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Toughening Shape-Memory Epoxy Resins via Sacrificial Hydrogen Bond

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Fracture Toughness Test

Fracture toughness tests were conducted to evaluate the brittleness of thermosets by notched three-point bending test. The size of resins was about 25 mm×5 mm×2.5 mm and the speed was set as 2 mm/min. According to the previous method,[1] the critical stress intensity factors (K_{IC}) were calculated using the following equations:

$$x=\frac{a}{W} \quad \text{Equation (S1)}$$

$$f(x)=\frac{(2+x)\,(0.886+4.64x-13.32x^2+14.72xx^3-5.6x^4)}{(1-x)^{3/2}} \quad \text{Equation (S2)}$$

$$K_{IC}=\frac{P_Q}{BW^{1/2}}\cdot f(x) \quad \text{Equation (S3)}$$

where a is the crack length ($0.45<\frac{a}{W}<0.55$), P_Q is the maximum load, W and B are the width and thickness of the sample, respectively.

Table S1 The mole number of different samples.

Samples	Number of moles of epoxy group (mmol)	Number of moles of VU-HDE (mmol)
EP-V-1.0	25.50	4.46
EP-V-1.1	25.50	4.78
EP-V-1.2	25.50	5.10
EP-V-1.3	25.50	5.42
EP-V-1.4	25.50	5.74
EP-V-1.5	25.50	6.06

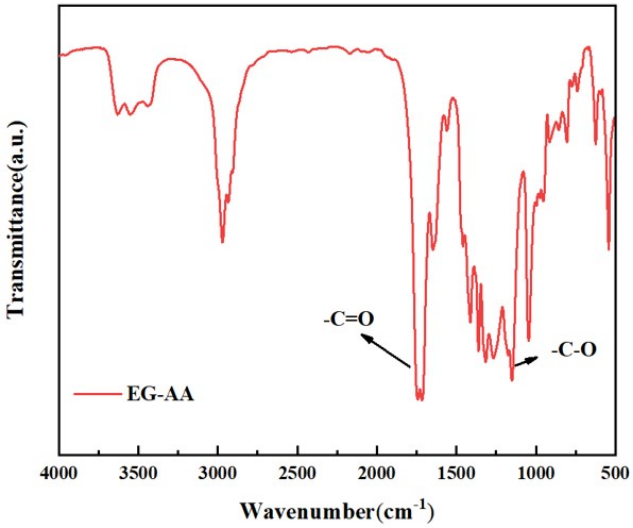

Figure S1. FT-IR of EG-AA.

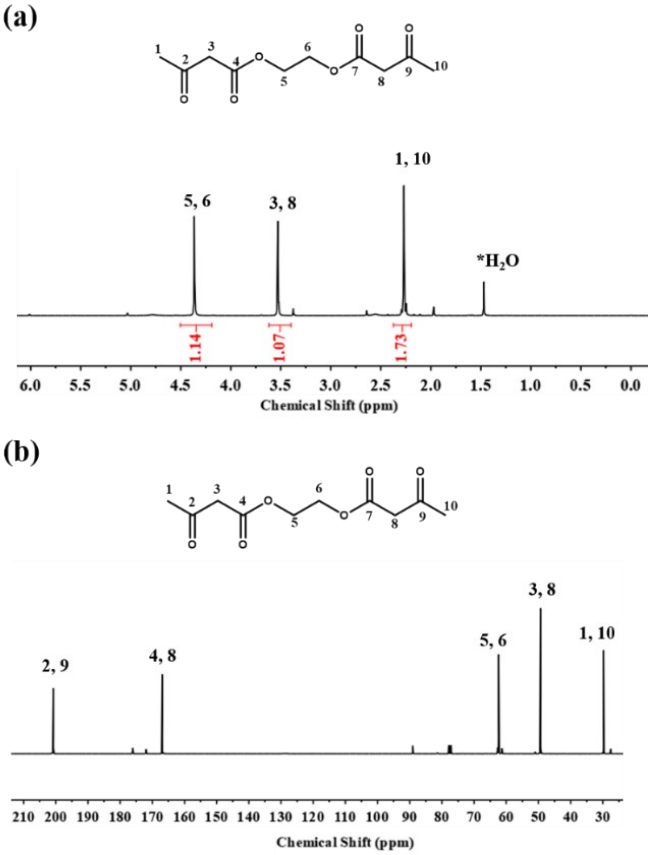

Figure S2. (a) ^{1}H NMR of EG-AA, (b) ^{13}C NMR of EG-AA.

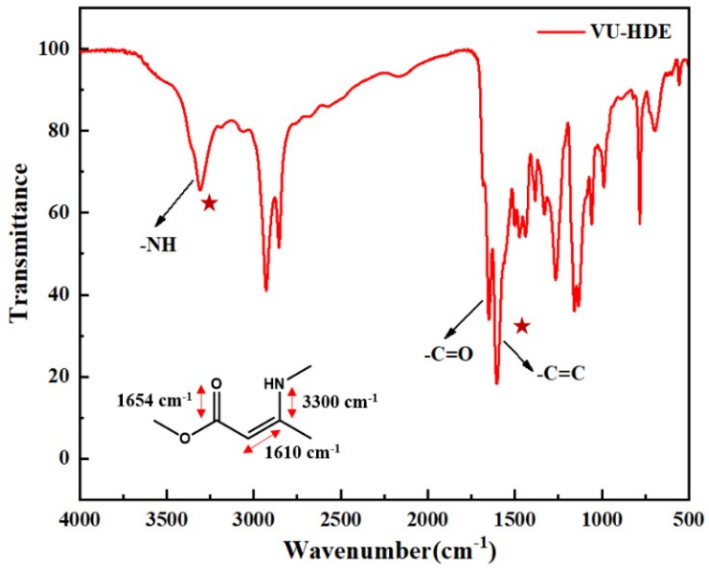

Figure S3. FT-IR of VU-HDE

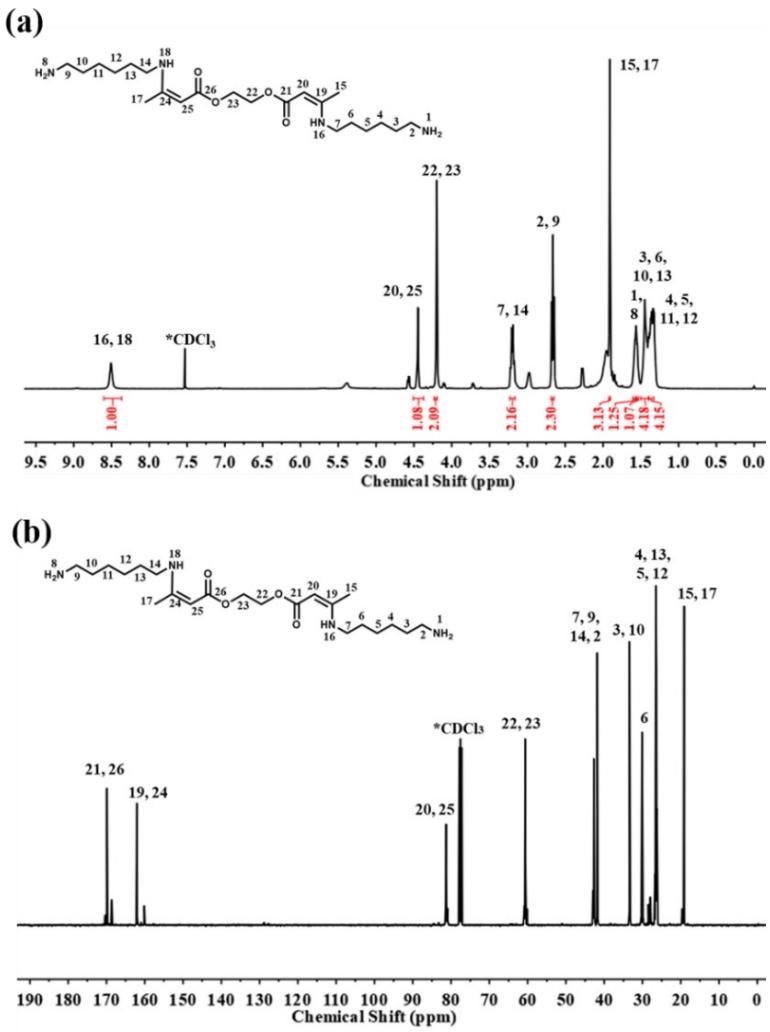

Figure S4. (a) ^{1}H NMR of VU-HDE, (b) ^{13}C NMR of VU-HDE.

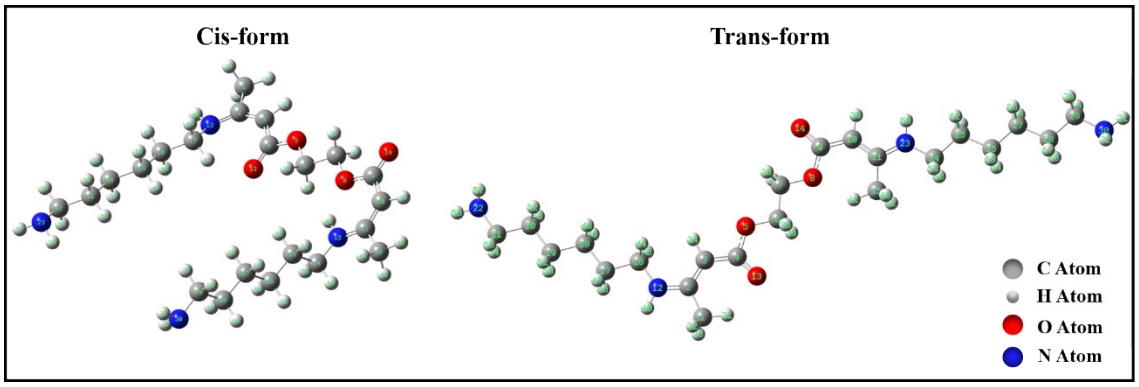

Figure S5 The geometric configuration features and atom positions of VU-HDE

Table S2 The geometric values for VU-HDE

	Interatomic distance (Å)	
Type of the bond	**Cis-form**	**Trans-form**
C_3-C_4	1.45	1.44
C_3-H_{34}	1.08	1.08
C_2-N_{12}	1.37	1.37
C_4-O_5	1.37	1.40
C_4=O_{13}	1.22	1.25
N_{12}-H_{40}	1.01	1.00

The corner markers represent the positions of atoms.

The antisymmetric stretching vibration of C=O groups were reasonably decomposed into six Gaussian peaks according to methods that reported by previous work.[2, 3]

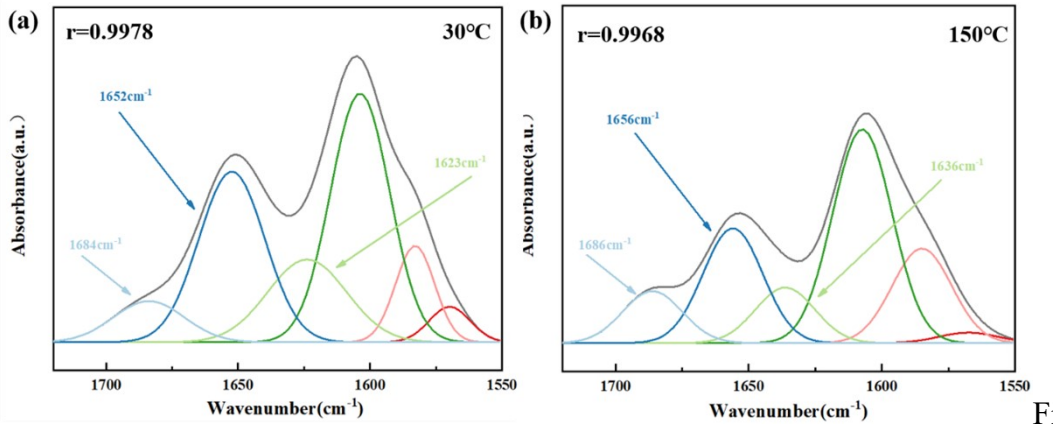

Figure S6. Infrared peak-splitting of FT-IR spectra under 30°C and 150°C for EP-V-1.3.

The degree of hydrogen bonding is calculated by the ratio of peak area according to Equation (S4). The results are showed in Table S2 and S3.

$$X_{B,CO\%}=\frac{A_{Ordered\ H-bond}+A_{Disordered\ H-bond}}{A_{Free\ -C=O}+A_{Ordered\ H-bond}+A_{Disordered\ H-bond}}$$

Equation (S4)

Table S3. Results of infrared peak-splitting of FT-IR spectra (30 ℃) for EP-V-1.3

	Free –C=O	**Disordered H-bond**	**Ordered H-bond**
Wavenumber(cm^{-1})	1684	1652	1623
Anlytc aera	2.48	9.58	5.57
Aera%	7.18	27.70	16.09
$X_{B,CO}$%		85.93%	

Table S4. Results of infrared peak-splitting of FT-IR spectra (150 ℃) for EP-V-1.3

	Free –C=O	**Disordered H-bond**	**Ordered H-bond**
Wavenumber(cm^{-1})	1686	1656	1636
Anlytc aera	2.59	5.73	2.77
Aera%	9.60	21.22	10.21
$X_{B,CO}$%		76.65%	

Curing behaviors

The Kissinger equation was used to calculate the non-isothermal curing reaction process (Equation S4), where β is the heating rate during the DSC test (K/min), Tp is the peak temperature in curves(K), R is 8.314 J/(mol*K). According to equation S7, we can obtain the number of activation energy (KJ/mol), which represents the degree of difficulty of curing reaction.[4]

$$\frac{d(ln\beta/Tp^2)}{d(\frac{1}{Tp})}=-\frac{\Delta Ea}{R}$$

Equation (S4)

Table S5. The parameters of EP-V-1.3 curing reaction based on DSC

β/(K/min)	Tp/K	$ln[\beta \cdot Tp^{-2}/(K \cdot min)^{-1}]$	$1000*Tp^{-1}/K^{-1}$
5	363.02	-10.1795	2.7547
10	376.74	-9.5605	2.6544
15	384.78	-9.1973	2.5989

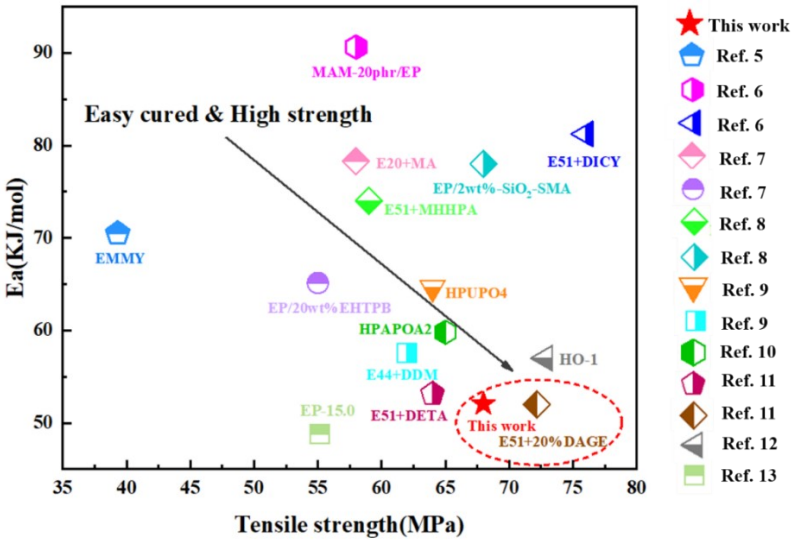

Figure S7. The activation energy and tensile strength of different epoxy resins (DGEBA) system.[5-13]

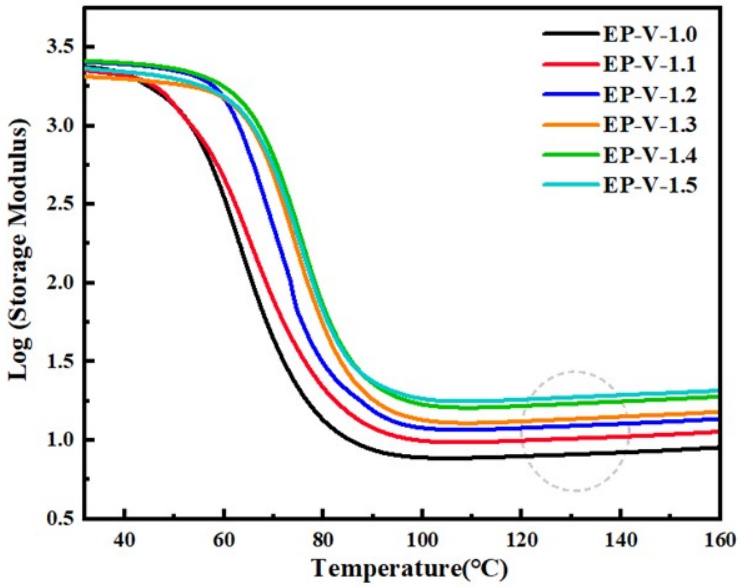

Figure S8. (a) The log axis of the storage modulus of different samples (Tg+60 ℃)

Table S6. Glass transition temperature (Tg), storage modulus at Tg + 60 ℃ and ν_e of six samples

	Tg (℃)	Tg+60 (℃)	Storage modulus (MPa)	ν_e (mol·m^{-3})
EP-V-1.0	67.39	127.39	8.08	809.08
EP-V-1.1	68.86	128.86	10.23	1019.90
EP-V-1.2	74.03	134.03	12.53	1233.82
EP-V-1.3	77.40	137.40	14.02	1369.76
EP-V-1.4	78.24	138.24	17.59	1714.52
EP-V-1.5	78.39	138.39	19.31	1881.41

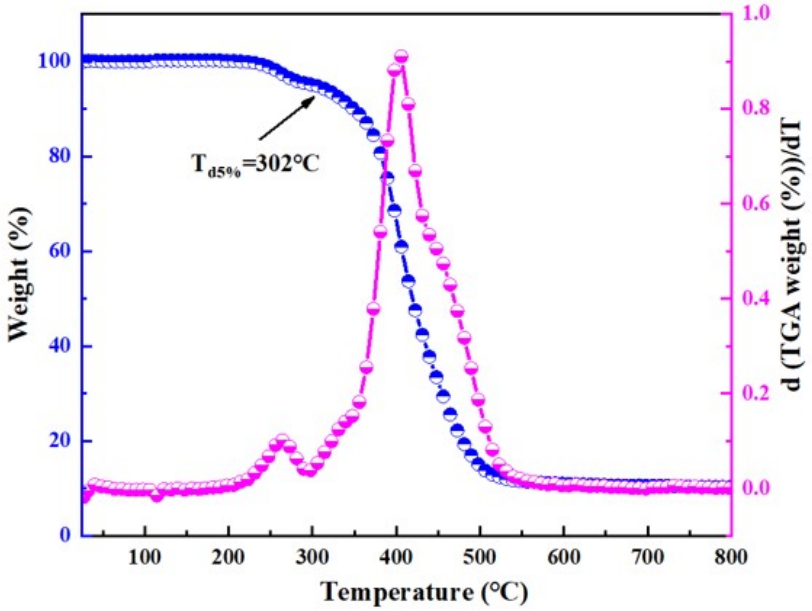

Figure S9. (a) TGA curves of EP-V-1.3

Table S7. Mass change of EP-V-1.3 in water, acid and base solution after 7 days.

Solution	Concentration(mol/L)	Mass change (+%)
H_2O	-	0.60
HCl	0.01	1.09
	0.1	11.7
	1	24.86
	2	23.10
	6	77.62
H_2SO_4	0.01	1.07
	0.1	5.33
	1	20.60
	2	25.77

	6	22.94
NaOH	0.01	0.82
	0.1	0.43
	1	1.20
	2	0.39
	6	0.32

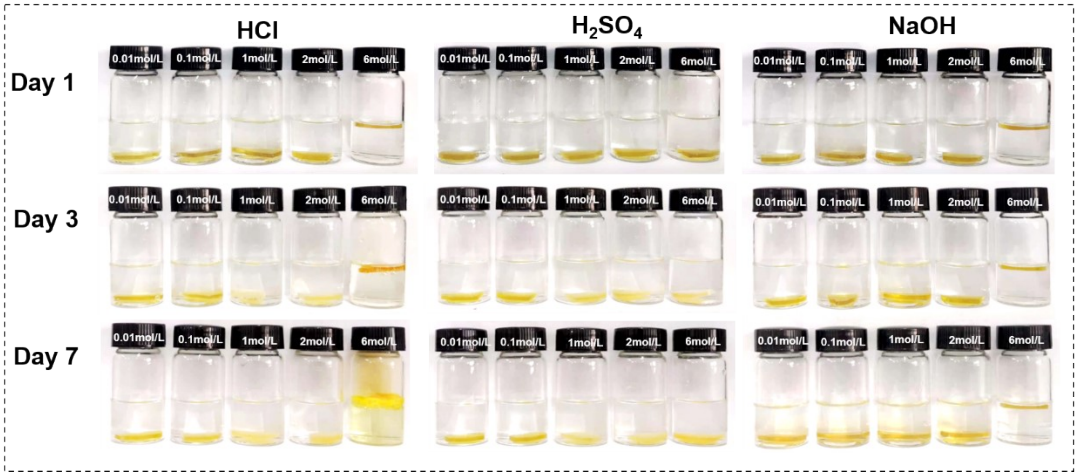

Figure S10. Digital photos of acid-base resistance property of EP-V-1.3

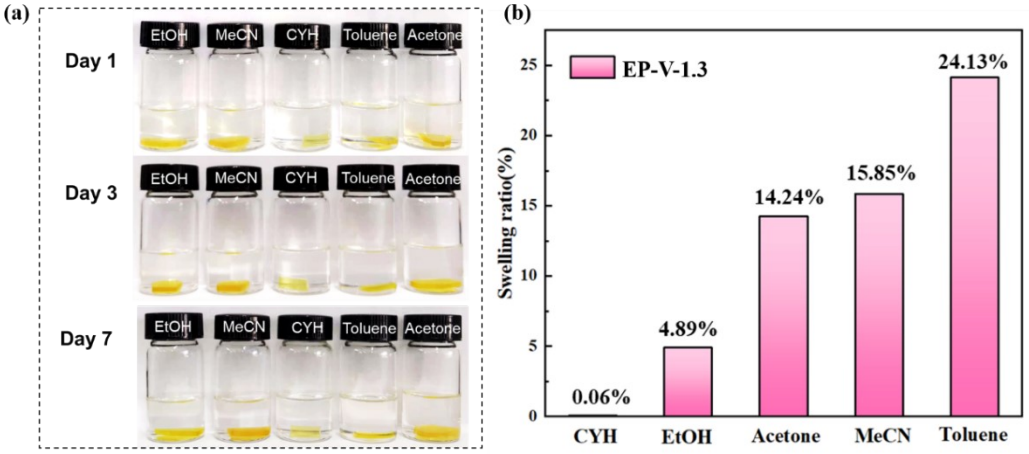

Figure S11. (a) Digital photos of solvent resistance of EP-V-1.3(1 day, 3 day, 7 day), (b) swelling ratio of EP-V-1.3 in different solvents (the swelling ratio of prepared resin are determined by comparison of weights of the resin before and after soaking in organic solvents).

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