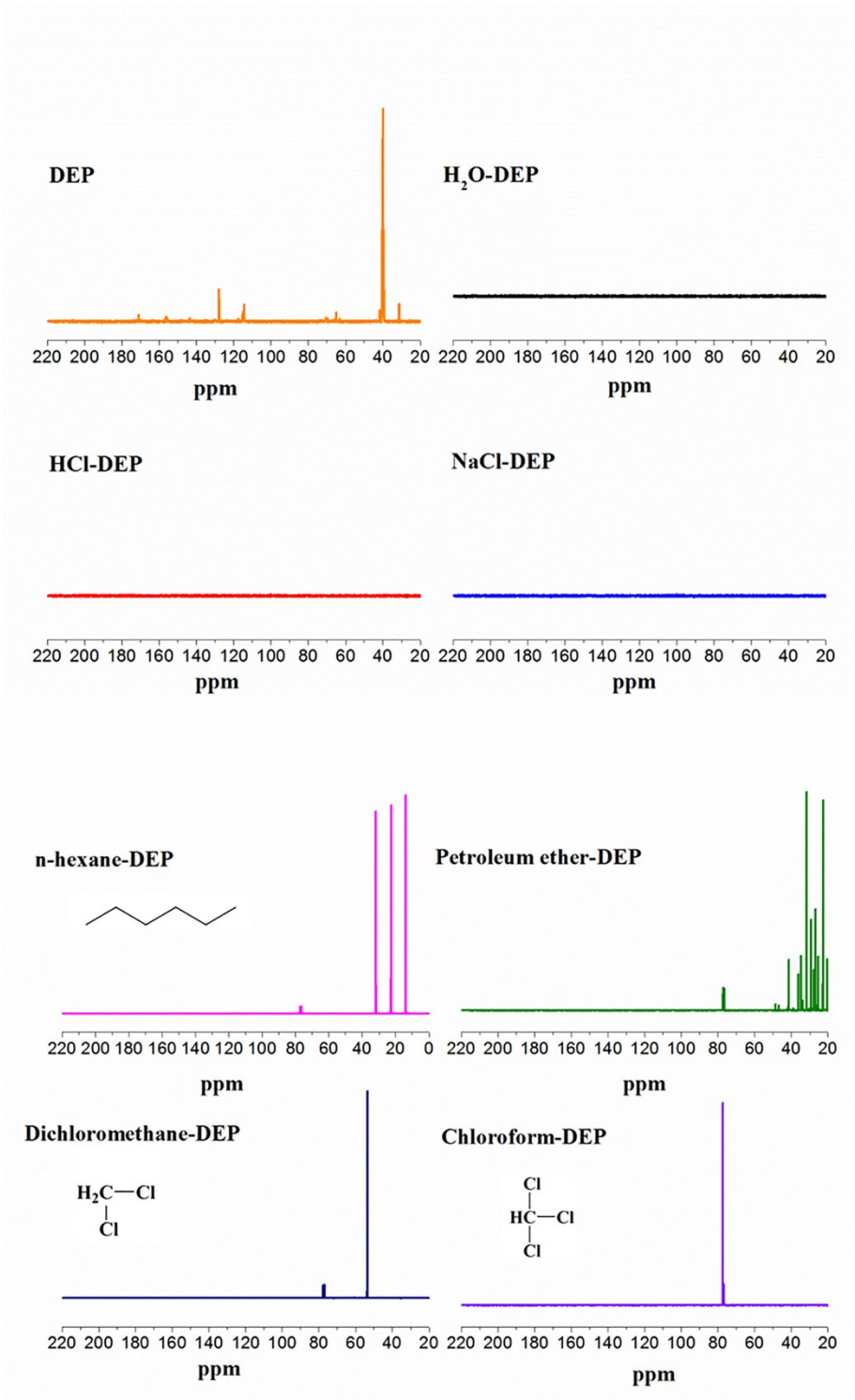

Figure S27. ^{13}C-NMR spectra of H_2O, HCl, NaCl, n-hexane, petroleum, dichloromethane and chloroform solutions after DEP soaked in them for 48 h.

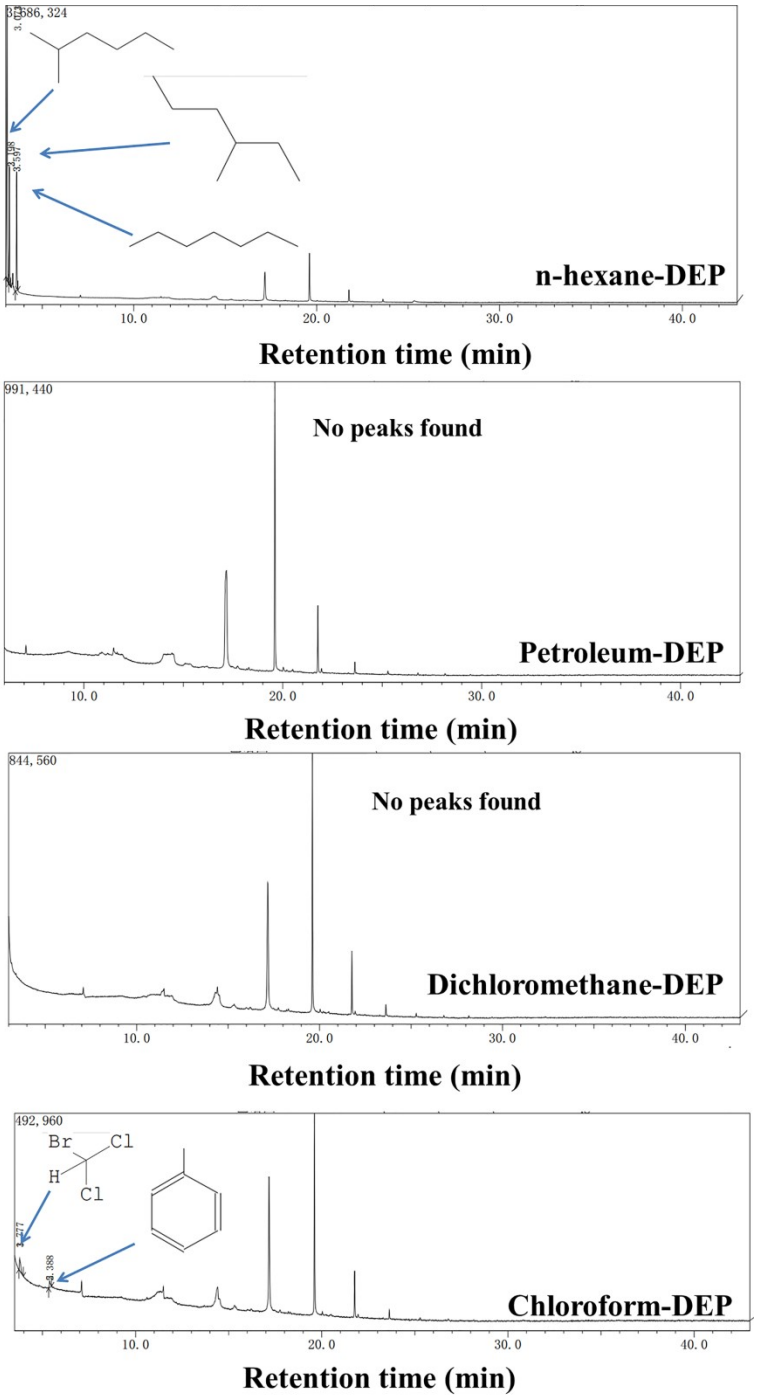

Figure S28. GC-MS spectra of n-hexane, petroleum, dichloromethane and chloroform solutions after DEP soaked in them for 48 h.

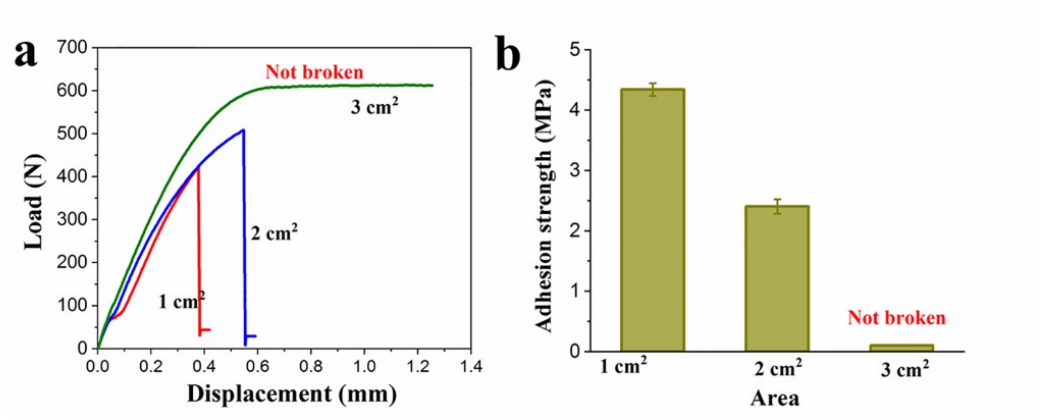

Figure S29. a, b, (a) Lap shear strength curves and (b) adhesion strength of various DEP layer sizes between Al slides.

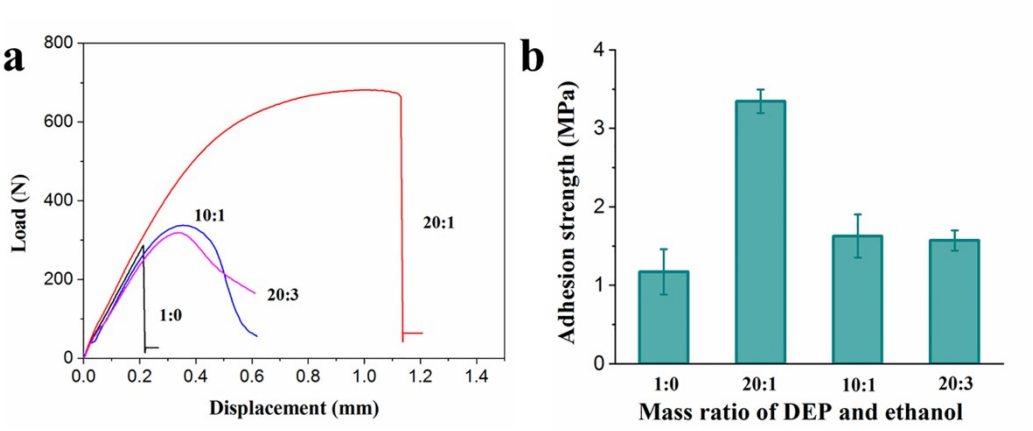

Figure S30. a, b, (a) Lap shear strength curves and (b) adhesion strength of DEP used as underwater adhesive with different ethanol content (DEP layer size: 2×1 cm^2).

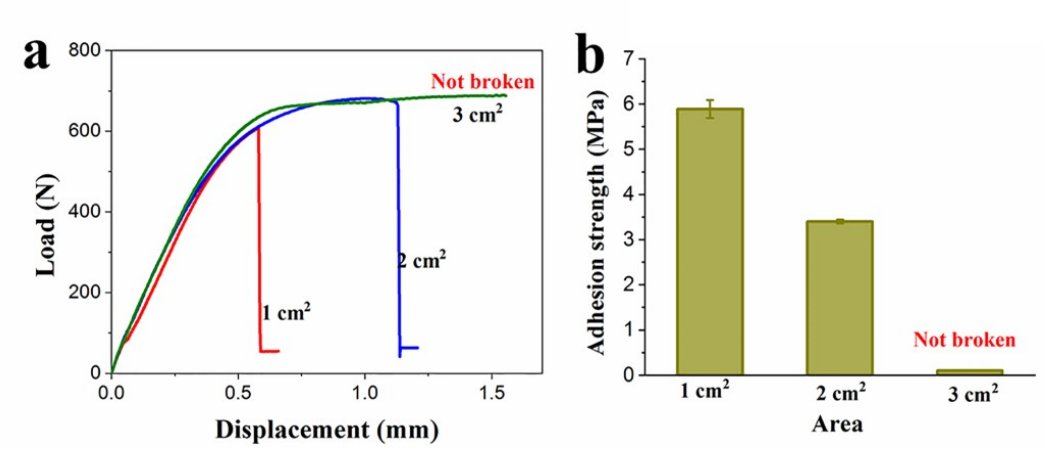

Figure S31. a, b, (a) Lap shear strength curves and (b) adhesion strength of various DEP layer sizes between Al slides.

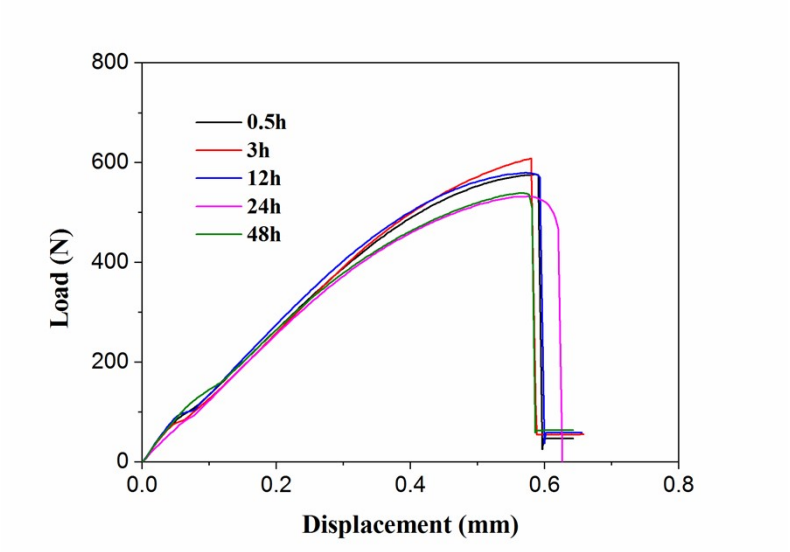

Figure S32. Lap shear strength curve of DEP-C_2H_5OH (20:1) used as underwater adhesive after soaked in water for different times (DEP layer size: 2×0.5 cm^2).

Table S1 Surface elemental composition of EP and DEP by XPS spectra.

Samples	Surface elemental composition (%)				
	C	N	O	O/C	N/C
EP	81.51	2.61	15.88	0.195	0.032
DEP	81.88	1.41	16.71	0.204	0.017

Table S2 Surface elemental composition of DEP-H_2O and DEP-C_2H_5OH by XPS spectra.

Samples	Surface elemental composition (%)				
	C	N	O	O/C	N/C
DEP-H_2O	77.38	1.5	21.12	0.273	0.019
DEP-C_2H_5OH	76.67	0.98	22.36	0.292	0.013

Table S3 Comparison of adhesion strength among different adhesives.

Adhesives		**Adhesion strength (MPa)**	**Reference**	**Corresponding letters in Fig.3g**
HMWM-based supramolecular adhesives	Hydrogen-bonded supramolecular polymer	1.3	Ref 32	a
	PXNT hydrogel	0.0004	Ref 33	b
LMWM-based supramolecular Adhesives	Supramolecular homopolymer (A)n	2.0	Ref 34	c
	AESOIPA	2.3	Ref 35	d
	poly(TA-DIB-Fe) copolymer	2.5	Ref 36	e
	AMN/IBU adhesive	0.045	Ref 37	f
	DB24C8-COOH/ Pentaerythrotol	4.174	Ref 38	g
	This work	**4.34**	\	\
Other adhesives	Multifber hydrogel	0.01	Ref 39	h
	BSA	2.8	Ref 40	i
	Soft dendritic microparticles	1.3	Ref 41	j
	AZOs	1.34	Ref 42	k
	Ionogel adhesive	1.0	Ref 43	l

Table S4 Comparison of adhesion strength among different underwater adhesives.

Underwater adhesives		**Adhesion strength (MPa)**	**Reference**	**Corresponding letters in Fig.4e**
Supramolecular adhesives	DB24C8-COOH/ Pentaerythrotol	3.23	Ref 38	a
	CB[8] supramolecular hydrogel	2.2	Ref 44	b
	This work	**5.88**	\	\
Other adhesives	HBPA	0.25	Ref 45	c
	NCA	1.8	Ref 46	d
	Nanocrystal reinforced hydrogel networks	3	Ref 47	e
	HyPPos	0.1	Ref 48	f
	Anth-PEI glues	0.6	Ref 49	g
	Nucleobase-Driven Nonswellable Adhesive	0.000124	Ref 50	h
	gallol-functionalized underwater adhesive	4	Ref 51	i
	Hetero-Polyacid-Based Underwater Adhesive	0.0000146	Ref 52	j
	Mussel-Inspired Adhesives	1.2	Ref 53	k