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Supporting Information

Parthenocissus-inspired, strongly adhesive, efficiently self-healing polymer for energetic adhesive applications

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Supplementary Methods

Materials:

GAP (Hydroxyl value=29.47 mgKOH g⁻¹) were supplied from Liming Research Institute of Chemical Industry (China). Isophorone diisocyanate (IDI, 98%), 4,4'-methylenedianiline (MDA, 99%), diphenyl methane-4,4'-diisocyanate (MDI, 98%) and isophorone diamine (IDA, 99%) were purchased from Macklin Inc.. All other chemical reagents are of analytical grade, no further purification is required in this work.

Synthesis of polymer GAP-IDI-MDA:

A typical polymerization procedure for GAP_{0.5}-IDI-MDA_{0.5} is described below. First, GAP (3.8076 g) was placed into a roundbottomed flask equipped with a vigorous stirring. Then the mixture was heated to 90 °C in an oil bath, and dried under vacuum for 2 hours to remove moisture. Afterwards, IDI (0.4662 g, 2.1 mmol) was dissolved in 5 mL DMF, dropwise added into the flask, and the mixture was continuously stirred for 30 min in a N₂ atmosphere. After this, the mixture was added by one drop of dibutyl tin dilaurate (DBTDL). After 3 h, the temperature was reduced to 0 °C, and MDA (0.1983 g, 1.0 mmol) dissolved in 10 mL DMF was slowly added to the above system. Kept stirring for 30 min at 0 °C, the reaction mixture was then heated to 90 °C for another 12 h. After being cooled to room temperature, methanol (3 mL) was added for removing residual isocyanate. The mixture was poured into a polytetrafluorethylene (PTFE) mold and dried at 90 °C for 48 h in an air-circulating oven and followed by subjecting vacuum evaporation to remove the residual solvent at 75 °C for 12 h (Fig. S1). The same procedure was used to prepare different polymers with different GAP/MDA, as summarized in the Table S1.

Synthesis of polymer GAP_{0.5}-MDI-IDA_{0.5}:

First, GAP (3.8076 g) was placed into a round-bottomed flask equipped with a vigorous stirring. Then the mixture was heated to 90 °C in an oil bath, and dried under vacuum for 2 hours to remove moisture. Afterwards, MDI (0.5255 g, 2.1 mmol) was dissolved in 5 mL DMF, dropwise added into the flask, and the mixture was continuously stirred for 30 min in a N₂ atmosphere.

After this, the mixture was added by one drop of dibutyl tin dilaurate (DBTDL). After 3h, the temperature was reduced to 0 °C, and IDA (0.1703 g, 1.0 mmol) dissolved in 10 mL DMF was slowly added to the above system. Kept stirring for 30 min at 0 °C, the reaction mixture was then heated to 90 °C for another 12 h. After being cooled to room temperature, methanol (3 mL) was added for removing residual isocyanate. The mixture was poured into a polytetrafluorethylene (PTFE) mold and dried at 90 °C for 48 h in an air-circulating oven and followed by subjecting vacuum evaporation to remove the residual solvent at 75 °C for 12 h (Fig. S1).

Preparation of energetic composite materials (ECM):

First, 5 g adhesive was dissolved in 100 mL ethyl acetate, and then 5 g TATB was dispersed into ethyl acetate with vigorous stirring about 1000 r min⁻¹ at 60 °C. After evaporating most of the solvent, the composite mixture became slurry-like. The product was then dried in oven at 60 °C for 12 h.

Materials and Characterization

Characterization of adhesives: ¹H NMR spectra were recorded on a Bruker AVANCE III 500 MHz NMR spectrometer using CDCl₃ as solvent. FTIR spectra were recorded using a Bruker Tensor II spectrometer equipped with an attenuated total reflectance (ATR) accessory and a heating device. The temperature-dependent FTIR data were selected to perform 2D correlation analysis and the temperature interval was controlled as 10 °C in the range of 30–90 °C. In the 2D correlation FTIR spectra, the red and blue colors define the positive and negative correlation intensities, respectively. X-ray diffraction (XRD) analysis was carried out using an X-ray diffractometer (Bruker D8 Advance), which is equipped with a Cu K α source and works in the 2 θ range of 5–60 at 40 kV and 40 mA. The gel permeation chromatography (GPC) (Waters 1515) was employed for evaluation of molecular weight. TGA measurement was performed on Mettler 851e instrument with a heating rate of 10 °C min⁻¹ from 50 to 600 °C under nitrogen atmosphere. DSC experiments were carried out on a TA instrument DSC-25 at the heating rates of 5,10,15,20 °C min⁻¹ under nitrogen atmosphere. The surface morphologies of polymeric films were observed

using AFM (Bruker Multimode 8) with the tapping mode. SAXS measurements were conducted on a Bruker Nano STAR system and Cu K α radiation ($\lambda = 0.1541$ nm) was used as the X-ray source. Mechanical tensile tests were performed on a Shimadzu AGS-X tester with a 50 N load following the standard strain/stress procedure. The temperature sweeps of dynamic mechanical behavior of polymeric samples were obtained using TA DMA Q800 in tensile mode (dynamic strain: 0.01 %). TA DMA Q800 instrument was also used in the stress relaxation tests, and samples were subjected to a strain of 100 % that was preserved constant for relaxation time of 30 min. Dimensions of the samples were measured by a standard Vernier caliper. The tensile adhesion test was used to evaluate the self-adhesion of different substrate surfaces. The substrate without contaminants was cut into 2×1 cm² splines. To evaluate the self-healing ability of the EPU adhesives, specimens ($30 \times 10 \times 1$ mm³) were completely cut in half in the atmosphere. Then, the two pieces of the EPU specimens were manually merged and healed under room temperature during different period of time. The healed specimens were again subjected to tensile tests. The healing efficiency (η) is defined as the ratio of the restored elongation at break to the original fracture strain. The adhesive is dissolved in ethyl acetate. After evaporating most of the solvent, the composite mixture became slurry-like and was dripped between the two substrates with an overlapping area of 1×1cm². After drying in a 60 °C oven, the samples were obtained, and were pulled by a Shimadzu AGS-X tester at a strain rate of 100 mm min⁻¹ until the joint cracks. The adhesion strength is calculated by the maximum load divided by the initial overlapping area.

Characterization of ECM: Mechanical test was performed on a Shimadzu AGS-X tester with a 50 N load following the standard strain/stress procedure at room temperature. The combustion process was recorded by a high-speed camera (Phantom VEO-E 310). FTIR spectra were recorded using a Bruker Tensor II spectrometer equipped with an attenuated total reflectance (ATR) accessory. Optical microscopy images of the scratch self-healing process of the EPU-based ECMs were obtained by Olympus (BX53) optical microscope. The EPU-based ECMs was scratched (length: 10 mm, width: 65 µm, depth: 0.5 mm) by a scalpel and placed in the atmosphere, and optical microscopy was used to monitor the self-healing process.



Fig. S1 Synthetic route of (a)GAP_{0.5}-MDI-IDA_{0.5} and (b)GAP_x-IDI-MDA_y.

	GAP (mol)	IDI (mol)	MDA (mol)	wt % of GAP ^a
GAP _{0.5} -MDI-IDA _{0.5}	1.0	2.1	1.0	84.6
GAP _{0.7} -IDI-MDA _{0.3}	1.4	2.1	0.6	90.1
GAP _{0.5} -IDI-MDA _{0.5}	1.0	2.1	1.0	85.1
GAP _{0.3} -IDI-MDA _{0.7}	0.6	2.1	1.4	79.0

Table S1 Polymer information.

^a Based on the weight percentages of GAP included in the total monomer weight.



Fig. S2 FTIR spectra of EPU adhesives in the wavenumber range (a) from 700 to 4000 cm⁻¹ and (b) from 1000 to 2300 cm⁻¹.



Fig. S3 ¹H NMR spectrum of GAP_{0.5}-IDI-MDA_{0.5} in CDCl₃ (500 MHz).



Fig. S4 ¹H NMR spectrum of GAP_x -IDI-MDA_y in CDCl₃ (500 MHz). The ratios of the signals on -CH₂- of GAP (highlighted in purple) and phenyl ring protons of MPU moieties (highlighted in red) confirm the incorporation of the corresponding mol% of GAP and MPU.

	Theoretical ratio (GAP/MPU)	Calculated ratio (GAP/MPU)
GAP _{0.5} -MDI-IDA _{0.5}	0.5/1.0	0.57/0.90
GAP _{0.7} -IDI-MDA _{0.3}	0.7/0.3	0.73/0.27
GAP _{0.5} -IDI-MDA _{0.5}	0.5/0.5	0.53/0.47
GAP _{0.3} -IDI-MDA _{0.7}	0.3/0.7	0.33/0.67

Table S2 GAP/MPU ratio calculated based on ¹H NMR.

	wt% of GAP ^a	M_n^{-1}	M_n^2	PDI^{l}	PDI ²
GAP _{0.5} -MDI-IDA _{0.5}	84.6	7179	34105	3.2	3.0
GAP _{0.7} -IDI-MDA _{0.3}	90.1	8539	37442	2.5	2.3
GAP _{0.5} -IDI-MDA _{0.5}	85.1	7317	33238	3.0	3.1
GAP _{0.3} -IDI-MDA _{0.7}	79.0	6664	39406	2.8	3.3

 Table S3 The molecular weight of EPU adhesives.

^a Based on the weight percentages of GAP included in the total monomer weight;

¹ refers to prepolymer;

² refers to adhesive.

Samula	Maximum stress	Young's modulus	Maximum Strain
Sample	(kPa)	(kPa)	(%)
GAP _{0.7} -IDI-MDA _{0.3}	29.1	36.1	13,399
GAP _{0.5} -IDI-MDA _{0.5}	142.7	524.8	5,269
GAP _{0.3} -IDI-MDA _{0.7}	330.3	815.4	311

Table S4 The mechanical properties of EPU adhesives.



Fig. S5 DMA curves of (a) GAP_{0.5}-MDI-IDA_{0.5}, (b) GAP_{0.7}-IDI-MDA_{0.3}, (c) GAP_{0.5}-IDI-MDA_{0.5} and (d) GAP_{0.3}-IDI-MDA_{0.7}. Loss modulus (G') and storage modulus (G') of films versus temperature at 1 Hz.



Fig. S6 Synchronous (I) and asynchronous (II) 2D correlation FTIR spectra of GAP_{0.5}-MDI-IDA_{0.5}.

Quantum Chemical Calculations

1. Method

We determined the initial complex structures from the selected conformations by AutoDock package and calculated the binding energies of these complexes. Each of monomer and complex is optimized at the level of B3LYP/6-31G and then calculated the single-point energies in vacuum by Gaussian 09 software. Using Chimera software displays the H-bond of complex.

The formula of single-point energy:

$$\Delta E_{H\text{-Bond}} = E_{comp} - (E_{moll} + E_{mol2})$$

2. Monomer structres

The three optimized structures of urea and carbamate are shown in Fig. S7.



Fig. S7 Three optimized structures of urea and carbamate.

3. Calculation results

The structure of A-A is as shown:



Fig. S8 Optimized structure of A-A ($E_{comp} = -2058.2026$ a.u.).

The H-bond energy is:

$$\Delta E_{H-Bond} = E_{comp} - (E_{moll} + E_{mol2}) = -21.21 \text{ kcal/mol}$$

The structure of A-B is as shown:



Fig. S9 Optimized structure of A-B ($E_{comp} = -1968.58$ a.u.).

The H-bond energy is:

$$\Delta E_{H-Bond} = E_{comp} - (E_{mol1} + E_{mol2}) = -23.84 \text{ kcal/mol}$$

The structure of B-B is as shown:



Fig. S10 Optimized structure of B-B ($E_{comp} = -1878.9460 \text{ a.u.}$).

The H-bond energy is:

$$\Delta E_{H-Bond} = E_{comp} - (E_{moll} + E_{mol2}) = -22.21 \text{ kcal/mol}$$

The structure of A-C is as shown:



Fig. S11 Optimized structure of A-C ($E_{comp} = -1897.27 \text{ a.u.}$).

The H-bond energy is:

$$\Delta E_{H-Bond} = E_{comp} - (E_{moll} + E_{mol2}) = -11.99 \text{ kcal/mol}$$

The structure of B-C is as shown:



Fig. S12 Optimized structure of B-C ($E_{comp} = -1807.64 \text{ a.u.}$).

The H-bond energy is:

 $\Delta E_{H-Bond} = E_{comp} - (E_{moll} + E_{mol2}) = -14.56 \text{ kcal/mol}$



Fig. S13 Optical microscope images demonstrating self-healing of GAP_{0.5}-MDI-IDA_{0.5}.

	N (%)	C (%)	H (%)	O (%)	Assumed chemical formula
GAP _{0.5} -MDI-IDA _{0.5}	36.93	42.31	5.61	15.15	$C_{3.53}H_{5.61}O_{0.95}N_{2.64}$
GAP _{0.3} -IDI-MDA _{0.7}	34.88	45.36	6.19	13.57	$C_{3.78}H_{6.19}O_{0.85}N_{2.49}$
GAP _{0.5} -IDI-MDA _{0.5}	37.33	41.63	5.19	15.84	$C_{3.47}H_{5.19}O_{0.99}N_{2.67}$
GAP _{0.7} -IDI-MDA _{0.3}	38.58	39.90	5.84	15.69	$C_{2.76}H_{5.84}O_{0.98}N_{2.76}$

Table S5 EPU adhesives element composition and assumed chemical formula.

$Q \left(J \ g^{-1}\right)$	$\Delta_{c}H^{0}~(kJ~g^{-1})$	$\Delta_{\rm f} H^0 (kJ \; g^{1})$
1626	-21.67	-0.23
1306	-22.89	-0.83
1657	-21.90	+0.83
1805	-21.38	+1.95
	Q (J g ⁻¹) 1626 1306 1657 1805	Q (J g ⁻¹) $\Delta_c H^0$ (kJ g ⁻¹)1626-21.671306-22.891657-21.901805-21.38

Table S6 EPU adhesives heat release, combustion heat and enthalpy of formation.

 $\Delta_{\!c} H^0\!\!:$ Heat of combustion; $\Delta_{\!f} H^0\!\!:$ Enthalpy of formation.

Table S7	Thermal	decomposition	temperature and	l activation	energy of EPU	adhesives at	different l	heating rates.
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		F			
β	5 °C min ⁻¹	10 °C min ⁻¹	15 °C min ⁻¹	20 °C min ⁻¹	Ea
GAP _{0.3} -IDI-MDA _{0.7}	245.55 °C	255.61 °C	263.51 °C	268.75 °C	124.45 kJ mol ⁻¹
GAP _{0.5} -IDI-MDA _{0.5}	246.19 °C	257.95 °C	264.88 °C	269.12 °C	131.42 kJ mol ⁻¹
GAP _{0.7} -IDI-MDA _{0.3}	244.22 °C	256.08 °C	263.58 °C	268.26 °C	130.42 kJ mol ⁻¹



Fig. S14 Comparison of the self-healing time, effiency and adhesive strength of the GAP_{0.7}-IDI-MDA_{0.3} with other self-

healing adhesive polymers reported recently.1-9



 $\textbf{Fig. S15} \ Plot \ of \ ln(\beta/T2 \ p) \ vs. \ -1/RT_p \ for \ (a) \ GAP_{0.7}\text{-}IDI-MDA_{0.3}, \ (b) \ GAP_{0.5}\text{-}IDI-MDA_{0.5} \ and \ (c) \ GAP_{0.3}\text{-}IDI-MDA_{0.7}, \ (b) \ GAP_{0.5}\text{-}IDI-MDA_{0.5} \ and \ (c) \ GAP_{0.3}\text{-}IDI-MDA_{0.7}, \ (c) \ GAP_{0.5}\text{-}IDI-MDA_{0.5} \ and \ (c) \ GAP_{0.5}\text{-}IDI-MDA_{0.7}, \ (c) \ GAP_{0.5}\text{-}IDI-MDA_{0.7}, \ (c) \ GAP_{0.5}\text{-}IDI-MDA_{0.5} \ and \ (c) \ GAP_{0.5}\text{-}IDI-MDA_{0.7}, \ (c) \ GAP_{0.5}\text{-}IDI-MDA_{0.7}, \ (c) \ GAP_{0.5}\text{-}IDI-MDA_{0.5}, \ (c) \ GAP_{0.5}\text{-}IDI-MDA_{0.7}, \ (c) \ GAP_{0.5}\text{-}IDI-MDA_{0.5}, \ (c) \ (c) \ GAP_{0.5}\text{-}IDI-MDA_{0.5}, \ (c) \$

	1.4	T _b	T _{SADT}	ΔS^{\neq}	$\Delta \mathrm{H}^{\neq}$	ΔG^{\neq}
	IIIA	(°C)	(°C)	$(J mol^{-1}K^{-1})$	(kJ mol ⁻¹)	(kJ mol ⁻¹)
GAP _{0.3} -IDI-MDA _{0.7}	27.67	248.93	230.72	+14.78	+120.30	+112.86
GAP _{0.5} -IDI-MDA _{0.5}	29.20	250.75	233.39	+27.49	+127.21	+113.29
GAP _{0.7} -IDI-MDA _{0.3}	29.03	250.77	233.28	+26.08	+126.21	+113.00

Table S8 GAP-IDI-MDA series EPU adhesives kinetics, thermodynamics and thermal stability parameters.

Bonding energy calculation

Autodock package was utilized to determine the representative conformations of these four complexes. Then, we use the semi-empirical PM6 method to optimize each monomer and complex, and calculate their single point energies at the PM6/6-31G level to describe the non-bonding interaction.

The formula of single-point energy:

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\Delta Ebind \ vacu = Ecomp \ vacu - ( \ Emol1 \ vacu + Emol2 \ vacu )
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Where $\Delta Ebind vacu$ is the bonding energy between EPU and solid molecules, *Emol1 vacu* and *Emol2 vacu* respectively represent the energy of the polymer and small molecules in the optimized conformation, and *Ecomp vacu* is the total energy

of the optimized complex conformation. The calculated results are list in Table S9 and shown in Fig. S16.

No	small	Ecomp vacu	Emollvacu	Emol2 vacu	$\Delta E bind vacu$
INO.	molecules	(a. u.)	(a. u.)	(a. u.)	(kcal mol ⁻¹)
a		-0.380101	-0.310604	-0.041088	-17.83
b	د قور قر د قورقی قر د قورقر د قو	-0.316192	-0.310604	-0.017688	-14.61
с	ه و شوره و ر شور شر و ه و	-0.298125	-0.310604	-0.031938	-12.21
d	ی فرق گونی ای فرقی کی ای فرقی ای فرقی ای فرقی	-0.362384	-0.310604	-0.037449	-8.99

Table S9 The Bonding energy calculation results.
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Fig. S16 The optimized configurations of EPU with TATB, 1,3,5-triaminobenzene, 1,3,5-trinitrobenzene, and hexamethylbenzene.



Fig. S17 XPS N 1s spectra of (a) TATB and (b) EPU-based ECMs

	Strongth (MBa)	Voung's modulus (MDa)	Toughness
	Suengui (MFa)	roung's modulus (Mra)	(MJ m ⁻³)
EPU-based ECMs	1.39	2.67	8.05
EPU	0.03	0.04	1.98

 Table S10 The mechanical parameters of EPU-based ECMs and EPU.



Fig. S18 Optical microscope images demonstrating self-healing of EPU-based ECMs.



Fig. S19 Schematic diagram of ignition and combustion test.

NEPU-based ECMs	270 ms	618 ms
4	3	4
669 ms	969 ms	1269 ms
· · ·		2 cm

Fig. S20 Sequential open-combustion images of NEPU-based ECMs (Spline size: 40×10×1 mm³).

Movie S1. Demonstration shows the rapid self-healing of GAP_{0.7}-IDI-MDA_{0.3} film at room temperature.

Movie S2. Demonstration shows strong adhesion of GAP_{0.7}-IDI-MDA_{0.3} to glass substrate.

Movie S3. Demonstration shows the fast crack-healing ability of EPU-based ECMs.

Movie S4. Demonstration shows the ignition and combustion process of EPU-based ECMs.

Movie S5. Demonstration shows the ignition and combustion process of NEPU-based ECMs.

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