Emerging polyhydroxyurethane as sustainable thermosets: a structure-property relationship

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Supporting Informations

Additional experimental details, materials, and methods, including monomer mass and 1H-NMR spectra, FTIR results, representative tensile stress-strain curves, and photographs of the reprocessed samples.

Contents

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List of Figures

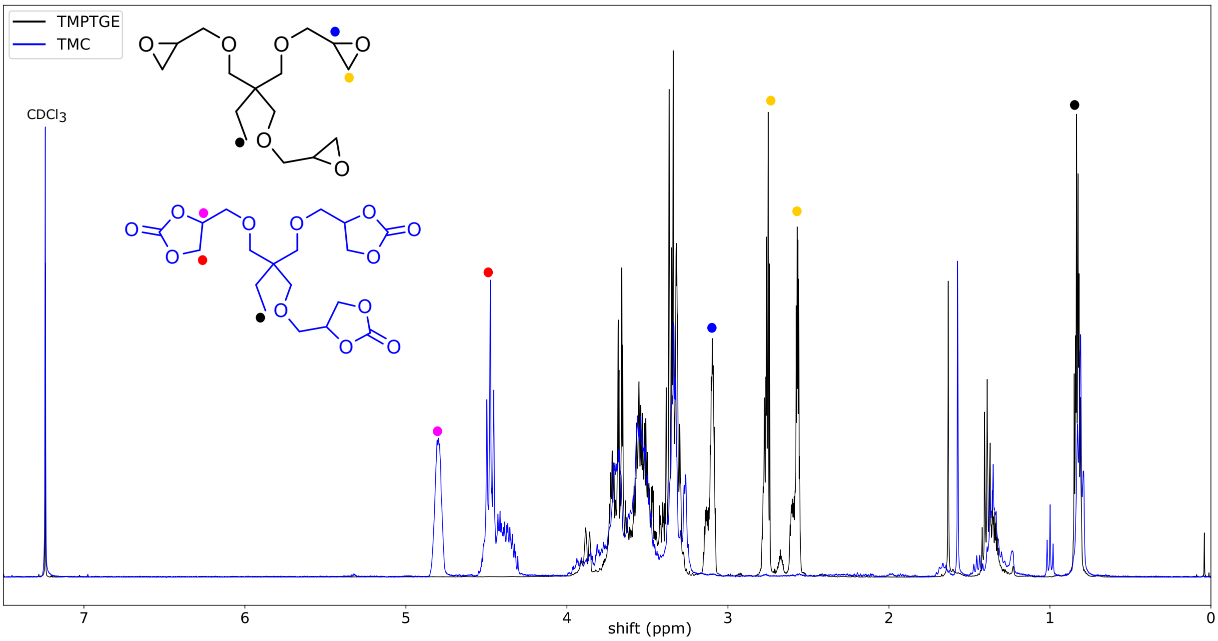
1 Carbonate Precursors

1.1 Cyclic Carbonates properties

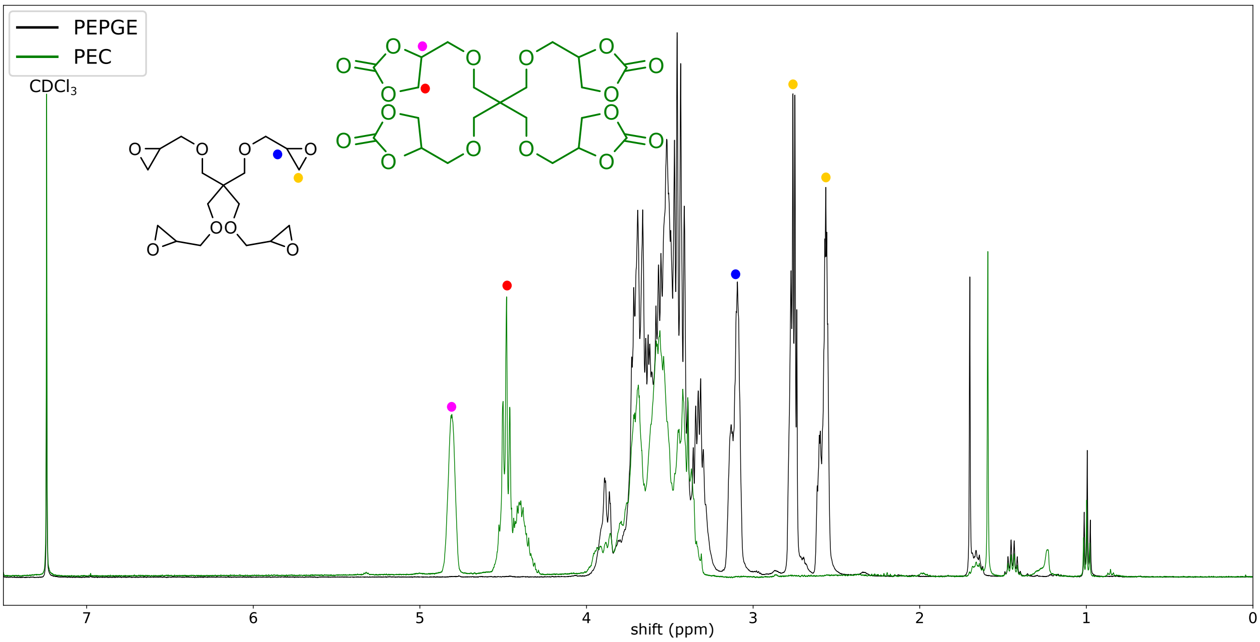
Name	Ref	CEW (g/eq)	M_n (g/mol)	Functionnality	$T_{d_{5\%}}$ (°C)	T_g (°C)	$\eta_{25^\circ C}$ (Pa.s)	$\eta_{50^\circ C}$ (Pa.s)
TriMethylol propane triCarbonate	TMC	175	530	2.9	236	-19	148	6
PentaErythritol Carbonate	PEC	180	709	3.9	232	-7	863	30
GlycErol Carbonate	GEC	170	495	2.9	224	-25	30	2.4
SorBitol Carbonate	SBC	260	-	-	239	3	65000	2050
Carbonated SoyBean Oil	CSBO	310	1083	3.5	336	-23	120	7

Supp. Tab. 1: Characteristics of the synthesized cyclic carbonates

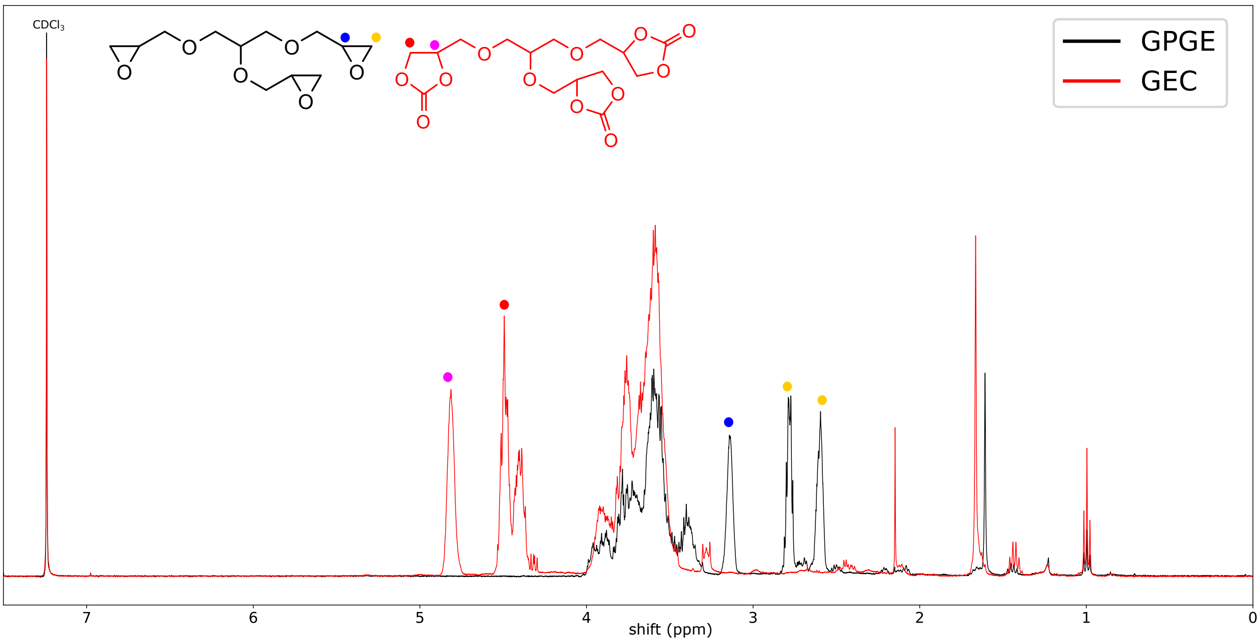
1.2 ^{1}H-NMR



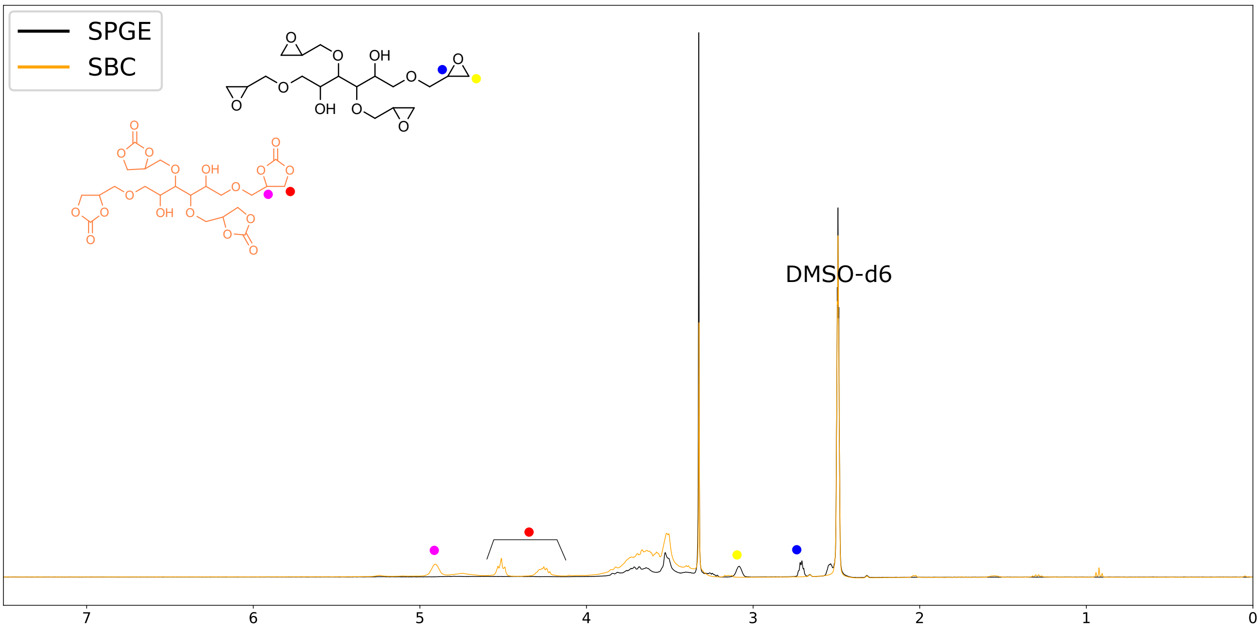
Supp. Fig. 1: ^{1}H-NMR of the Trimethylol Propane Triglycidyl Ether (TMPTGE) and the Trimethylol Propane Carbonate (TMC)



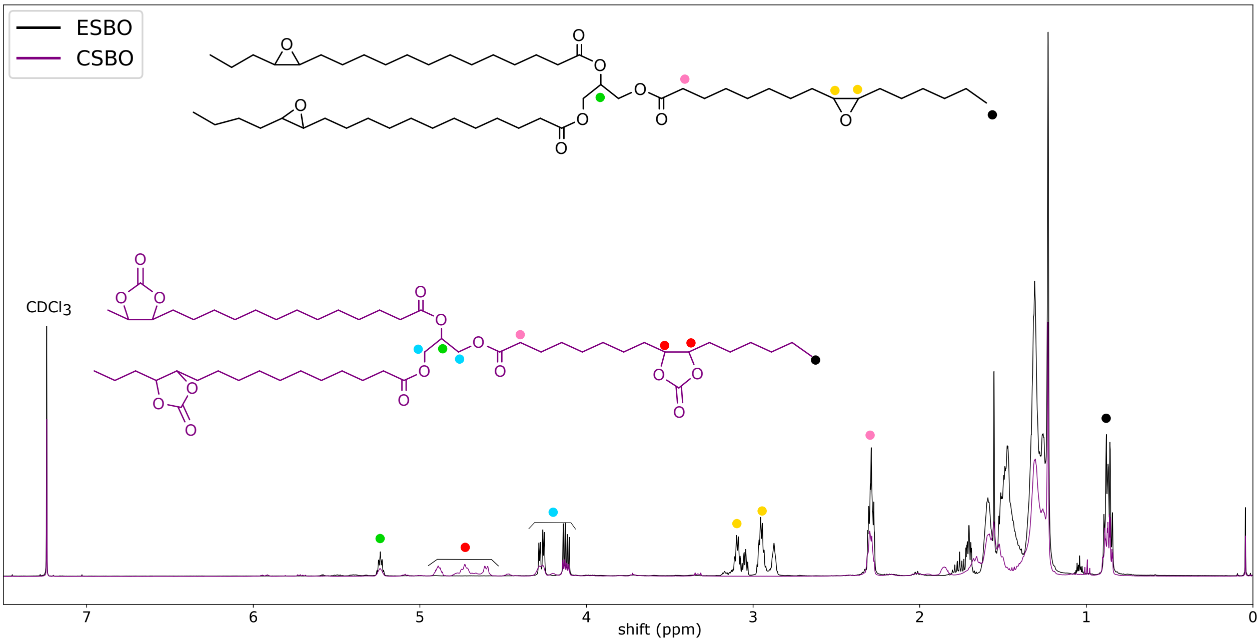
Supp. Fig. 2: ^{1}H-NMR of the Pentaerythritol Polyglycidyl Ether (PEPGE) and the Pentaerythritol Carbonate (PEC)



Supp. Fig. 3: ^{1}H-NMR of the Glycerol Polyglycidyl Ether (GPGE) and the Glycerol Carbonate (GEC)

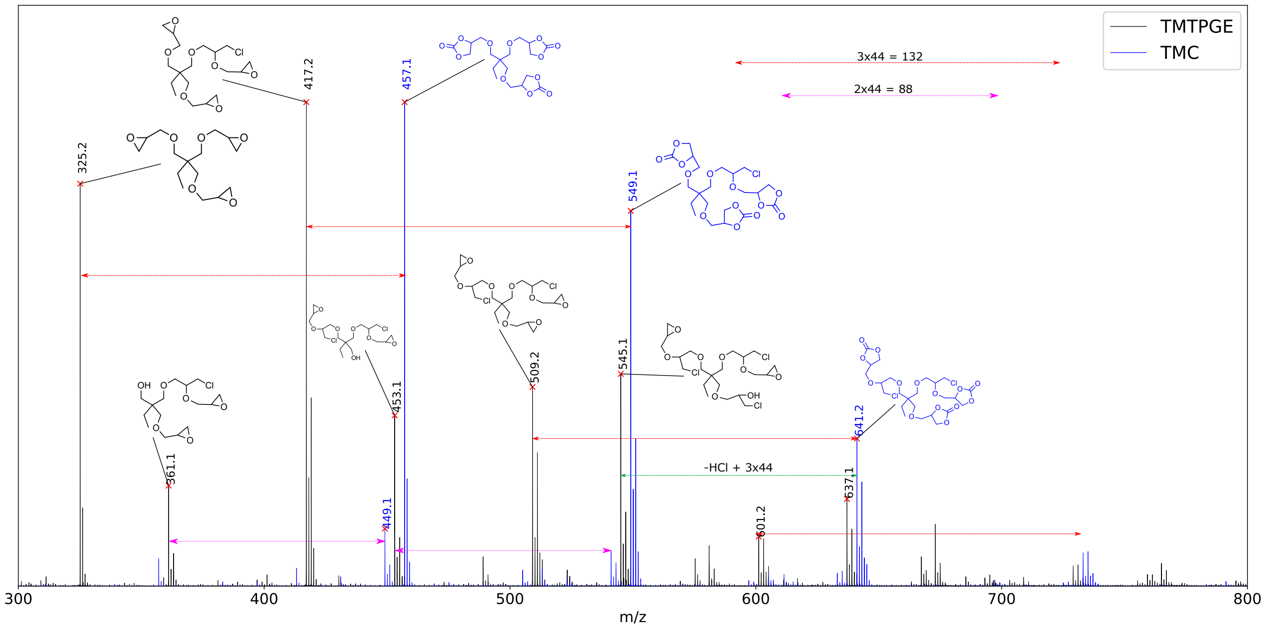


Supp. Fig. 4: [1]H-NMR of the Sorbitol PolyGlycidyl Ether (SPGE) and the Sorbitol Carbonate (SBC)

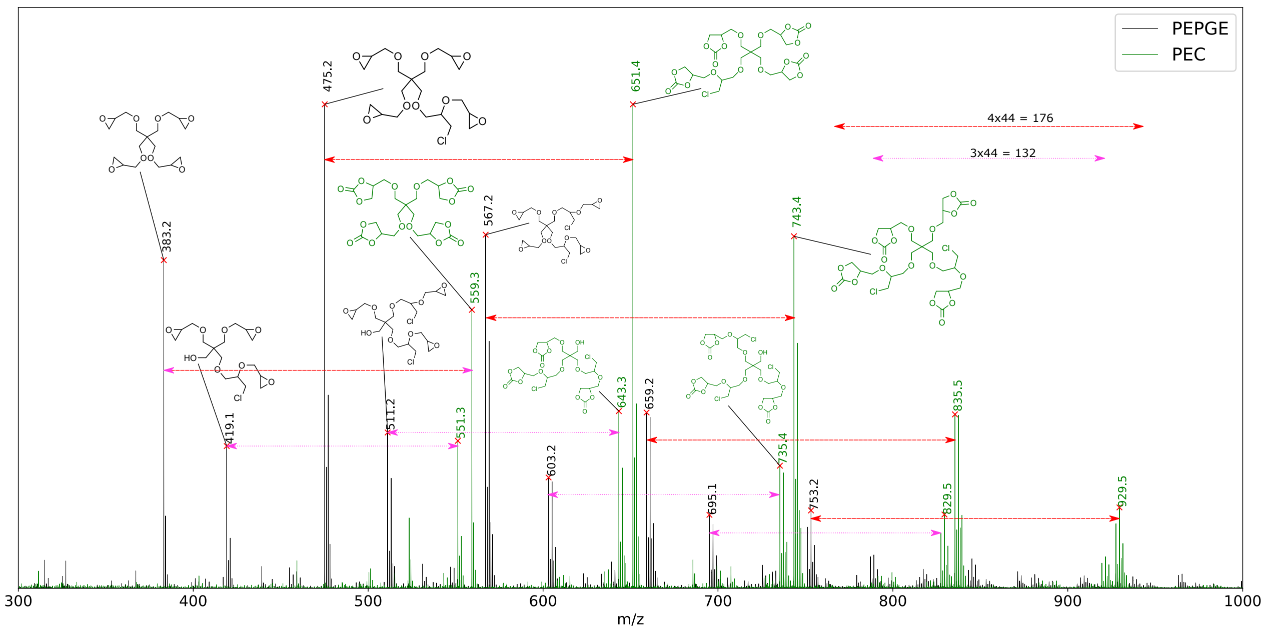


Supp. Fig. 5: [1]H-NMR of the Epoxidized SoyBean Oil (ESBO) and the Carbonated SoyBean Oil (CSBO)

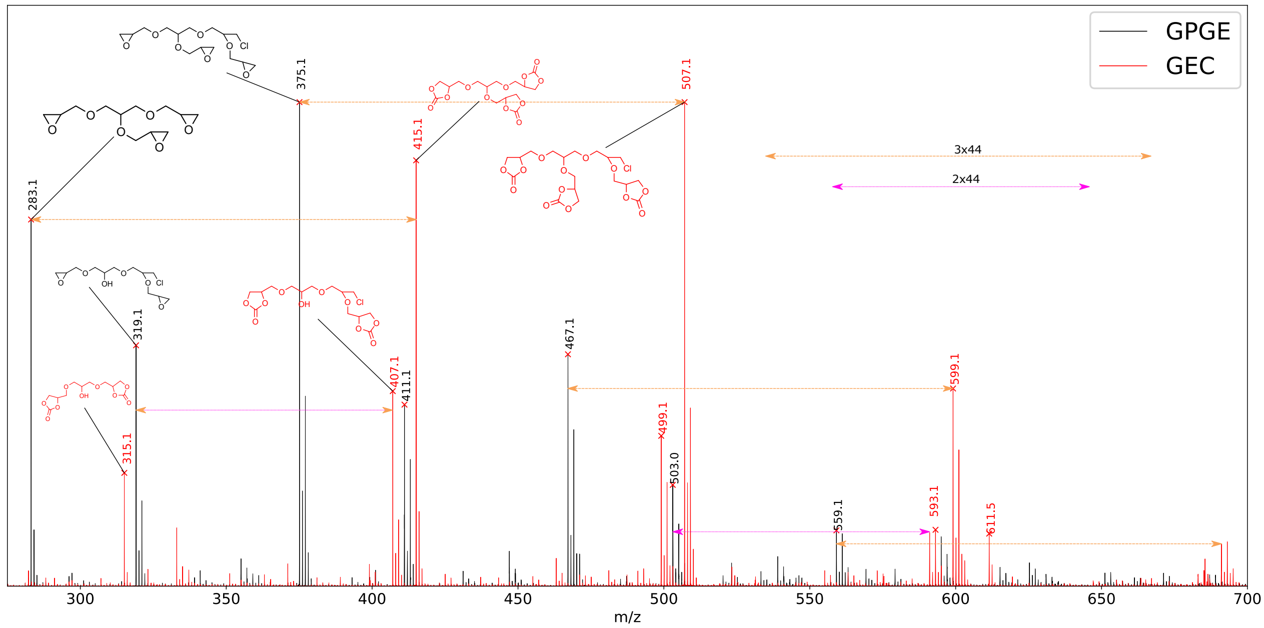
1.3 Mass Spectrometry



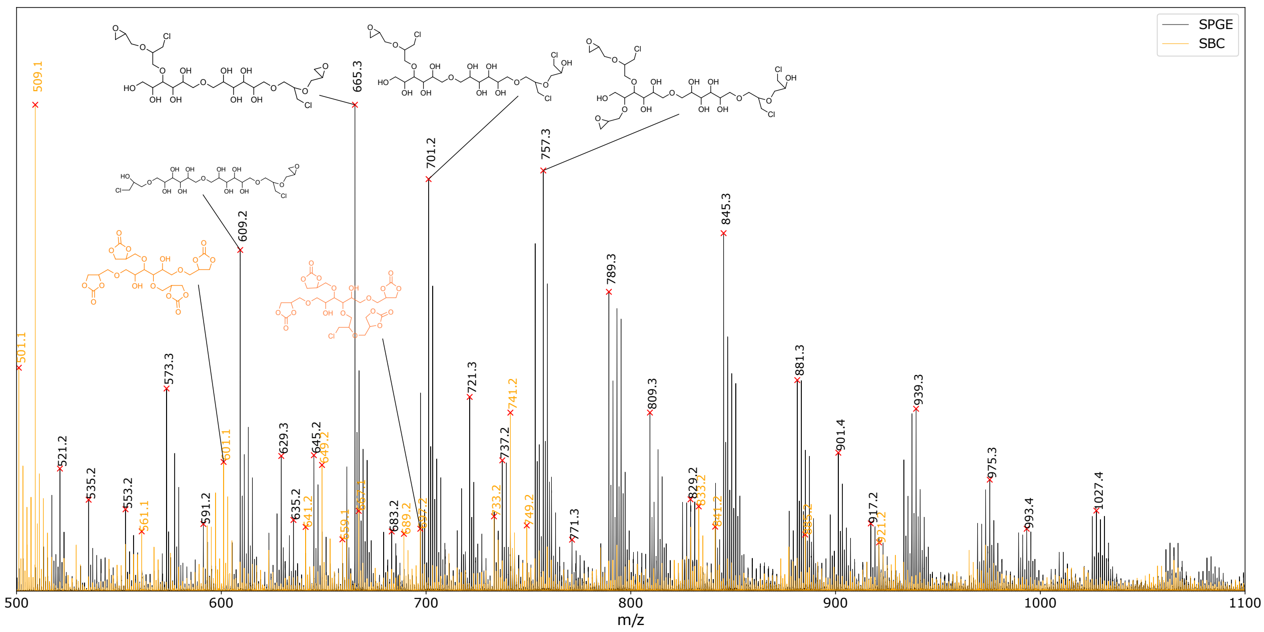
Supp. Fig. 6: Mass spectrometry of the Trimethylol Propane Triglycidyl Ether (TMPTGE) and the Trimethylol Propane Carbonate (TMC)



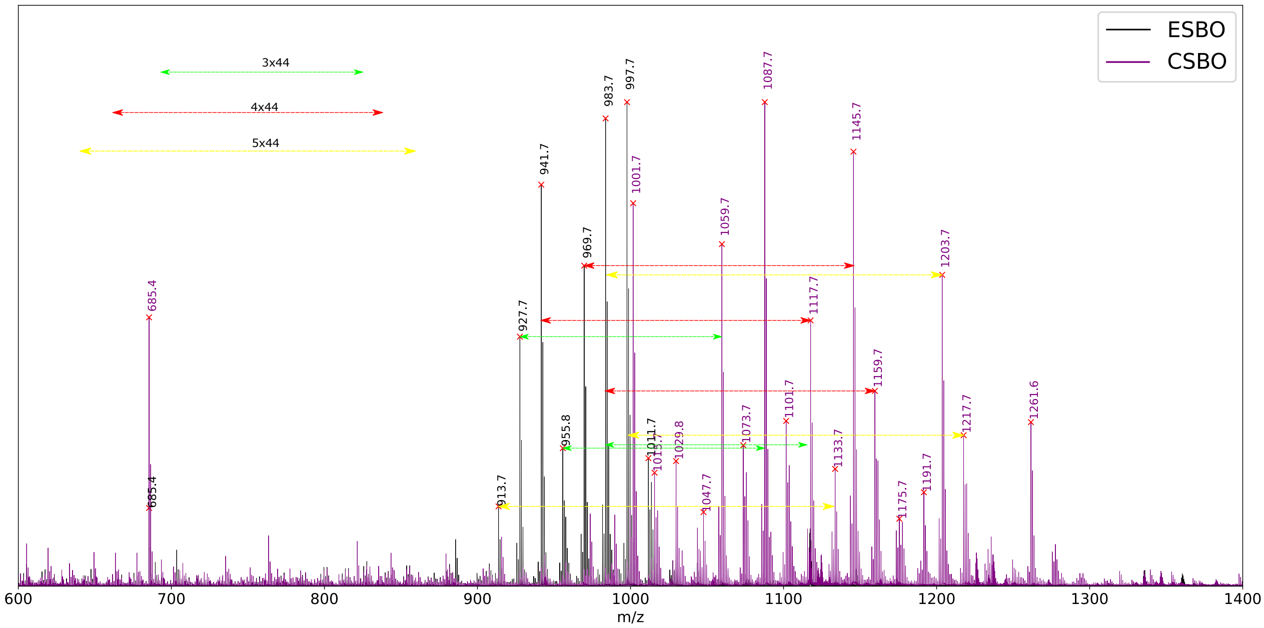
Supp. Fig. 7: Mass spectrometry of the Pentaerythritol Polyglycidyl Ether (PEPGE) and the Pentaerythritol Carbonate (PEC)



Supp. Fig. 8: Mass spectrometry of the Glycerol Polyglycidyl Ether (GPGE) and the Glycerol Carbonate (GEC)

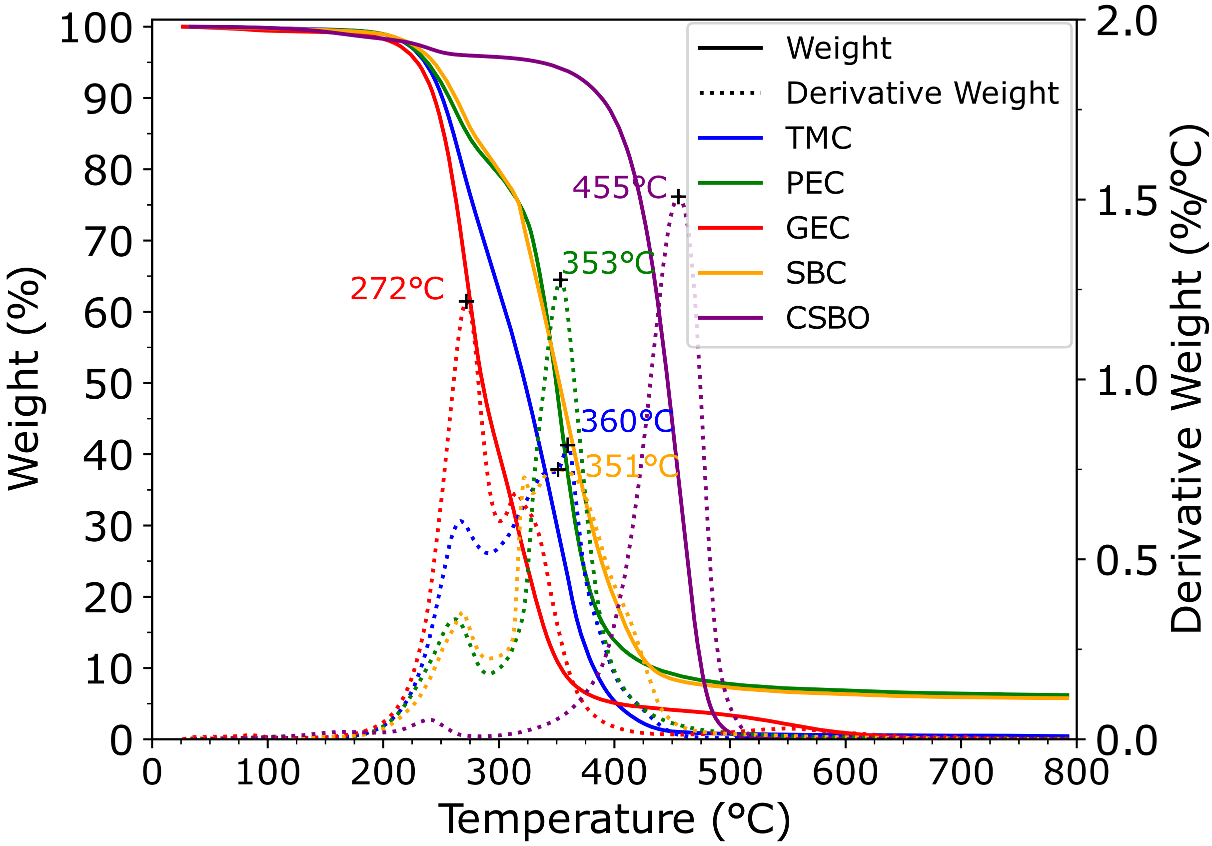


Supp. Fig. 9: Mass spectrometry of the Sorbitol PolyGlycidyl Ether (SPGE) and the Sorbitol Carbonate (SBC)

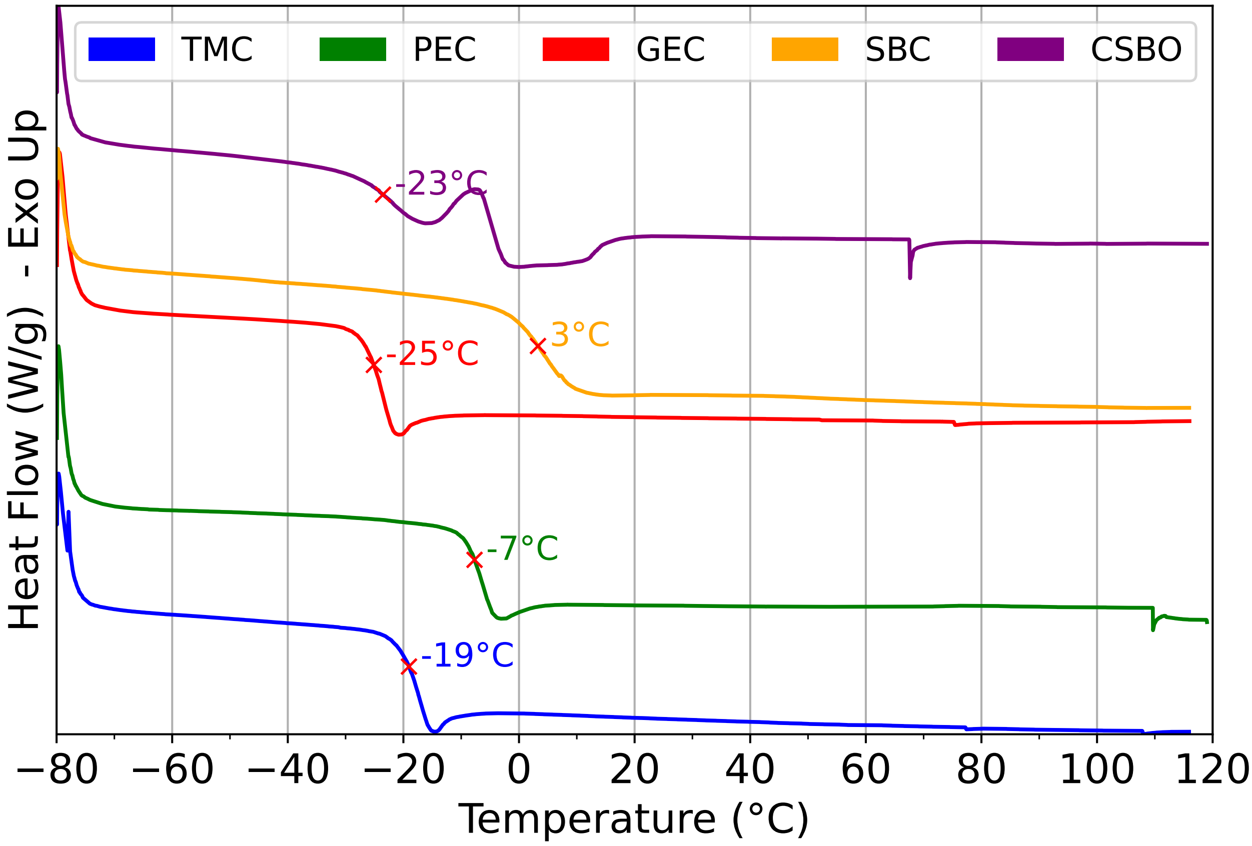


Supp. Fig. 10: Mass spectrometry of the Epoxidized SoyBean Oil (ESBO) and the Carbonated SoyBean Oil (CSBO)

1.4 Thermophysical properties of the carbonates

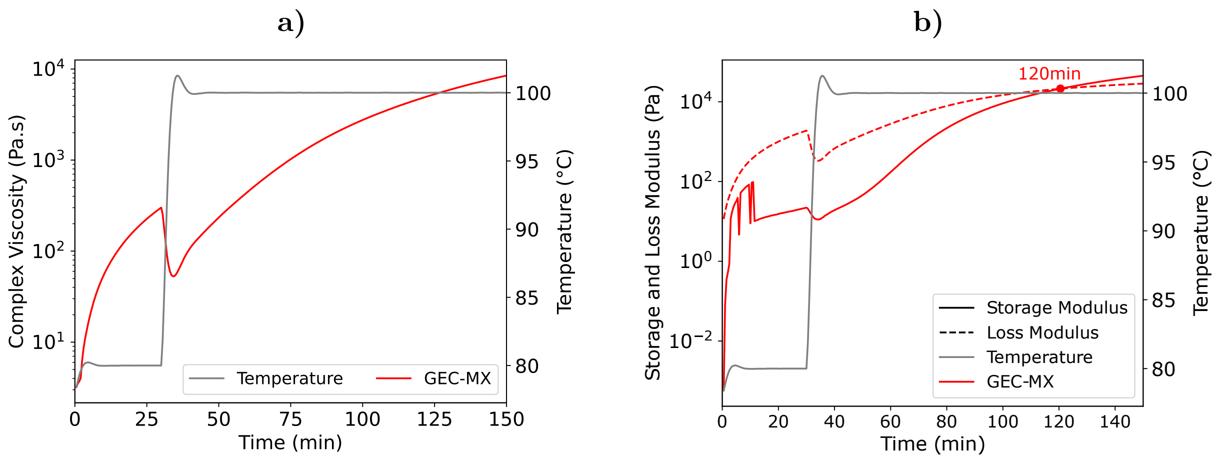


Supp. Fig. 11: TGA of the synthesised cyclic carbonates



Supp. Fig. 12: DSC of the synthesised cyclic carbonates

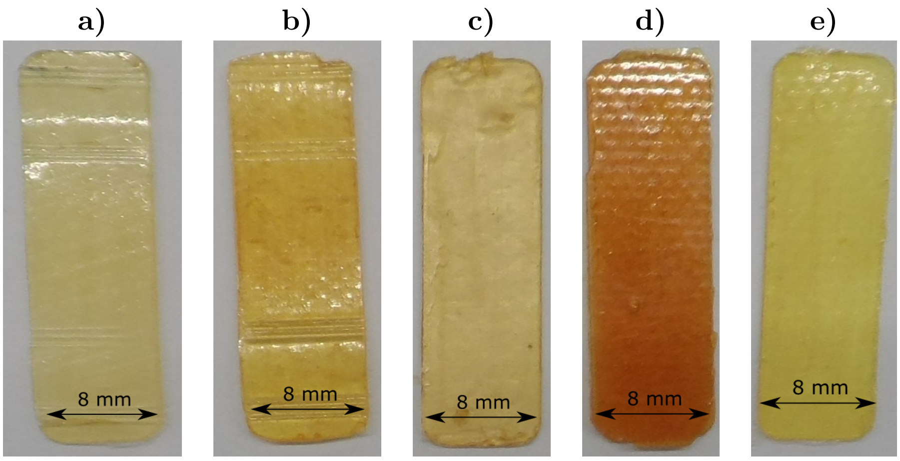
2 Rheology of curing polyhydroxyurethanes



Supp. Fig. 13: Two step (80°C & 100°C) isothermal curing of the GEC-MX formulation. a)Complex viscosity, and b) Storage and Loss Modulus evolution with gel point

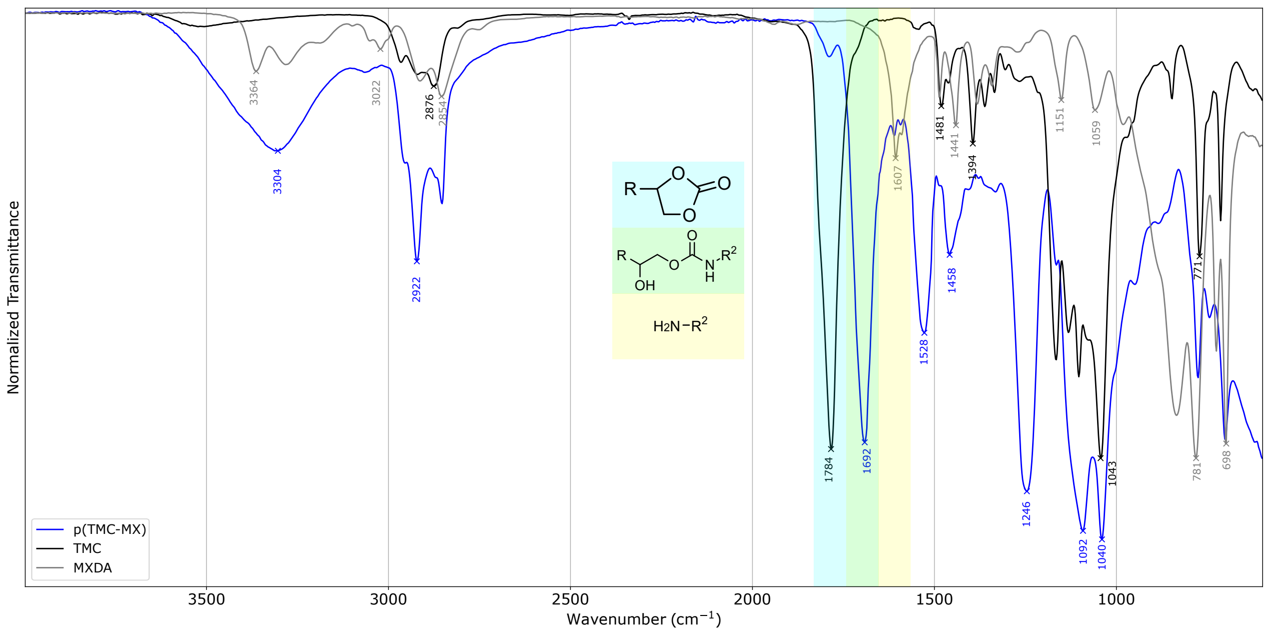
3 Cured polyhydroxyurethanes, complementary characterizations

3.1 Polymers Pictures

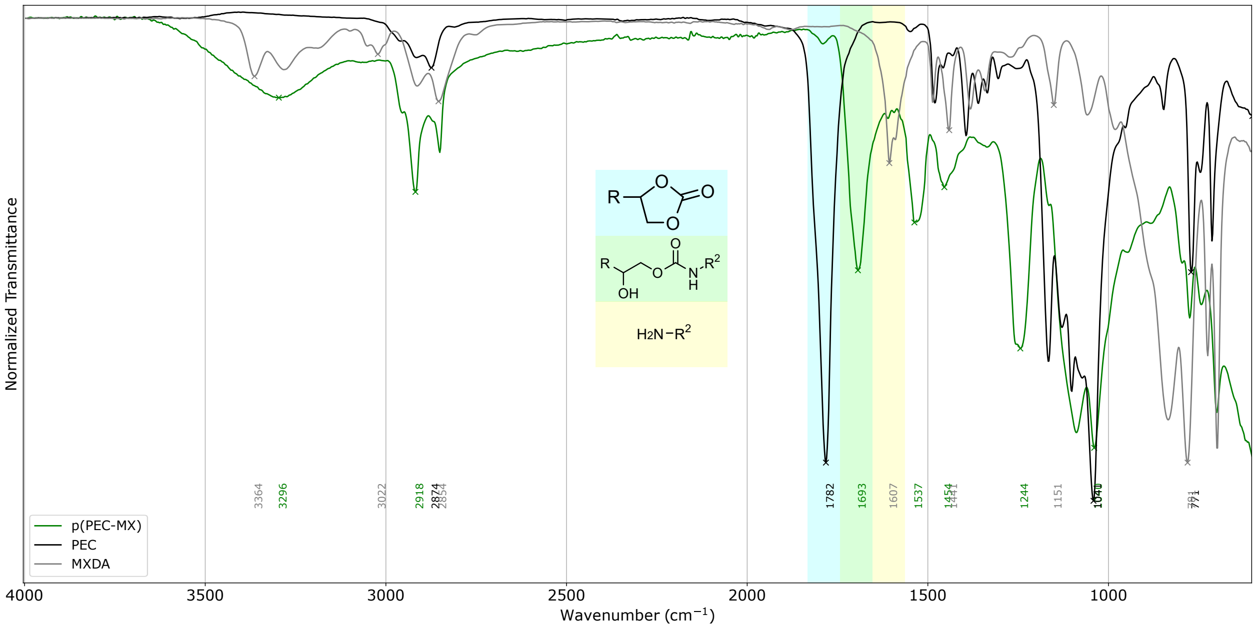


Supp. Fig. 14: Photos of polymerized PHUs a) p(TMC-MX) b) p(PEC-MX) c) p(GEC-MX) d) p(SBC-MX) and e) p(CSBO-MX)

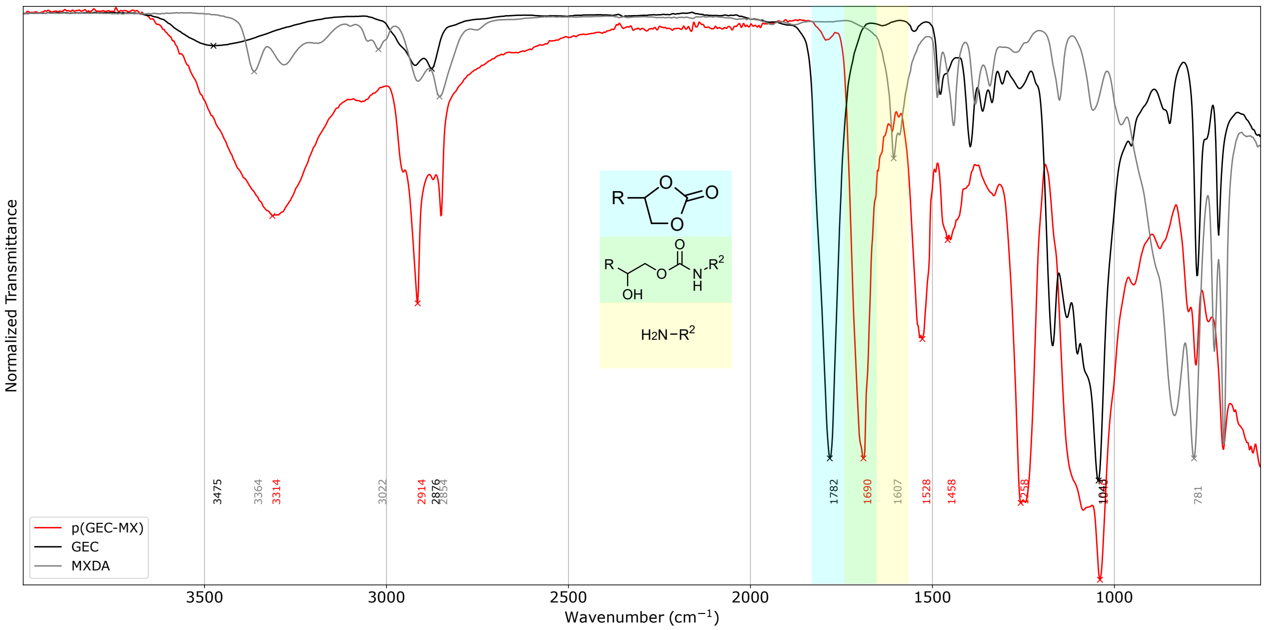
3.2 FTIR



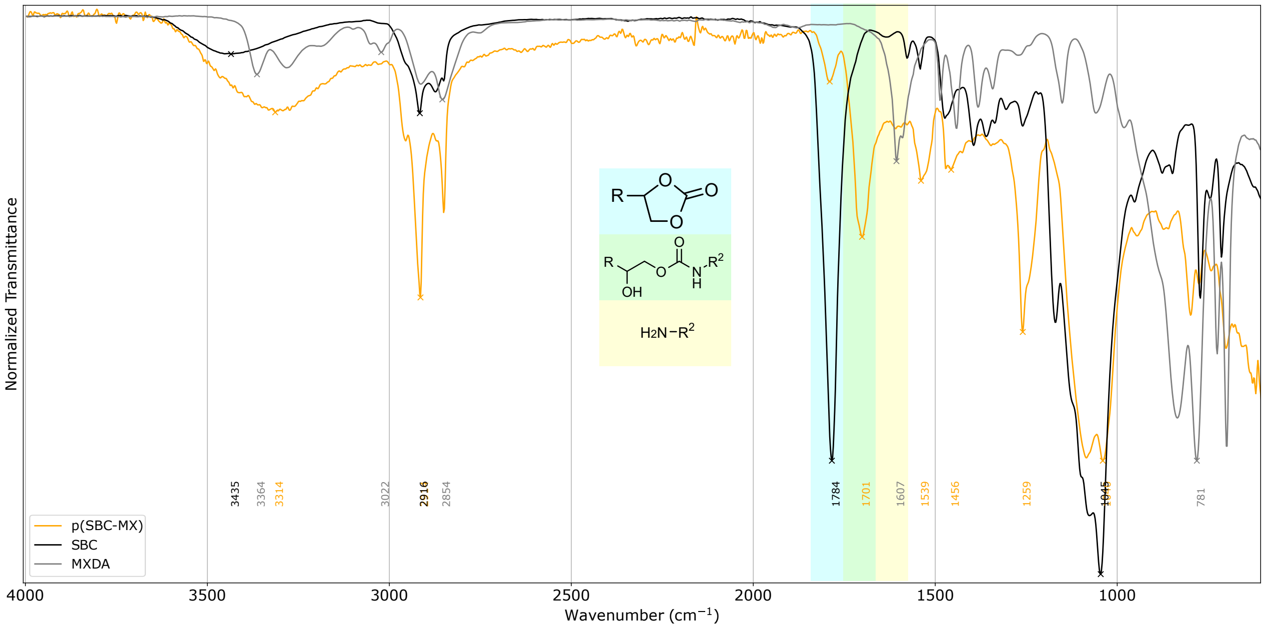
Supp. Fig. 15: FTIR of the p(TMC-MX) and its corresponding monomers



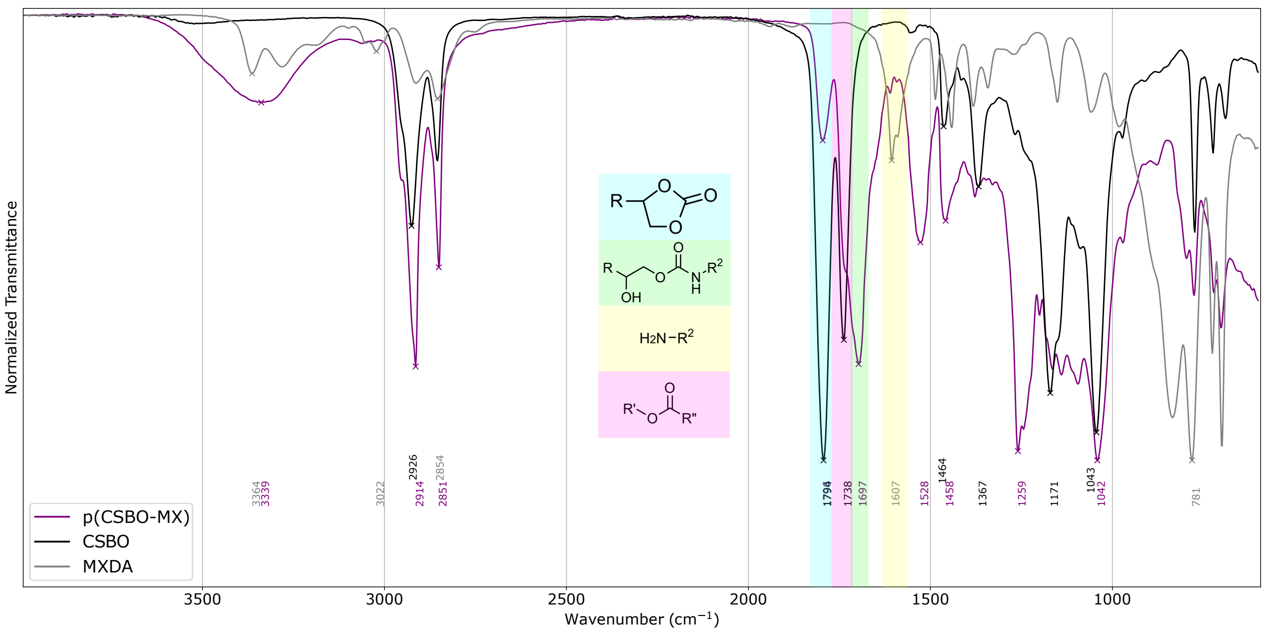
Supp. Fig. 16: FTIR of the p(PEC-MX) and its corresponding monomers



Supp. Fig. 17: FTIR of the p(GEC-MX) and its corresponding monomers



Supp. Fig. 18: FTIR of the p(SBC-MX) and its corresponding monomers



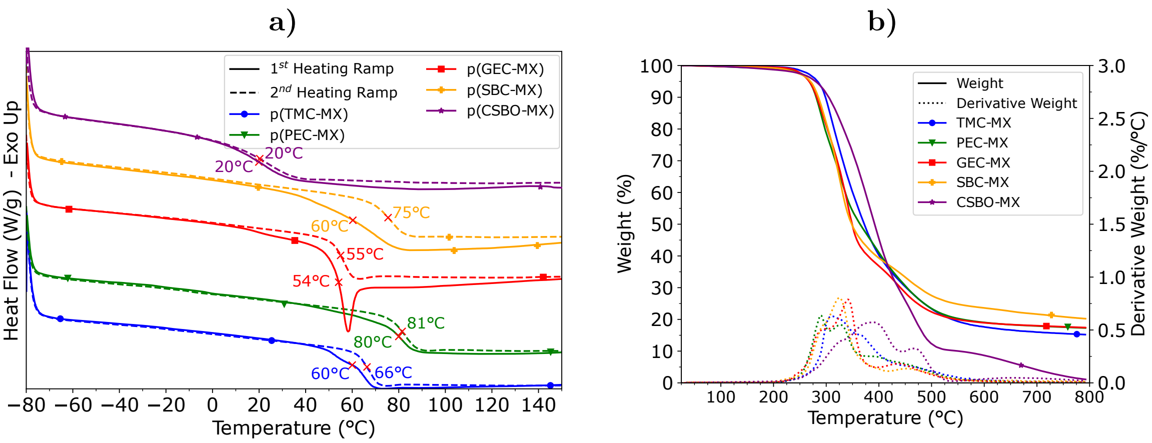
Supp. Fig. 19: FTIR of the p(CSBO-MX) and its corresponding monomers

3.3 Swelling and Gel Content

Formulation	SI_{THF} (%)	$SI_{Toluene}$ (%)	GC_{THF} (%)	$GC_{Toluene}$ (%)	MU (%)	WU (%)
p(TMC-MX)	56.6 ± 1.73%	0.14 ± 0.12%	99.76 ± 0.44%	98.43 ± 0.8%	2.6 ± 0.1%	13 ± 1%
p(PEC-MX)	0.72 ± 0.16%	0.87 ± 0.61%	98.24 ± 0.17%	98.62 ± 0.65%	3.5 ± 0.4%	25 ± 1%
p(GEC-MX)	3.14 ± 0.88%	0.76 ± 0.16%	99.76 ± 0.41%	98.88 ± 0.8%	2.5 ± 0.5%	47 ± 2%
p(SBC-MX)	0.81 ± 0.66%	0.44 ± 0.56%	99.03 ± 0.39%	98.76 ± 0.46%	3.3 ± 0.3%	30 ± 4%
p(CSBO-MX)	239.28 ± 18.04%	54.04 ± 1.03%	74.59 ± 1.6%	93.67 ± 0.97%	1.1 ± 0.7%	5 ± 1%

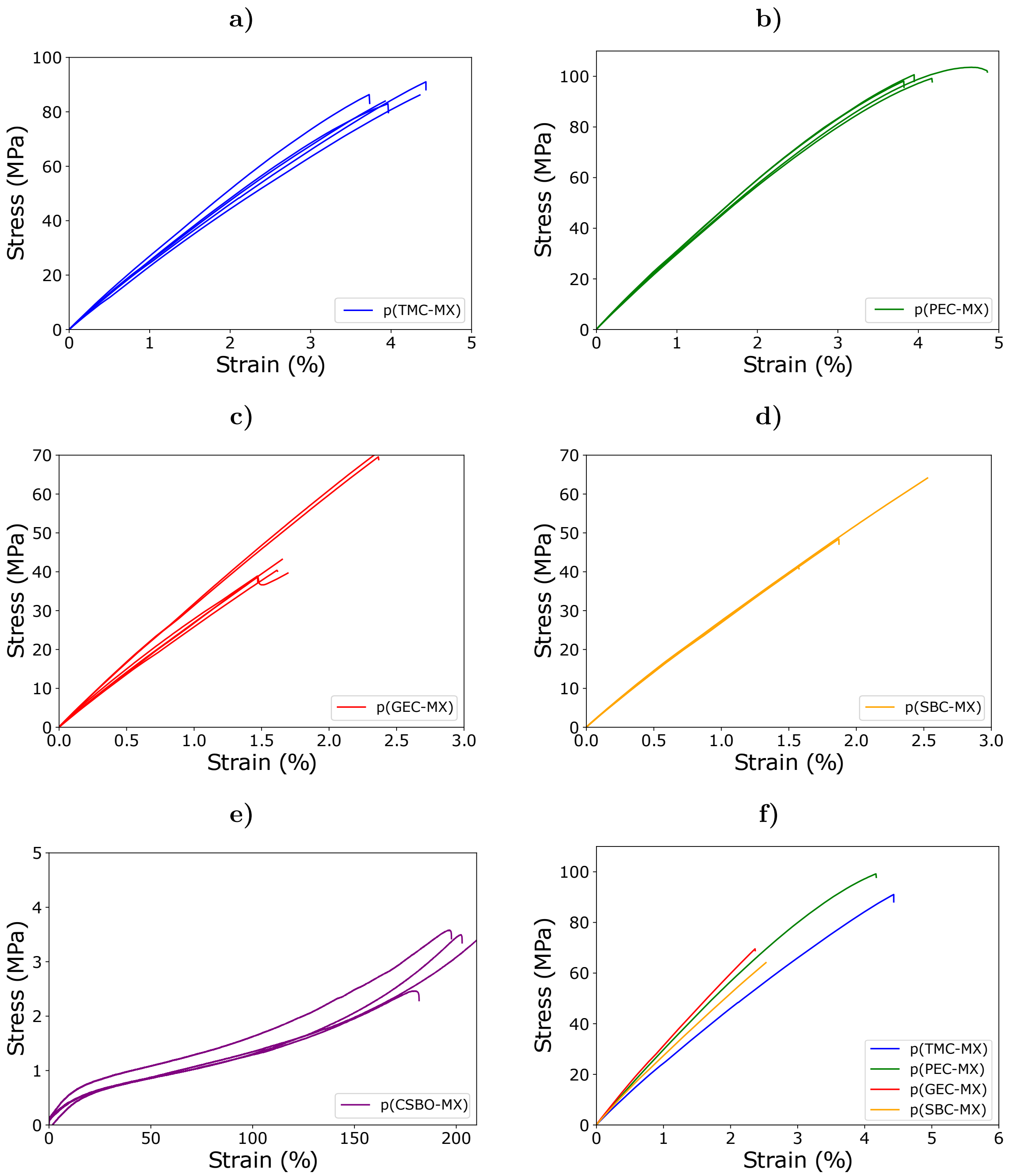
Supp. Tab. 2: Gel content and swelling index of the PHU thermosets

3.4 DSC and TGA



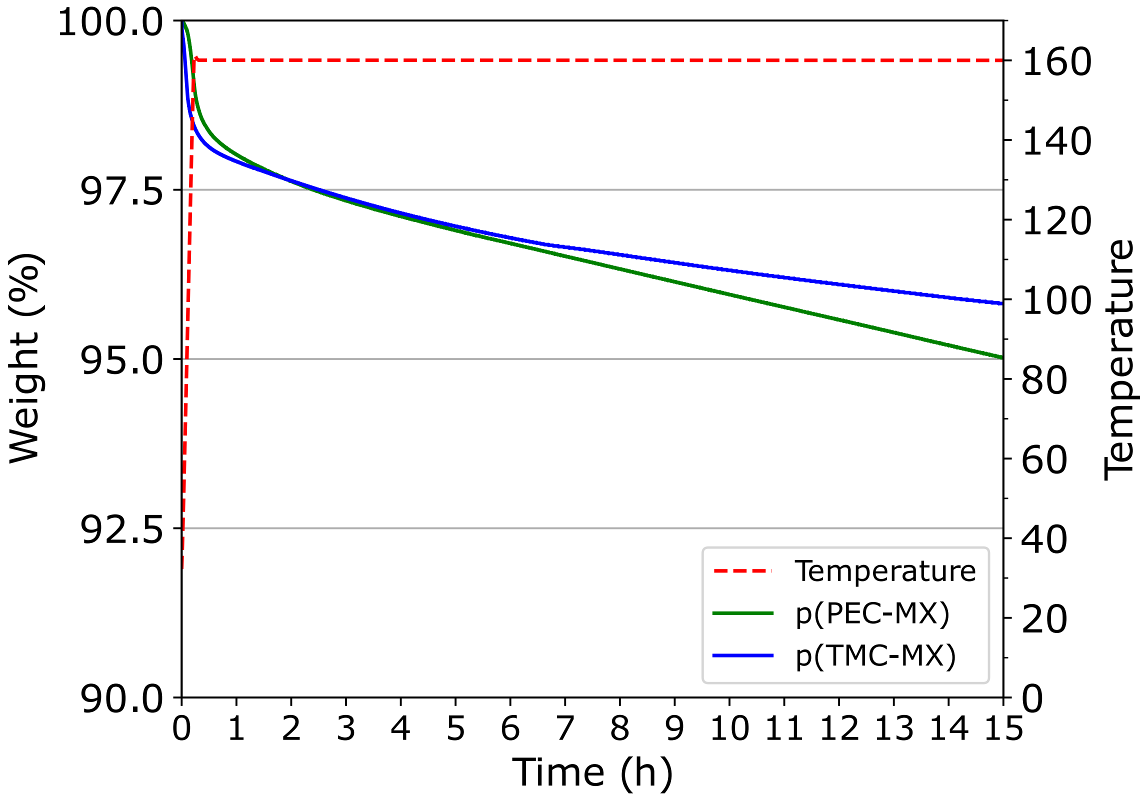
Supp. Fig. 20: a) DSC heating ramp of the cured PHU formulations b) TGA under N_2 flow

3.5 Monotonic Tensile Strain-Stress Curves

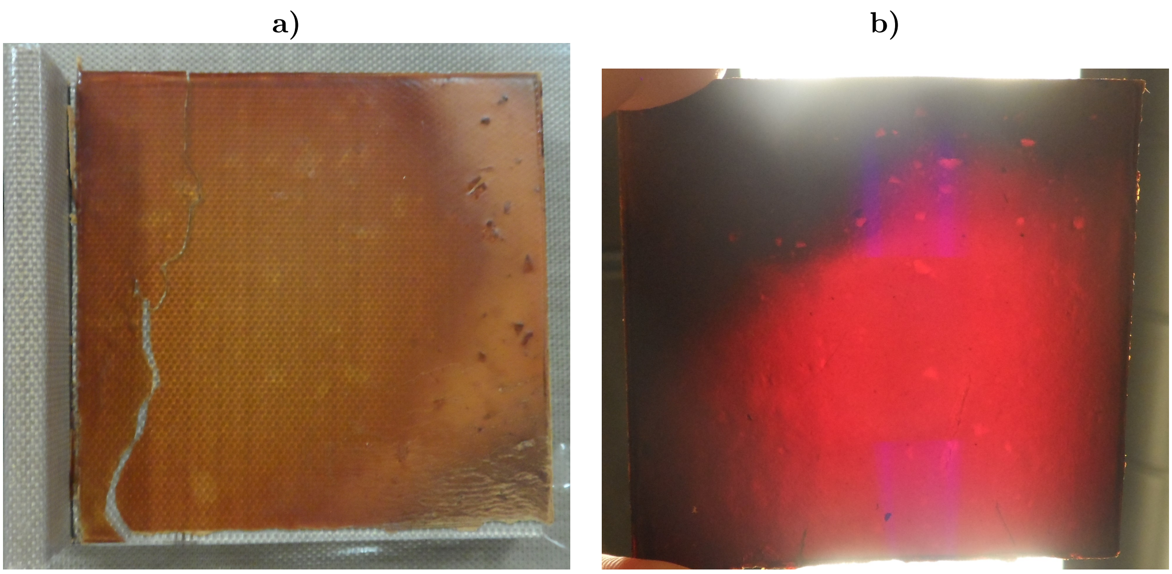


Supp. Fig. 21: Tensile strain-stress curves of the PHUs formulations. a) p(TMC-MX) b)p(PEC-MX) c)p(GEC-MX) d)p(SBC-MX) e)p(CSBO-MX) and f) representative tensile curve of all PHUs

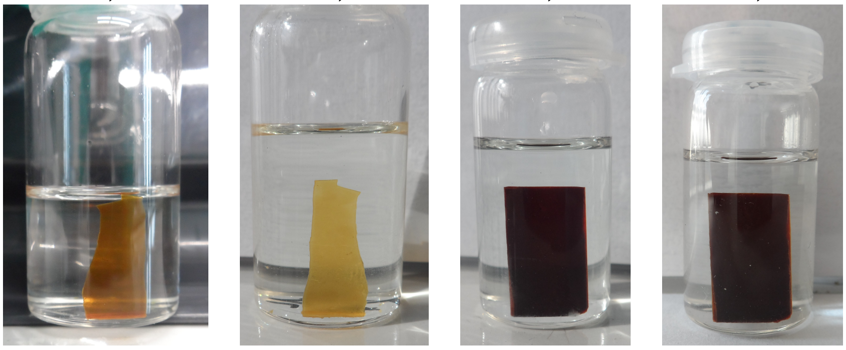
3.6 Reprocessing of PHUs



Supp. Fig. 22: Isothermal TGA of p(PEC-MX) and p(TMC-MX) thermoset at 160°C for 15h



Supp. Fig. 23: Reprocessed PHU a) p(TMC-MX) b)p(PEC-MX)



Supp. Fig. 24: Reprocessed PHU samples in THF solvent a) p(TMC-MX) t=0, b) TMC-MX t=3 weeks, c) p(PEC-MX) t=0, and d) p(PEC-MX) t=3 weeks

Sample		T_α (°C)	$E'_{glassy} 25°C$(MPa)	$E'_{rubbery}$(MPa)	$\nu'_{E'}(mol/m^3)$	Recovered E' (%)
p(TMC-MX)	original	68	3120	5.3	559	-
p(TMC-MX)	reprocessed	81	1600	7.2	712	51.3
p(PEC-MX)	original	92	3996	13.8	1335	-
p(PEC-MX)	reprocessed	107	3921	11.1	1036	98.1

Supp. Tab. 3: Thermo-mechanical properties of reprocessed p(TMC-MX) and p(PEC-MX) formulations