Electronic Supplementrary Information

Build-to-specification vanillin and phloroglucinol derived biobased epoxy-amine vitrimers

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[1]H Nuclear magnetic resonance (NMR)

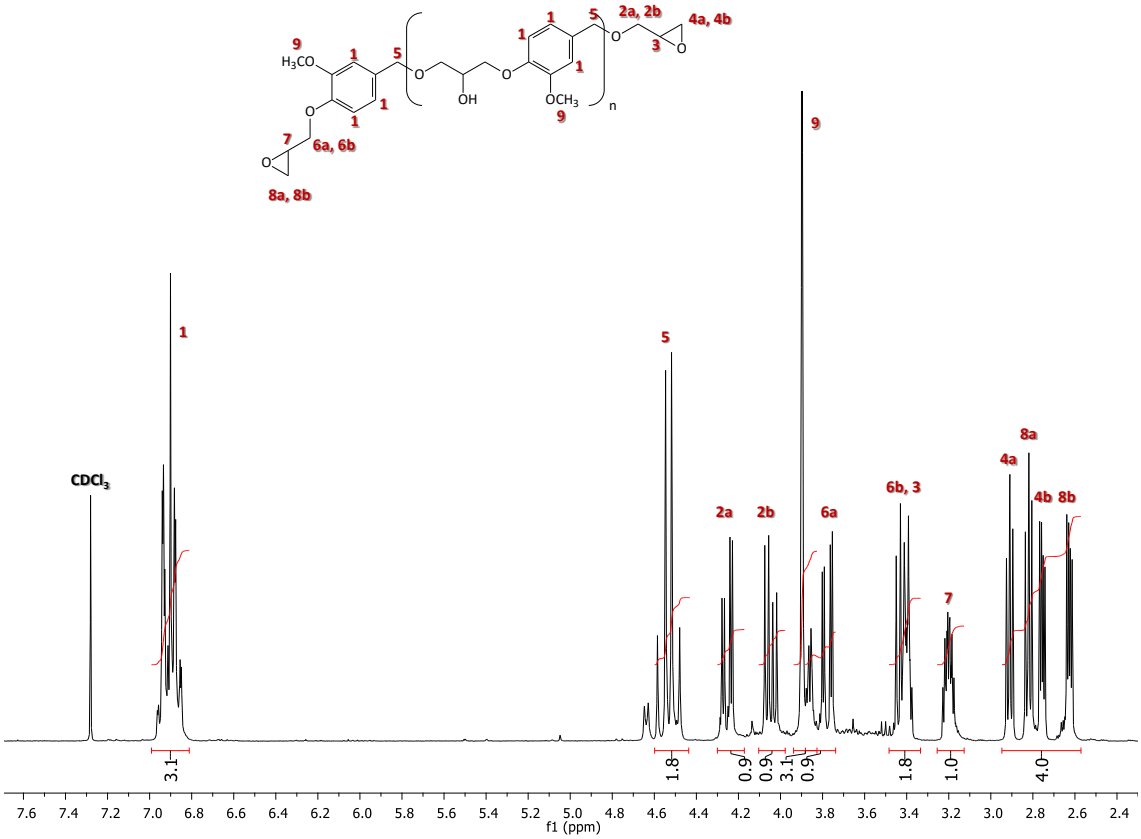

Figure S1: [1]H NMR spectra of DGEVA – NMR 300MHz – $CDCl_3$

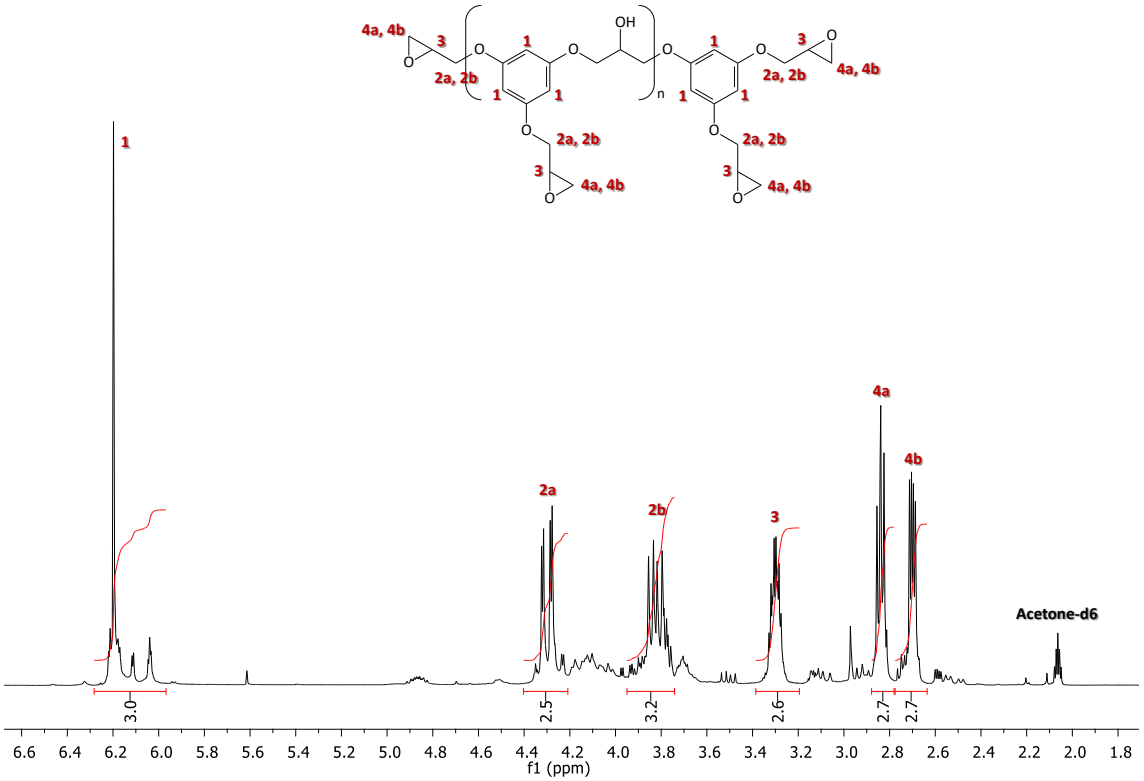

Figure S2: ^{1}H NMR spectra of PHTE – NMR 300MHz – Acetone-d_6

Differential Scanning Calorimetry (DSC) for setting the curing conditions

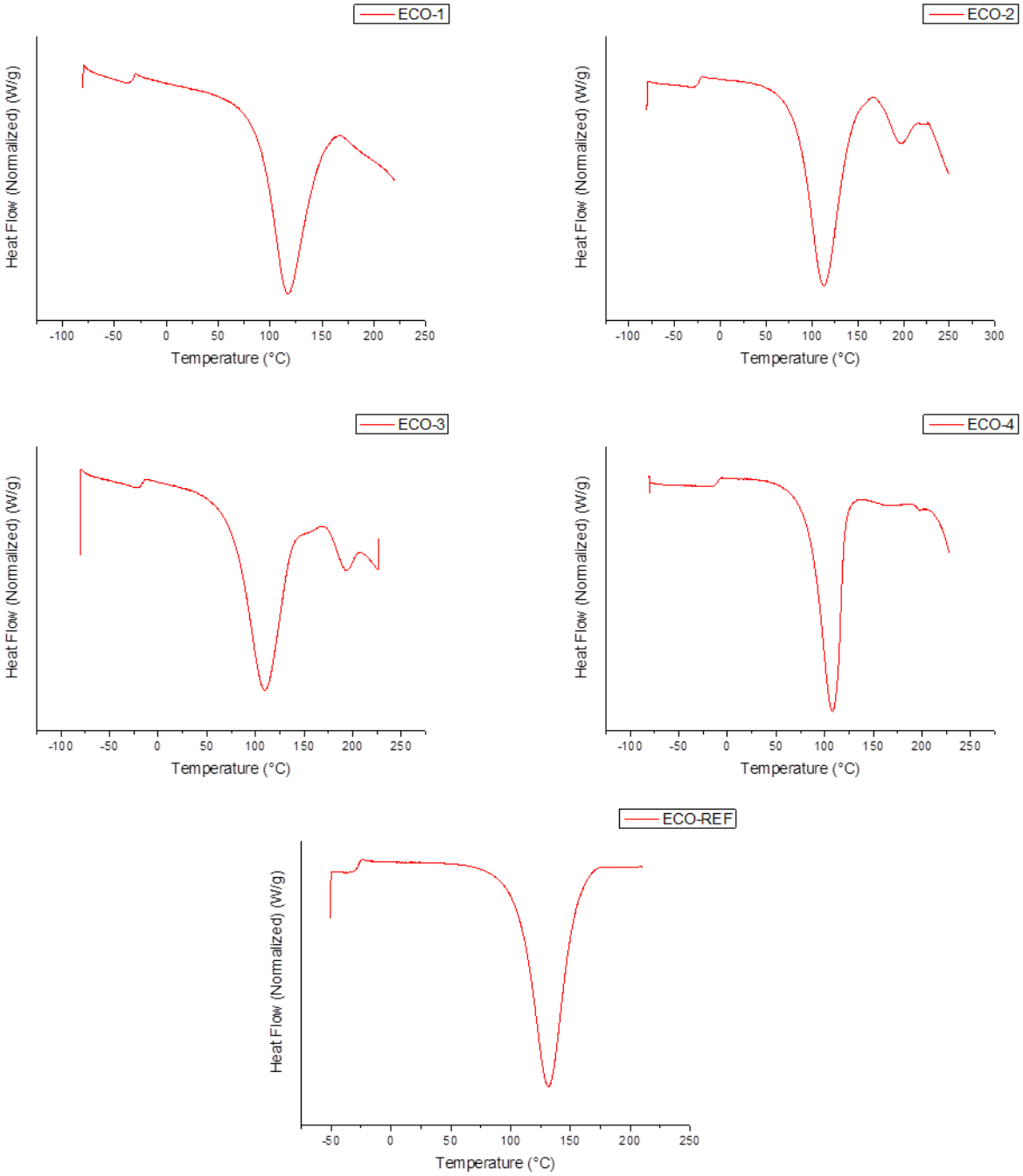

Figure S3: DSC thermograms for all the prepared formulations from which curing conditions were determined.

Fourier-Transform Infrared (FTIR)

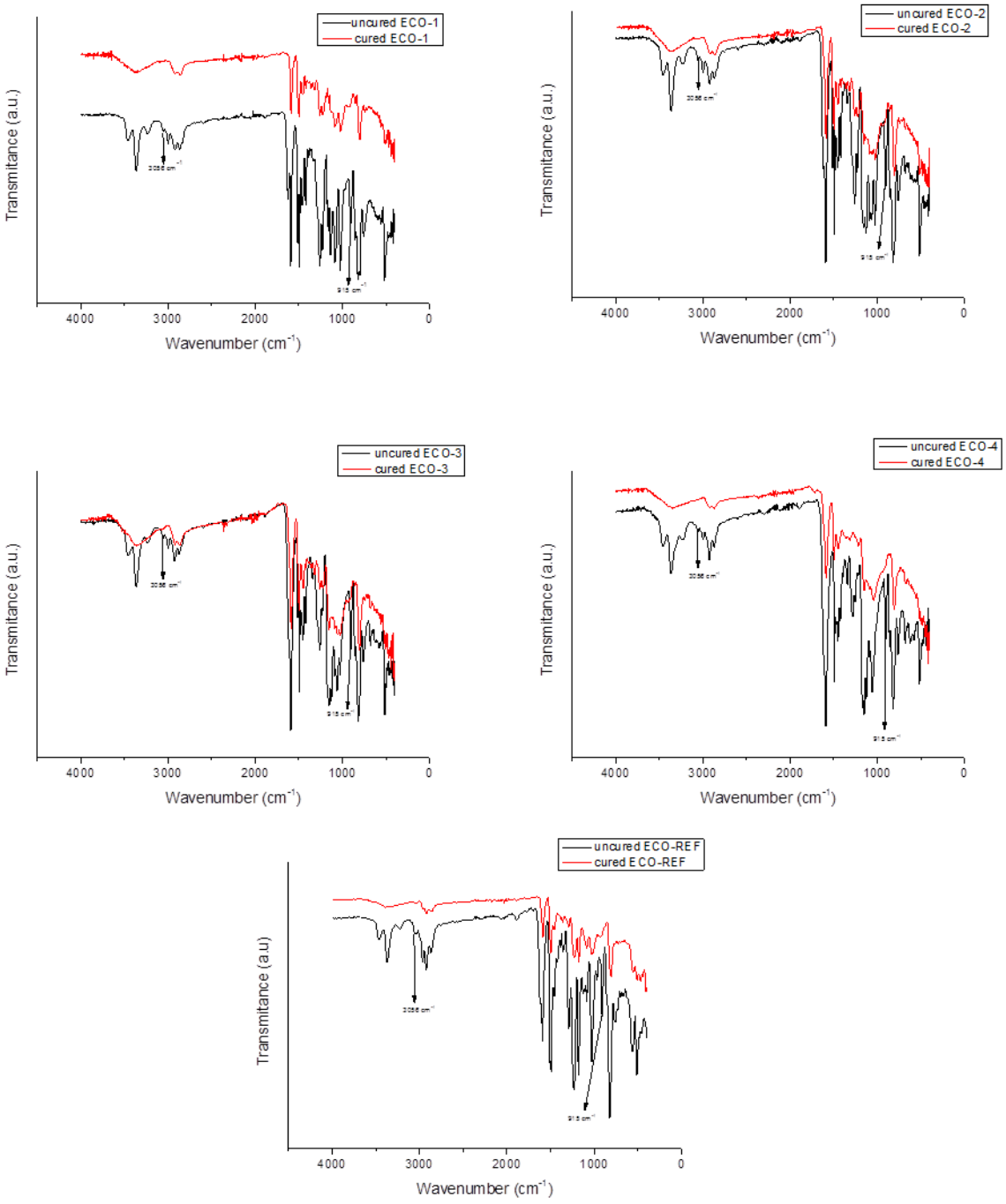

Figure S4: FTIR spectra of uncured (black trace) and cured (red trace) epoxy resin systems. The disappearance of bands corresponding to the epoxy group at 915 cm^{-1} (C-O stretching of oxirane ring) and 3056 cm^{-1} (C-H stretching of oxirane ring) was used as criteria to establish that the curing was complete.

DSC for determining the Tg

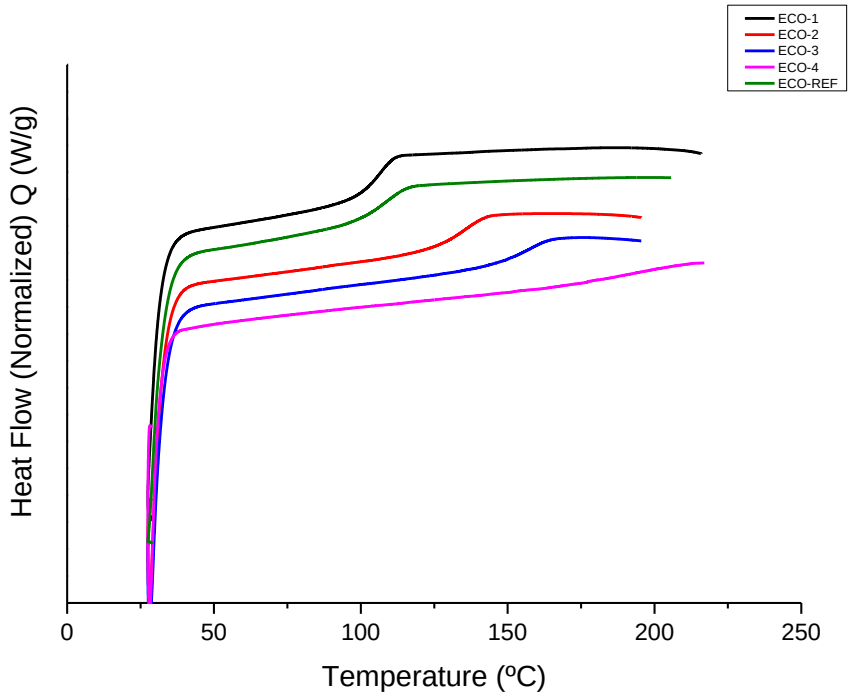

Figure S5: DSC thermograms for all the prepared epoxy networks from which the T_g values were determined for each formulation: 105 °C for ECO-1; 135 °C for ECO-2; 157 °C for ECO-3; 194 °C for ECO-4; and 107 °C for ECO-REF. It can be observed the absence of other exothermic peaks associated to residual curing

Dynamic mechanical analysis (DMA)

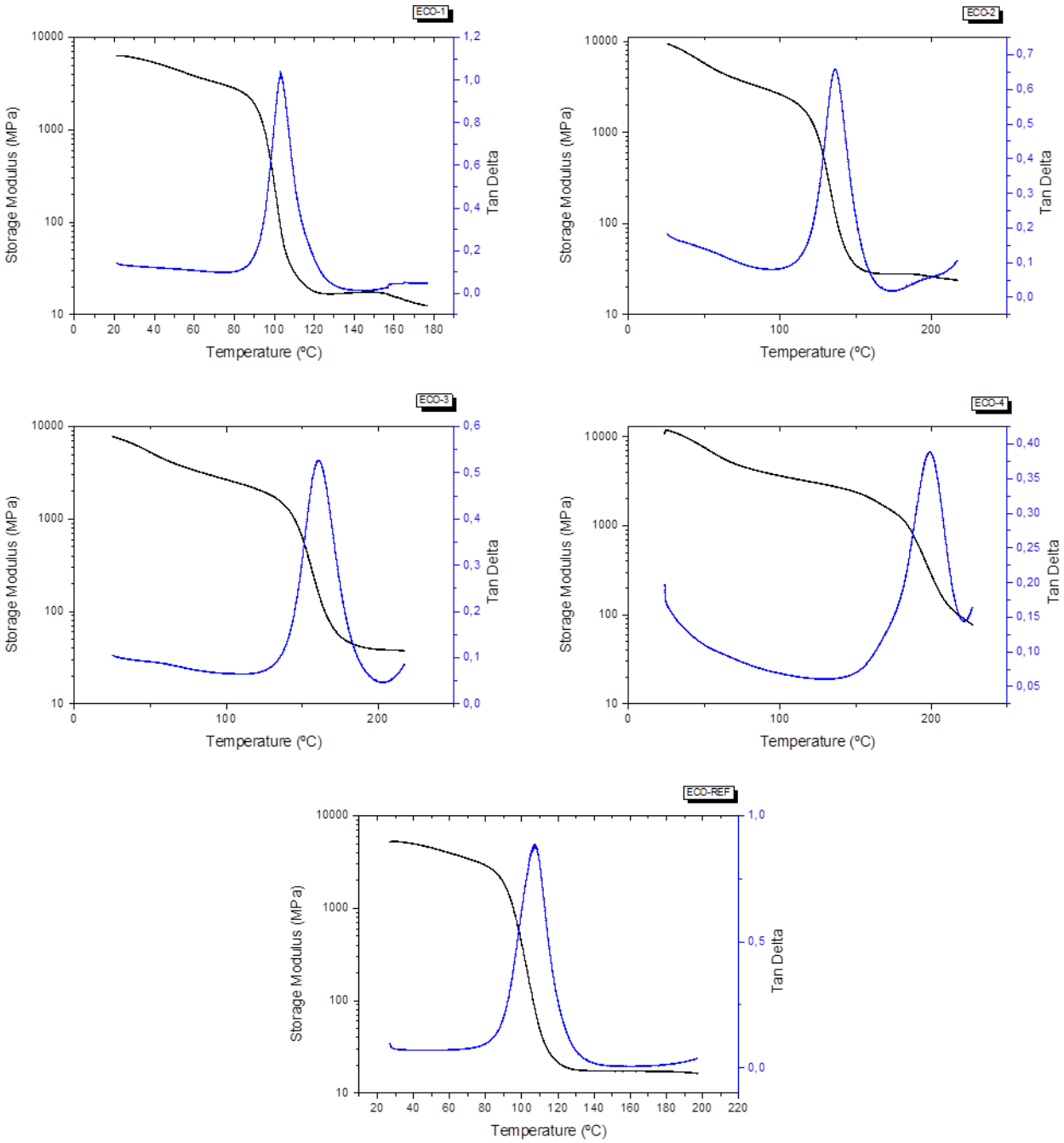

Figure S6: DMA curves obtained for the prepared vitrimers, representing storage modulus and tan delta versus temperature. T_g values were determined for each formulation from the maximum of tan delta: 103 °C for ECO-1; 137 °C for ECO-2; 160 °C for ECO-3; 197 °C for ECO-4; and 108 °C for ECO-REF. E' (30 °C) and E' (T_g + 30 °C) values were also determined from these curves: 6.10^3 MPa and 17 MPa for ECO-1; 9.10^3 MPa and 28 MPa for ECO-2; 7.10^3 MPa and 41 MPa for ECO-3; 11.10^3 MPa and 83 MPa for ECO-4; and 7.10^3 MPa and 16 MPa for ECO-REF (for E' (30 °C) and E' (T_g + 30 °C) respectively).

Thermogravimetric analysis (TGA)

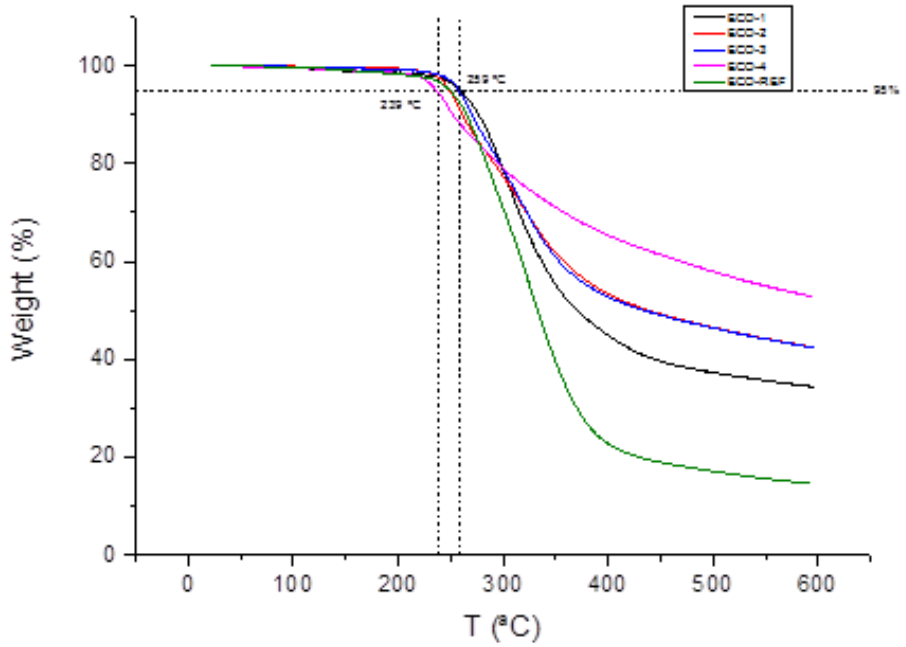

Figure S7: TGA thermogram of the prepared vitrimers representing the weight loss versus temperature. T_d(5%) was determined for each formulation as the temperature at which the material has lost 5% of its weight: 259 °C for ECO-1; 251 °C for ECO-2; 257 °C for ECO-3; 239 °C for ECO-4; and 252 °C for ECO-REF.

Mechanical tests

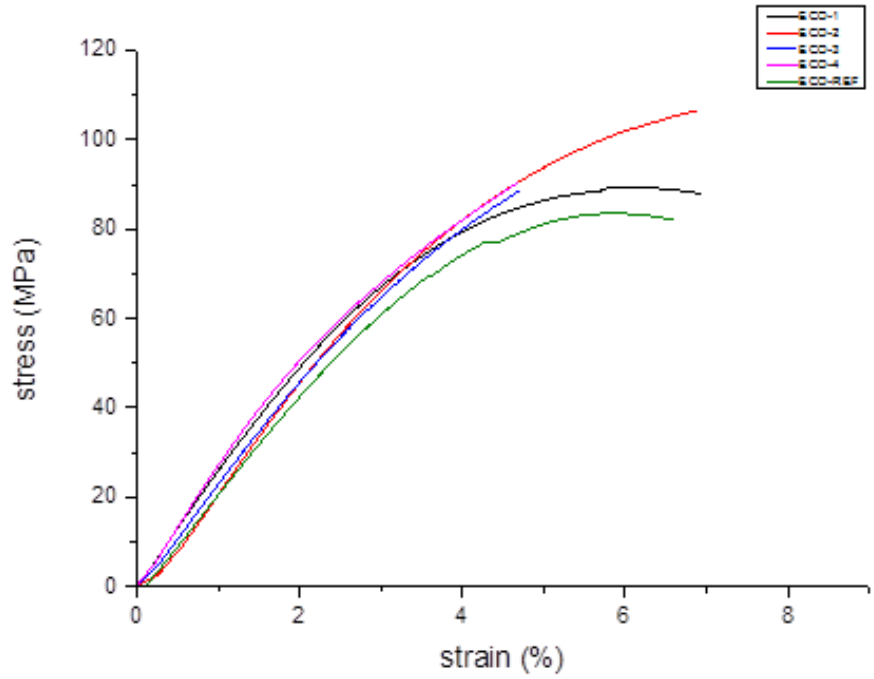

Figure S8: Stress-strain curves for the prepared epoxy networks

Stress relaxation

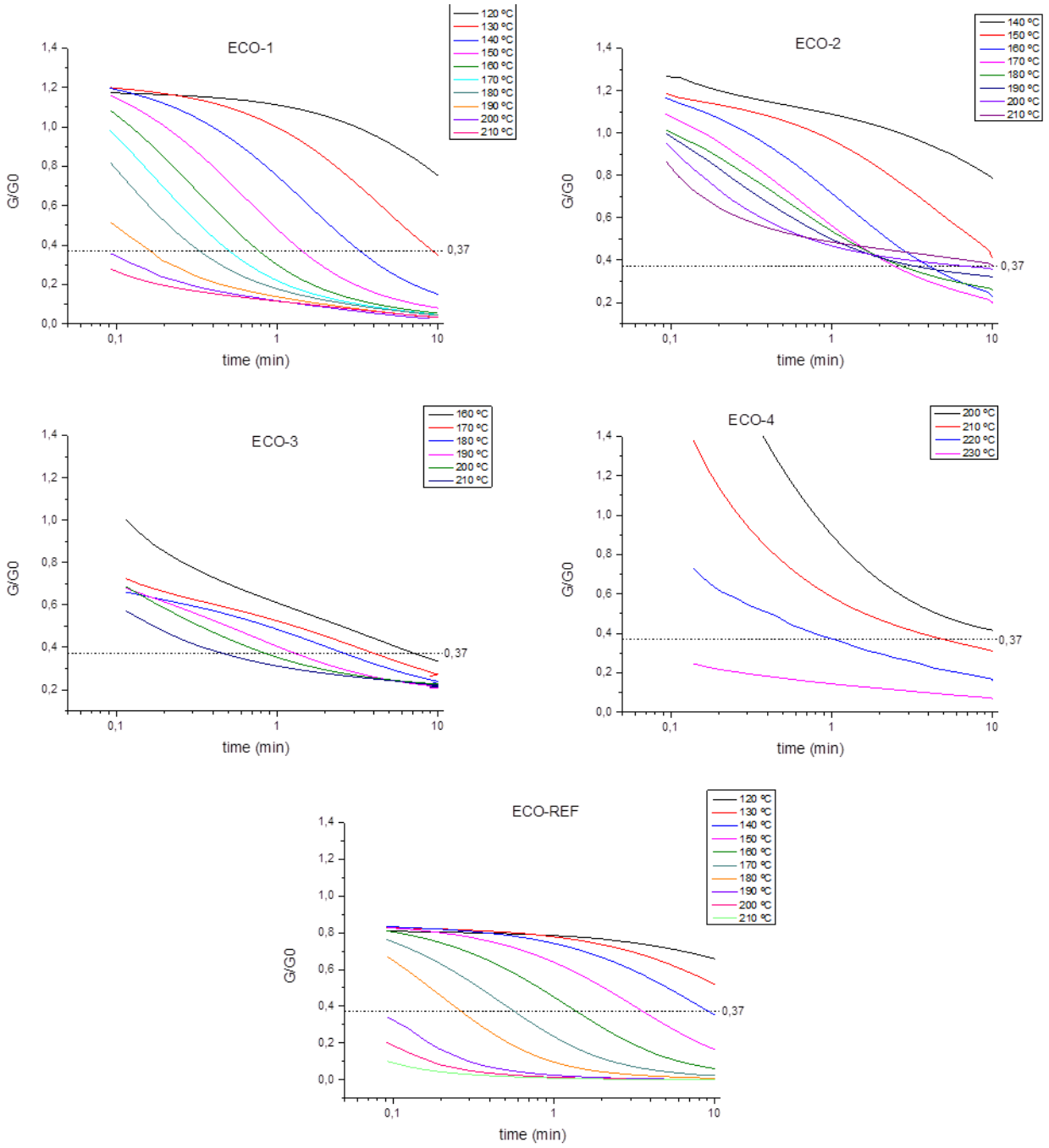

Figure S9: Normalized stress relaxation curves for all the prepared vitrimers at different temperatures from which their relaxation times were determined at temperatures 20 °C and 50 °C above their T_g.

DSC for determining the Tg of the residues of the TGA isothermals

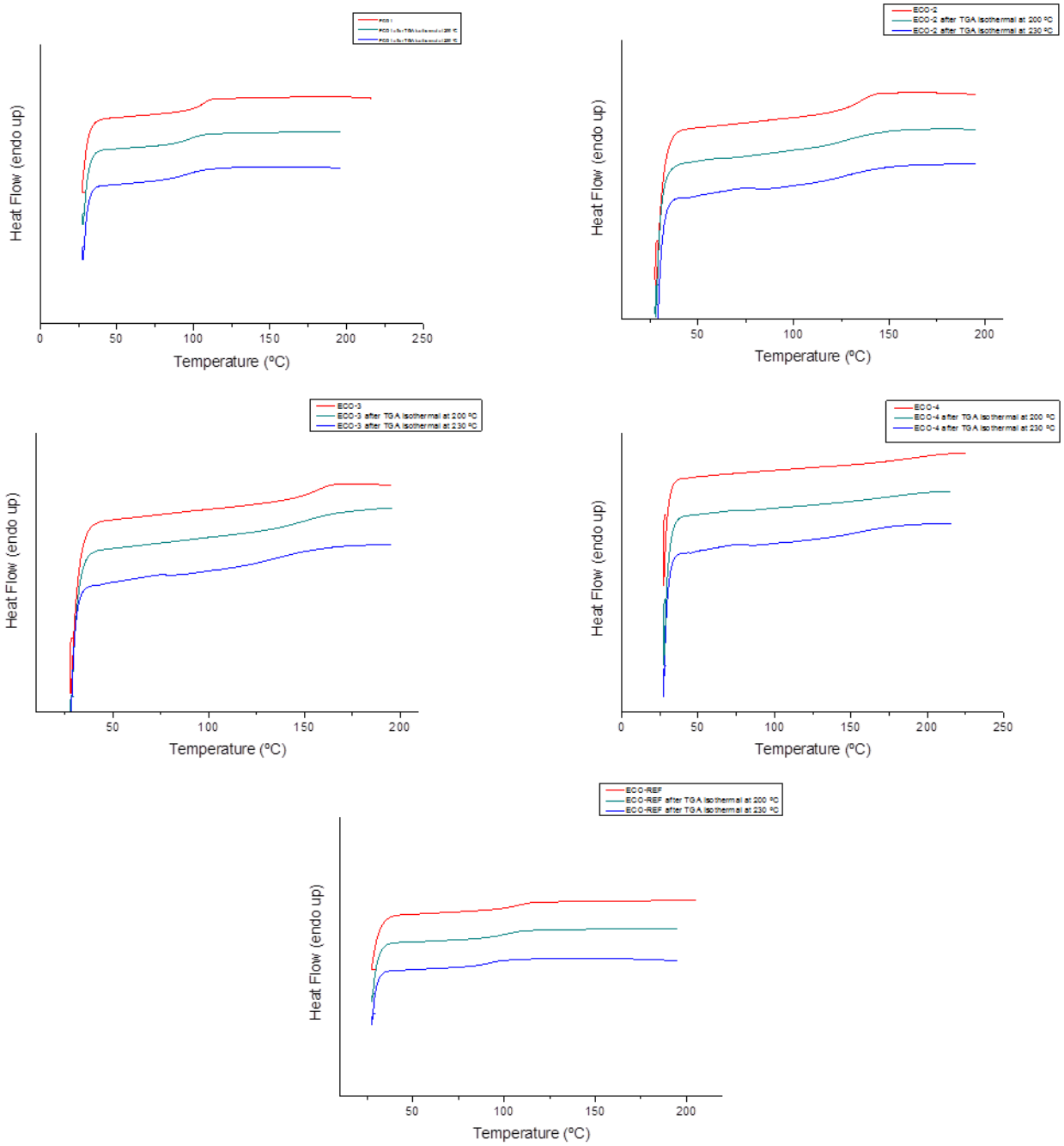

Figure S10: DSC thermograms for the residues obtained after the TGA isothermals (20 min) at 200 °C and 230 °C for all the prepared vitrimers. T_g values after these isothermals were determined and compared to the T_g of the pristine epoxy for each formulation: 105 °C, 97 °C and 95 °C for ECO-1 (untreated, after 20 min at 200 °C and after 20 min at 230 °C respectively); 135 °C, 131 °C and 129 °C for ECO-2 (untreated, after 20 min at 200 °C and after 20 min at 230 °C respectively); 157 °C, 152 °C and 137 °C for ECO-3 (untreated, after 20 min at 200 °C and after 20 min at 230 °C respectively); 194 °C, 177 °C and 162 °C for ECO-4 (untreated, after 20 min at 200 °C and after 20 min at 230 °C respectively); and 107 °C, 102 °C and 92 °C for ECO-REF (untreated, after 20 min at 200 °C and after 20 min at 230 °C respectively).