Supporting information

High Performance Dynamic Covalent Crosslinked Polyacylsemicarbazide
Composites with Self-healing and Recycling Capabilities

Shuo Wang[1], Daihua Fu[1], Xiaorong Wang[3], Wuli Pu[1], Alfonso Martone[2], Xili Lu[1],

Marino Lavorgna[2], Zhanhua Wang[1],*, Eugenio Amendola[2,*], and Hesheng Xia[1],*

[1] State Key Laboratory of Polymer Materials Engineering, Polymer Research Institute, Sichuan University, Chengdu, 610065, China

Email: zhwangpoly@scu.edu.cn; xiahs@scu.edu.cn

[2] Institute of Polymers, Composites and Biomaterials, National Research Council, P.le Fermi, 1-80055 Portici, Naples, Italy

Email: amendola@unina.it

[3] School of Petrochemical Engineering, Liaoning Shihua University, Fushun, Liaoning 113001, China

Table of contents

Synthesis of ASC model compound (2-acetyl-N-cyclohexylhydrazine-1-carboxamide): acetyl hydrazide (10 mmol, 0.74 g) and cyclohexyl isocyanate (CHI, 10 mmol, 1.25 g) dissolved in 15 mL tetrahydrofuran (THF) were charged to a 20 mL glass bottle with a magnetic stir bar. The product was precipitated out of the solution after reacting for 10 minutes at RT, then collected by vacuum filtration and washed with cold THF. The resulting product was dried in an oven at 80 ℃ for 12 h.

NMR study of small model compounds:

2-acetyl-N-cyclohexylhydrazine-1-carboxamide (0.18 mmol, 0.036 g) and benzoylhydrazide (0.18 mmol, 0.025 g) were dissolved in 5 mL DMSO-d_6. The resulting solution was divided in 7 NMR tubes. The 7 samples were reacted at 120 ℃ for 0, 3, 10, 21, 24, 35 and 40 h, then was characterized by ^{1}H NMR spectroscopy.

Determination of the reaction order for the ASC dissociation: In order to avoid the influence of the ASC moiety reversible reaction, we added benzylamine which is 5 times the amount of 2-acetyl-N-cyclohexylhydrazine-1-carboxamide into the reaction system. Benzylamine with high reactivity (compared to hydrazide) can effectively capture the cyclohexyl isocyanate produced by the dissociation of the 2-acetyl-N-cyclohexylhydrazine-1-carboxamide. Thus, the dissociation reaction of the 2-acetyl-N-cyclohexylhydrazine-1-carboxamide can be regarded as an irreversible reaction. 2-acetyl-N-cyclohexylhydrazine-1-carboxamide and benzylamine were dissolved in an appropriate amount of DMSO-d_6 at a molar ratio of 1:5 and divided into 5 NMR tubes. The 5 samples were reacted at 140 ℃ for 7, 15, 30, 45, and 60 minutes. If the reaction rate is only proportional to the concentration of 2-acetyl-N-cyclohexylhydrazine-1-carboxamide according to the equation S1, it can be proved that the dissociation reaction of the ASC group is a first-order reaction.

$-\mathrm{d}c/\mathrm{d}t = kc$ (Equation S1)

Determine the dissociation kinetics of ASC moieties: 2-acetyl-N-cyclohexylhydrazine-1-carboxamide (0.7 mmol, 0.14 g) and benzylamine (3.5 mmol, 0.375 g) were dissolved in 15 mL DMSO-d_6. The obtained solution is divided evenly

into 25 NMR tubes, and they react at varying temperatures (100, 110, 120, 130, 140 °C) for different times (0, 15, 30, 45, 60 min). The dissociation rate constant (k_d) is the slop of ln (c_t/c_0)-t at various temperatures.

Since the dissociation reaction of ASC is a first-order kinetic, the reaction rate constant at different temperatures can be calculated from:

$$\ln (c_t/c_0) = -k_d t \quad\quad\quad \text{(Equation S2)}$$

The dissociation activation energy: The dissociation activation energy can be calculated by Arrhenius equation:

$$\ln k = \ln A - E_a/RT \quad\quad\quad \text{(Equation S3)}$$

Cross-linking density χ

The cross-linking density χ of PASCs are defined as[1]:

$$\chi = \sum_{f=3}^{\infty} \frac{f}{2} C_f$$

(Equation S4)

Where χ is the cross-linking density of PASCs, where f is the functionality of the reactants and C_f is the concentration of reactant with functionality f, expressed as moles per volume of a fully cured polymer.

GPC: HMDI (2 mmol, 0.53 g) and ADH (2 mmol, 0.35 g) were stirred in 30 ml DMF at RT for 1 h. The obtained linear PASC-ADH-HMDI suspension was divided into 5 glass bottles evenly after adding 3 mmol 2-acetyl-N-cyclohexylhydrazine-1-carboxamide. Then, they were reacted for 0, 1, 2, 5, 10 h at 120 °C. Samples were performed on GPC.

Stress relaxation analysis: The calculation model of relaxation activation energy of PASC is the Maxwell model. The formula for calculating the relaxation modulus is as:

$$E(t) = E_0 \exp(-t/\tau) \quad\quad\quad \text{(Equation. S5)}$$

Where $E_{(t)}$ is the stress relaxation modulus at time t, E_0 is the initial value and τ is the relaxation time. τ is defined as the time when stress relaxation modulus reaches about 37% (1/e) of its initial value ($E/E_0 = 1/e$). τ of PASC-ADH-HMDI-0.09 is determined by temperature of 125-145 °C in this work. Besides, the relationship of the relaxation time τ and temperature follows the Arrhenius equation[2, 3]:

$$\tau_{(T)} = \tau_0 \exp(E_{a,r}/RT) \tag{Equation. S6}$$

Where $\tau_{(T)}$ is the relaxation time at actual temperature, τ_0 is the characteristic relaxation time at infinite T, $E_{a,r}$ is the relaxation activation energy (kJ·mol^{-1}) of the PASC-ADH-HMDI-0.09, R is the universal gas constant and T (K) is the temperature at the stress relaxation is performed.

Recycling experiment of CFRP-2 composite: Firstly, a CFRP-2 prepreg (50 × 60 × 0.22 mm, L × W × H) was used to study the recycling mechanism and clarify the feasibility. The CFRP-2 prepreg was swelled in 50 mL DMSO for 24 h at RT. Solvent molecules continued to diffuse into the matrix resin network, and the sheet expanded and loosened continually (Figure S9). Then, the container was placed in a 110 °C oven for 5 h. When the temperature dropped to room temperature, we removed the solution from the container. The CFs were washed three times with DMSO and ethanol, then dried in an 80 °C oven. PASC can be precipitated from DMSO by adding poor solvent ethanol. Excess ethanol was added, followed by centrifugalizing and washing to remove solvent. Finally, PASC was dried in an 80 °C oven for 12 h. About 78.2 wt% of PASC from the composite was recycled. The recycled CFs were characterized by SEM, XRD, XPS, Raman spectroscopy and tensile test of single-layer regenerated CFRP-2 prepreg. The regenerated PASC-ADH-HMDI-0.09 polymers were characterized by uniaxial tensile measurement after hot pressing.

Secondly, we used 300 mL DMSO solvent to swell the ten-layer CFRP-2 laminate (150 × 150 × 2.2 mm, L × W × H) for 24 hours at room temperature. CFRP-2 composite laminate became loose and the layers were no longer tightly connected with each other. We transferred it to another glass container containing 300 mL

DMSO and heated at 110 °C for 5 h. The single-piece carbon fiber fabric was taken out and washed with DMSO and ethanol three times respectively. About 70.1 wt% of PASC was recycled from composite laminates. We reprocessed the recycled carbon fiber and PASC-ADH-HMDI-0.09 polymers into short beam shear (SBS) test specimens. The interlaminar shear strength (ILSS) of regenerated laminates was characterized. Tensile experiment of single-layer regenerated CFRP-2 prepreg was also tested.
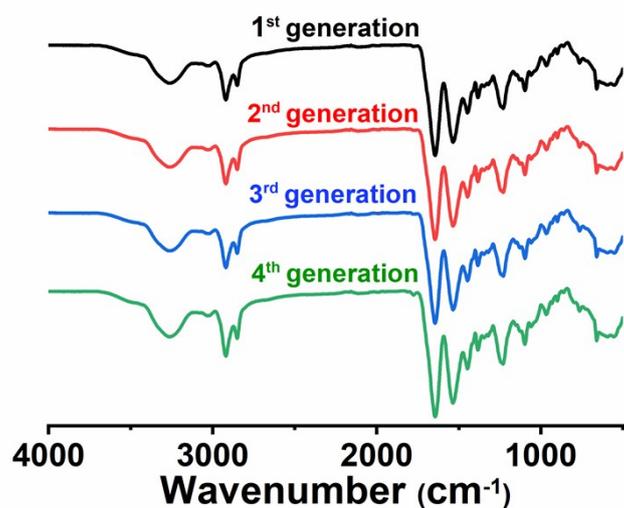
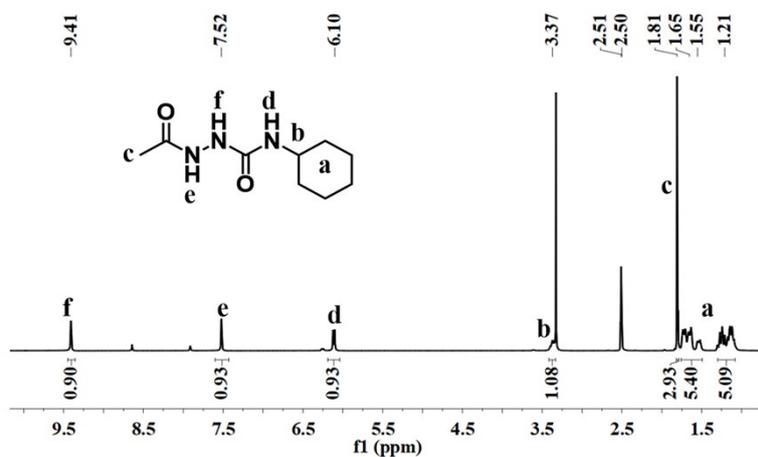**Figure S1.** ATR-FTIR spectra of PASC-ADH-HMDI-0.09 after multiple reprocessing cycles.

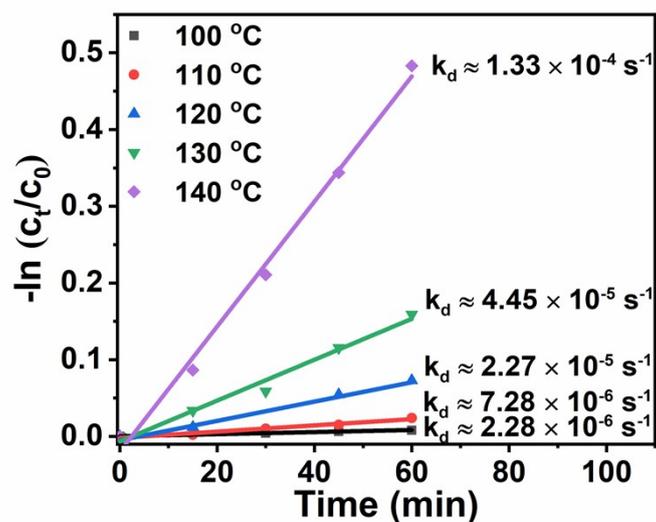**Figure S2.** ^{1}H NMR spectra (400 MHz, DMSO-d_6, 298 K) of 2-acetyl-N-cyclohexylhydrazine-1-carboxamide.

Figure S3. Linear fitting of -ln(c_t/c_0) versus time at different temperatures (equation S2).
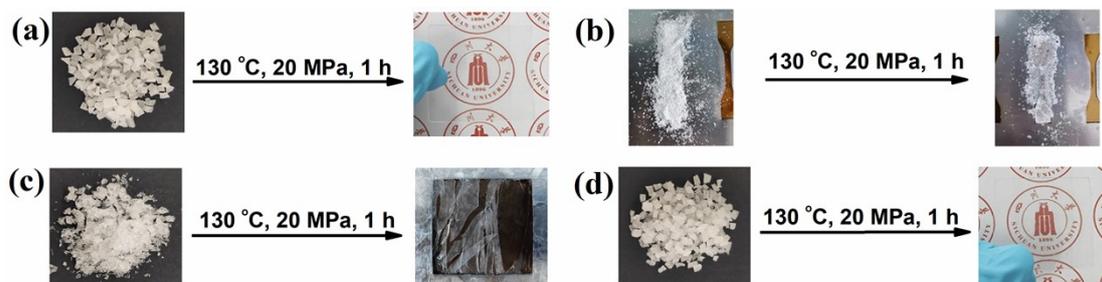

Figure S4. Hot-shaping conditions and appearance of PASCs. (a) PASC-ADH-HMDI-0.09, (b) PASC-IPDH-HMDI-0.07, (c) PASC-BDH-HMDI-0.09, (d) PASC-DDH-HMDI-0.08.
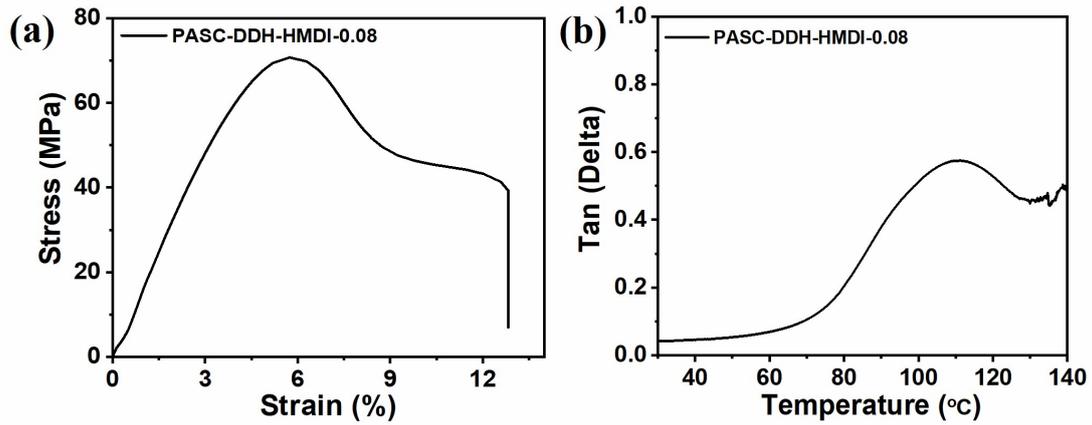
Figure S5. (a) Stress–strain and (b) DMA curves of PASC-DDH-HMDI-0.08.
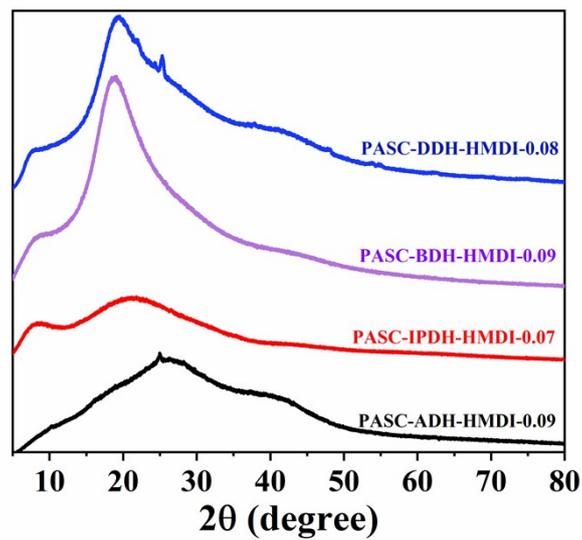

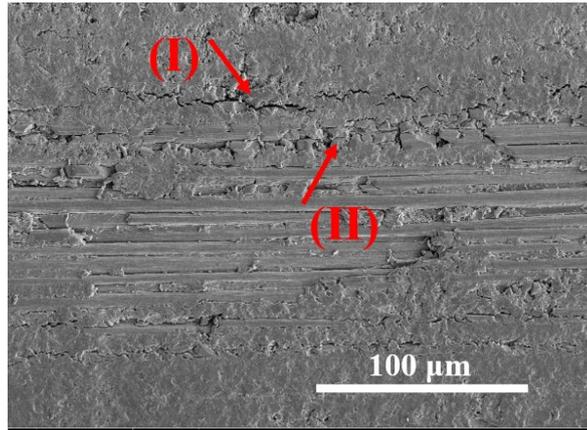**Figure S6.** XRD curves of different PASCs.

Figure S7. (Ⅰ) Delamination between resin and CF, reversible damage; (Ⅱ) Rupture of fiber, irreversible damage.

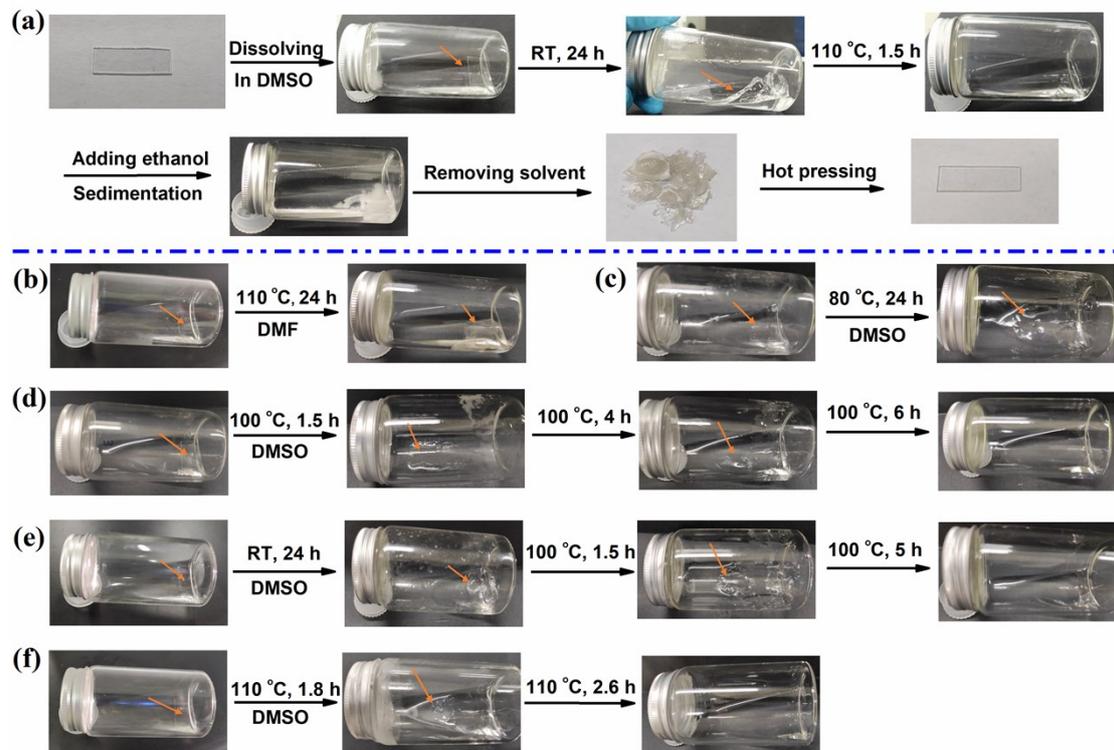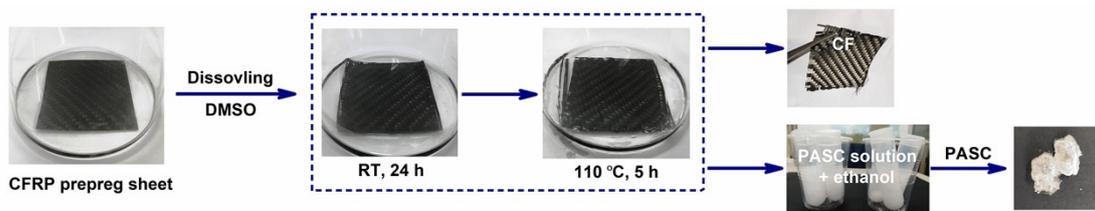**Figure S8.** Solvolytic recycle of PASC-ADH-HMDI-0.09 in solvents.

Figure S9. The recycling process of the single-layer CFRP-2 prepreg with dimension of 60 mm × 50 mm × 0.22 mm (L × W × H) in DMSO.
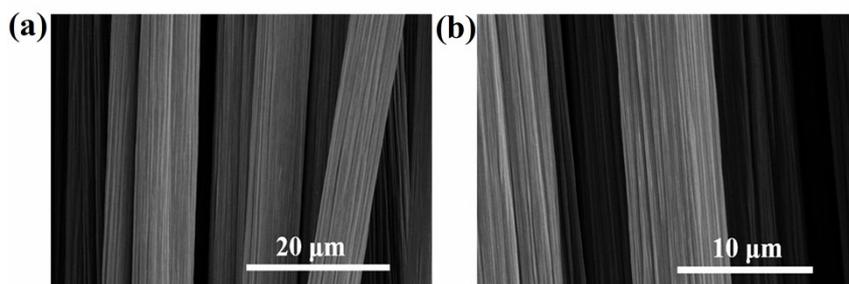

Figure S10. Highly magnified images of the surface of recycled CF.
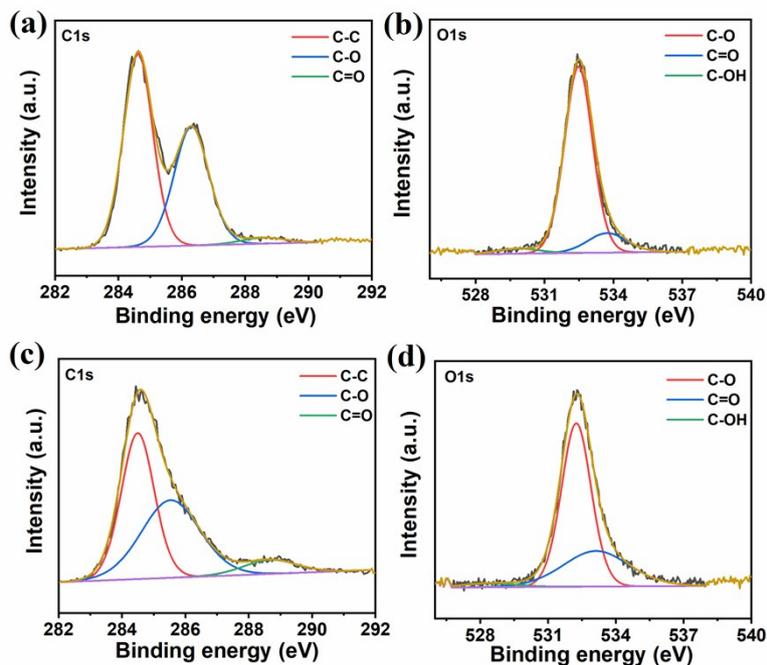
Figure S11. High-resolution XPS spectra of the virgin and recycled CFs. (a) and (b) the virgin CFs. (c) and (d) the recycled CFs.
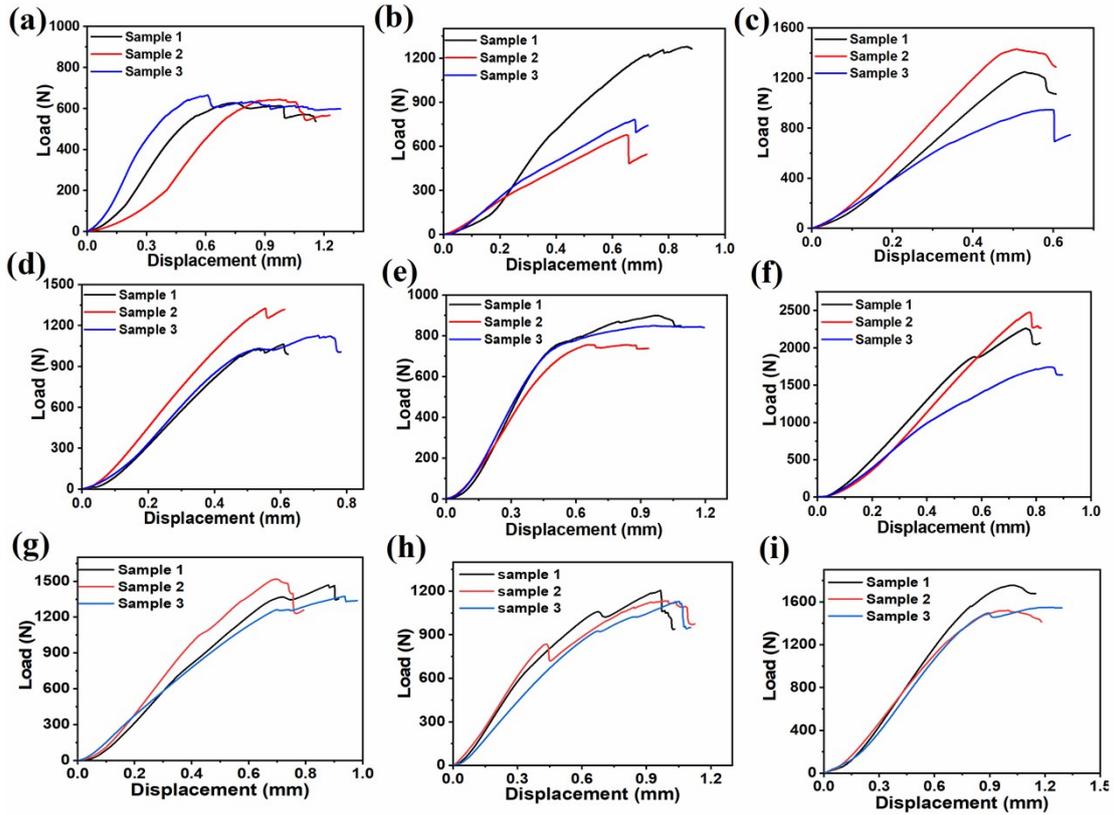
Figure S12. Short beam shear (SBS) curves of PASC-ADH-HMDI-0.09/CF composites. (a) CFRP-1 composite under 2 MPa at 130 ℃ for 1 h. (b) CFRP-1 composite under 10 MPa at 130 ℃ for 1 h. (c) CFRP-1 composite under 20 MPa at 130 ℃ for 1 h. (d) CFRP-1 composite under 25 MPa at 130 ℃ for 1 h. (e) CFRP-1 composite under 30 MPa at 130 ℃ for 1 h. (f) CFRP-2 composite under 20 MPa at 130 ℃ for 1 h. (g) Destroyed CFRP-2 composite samples are healed under 6 MPa at 130 ℃ for 1 h at first time. (h) Destroyed CFRP-2 composite samples are healed under 6 MPa at 130 ℃ for 1 h at second time. (i) Regenerated CFRP-2 composite samples prepared by recycled CFs and PASC-ADH-HMDI-0.09

Table S1. The monomer ratio and experimental condition of PASCs synthesis

Samples	[a] Molar ratio	Cross-linking density χ (mmol/cm3)	Experimental conditions	Dihydrazide (mmol)	HMDI (mmol)	tri-HDI (mmol)
PASC-ADH-HMDI-0	1 : 1 : 0	0	RT,10 min	10.00	10.00	0.00
PASC-ADH-HMDI-0.05	60 : 59 : 2/3	0.05	RT,10 min	20.00	19.67	0.22
PASC-ADH-HMDI-0.07	41 : 40 : 2/3	0.07	RT,10 min	20.50	20.00	0.33
PASC-ADH-HMDI-0.09	31 : 30 : 2/3	0.09	RT,10 min	20.67	20.00	0.44
PASC-ADH-HMDI-0.25	11 : 10 : 2/3	0.25	RT,10 min	22.00	20.00	1.33
PASC-ADH-HMDI-0.45	6 : 5 : 2/3	0.45	RT,10 min	20.00	16.67	2.22
PASC-IPDH-HMDI-0.07	31 : 30 : 2/3	0.07	RT, 3 min	25.50	15.00	0.33
PASC-BDH-HMDI-0.09	31 : 30 : 2/3	0.09	RT, 5 min	15.50	15.00	0.33
PASC-BDH-HMDI-0.08	31 : 30 : 2/3	0.08	Δ, 20 min	15.50	15.00	0.33

[a] The molar ratio refers to dihydrazide: HMDI: tri-HDI.

Table S2. Molding capabilities of PASCs under normal hot pressing.

Samples	Hot-pressing conditions	Can it be shaped?
PASC-ADH-HMDI	130 ℃, 1 h, 20 MPa	Yes
PASC-DDH-HMDI	130 ℃, 1 h, 20 MPa	Yes
PASC-BDH-HMDI	130 ℃, 1 h, 20 MPa	No
PASC-IPDH-HMDI	130 ℃, 1 h, 20 MPa	No

Table S3. The normalize relaxation modulus corresponding with the relaxation time of PASC-ADH-HMDI-0.09

Temperature (℃)	E/E_0	Relaxation (s)
125	0.367	38.61
130	0.367	34.83
135	0.367	31.63
140	0.367	25.17
145	0.367	18.98

Table S4. The compositions of the virgin CFs and the recycled CFs obtained from the XPS analyses.

CFs	Atomic ratio (%)	
	C	O
Virgin	81.78	18.22
Recycled	81.34	18.66

Table S5. The percentage areas of the deconvoluted signals obtained from the XPS spectra for the virgin CFs and the recycled CFs.

CFs	Component	Binding energy (eV)	Function groups	% of total area
Virgin	C	284.62	C-C	56.31
		288.56	C=O	2.58
		286.30	C-O	41.11
Recycled	C	284.50	C-C	47.68
		288.67	C=O	7.39
		285.53	C-O	44.93

Table S6. Comparison of the mechanical properties of PASC-ADH-HMDI-0.09 with other reported high-performance dynamic covalent polymers in previous literature[3-18].

Sample	Dynamic motifs	Young's modulus (GPa)	Stress at break (MPa)	Healing efficiency (%)	Reprocessing conditions	References
Vinylogous urethane/urea	Vinylogous urethane/urea	1.43-2.2	~40-90	Not discussed	150 ℃, 30 min/180 ℃, 5 min/150 ℃, 55 min	3-5
Polyurethanes with DA	DA	2.37-2.70	53.7-87.8	66.3-94.4	Not discussed	6-8
Poly-PME	Transesterification	1.43-1.97	48.6-52.1	Not discussed	150 ℃, 4 t, 1 h	9
PUU	Hinder urea bond	1.71-1.87	39.5-45.2	95	100 ℃, 300 kPa, 20 min	10
Polylactide vitrimer	Transesterification	1.5-1.8	49-60	44-102	Not discussed	11
Polyimine	Imine exchange	~1	~ 40	Not discussed	80 ℃, 90 KPa, 40 min/RT, 90 KPa, 96 h	12
Epoxy-anhydride	Transcarbamoylation	~1.8	~55	Not discussed	240 ℃, 3 min	13
PHU	Transesterification	1.6	53	Not discussed	160 ℃, 4 MPa, 8 h	14
Epoxy with imine amine exchange	Imine exchange	2.02-2.11	81-86	Not discussed	180 ℃, 15 MPa, 20 min	15
PASC-HM-0.07	Acylsemicarbazide	1.74	63.6	99.7	140 ℃, 15 MPa, 1 h	16
PTU	Thiocarbamate bond	2.0	62.7	Not discussed	80 ℃, 3 MPa, 30 min	17
Epoxy with exchangeable aromatic disulfide	Disulfide bonds	Not discussed	63.15	Not discussed	180 ℃, 1 h	18
PASC-ADH-HMDI-0.09	Acylsemicarbazide	2.84	100.12	94.2	130 ℃, 20 MPa, 1 h	This work

Table S7. Comparison with high-performance epoxies and their composite[15, 18-20]

	T_g (℃)	Tensile Modulus (GPa)	Tensile Strength (MPa)	Elongation at break (%)	ILSS (MPa)	References
[a] PRIME™ 20LV	82.8-87	3.2-3.5	69-75	3-4.1	47.0-56.9	
[b] Araldite® LY 1556	140-155				75.2-77.2	
Epoxy with imine amine exchange	170-172	2.02-2.11	81-86	8.6-15		15
Epoxy with exchangeable aromatic disulfide	147		63.15			18
Epoxy with aromatic disulfide metathesis	130		88	7.1	29-37	19
Epoxy with transesterification	30.1	0.0038-0.73	3.0-37.7	4.6-144.9		20
PASC-ADH-HMDI-0.09	123	2.84	100.12	5.21	40.1	This work

[a] Data is obtained from the Gurit company. [b] Data is obtained from the Huntsman Advanced Materials.

References

1. L. W. Hill, *Prog. Org. Coat.*, 1997, **31**, 235-243.
2. L. H. Sperling, *Introduction to physical polymer science*, John Wiley & Sons, 2005.
3. W. Denissen, G. Rivero, R. Nicolaÿ, L. Leibler, J. M. Winne and F. E. Du Prez, *Adv. Funct. Mater.*, 2015, **25**, 2451-2457.
4. W. Denissen, I. De Baere, W. Van Paepegem, L. Leibler, J. Winne and F. E. Du Prez, *Macromolecules*, 2018, **51**, 2054-2064.
5. Y. Spiesschaert, M. Guerre, I. De Baere, W. Van Paepegem, J. M. Winne and F. E. Du Prez, *Macromolecules*, 2020, **53**, 2485-2495.
6. Y. Heo and H. A. Sodano, *Adv. Funct. Mater.*, 2014, **24**, 5261-5268.
7. Y. Heo, M. H. Malakooti and H. A. Sodano, *J. Mater. Chem. A*, 2016, **4**, 17403-17411.
8. Y. Heo and H. A. Sodano, *Compos. Sci. Technol.*, 2015, **118**, 244-250.
9. M. Delahaye, J. M. Winne and F. E. Du Prez, *J. Am. Chem. Soc.*, 2019, **141**, 15277-15287.
10. Y. Zhang, H. Ying, K. R. Hart, Y. Wu, A. J. Hsu, A. M. Coppola, T. A. Kim, K. Yang, N. R. Sottos, S. R. White and J. Cheng, *Adv. Mater.*, 2016, **28**, 7646-7651.
11. J. P. Brutman, P. A. Delgado and M. A. Hillmyer, *ACS Macro Lett.*, 2014, **3**, 607-610.
12. P. Taynton, K. Yu, R. K. Shoemaker, Y. Jin, H. J. Qi and W. Zhang, *Adv. Mater.*, 2014, **26**, 3938-3942.
13. D. Montarnal, M. Capelot, F. Tournilhac and L. Leibler, *Science*, 2011, **334**, 965-968.
14. D. J. Fortman, J. P. Brutman, C. J. Cramer, M. A. Hillmyer and W. R. Dichtel, *J. Am. Chem. Soc.*, 2015, **137**, 14019-14022.
15. S. Wang, S. Ma, Q. Li, X. Xu, B. Wang, W. Yuan, S. Zhou, S. You and J. Zhu, *Green Chem.*, 2019, **21**, 1484-1497.
16. D. Fu, W. Pu, J. Escorihuela, X. Wang, Z. Wang, S. Chen, S. Sun, S. Wang, H. Zuilhof and H. Xia, *Macromolecules*, 2020, **53**, 7914-7924.
17. C. Cui, X. Chen, L. Ma, Q. Zhong, Z. Li, A. Mariappan, Q. Zhang, Y. Cheng, G. He and Z. Dong, *ACS Appl. Mater. Interfaces*, 2020, **12**, 47975-47983.
18. H. W. Si, L. Zhou, Y. P. Wu, L. X. Song, M. Kang, X. L. Zhao and M. Chen, *Compos Part B-Eng*, 2020, **199**, 108278.
19. A. R. de Luzuriaga, R. Martin, N. Markaide, A. Rekondo, G. Cabañero, J. Rodríguez and I. Odriozola, *Mater. Horiz.*, 2016, **3**, 241-247.
20. K. Yu, Q. Shi, M. L. Dunn, T. Wang and H. J. Qi, *Adv. Funct. Mater.*, 2016, **26**, 6098-6106.