Green enzymatic synthesis and processing of poly (*cis*-9,10-epoxy-18-hydroxyoctadecanoic acid) in supercritical carbon dioxide ($scCO_2$).

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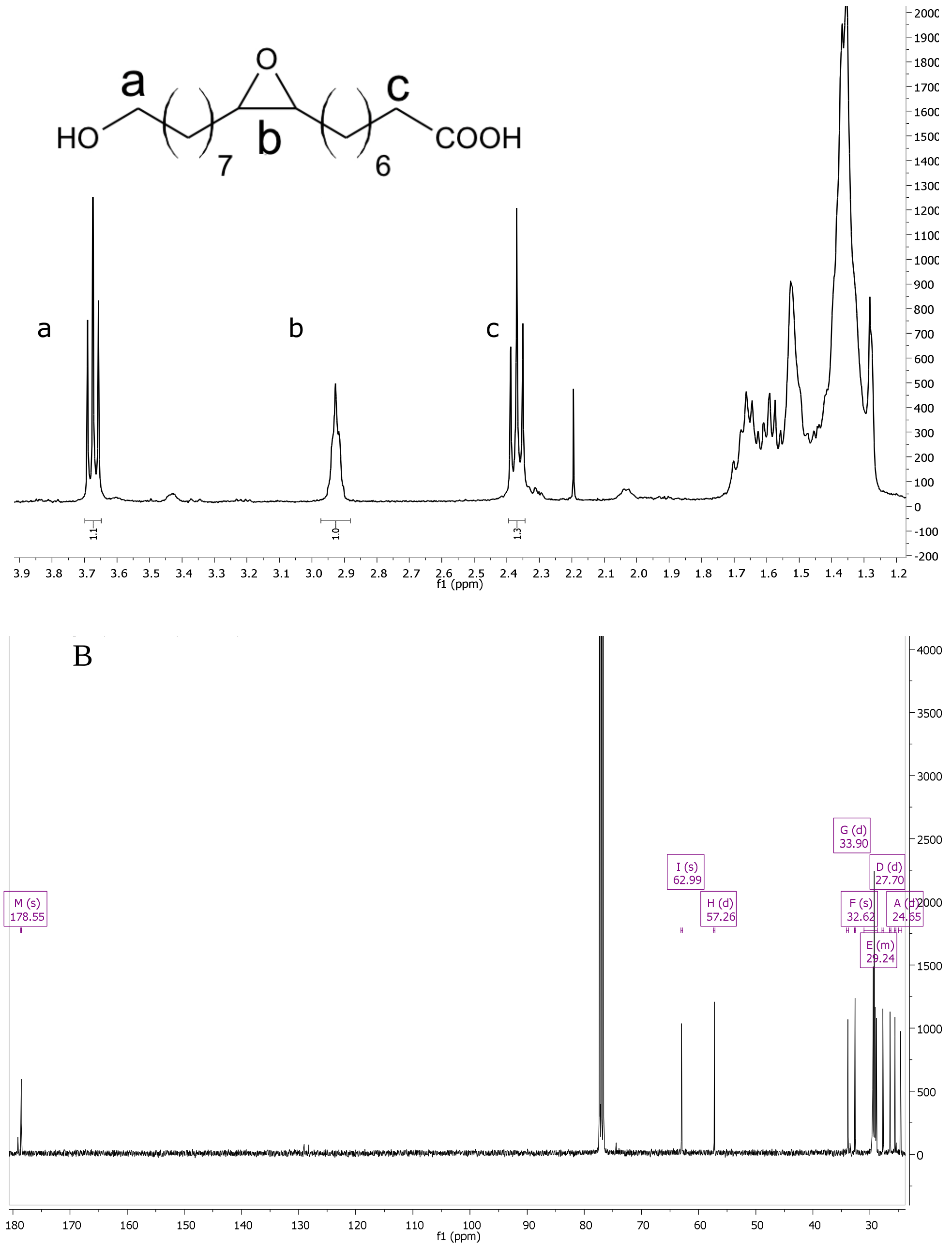
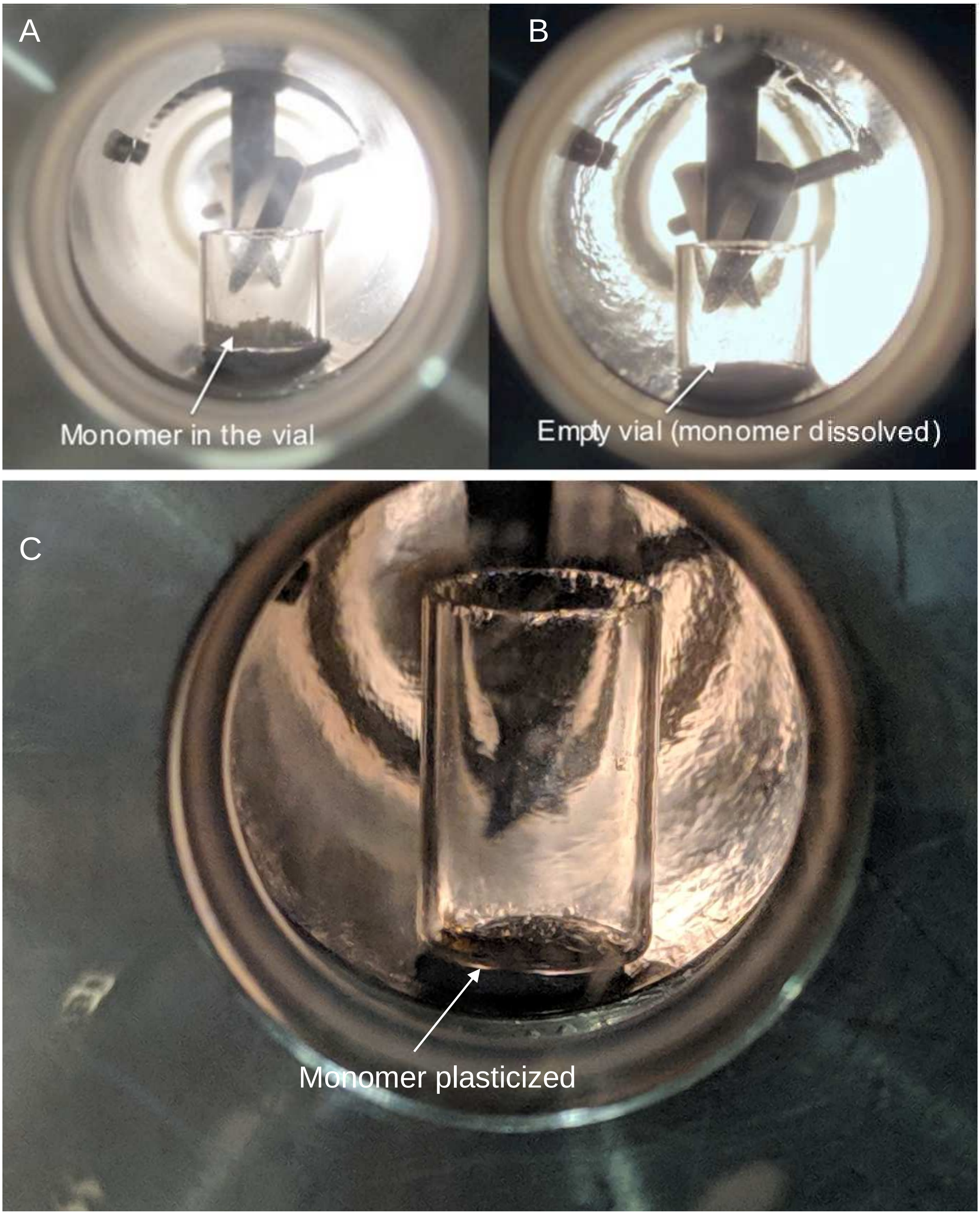
KEYWORDS. Supercritical CO2, birch bark, EFA monomer, lipase, Calb, enzymatic polymerisation, UV curing



Supplementary Figure 1. A) CHA post recrystallization showing that our procedure does not cause the opening of the epoxy group. Showing the areas ratio (1:1) between the epoxide and the protons nearby the end-groups remain constant. C) C^{13}NMR of the monomer recrystallized. Showing the carbon of the epoxide group (57.26 ppm)



Supplementary Figure 2. Visual observation of the solubility of EFA in CO2: A) Initial state of the monomer in the form of a powder (room temperature and pressure). B) Empty vial indicative of the dissolution of the monomer in CO2 (85 °C and 275 bar). C) Monomer deposited in CO_2 swollen fluid state indicative of melting (35℃ and 274 bar).

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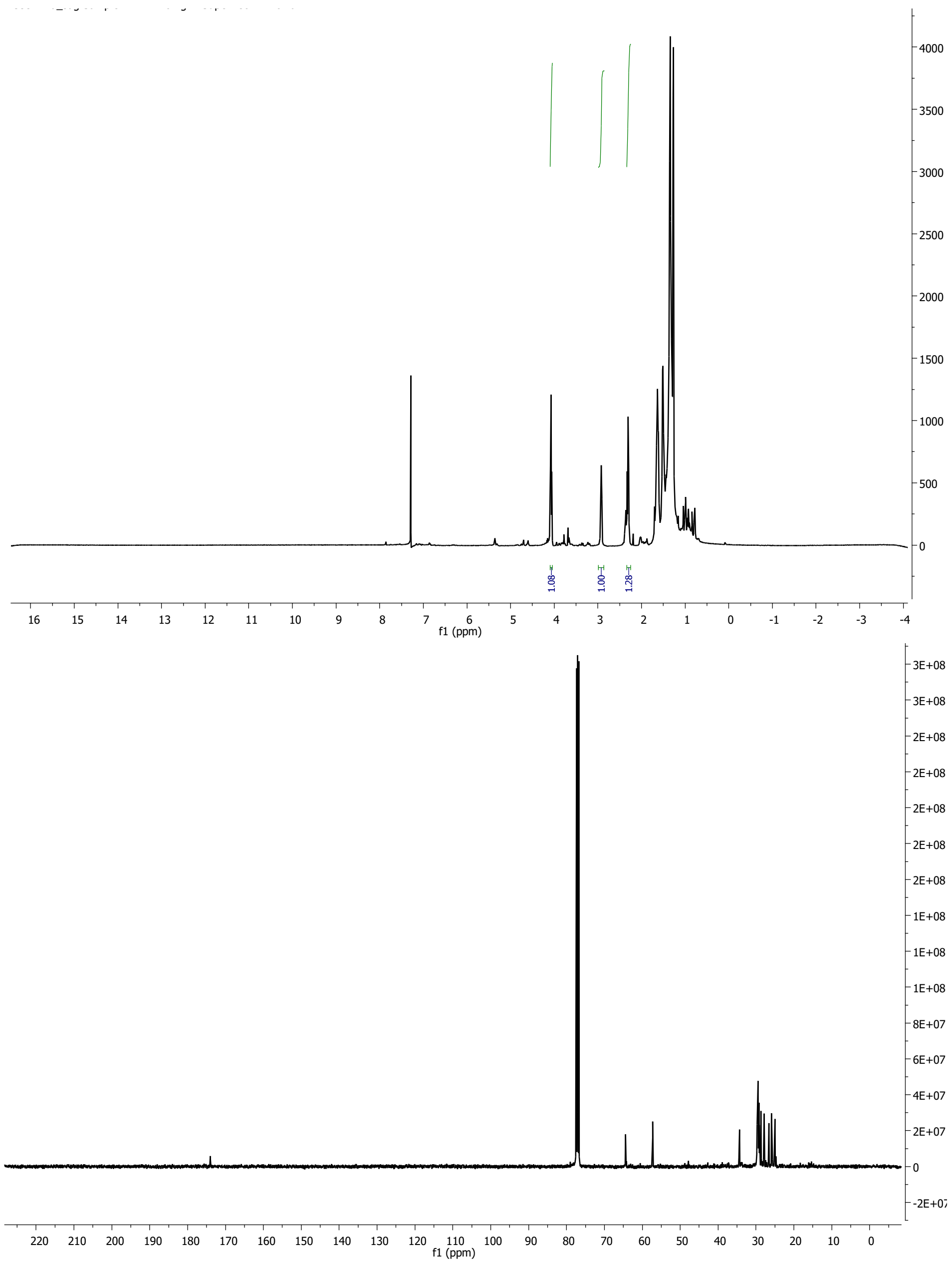
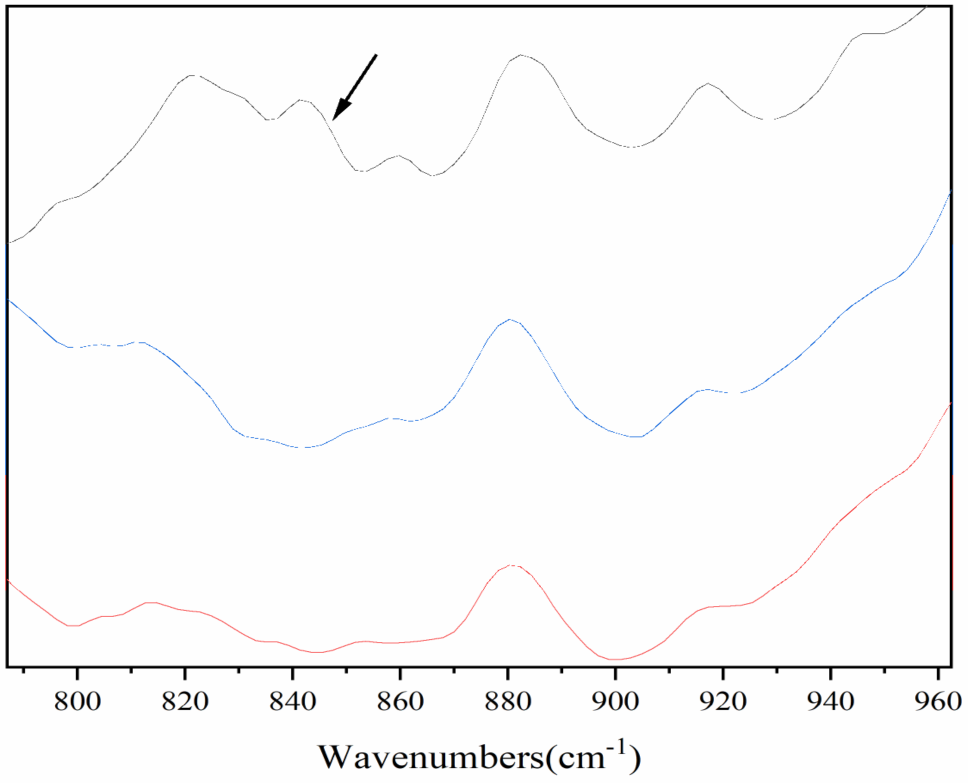
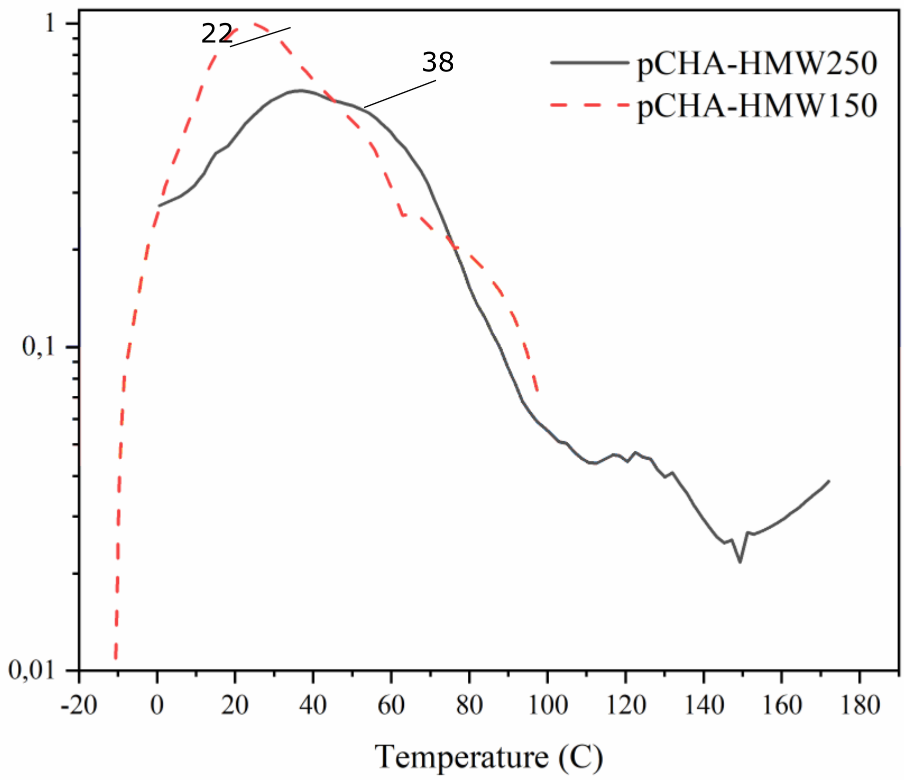


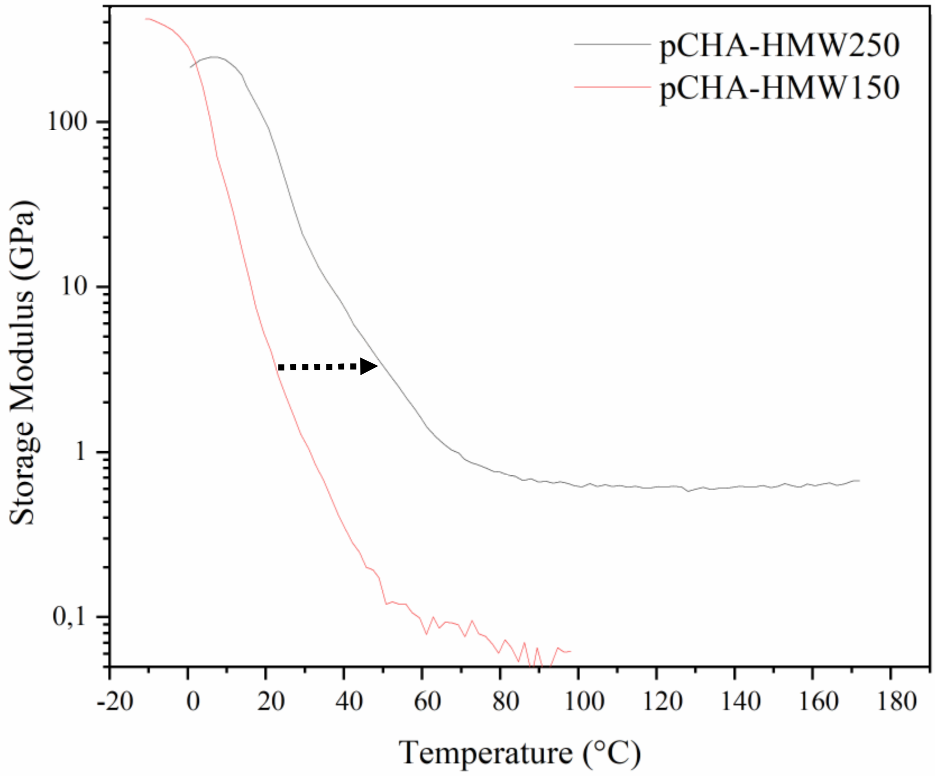
Supplementary Figure 3. pCHA analysis by proton(A) and carbon (B) NMR showing no extraneous peak and a ratio 1:1 between the epoxy group and the peaks at 4.1 (2H, t, J = 6.5 Hz, −CH2O−) and 2.3 (2H, t, J = 7.5 Hz, −COCH2−).

Supplementary Figure 4. Crosslinked pCHA-HMW in THF. The material produce was largely insoluble even after 72 h of constant stirring in THF (RT).

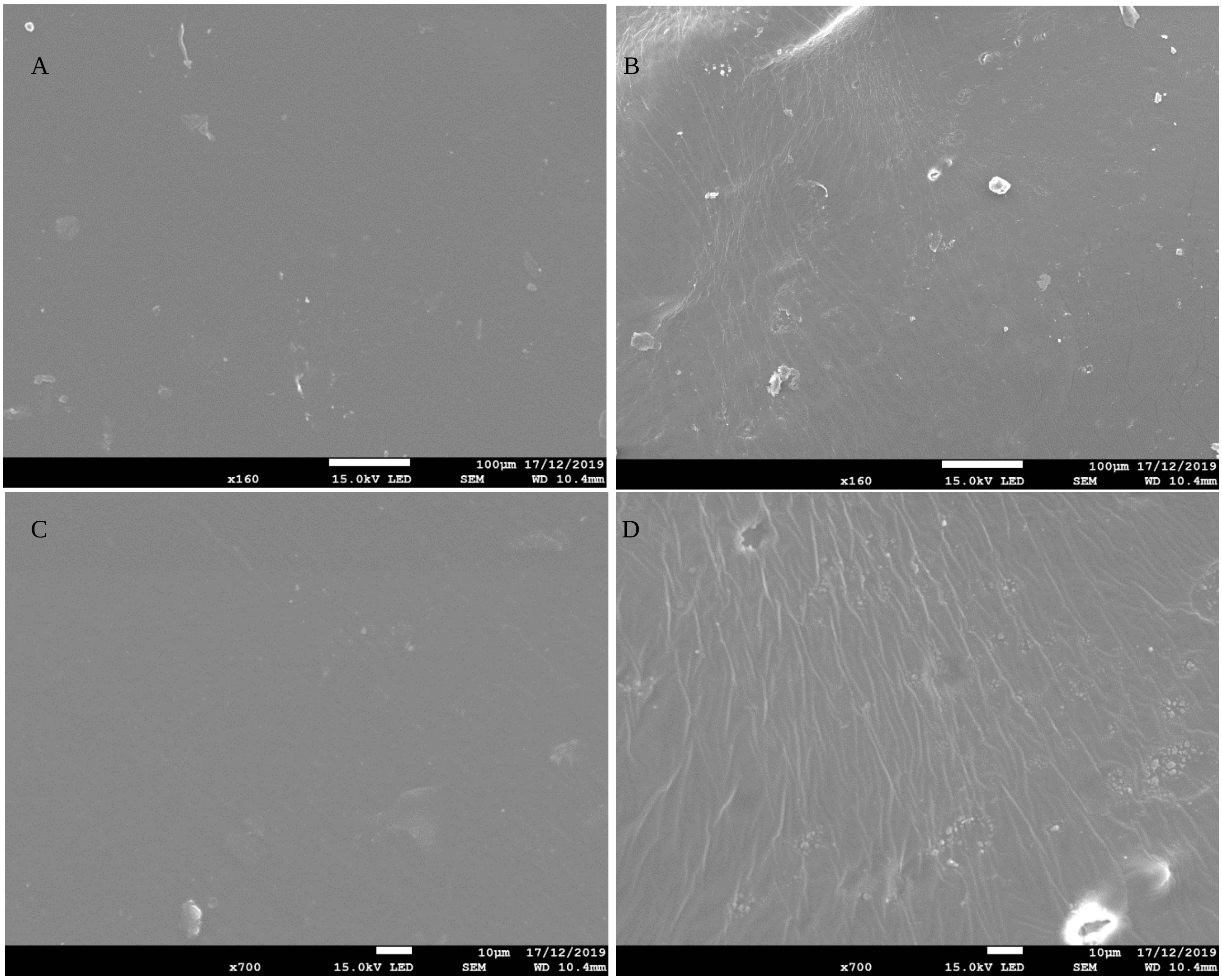


Supplementary Figure 5. FTIR-spectra of the bands between 800-950 cm^{-1}. A comparison between pCHA-uncured (black line) and pCHA-cured at 150 C (blue line) and 250 C (red line). The arrow indicates the vibrational peak representing the epoxide group in the uncured monomer.

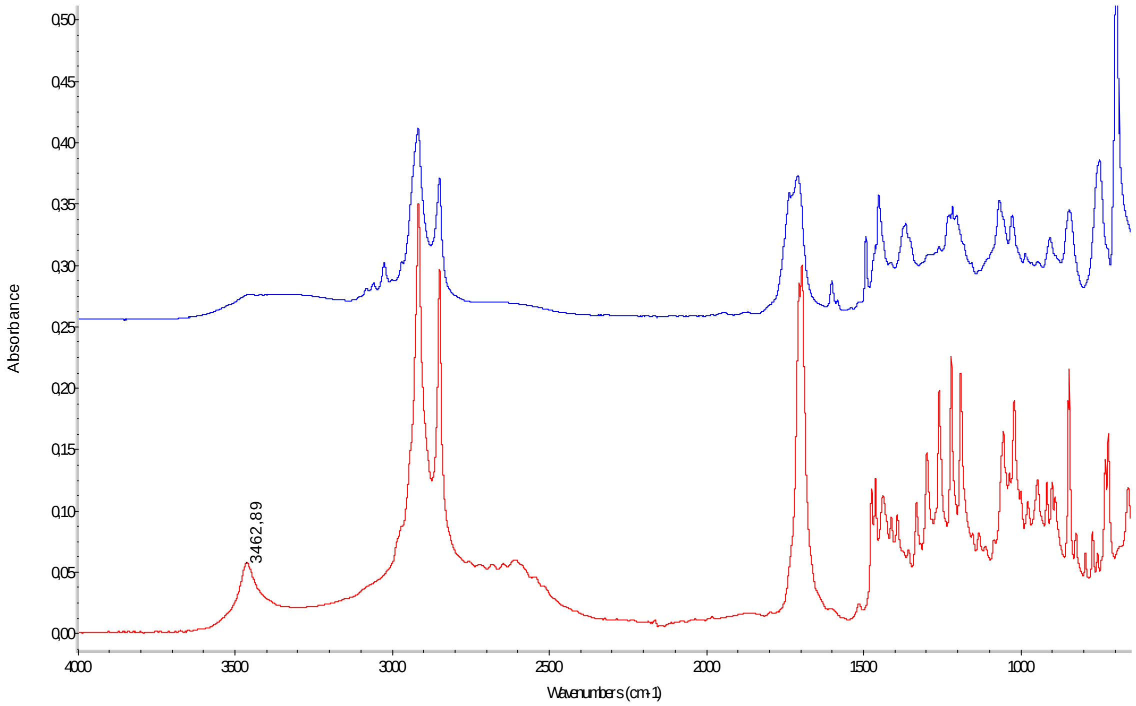

1
0,1
0,01
-20
0
20
40
60
80
100
120
140
160
180
Temperature (C)
22
38
pCHA-HMW250
pCHA-HMW150

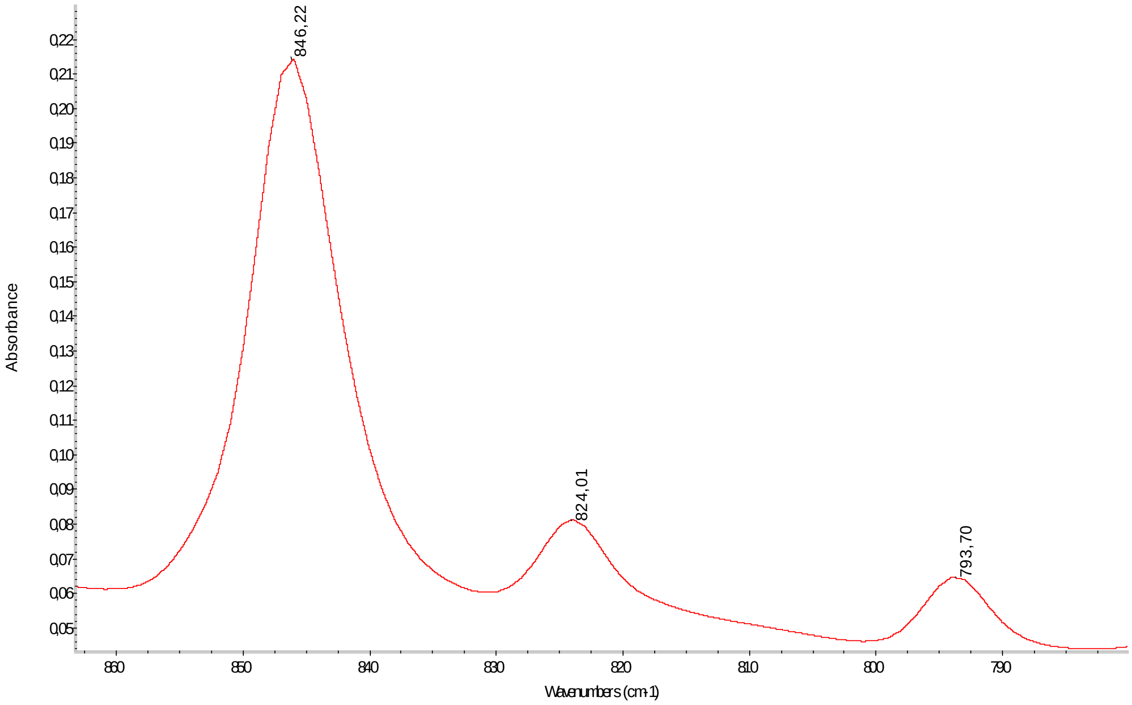

Storage Modulus (GPa)
100
10
1
0,1
-20
0
20
40
60
80
100
120
140
160
180
Temperature (°C)
pCHA-HMW250
pCHA-HMW150

Supplementary Figure 6. A)Tan Delta of pCHA-HMW cured material. The material was cured at 150 ºC (red dotted line) and subsequently at 250 ºC (black line). Post-curing effect on glass transition temperature of pCHA-HMW cured material. B) Comparison between the G’ of pCHA-HMW cured at 150 ºC (red line) and 250 ºC (black line). The shift of the G’ likely indicates a higher crosslinking density.



Supplementary Figure 7. Micrographs of pCHA-LMW (A and C) and CHA-cured (B and D) Observed prior to any treatment with scCO2





Supplementary Figure 8. Top. Comparison of the full FTIR spectra of recrystallized CHA (red line) and UV cured CHA (blue line). In particular it is possible to see that the -OH vibrational peak broadens after the curing reaction as shown when curing with the diamine. Bottom. Shows the features of small intensity vibrations around 794, 824 and 846 cm^{-1} are attributed to the C-O-C stretching modes of oxirane rings