Electronic Supplementary Material (ESI) for Polymer Chemistry.

Reinforced poly(hydroxyurethane) thermosets as high performance adhesives for aluminum substrates

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Synthesis and characterizations of TMPTC

Figure S1: ^{1}H NMR spectra of TMPTE and TMPTC
Figure S2: FTIR spectra of TMPTE and TMPTC
Figure S3: ^{1}H NMR spectra of GPTMS and C-GPTMS
Figure S4: FTIR spectra of GPTMS and C-GPTMS
Figure S5: TGA of
  a) PHUs reinforced by 3wt% of ZnO, GPTMS-ZnO and C-GPTMS-ZnO fillers
  b) PHUs reinforced by 5wt% of ZnO, GPTMS-ZnO and C-GPTMS-ZnO fillers
Figure S6: TEM micrographs of
  a) reinforced non-functionalized (PHU 5N),
  b) epoxy functionalized (PHU-5E) and c) cyclic carbonate functionalized (PHU 5C) formulations. (scale bar = 1µm).
Figure S7: DSC of PHUs reinforced by 3, 5wt% of ZnO, GPTMS-ZnO and C-GPTMS-ZnO fillers.

Synthesis of 4,4'-(((2-ethyl-2-(((2-oxo-1,3-dioxolan-4-yl)methoxy) methyl) propane-1,3-diyl) bis(oxy))bis(methylene))bis(1,3-dioxolan-2-one) (TMPTC).

TMPTC was synthesized by coupling CO_2 with epoxide, using a bicomponent organocatalyst that combined tetrabutylammonium iodide (TBAI) as catalyst with 1, 3-bis(2-hydroxyhexafluoroisopropyl)benzene as activator. 34g (0.112 mol) of trimethylolpropane triglycidyl ether (TMPTE) was introduced in a 80 ml high pressure cell equipped with a mechanical stirrer and prior addition of 2.5 mol% (with respect to the epoxy content) of bicomponent organocatalyst combining TBAI (2.81mmol, 1.0384 g) and 1,3-bis(2-hydroxyhexafluoroisopropyl)benzene (2.81mmol, 0.698 mL). Then the reaction mixture was heated to 80^0C prior equilibration of the cell at a CO_2 pressure of 100 bar for 24 h. The reactor was depressurized slowly to release unreacted CO_2. The resulting product was collected as a viscous liquid that was used without any further purification.

The complete conversion of TMPTE into TMPTC was confirmed by ^{1}H NMR spectroscopy with the disappearance of the peaks characteristic of -C*H*-O- and -CH_2-O- of epoxides at 3.15 and 2.5-2.8 ppm, respectively, and the appearance of new signals of -C*H*-OC(=O)O- and –CH_2- OC(=O)O- of cyclic carbonates at 4.8 and 4.25-4.6 ppm, respectively (Figure S1). Formation of the cyclic carbonate was further confirmed by FT-IR spectroscopy highlighting the presence of a strong signal at 1789 cm^{-1} corresponding to the elongation of the C=O group (Figure S2).

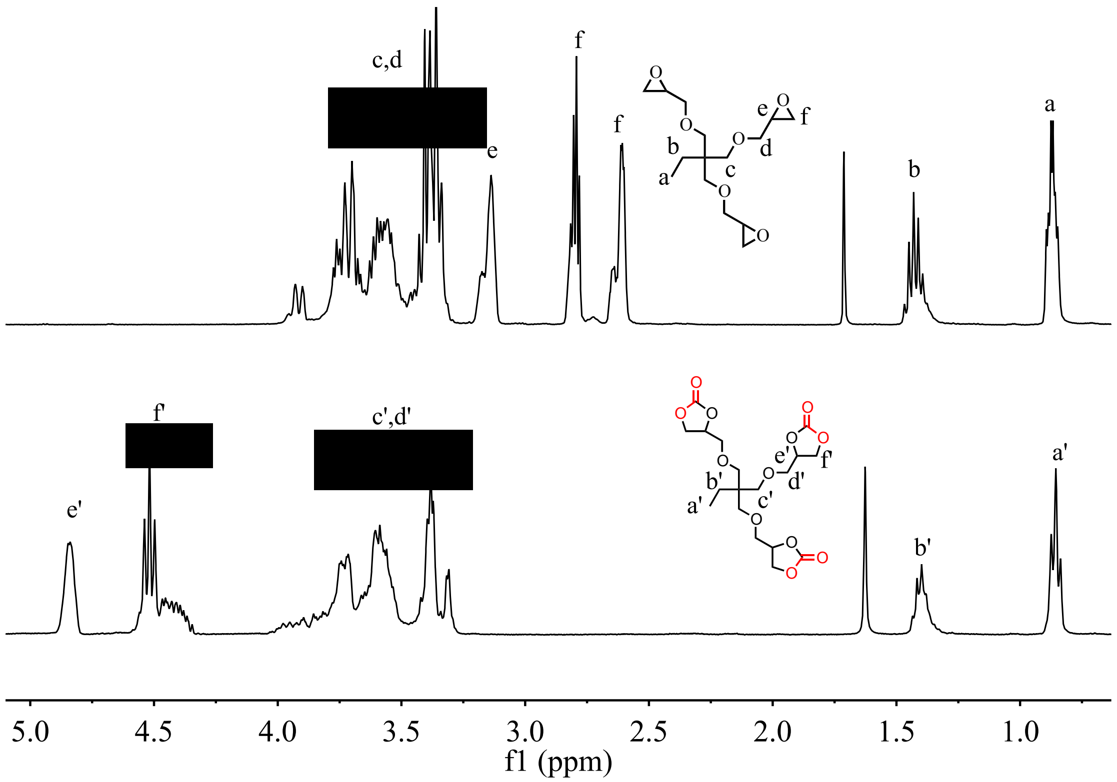

Figure S1: ^{1}H NMR spectra of TMPTE (top) and TMPTC (bottom).

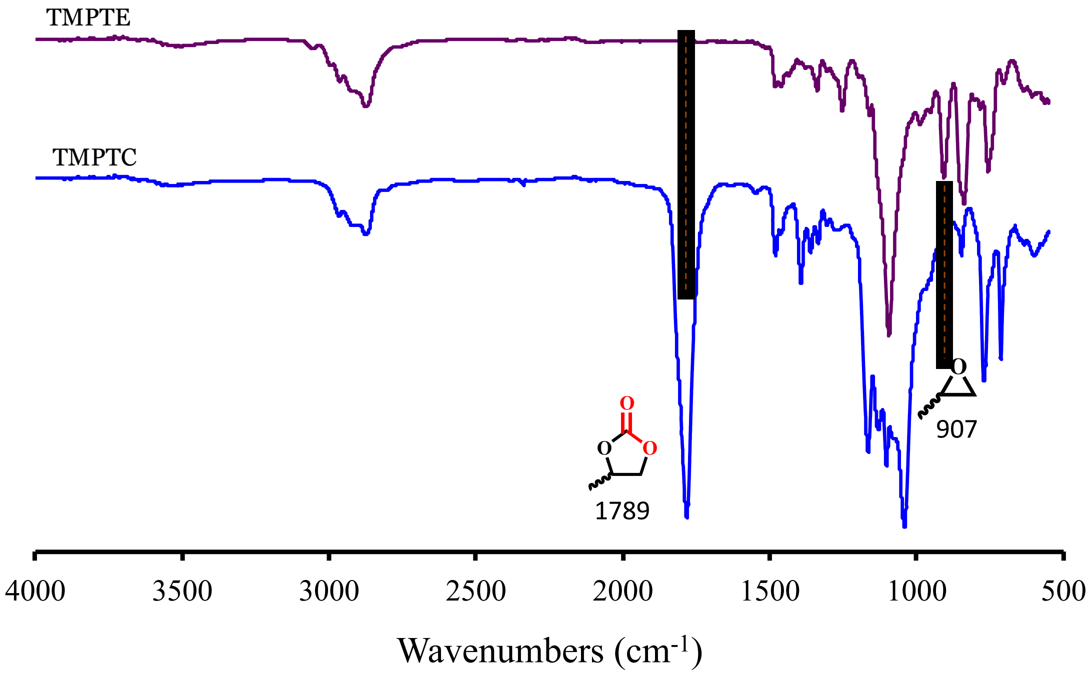

Figure S2: FTIR spectra of TMPTE and TMPTC

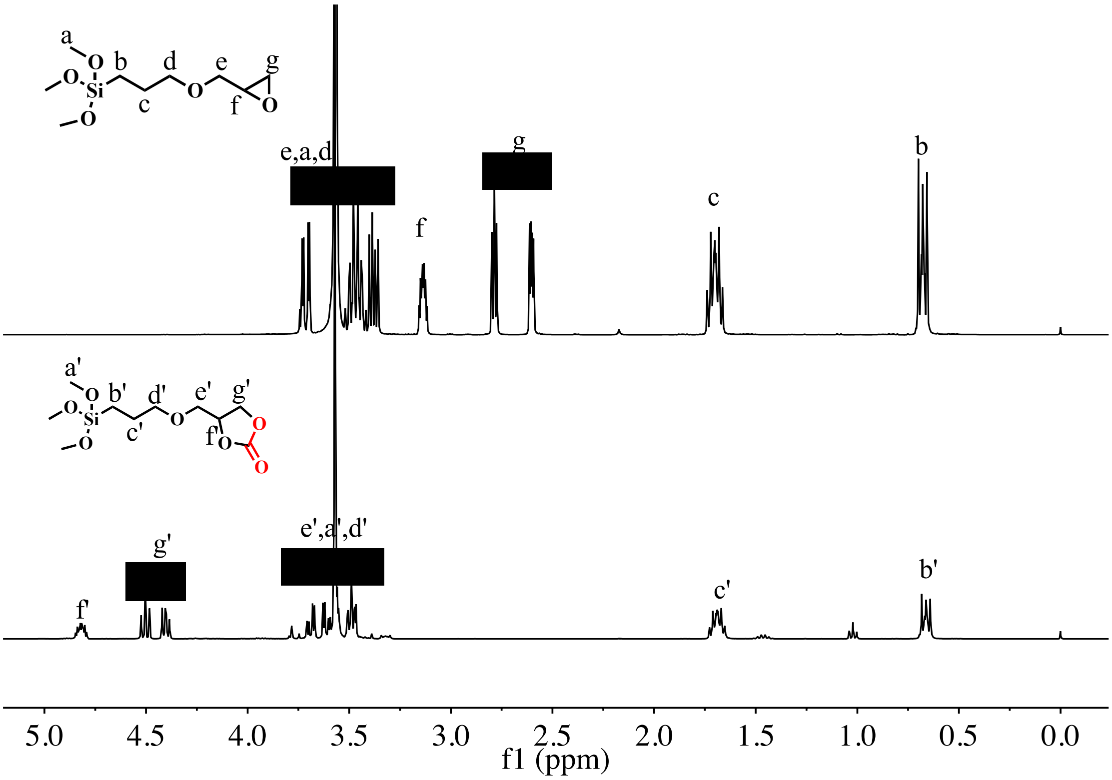

Figure S3: ^{1}H NMR spectra of GPTMS (top) and C-GPTMS (bottom)

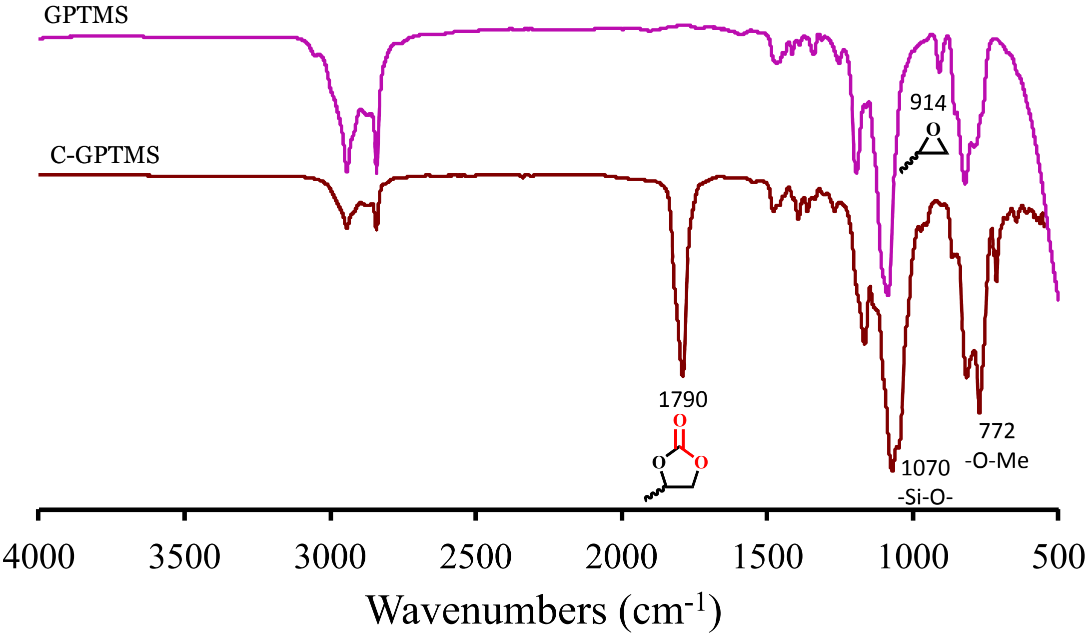

Figure S4: FTIR spectra of GPTMS and C-GPTMS

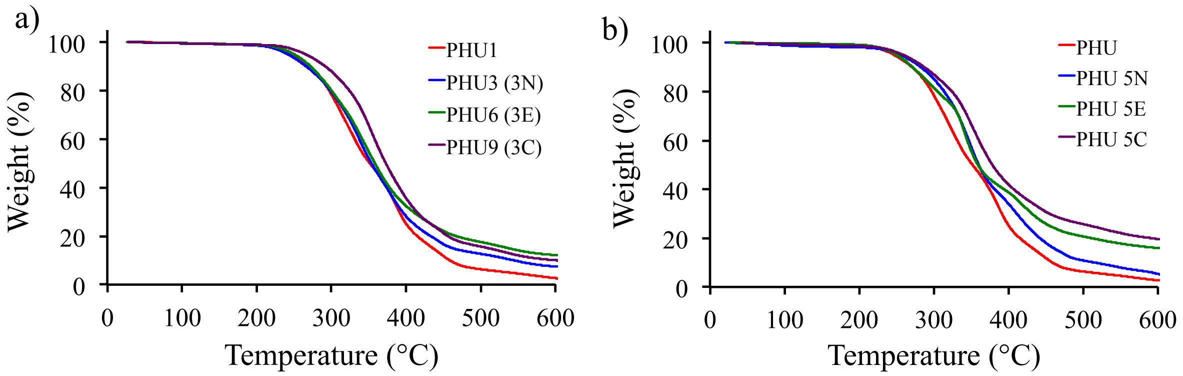

Figure S5: TGA of a) PHUs reinforced by 3wt% of ZnO, GPTMS-ZnO and C-GPTMS-ZnO fillers. b) PHUs reinforced by 5wt% of ZnO, GPTMS-ZnO and C-GPTMS-ZnO fillers.

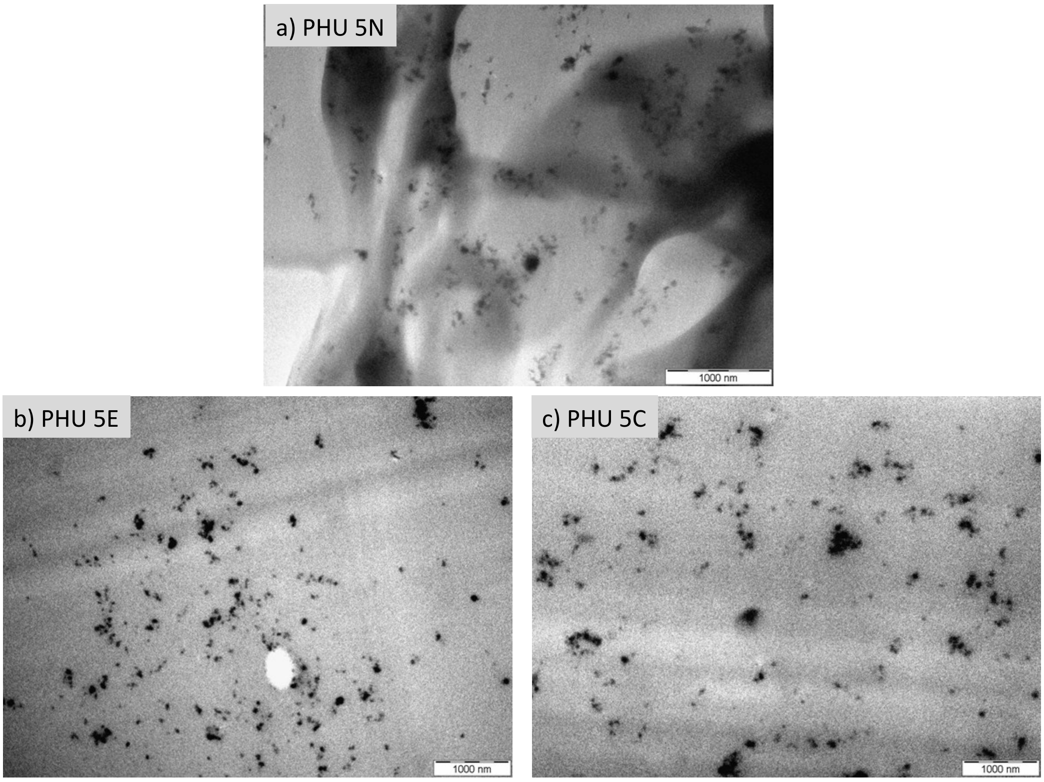

Figure S6. TEM micrographs of a) reinforced non-functionalized (PHU 5N), b) epoxy functionalized (PHU-5E) and c) cyclic carbonate functionalized (PHU 5C) formulations. (scale bar = 1μm).

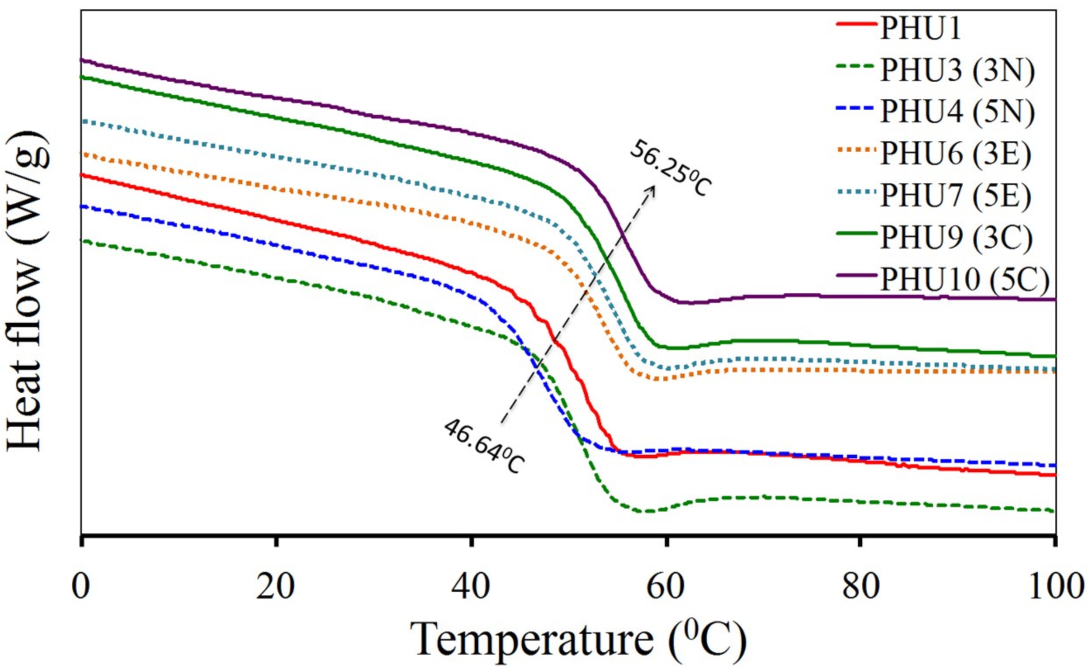

Figure S7: DSC of PHUs reinforced by 3, 5wt% of ZnO, GPTMS-ZnO and C-GPTMS-ZnO fillers.