# **Supporting information**

Hydrophobic Deep Eutectic Solvent Based Hydrophobic Polymer Adhesive with On-demand Detachability, Strong Broad-Spectrum Adhesion in Air/Aquatic Environments

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### Molecular dynamics (MD) simulation details

The structure optimization of all molecules was performed using the BDF quantum chemistry software,<sup>46-50</sup> with the PBEO-D3(B,J)/6-31G(d,p) level. The restrained electrostatic potential <sup>S1</sup> (RESP) charge calculated by Multiwfn program was used to define atomic charges of the molecules. <sup>53</sup> The force field were generated by sobtop <sup>S2</sup> program with GAFF2 force field <sup>S3</sup>. To account for the flexibility of water, the SPC/Fw model <sup>S4</sup> was used for water molecules.

MD stimulations were performed using the GPU version of Gromacs 2020.6 package. <sup>S5</sup> A periodic box was created using Packmol <sup>54</sup> for the subsequent MD simulation. A cut-off radius of 1.4 nm was set for both van der Waal and electrostatic interactions. The electrostatic interactions were evaluated through the particle-mesh-Ewald (PME) method. <sup>S6</sup> The equilibration in a NPT ensemble for 10 ns with 0.5 fs step, where the pressure and temperature was controlled with Berendsen barostat and velocity-rescale thermostat. <sup>S7-8</sup> After equilibration, a 20 ns production run with step 0.5 fs was simulated for subsequent analysis, where the pressure and temperature was controlled with method. <sup>S9</sup>

### Swelling Behavior

Swelling behavior of the adhesives were evaluated by the traditional swelling method. The sample was soaked in deionized water until achieving swelling equilibrium at ambient temperature. The swelling ratio (SR) is calculated as follows

swelling ratio = 
$$\frac{W_s - W_i}{W_i}$$

where  $W_s$  and  $W_i$  refer to the weights of the swollen and original samples, respectively.

## Shear Adhesion Force Test

Lap-shear testing was carried out on CMT4202GD universal testing machine (China) to investigate the adhesive strength of the adhesives. Adhesives (15 mm × 15 mm × 1 mm) were sandwiched in different substrates illustrated as the schematic structure (Fig. 4b). The tensile speed was set at 50 mm/min. At least three specimens were measured for each adhesive sample. The tested adherends included steel, wood, paper, copper, glass, polyvinyl chloride (PVC), polypropylene (PP), cotton, acrylonitrile butadiene styrene (ABS), epoxy glass cloth (FR-4), PTFE and polyurethane (PU). The adhesion strength was calculated using the following equation, adhesive strength =  $F_{max}/S$ , where  $F_{max}$  refers to the maximum load strength and S means the adhesive area of the adhesive sample.

The adhesion environments included air, deionized water, seawater, HCl solution (1 mol/L), and NaOH solution (1 mol/L). The seawater was simulated through the dissolution of NaCl (2.67 g), CaCl<sub>2</sub> (0.15 g), KCl (0.07 g), MgCl<sub>2</sub> (0.23 g), and MgSO<sub>4</sub> (0.32 g) in deionized water (96.56 g) and the corresponding seawater salinity was 3.44 g L<sup>-1</sup>.

### **Rheological Measurement**

Rheological measurements were examined on freshly prepared adhesives using a controlled stress rheometer (Malvern Bohlin Gemini HRnano) with a parallel plate geometry (25 mm diameter). The strain sweep from  $\gamma = 0.0001-1\%$  was to determine the linear viscoelastic region of adhesive gels. G' and G'' were also obtained as a function of temperature ranging from 10 °C to 150 °C. The viscosity of the adhesive as a function of shear rate and temperature ranging from 10 °C to 150 °C were also investigated at  $\gamma = 0.01\%$  of strain amplitude and 10 rad s<sup>-1</sup> of frequency. *Self-healing characterization of adhesive* 

In order to examine the self-healing ability of the samples visibly, the adhesive was stained in pink using edible pigment, which has no influence on self-healing. The adhesive was cut into two parts. The two parts were heated to 60 °C and connected together end to end into a whole one. **Statistical Analysis:** 

All experiments were examined at least three times ( $n \ge 3$ ) for each sample, and the mean value (±standard deviation, SD) was echibited in the figures. Statistical analysis was conducted using Origin 2021.



**Fig. S1** Two monomers, PEGDA and DMPA can form uniformly transparent liquid with HDES and are almost insoluble in water.



Fig. S2 Color bar of mapped function sign( $\lambda_2$ ) $\rho$  in IGMH maps and the representation of each colors. <sup>52</sup>



**Fig. S3** At ambient temperature, the network is soft and can be bent (a), twisted (b), stretched (c) and torn into pieces (d).



Fig. S4 Stress-strain curve of the adhesive.



**Fig. S5** Photos of the softness of the adhesive under different temperature, (a) room temperature, (b) 60 °C.

Aliphatic acid	Carbon chain length of aliphatic acid	Adhesive strength (kPa)
acetic acid	2	186.9±22.7
butyric acid	4	153.1±43.3
hexanoic acid	6	267.5±25.7
caprylic acid	8	415.5±23.8
capric acid	10	148.3±21.3
lauric acid	12	251.9±40.9

**Table S1** Effect of alkyl chain length of acid components in HDES on the adhesive properties of the adhesives.

The adhered substrate was PTFE. The amounts of HDES, isobornyl acrylate, tertbutyl acrylate,

PEGDA, and DMPA were 500 mg, 1200 mg, 600 mg, 3 mg, and 7 mg, respectively.



**Fig. S6** Effects of the molar ratios of n-caprylic acid (HBA) and menthol (HBD) in HDES on the adhesion performance of P(IBOA-co-TBA).

Isobornyl acrylate (mg)	Tertbutyl acrylate (mg)	Molar ratios of isobornyl acrylate to tertbutyl acrylate	Adhesive strength (kPa)
0	1800	0:1	243.9±23.6
900	900	1:1	360.9±36.5
1200	600	2:1	484.2±5.3
1350	450	3:1	477.5±10.4
1440	360	4:1	458.1±17.8
1500	300	5:1	385.5±2.5
1800	0	1:0	347.8±7.0

**Table S2** Effect of molar ratios of two monomers on the adhesive properties of the adhesives.

The adhered substrate was PTFE. The amounts of HDES, PEGDA, and DMPA were 500 mg, 3 mg,

and 7 mg, respectively.

Isobornyl acrylate (mg)	Tertbutyl acrylate (mg)	Molar ratios of isobornyl acrylate to tertbutyl acrylate	Adhesive strength (kPa)
800	400	1:2	46.6±12.9
1200	600	1:2	415.5±23.8
1400	700	1:2	317.9±54.4
1600	800	1:2	339.2±64.0

 Table S3 Effect of the total weights of two monomers on the adhesive properties of the adhesives.

The adhered substrate was PTFE. The amounts of HDES, PEGDA, and DMPA were 500 mg, and 3

mg, respectively.

**Table S4** Effect of the cross-linker, PEGDA, on the adhesive properties of the adhesives.

PEGDA (mg)	Adhesive strength (kPa)
1.0	228.7±34.6
2.0	272.7±46.6
3.0	296.0±10.8
4.0	280.8±31.8
5.0	229.5±37.0
6.0	86.3±39.2

The adhered substrate was PTFE. The amounts of HDES, isobornyl acrylate, tertbutyl acrylate, and DMPA were 500 mg, 1200 mg, 600 mg, and 7 mg, respectively.



**Fig. S7** Lap-shear curve of the adhesives prepared with (a) different mass ratios of TBA and IBOA and (b) different cross-linker ratios of HDES. PTFE was used as adhered substrate.



**Fig. S8** Effect of different contents of monomers on adhesion strength of the adhesives adhered with PTFE.



**Fig. S9** Lap-shear test of two substrates adhered by the P(IBOA-co-TBA) adhesive at room temperature.



**Fig. S10** (a) Macroscopic adhesion tests of adhesive on versatile substrates with the bonding area of 2.25 cm<sup>2</sup>. (b) Photograph of the adhesive bonded wood to hold a total weight of 50 kg with a bonding area of 6 cm<sup>2</sup>.

	Adhesion				
Adhesive	strength for	Composition	Adhesion mode	Curing time	
	PTFE (kPa)				
<sup>3M</sup> VHB	93.5±14.01	Polyacrylate	Directly	/	
Kafuter <b>uo 4</b> 0	100 01 110 07	Madified cilena	Solvent	24 h	
N940	106.01±16.07	Woolfied silane	evaporation	24 n	
214500050	244 22+22 00		Solvent		
5200FC	244.32±22.08	polyurethane	evaporation	48 h	
3MDD910	214 46+0 77		In-situ		
SMDP810	314.46±9.77	polyacrylate	polymerization	24 h	
	245 24-21 00	thermoplastic	Temperature	20 •	
JW3748Q	345.24±21.90	resin	dependent	30 s	
		,	UV		
Kaluter K3100	339.94±56.01	/ Ethyl	polymerization	10 s	
			In-situ		
<sup>3</sup> ™AD118	389.41±12.91	.8 389.41±12.91	2.91 Cyanoacrylate	polymerization	10 s-40 s
		Ethyl	In-situ	aa = .	
<sup>3™</sup> AD125	407.0±24.04	Cyanoacrylate	polymerization	30 s-5 min	
		Ethyl	In-situ		
<sup>3™</sup> CA40H	400.35±16.09	Cyanoacrylate	polymerization	55	
			In-situ		
<sup>3M</sup> AD630	391.44±27.02	/	polymerization	24 h-72 h	
	472 44 22 42		In-situ		
<sup>3™</sup> DP100	472.41±22.13	epoxy resin	polymerization	48 N	
Kafuter <b>B7000</b>	588.48±29.12	/	/	48 h	
This work	458±40.87	HDES/polyacrylate	Temperature dependent	30 s	

**Table S5** Comparison of twelve commercial adhesives with our prepared adhesive.



Fig. S11 Adhesion strength of twelve commercial adhesives and our prepared adhesive.



**Fig. S12** Adhesion strengths of P(IBOA-co-TBA) adhesive to different substrate including steel, copper, glass, PVC, PP, ABS, FR-4, PFTE, and PU after 40 days immersed in the water.



Fig. S13 Photo P(IBOA-co-TBA) adhesive adhering to PTFE lifting a 1 kg weight.



**Fig. S14** (a) Photos after peeling using the cooling-peeling strategy show that due to interfacial adhesion failure, the adhesive remains on one side with no residue on the other side. (b) Photos after immersion in ethyl acetate, there is no residue on either substrate.



**Fig. S15** Changes in adhesion strength of adhesive to polytetrafluoroethylene after dissolving the adhesive in ethyl acetate and spin drying the ethyl acetate for six cycles

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