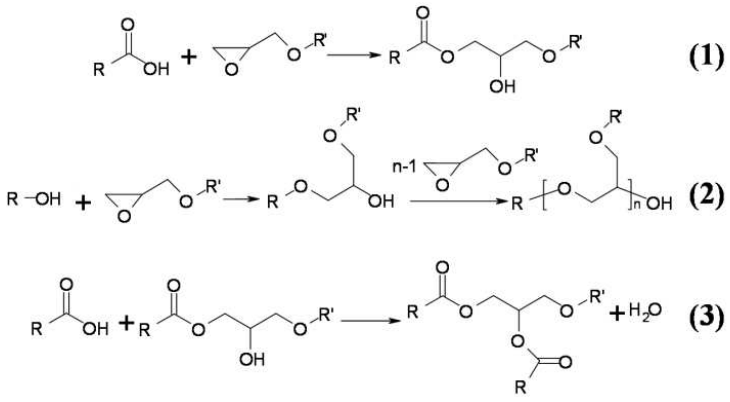
Supporting Information for

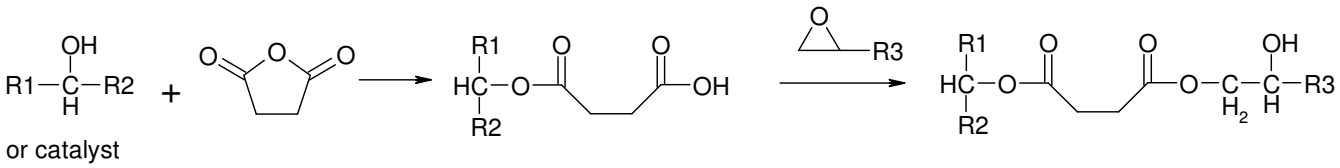
Metal-Catalyzed Transesterification for Healing and Assembling of Thermosets

Mathieu Capelot, Damien Montarnal, François Tournilhac, Ludwik Leibler*

I. Epoxy-acid and epoxy-anhydride reactions



Scheme 1. The three main reactions occuring during epoxy-acid networks curing: (1) addition-esterification of acids on epoxy rings (2) Etherification of epoxy groups (homopolymerization) (3) Fischer esterification of acids on hydroxyl groups.



Scheme 2. Epoxy-anhydride alternate ring-opening polymerization, yielding diesters. The hydroxyl group present at the end of these two steps can open a new anhydride and propagate the reaction. With an excess of epoxy rings, an homopolymerization process takes place (see reaction (2) on scheme 1).

II. Synthesis of epoxy-acid and epoxy-anhydride networks

Chemical reagents:

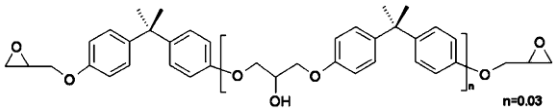
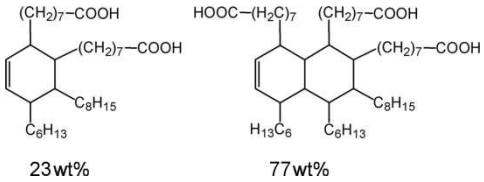
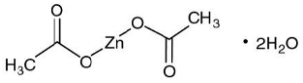
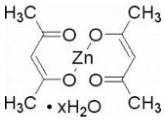
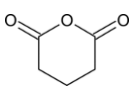
Chemical	Structure	Mw (g/mol)	Provider
DER332		174 per epoxy	Sigma Aldrich
Pripol 1040		296 per acid	Croda
$Zn(OAc)_2$, $2H_20$		219.5	Fischer Scientific
$Zn(acac)_2$, H_20		218.62	Acros
Glutaric Anhydride		114.1	Acros

Table 1. Reagents for networks synthesis.

All reagents were used without further purification.

Synthesis of soft networks:

In a 100 mL round-bottom flask are introduced about 20 g of the trimer acids (Pripol 1040, 296 g/mol_{COOH}) and the catalyst ($Zn(Ac)_2$, 2 H_2O) at different concentrations: 1 and 5 mol% to the COOH groups. Temperature is gradually increased from 100 °C to 180 °C while maintaining the mixture under vacuum. Evolution of acetic acid indicates that the fatty acids replace the acetates as ligands of Zn. The mixture is left at 180 °C under vacuum until not gas evolution is observed and catalyst particles are fully solubilized (3 h).

In a PTFE beaker are added the previous fatty acid mixture containing solubilized catalyst and DGEBA (1 epoxy ring to 1 acid). The mixture was heated to 130 °C until phase miscibility occurred, manually

stirred, and then quickly poured into a 10×10×0.15 cm^3 brass mold sandwiched with anti-adhesive silicone paper. The mold was placed in a heating press and left for at least 5 h at 130 °C.

Synthesis of hard networks:

In a PTFE beaker are added DGEBA (equivalent weight: 174) and $Zn(acac)_2$ (at 5mol% to the epoxy groups). The mixture is heated until homogenization (about 150°C), and glutaric anhydride is added. After a second heating to ensure complete miscibility, the mixture is poured into 10×10×0.15 cm^3 brass mold and cured at 140 °C for 12 hours.

4 syntheses were carried out:

Epoxy:Anhydride ratio	**DGEBA (g / $mmol_{epoxy}$)**	**Glutaric anhydride (g / mmol)**	**$Zn(acac)_2$ (mg / mmol)**
1:0.5	10.7 / 61.4	3.51 / 30.7	809 / 3.07
1:0.66	10.4 / 60.0	4.56 / 40.0	791 / 3.00
1:0.75	9.58 / 55.1	4.71 / 41.3	726 / 2.76
1:1	9.06 / 52.1	5.94 / 52.1	686 / 2.60

Table 2. Compositions of the different epoxy-anhydride networks.

The 4 materials were characterized by DSC and DMA:

Epoxy:Anhydride ratio	**Tg (DSC, °C)**	**E' (150°C, MPa)**
1:0.5	68	15
1:0.66	73	19
1:0.75	73	21
1:1	59	25

Table 3. Tg and storage modulus of the different epoxy-anhydride networks.

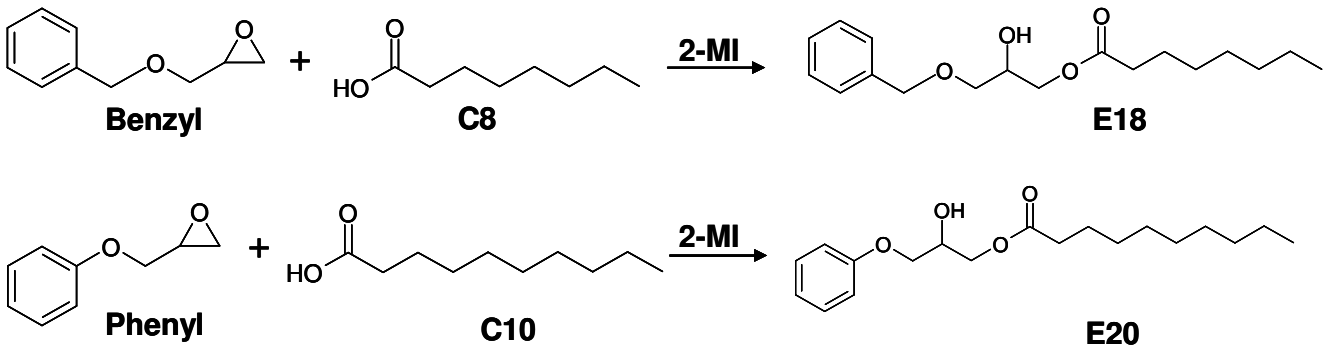
For DMA and DSC studies, please also see Montarnal *et al.*, *Science*, 2011, **334**, 965.

III. Synthesis of model molecules E18, E19, DE26 and DE29

Please note that, among other backside products, diesters and diols were also formed in small quantities.

β-hydroxylesters : octanoic ester of benzylglycidyl ether (E-18) and decanoic ester of phenylglycidylether (E-19)

The two syntheses follow the same preparation method: the carboxylic acid (1eq), the epoxyde (1eq) and 2-Methylimidazole (0.06eq) are introduced in a 25 mL round-bottom flask. The mixture is homogenized and left for reaction at 120 °C under a gentle nitrogen flow. Progression of both reactions is monitored by FTIR and considered as complete after 1h, when the signals of epoxy ring (915 cm^{-1}), ester (1735 cm^{-1}) and carboxylic acid (1705 cm^{-1}) do not evolve anymore.



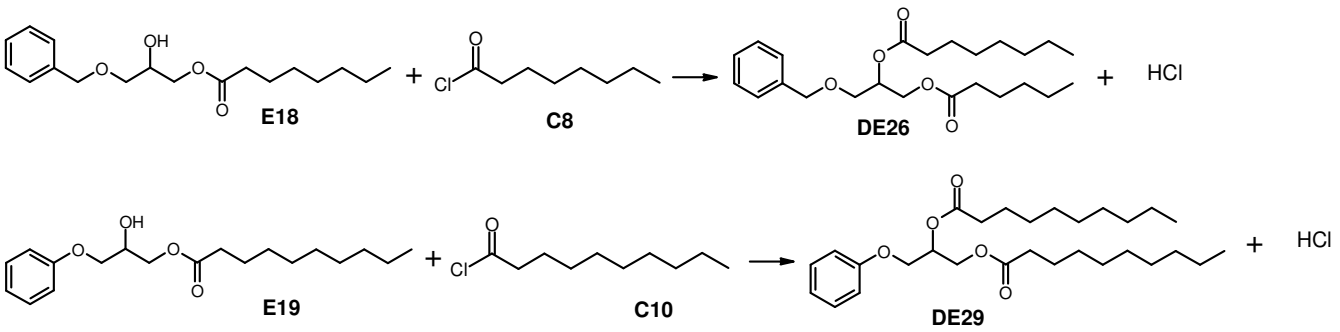
Scheme 3. Syntheses of E18 and E19.

Monoester	Acid (g / mmol)	Epoxide (g / mmol)	Catalyst (mg / mmol)
E18	octanoic acid: 4.40 / 30.6	benzylglycidyl ether 5.03 / 30.7	2-MI 150 / 1.83
E19	decanoic acid : 5.73 / 33.3	phenylglycidyl ether 5.05 / 33.6	2-MI 163 / 1.99

Table 4. Amount of reagents added during the syntheses of E18 and E19.

diesters: di-octanoic ester of benzylglycidyl ether (DE-26) and di-decanoic ester of phenylglycidylether (DE-29)

The syntheses proceed in two steps. In the first step, the corresponding β-hydroxylesters are synthesized as described above (1 h at 120 °C). Then, the mixture is cooled at room temperature and the corresponding acyl chloride is added dropwise. The mixture is then left to react at 50 °C overnight under a nitrogen flow.



Scheme 4. Second steps of the syntheses of DE26 and DE29.

Diester	Acid (g / $mmol_{epoxy}$)	Epoxide (g / mmol)	Acyl chloride (mg / mmol)	Catalyst (mg / mmol)
DE28	octanoic acid: 0.89 / 6.2	benzylglycidyl ether 1.01 g / 6.2	Octanoyl chloride 1.02 g / 6.3	2-MI 30 / 0.36
DE29	decanoic acid : 1.15 / 6.7	phenylglycidyl ether 1.00 / 6.7	Decanoyl Chloride 1.27 / 6.7	2-MI 33 / 0.40

Table 5. Amount of reagents added during the syntheses of DE26 and DE29.

IV. NMR

E18: ^{1}H NMR (400MHz, $CDCl_3$) δ/ppm = 0.80 (t, CH_3, J=6.9Hz), 1.2 (m, 4 CH_2, chain, 6H), 1.53 (m, CH_2, β-ester), 2.24 (m, CH_2, α-ester), 2.65 (m, CH_3, imidazole), 3.42 (dd, C$\underline{H_2}$CH(OH)CH_2O, J_{sysAB}= 9.6 Hz, J = 6Hz, 1H), 3.48 (dd, C$\underline{H_2}$CH(OH)CH_2O, J_{sysAB}= 9.6 Hz, J = 4.4 Hz, 1H), 3.55-3.62, 3.95 (tt, CH_2C$\underline{H}$(OH)CH_2O, J=6, 4.4 Hz), 4.06 (dd, CH_2CH(OH)C$\underline{H_2}$O, J_{sysAB}= 11.42 Hz, J = 6Hz, 1H), 4.11 (dd, CH_2CH(OH)C$\underline{H_2}$O, J_{sysAB}= 11.42 Hz, J = 4.4Hz, 1H), 4.48 (s, CH_2, benzyl), 4.97, 7.03 (d, CH, imidazole), 7-19-7.29 (m, CH, aromatic)

^{13}C NMR (100MHz, $CDCl_3$) δ/ppm = 14.08 (CH_3), 22.60 ($\underline{C}H_2CH_3$), 24.91 (CH_2, β-ester), 28.92 + 29.06 (CH_2 chain), 31.66 ($\underline{C}H_2CH_2CH_3$), 34.16 (CH_2, α-ester), 65.35 ((O$\underline{C}H_2$CHCH_2OC(O)), 68.93 (OC$H_2\underline{C}$HCH_2OC(O)), 70.89 (OCH_2C$\underline{H}$CH_2OC(O)), 73.44 (CH_2, benzyl), 127.77 + 127.85 (C *ortho* + C *para*), 128.50 (C *meta*), 137.68 (C-1 aromatic), 173.99 (C(O), ester).

E19: ^{1}H NMR (400MHz, $CDCl_3$) δ/ppm = 0.80 (t, CH_3, J=6.73Hz), 1.20 (m, CH_2, chain), 1.55 (m, CH_2, β-ester), 2.27 (m, CH_2, α-ester), 2.70 (m, CH_3, imidazole), 3.90 - 4.35 (m, H glycidyl, 5H), 5.14, 6.83 (CH, *ortho* aromatic), 6.90 (CH, *para* aromatic), 7.25 (CH, *meta* aromatic)

^{13}C NMR (100MHz, $CDCl_3$) δ/ppm = 14.12 (CH_3), 22.67 ($\underline{C}H_2CH_3$), 24.93 (CH_2, β-ester), 29.08 + 29.14 + 29.26 + 29.33 (CH_2 chain), 31.86 ($\underline{C}H_2CH_2CH_3$), 34.17 (CH_2, α-ester), 66.04 ((O$\underline{C}H_2$CHCH_2OC(O)), 68.61 (OCH_2CHCH_2OC(O)), 63.63 (OCH_2C$\underline{H}$CH_2OC(O)), 114.54 (C *ortho*), 121.36 (C *para*), 129.57 (C *meta*), 158.38 (C-1 aromatic), 174.09 (C(O), ester).

DE26: ^{1}H NMR (100MHz, $CDCl_3$) δ/ppm = 0.85 (t, CH_3, J=6.92Hz), 1.25 (m, 8 CH_2 chain), 1.6 (m, 2 CH_2, β-ester)), 2.3 (m, CH_2, α-ester), 2.79 (m, CH_3, imidazole), 3.65-3.75 (m, CH_2CH(OH)C$\underline{H_2}$O), 4.34 + 4.18 (dd, C$\underline{H_2}$CH(OH)CH_2O, J_{sysAB}= 11.88 Hz, J = 3.86 Hz, 6.39 Hz), 4.49-4.57 (m, CH_2 benzyl), 5.23 (m, CH_2 glycidyl), 7.26-7.35 (m, CH, aromatic)

^{13}C NMR (100MHz, $CDCl_3$) δ/ppm = 14.02 (CH_3), 22.58 ($\underline{C}H_2CH_3$), 24.95 (CH_2, β-ester), 28.90 + 29.03 (CH_2 chain), 31.65 ($\underline{C}H_2CH_2CH_3$), 34.12 (CH_2, α-ester), 62.67 (O$\underline{C}H_2$CHCH_2OC(O)), 68.3 (OCH_2C$\underline{H}$CH_2OC(O)), 70.04 (OC$H_2\underline{C}$HCH_2OC(O)), 73.32 ($\underline{C}H_2$ benzyl), 127.62 + 127.77 (C *ortho* + C *para*), 128.41 (C *meta*), 137.74 (C-1 aromatic), 173.10 + 173.30 (C(O), ester).

DE29: ^{1}H NMR (100MHz, $CDCl_3$) δ/ppm = 0.87 (t, 2 CH_3, J=6.7 Hz)), 1.24 (m, 12 CH_2 chain), 1.60 (m, 2 C$\underline{H_2}$CH_2C(O)), 2.31 (m, 2 C$\underline{H_2}$C(O)), 2.43, 2.85-2.9, 3.81, 4.09 (d, CHC$\underline{H_2}$O, J=5.1 Hz), 4.32 +

4.46 (dd, $OC\underline{H_2}CHCH_2O$, JsysAB = 12 Hz, J = 3.9 Hz, 6.06Hz), 5.38 (m, $OCH_2C\underline{H}CH_2O$), 6.90 (CH, *ortho* aromatic), 6.96 (CH, *para* aromatic), 7.25 (CH, *meta* aromatic), 7.43

^{13}C NMR (100MHz, $CDCl_3$) δ/ppm = 14.12 (CH_3), 22.68 ($\underline{C}H_2CH_3$), 24.91 (CH_2, β-ester), 29.07 + 29.12 + 29.29 +29.43 (CH_2 chain), 31.87 (C(O)), 34.13 + 34.29 ($C(O)CH_2$), 63.37 ($O\underline{C}H_2CHCH_2OC(O)$), 66.03 ($OCH_2CH\underline{C}H_2OC(O)$), 69.53 ($CH_2\underline{C}HCH_2$), 114.58 (C *ortho*), 121.33 (C *para*), 129.52 (C *meta*), 158.31 (C-1 aromatic), 173.14 +173.44 (C ester).

V. GCMS studies

The syntheses of E18 and E19 were catalyzed by 2-MI (6 mol%) in order to obtain exclusively the ester products. Since no purification was done afterwards, 2-MI stayed in the mixture during the transesterification reaction, in the GCMS studies.

Kinetics study with model molecules:

In a test tube are added the β-hydroxylesters **E18** and **E19** and 5 mol% of catalyst. The mixture is homogenized and heated at 150 °C under a gentle nitrogen flow. Aliquots are taken from the mixture at different times, dissolved in methanol (in concentrations about 3 mg/mL), and analyzed with Shimazu GC-2010 gas chromatograph coupled to mass spectrometry. The same characterization was repeated for a 1:1 molar mixture of diesters **DE26** and **DE29**, and a 1:1 molar mixture of β-hydroxyl ester **E18** and diester **DE29**.

Kinetics was followed using i) the ratio of area ([E17]+[E20])/([E18]+[E19]) for E18+E19 reaction ii) the ratio of area DE28/DE29 for E18 + DE29 reaction and iii) DE28/DE26 for DE26 + DE29 reaction.

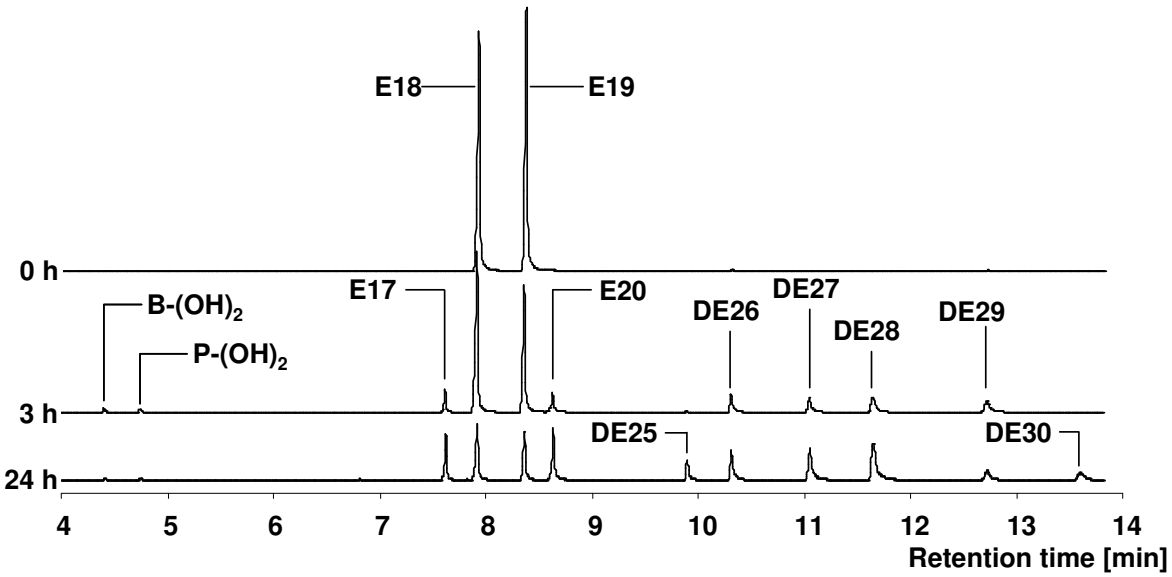


Figure 1. Gas chromatograms of a mixture of E18 and E19 heated at 150°C, without metal catalyst.

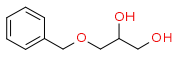
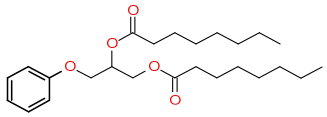
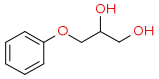
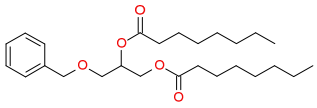
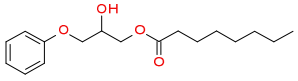
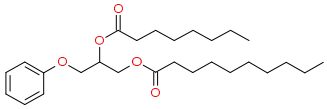
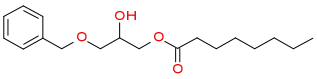
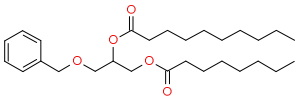
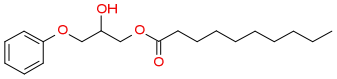
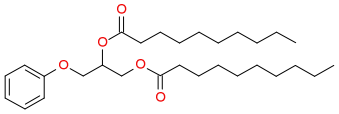
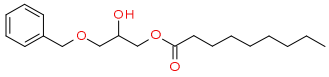
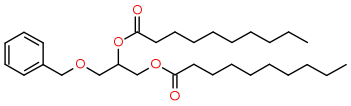
B-(OH)$_2$		**DE25**	
P-(OH)$_2$		**DE26**	
E17		**DE27**	
E18		**DE28**	
E19		**DE29**	
E20		**DE30**	

Table 6. Molecular structures of diesters and diols.

For MS attribution, please see Montarnal *et al.*, *Science*, 2011, **334**, 965.

VI. Welding tests

Welding experiments:

i) Epoxy-acid networks : Lap Shear experiments were carried out on an Instron 5564 tensile machine. Rectangular specimens (1.4×5×25 mm^3) were superposed on a 15 mm length and left under compression using a Mohr clamp (about 25 % compression) in an oven for varying times and temperature. After the mending process, tensile tests were performed on the assembly at a speed of 5 mm/min.

ii) Epoxy-anhydride networks: Rectangular specimens (1.4×5×25 mm^3) were superposed on a 15 mm length and maintained by a Mohr clamp tightened with a dynamometric screwdriver to apply a reproducible pressure. After the mending process, tensile tests were performed on the assembly at a speed of 0.1 mm/min.

Effect of the welding time:

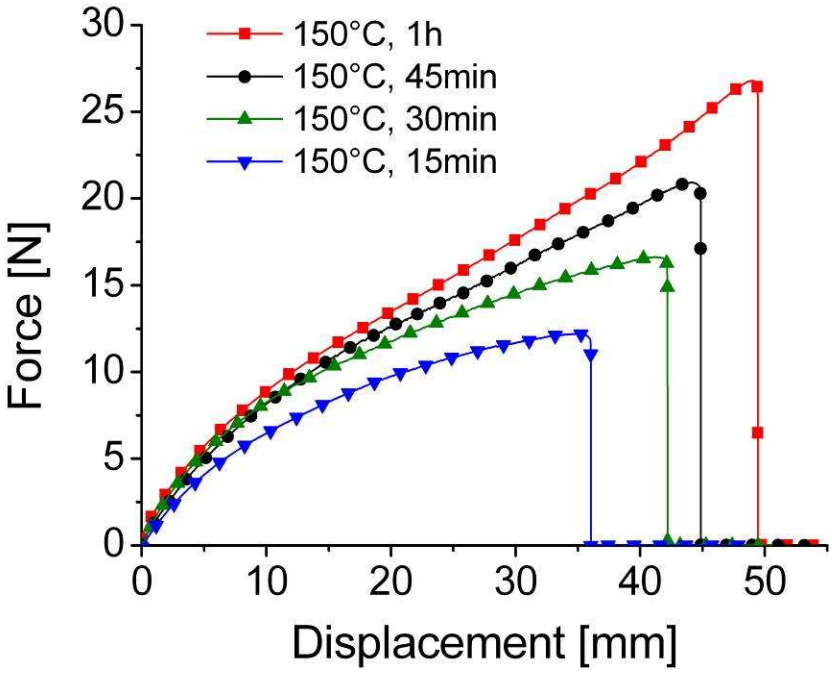


Figure2. Effect of the welding time.

Effect of the contact:

Maintaining a good contact between the two parts during the welding process is critical. Unfortunately, the material also relaxes during the process and does not recover the 25 % compression after the Mohr clip is released. A way to circumvent this issue is to first apply compression at low temperature to ensure a good adhesion between the surfaces but no relaxation, and then to perform the heating treatment without clips. In this way, the two parts could be assembled without modifying their shapes.

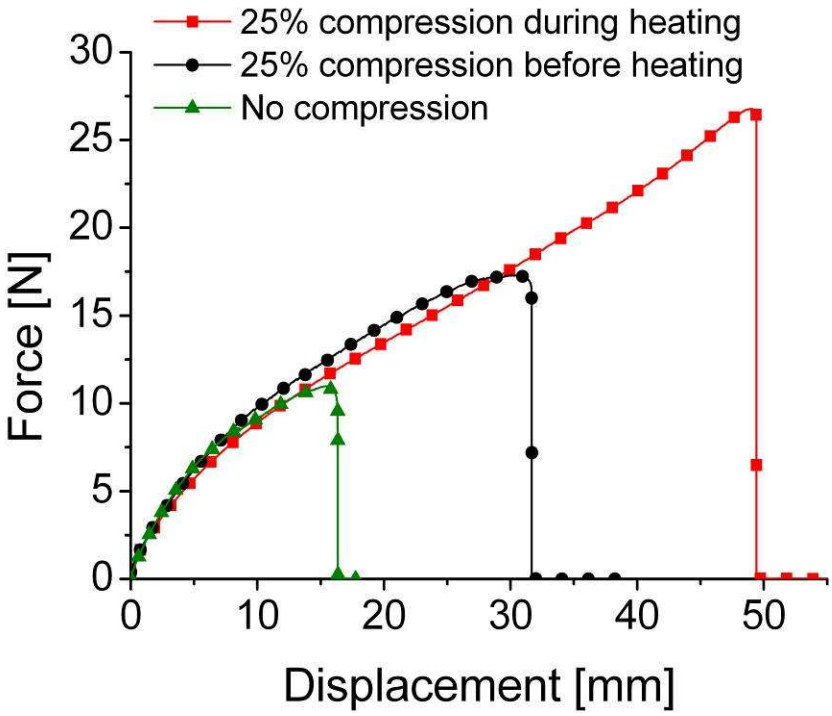


Figure 3.Effect of the contact on the welding efficiency.

Repetability of the welding:

The repeatability of the mending was tested using the two-part process (compression at 25 °C for two hours, then welding for 1 h at 150 °C) to avoid reducing the thickness of our sample at each test. Five consecutive tests were carried out on the same sample without significant loss changes in the mending properties. Control shows the stress at break when the assembly is mended for 1 h at room temperature.

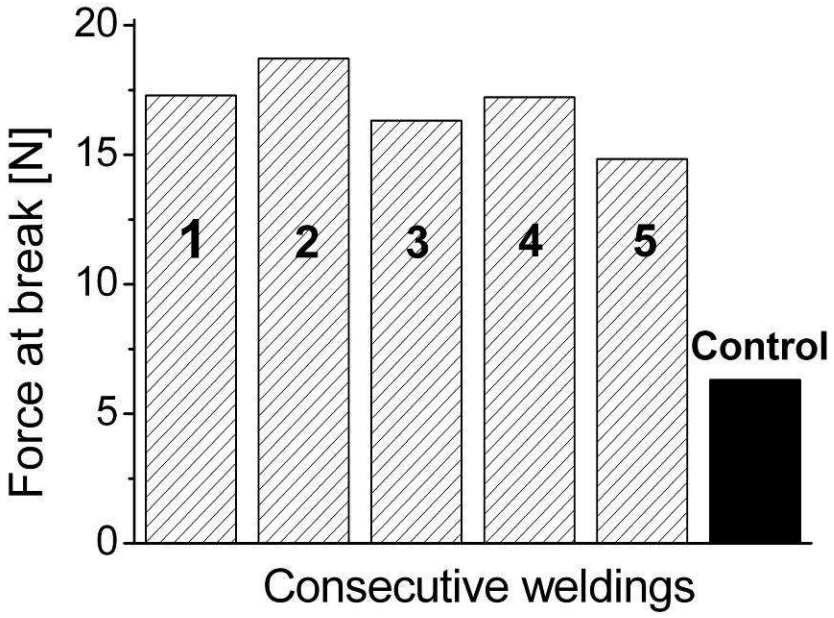


Figure 4. Several welding scan be done consecutively.

VII. FTIR

Curing was monitored by FTIR using a Bruker Tensor 37 spectrometer fitted with a Specac transmission Variable Temperature Cell. A thin layer of epoxy-glutaric anhydride mixture, with 10 mol% $Zn(acac)_2$, was sandwiched between KBr pellets and maintained with a solid holder in the VTC. Two epoxy/anhydride stoichiometries were tested: 1:1 and 1:0.5. Once the temperature is raised to 140°C, spectra are taken every every 20 minutes from 1.5h to 15h.

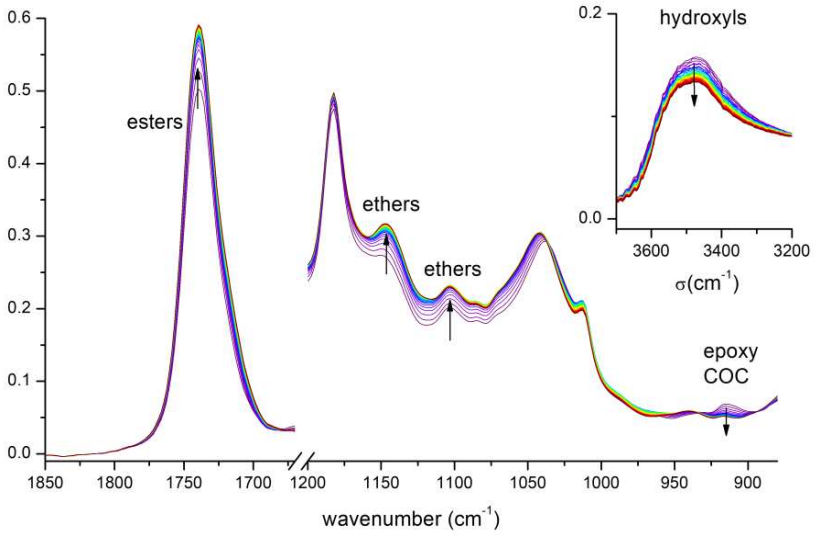


Figure 5. FTIR traces for the 1:0.5 stoichiometry.

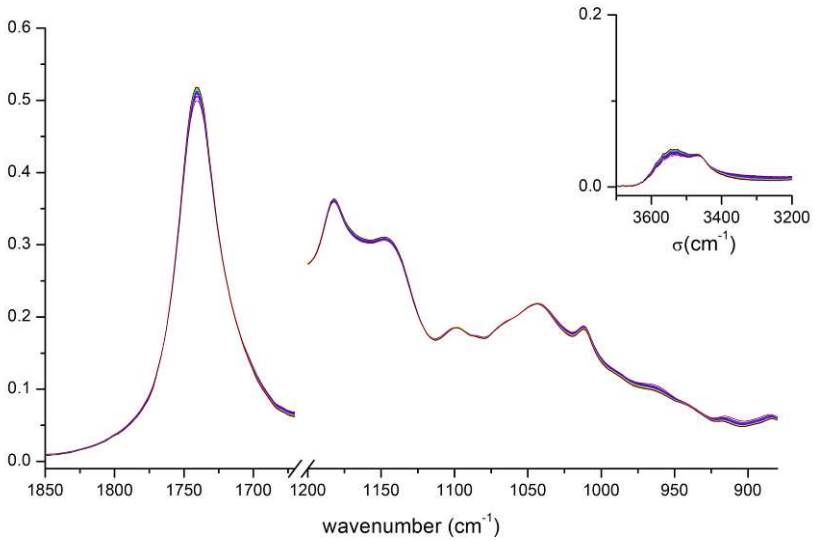


Figure 6. FTIR traces for the 1:1 stoichiometry.