Supporting information

Bio-based poly(hydroxyurethane) glues for metal substrates.

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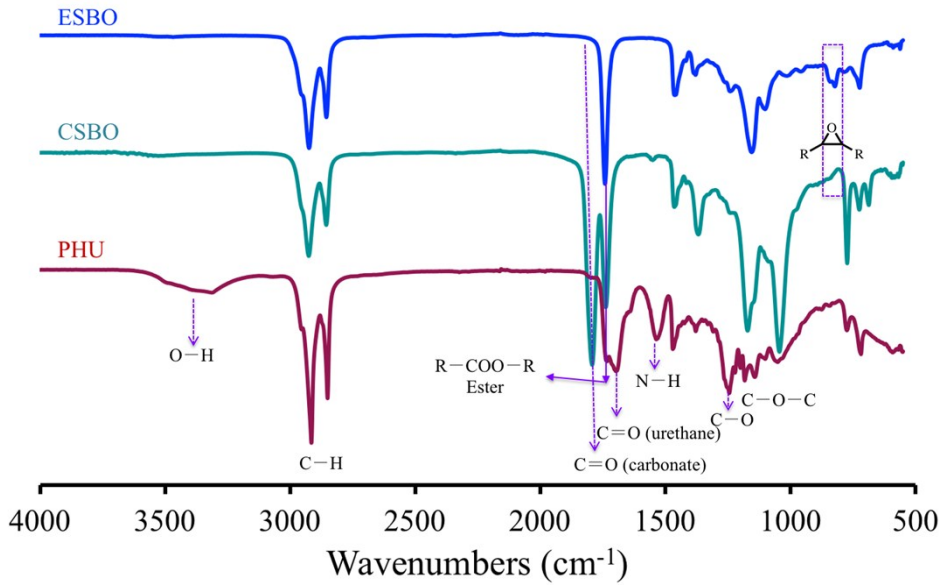

Figure S1. FTIR spectra of epoxidised soybean oil (ESBO), cyclic carbonated soybean oil (CSBO) and PHU-H (formed from CSBO/HMDA = 1/3 at 100 °C for 50 min).

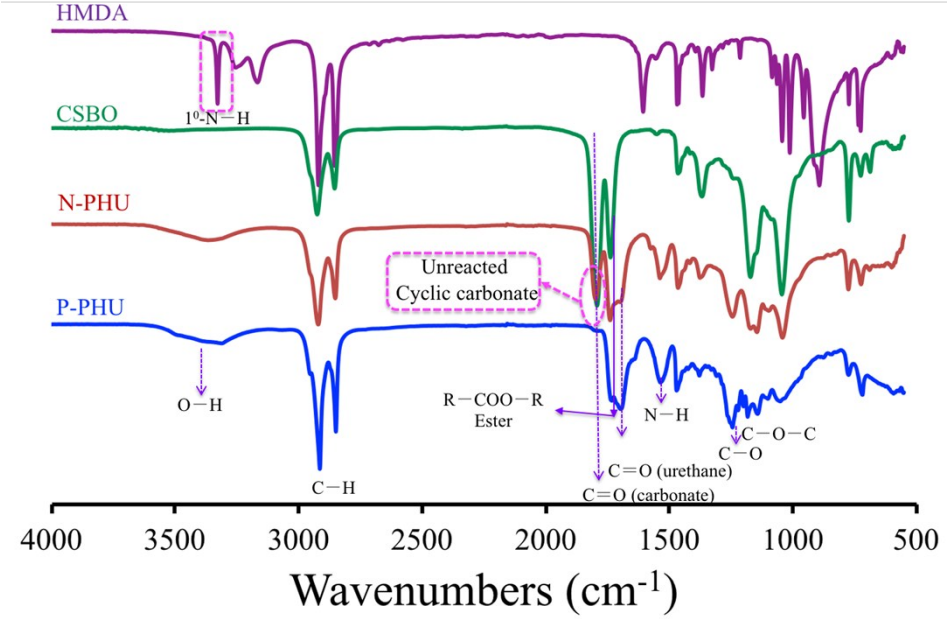

Figure S2. FTIR spectra used to determine the influence of mixing time on the conversion. The spectra of hexamethylene diamine (HMDA), cyclic carbonated soybean oil (CSBO), N-PHU (Not properly mixed polyhydroxyurethanes; mixed for 1 min at 50 ^{0}C) and P-PHU (properly mixed polyhydroxyurethanes; mixed for 3 min at 50 ^{0}C) after curing at 70 °C for 12 h and 100 °C for 4 h.

Effect of formulation mixing time on the stability of thermosets.

We performed the effect of formulation (CSBO/HMDA) mixing time (thus, A: mixed for 3 min at 50 ^{0}C and B: mixed for 1 min at 50 ^{0}C) on the stability of the thermosets towards organic solvents (DMF and THF). The samples were prepared by depositing formulations into teflon molds and curing at 70 ^{0}C for 12 h and 100 ^{0}C for 4 h. The stability of the PHU-thermoset films was performed by immersion in DMF and THF for 10 to 120 minutes (Figure S3). As can be seen, not properly mixed or inhomogeneous thermosets dissolved/broke into pieces due to insufficient mixing time (1 min) to obtain homogeneous formulations. Whereas properly mixed for 3 min, homogeneous thermosets sustain their structural integrity in organic solvents (THF and DMF). This study showed that, the effectively mixed formulations are crucial to obtain high performance materials.

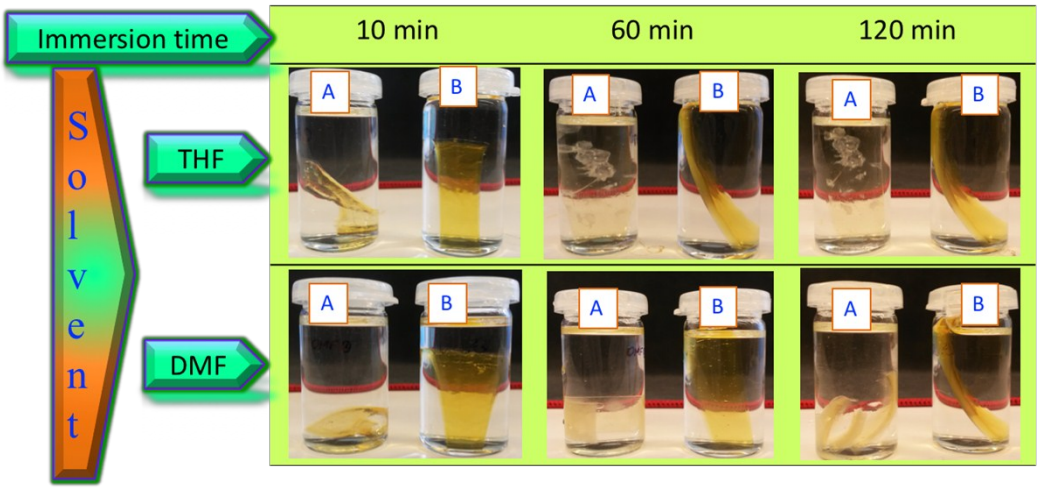

Figure S3. Effect of formulation mixing time on the stability of the PHU thermoset films within organic solvents (THF and DMF). A: on the left, formulation mixed for 1 min at 50 ^{0}C, B: on the right, formulation mixed for 3 min at 50 ^{0}C. The curing conditions were held constant (at 70 ^{0}C for 12 h and 4 h at 100 ^{0}C).

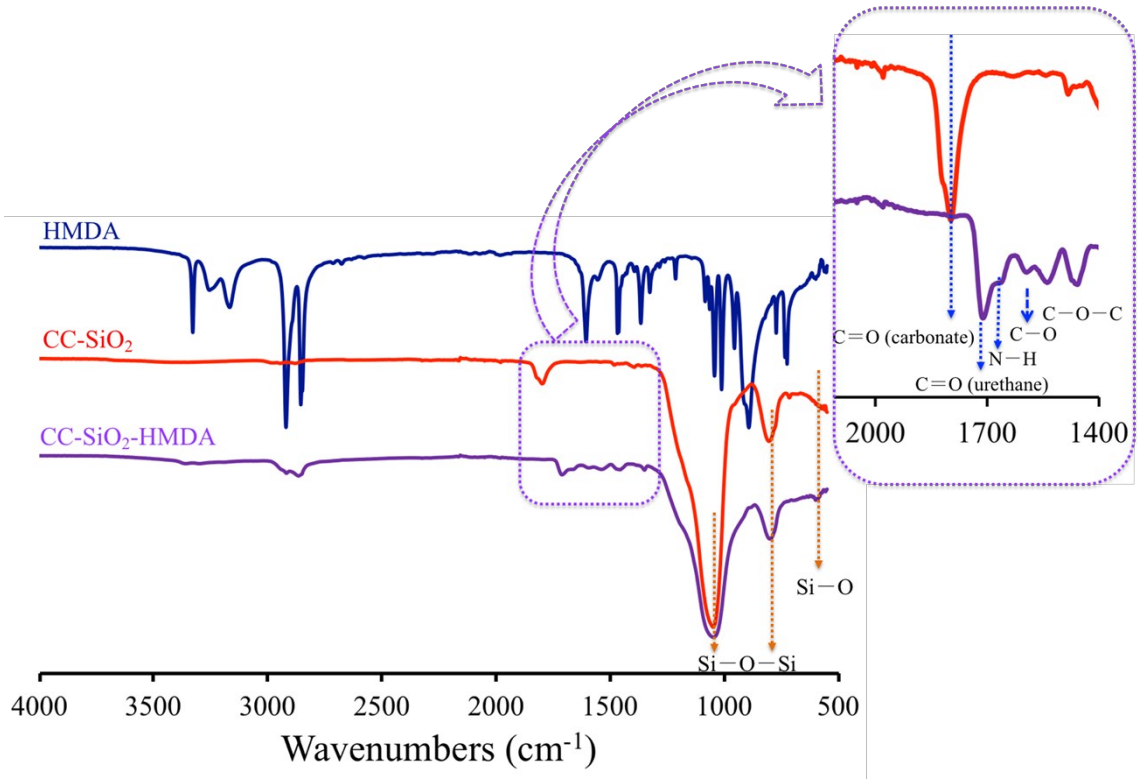

Figure S4. FTIR spectra used to highlight the reaction between cyclic carbonate functional fillers and HMDA. Spectra of HMDA, CC-SiO_2 and spectra after reaction between HMDA and CC-SiO_2 (CC-SiO_2-HMDA) in THF at 60 ^{0}C for 30 minutes followed by curing at 70 ^{0}C for 12 h and 100 ^{0}C for 4 h.

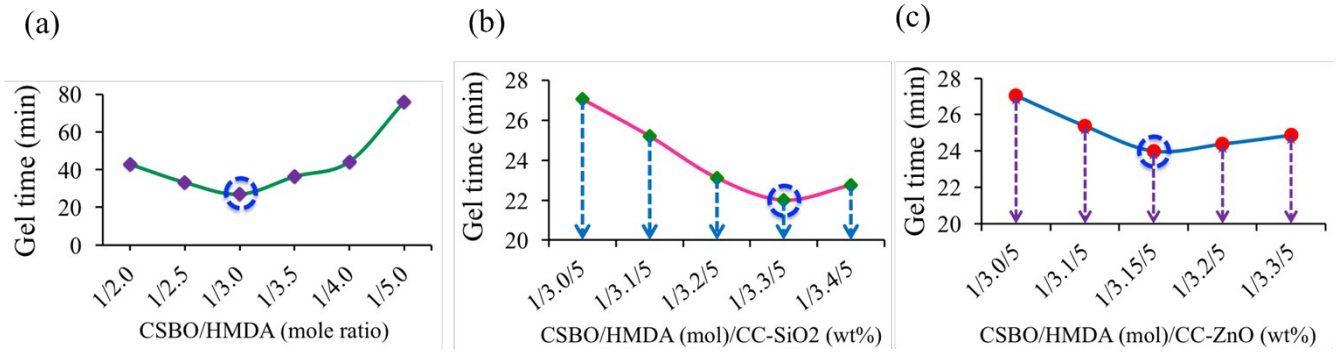

Figure S5. Optimisation of PHU and analogous nanocomposite formulations (a) Evolution of the gel time for various CSBO/HMDA molar compositions, (b) Gel time evolution for various CSBO/HMDA/CC-SiO_2 formulations and (c) Gel time evolution for various CSBO/HMDA/CC-ZnO formulations. All formulations were cured under solvent-free conditions at 100 °C and monitored by rheology. Blue star indicates the shortest gel time and best formulation molar ratios (thus, CSBO/HMDA-1/3, CSBO/diamines/CC-SiO_2 1/3.3/5 (mol/mol/wt%) and CSBO/diamines/CC-ZnO 1/3.15/5 (mol/mol/w%).

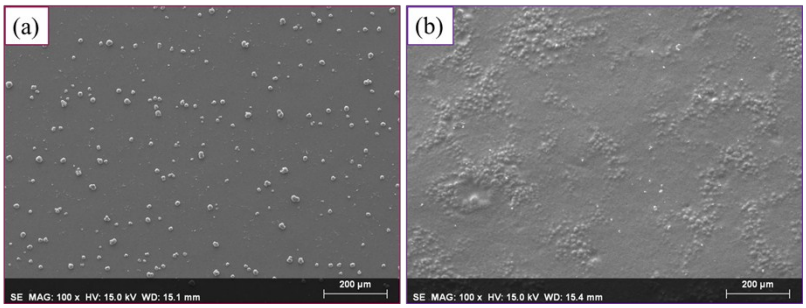

Figure S6. SEM images of PHUs coating reinforced with 5 wt% of (a) cyclic carbonate functional CC-SiO_2 fillers and (b) CC-ZnO fillers.

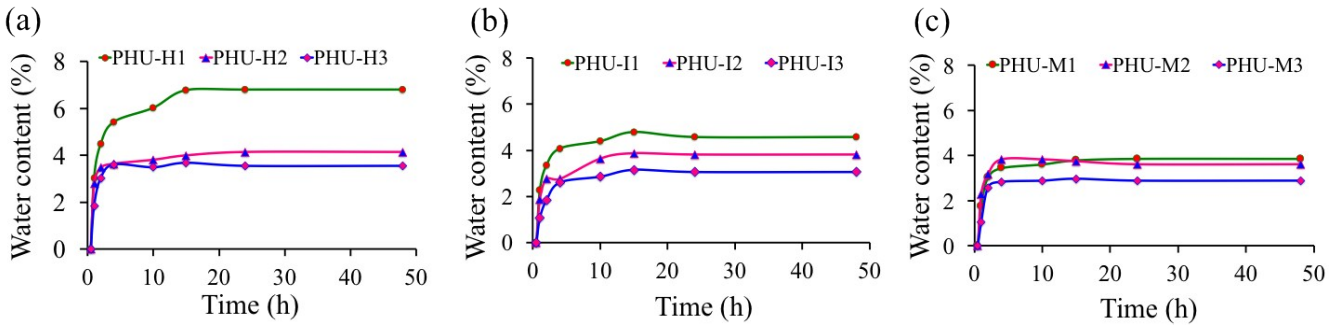

Figure S7. Water content evolution with time evaluated for PHUs and analogue nanocomposite freestanding films [dimensions: 0.5 cm (l) × 0.5 cm (t) × 0.5 cm (w)] prepared from [CSBO]/[diamine] formulations with 5wt% CC-SiO_2 or CC-ZnO. (a) PHU-H (CSBO/HMDA/fillers), (b) PHU-M (CSBO/MXDA/fillers), (c) PHU-I (CSBO/IPDA/fillers) and [PHU-H1, PHU-M1 and PHU-I1: unfilled PHUs, PHU-H2, PHU-M2 and PHU-I2: PHUs reinforced with 5wt% CC-SiO_2; PHU-H3, PHU-M3 and PHU-I3: PHUs reinforced with 5wt% CC-ZnO].

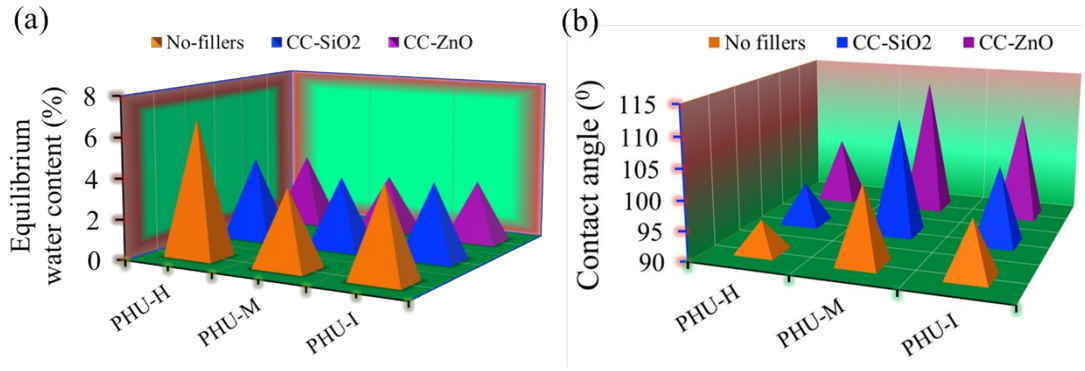

Figure S8. (a) Equilibrium water content (after 48 h of immersion) of PHUs and analogue nanocomposite freestanding films [dimensions: 0.5 cm (l) × 0.5 cm (t) × 0.5 cm (w)] prepared from [CSBO]/[diamine] formulations with 5wt% CC-SiO_2 or CC-ZnO. PHU-H (CSBO/HMDA/fillers), PHU-M (CSBO/MXDA/fillers), and PHU-I (CSBO/IPDA/fillers) and (b) Water contact angle measurements of PHU coatings.

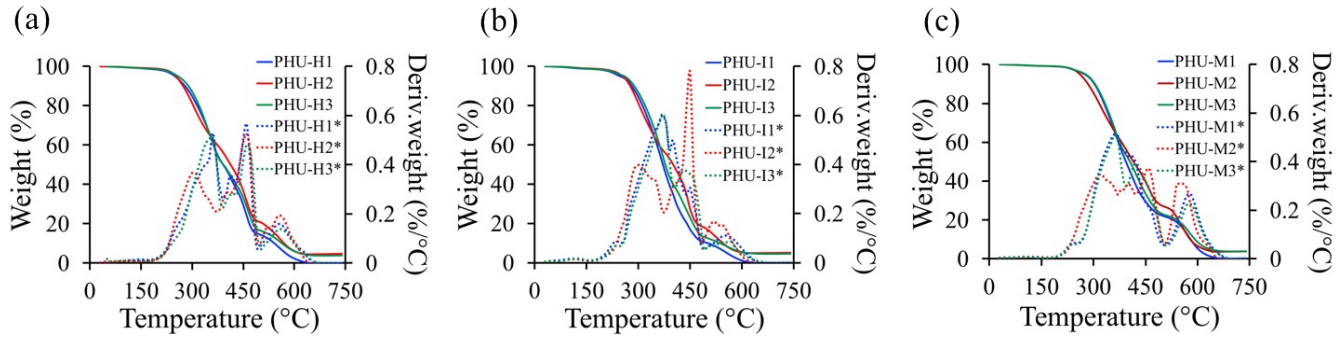

Figure S9: TGA and DTGA of (a) PHU-H (aliphatic), (b) PHU-I (cycloaliphatic) and (c) PHU-M (aromatic) [1: PHUs, 2: PHUs reinforced with 5 wt% CC-SiO_2, 3: PHUs reinforced with 5 wt% CC-ZnO and PHU*-Deriv.weight (%/^{0}C)].

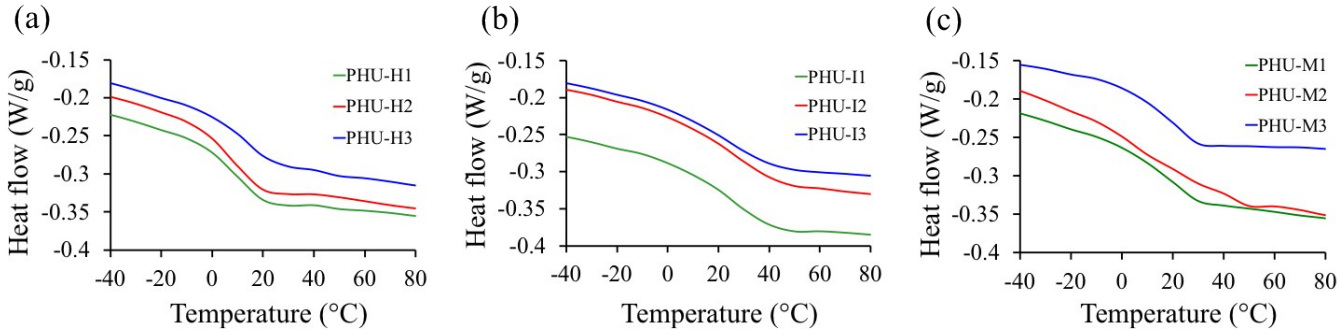

Figure S10: DSC thermograms of (a) PHU-H (from aliphatic amine), (b) PHU-I (from cycloaliphatic amine) and (c) PHU-M (from aromatic amine) and PHUs reinforced with 5 wt% CC-SiO_2 or CC-ZnO [1: PHUs, 2: PHUs reinforced with CC-SiO_2, 3: PHUs reinforced with CC-ZnO].

Table S1. Lap shear adhesion strength and failure pattern of bio-based PHU glues.

Sample code	Lap shear strength (MPa) Al-Al	Failure mode	Lap shear strength (MPa) SS-SS	Failure mode
PHU-H1	6.5 ± 0.49	C.F	4.9 ± 0.12	C.F
PHU-H2	8.8 ± 0.35	C.F	7.9 ± 0.27	C.F
PHU-H3	11.3 ± 0.28	C.F	10.1 ± 0.23	C.F
PHU-M1	6.4 ± 0.33	C.F	6.1 ± 0.49	C.F
PHU-M2	6.9 ± 0.26	C.F	6.4 ± 0.42	C.F
PHU-M3	7.5 ± 0.29	C.F	6.9 ± 0.15	C.F
PHU-I1	3.7 ± 0.54	C.F	3.5 ± 0.04	C.F
PHU-I2	4.6 ± 0.36	C.F	4.4 ± 0.98	A.F
PHU-I3	5.9 ± 0.52	A.F	4.6 ± 0.47	A.F

Bio-based PHU thermoset glues and analogues PHUs reinforced with 5 wt% CC-SiO_2 or CC-ZnO fillers; C.F: Cohesive failure, A.F: Adhesive failure. (PHU-H: aliphatic, PHU-M: aromatic and PHU-I: cyclic aliphatic thermosets). [PHU-H1, PHU-M1 and PHU-I1: unfilled PHUs, PHU-H2, PHU-M2 and PHU-I2: PHUs reinforced with 5wt% CC-SiO_2; PHU-H3, PHU-M3 and PHU-I3: PHUs reinforced with 5 wt% CC-ZnO].

Table S2. Adhesive performance of bio-based PHU nanocomposite thermoset glues compared with commercial PU as well as with reported PHUs.

Sample code	Cured at 25 ^{0}C for 48 h		Cured at 70 ^{0}C for 12 h and 100 ^{0}C for 4 h	
	Lap shear strength (MPa) Al-Al	Failure mode	Lap shear strength (MPa) SS-SS	Failure mode
Teromix-6700	12.5 ± 0.8	C.F	7.2 ± 0.4	C.F
Araldite®2000+	21.7 ± 0.2	C.F	11,2 ± 0.5	A.F
PHU(M-1)[1]: TMPTC/EDR-148	1.9 ± 0.2	C.F	6.5 ± 0.3	C.F
PHU-5C[2]: TMPTC/HMDA/PDMS/C-GPTMS-ZnO	3.3 ± 0.4	C.F	16.3 ± 1.4	C.F
PHU-H3: CSBO/HMDA/CC-ZnO	2.2 ± 0.9	C.F	11.3 ± 0.28	C.F

C.F: Cohesive failure and A.F: Adhesive failure

References:

1 A. Cornille, G. Michaud, F. Simon, S. Fouquay, R. Auvergne, B. Boutevin and S. Caillol, *Eur. Polym. J.*, 2016, **84**, 404–420.

2 S. Panchireddy, J.-M. Thomassin, B. Grignard, C. Damblon, A. Tatton, C. Jerome and C. Detrembleur, *Polym. Chem.*, 2017, **8**, 5897–5909