Inducing hardening and healability in poly(ethylene-*co*-acrylic acid) via blending with complementary low molecular weight additives

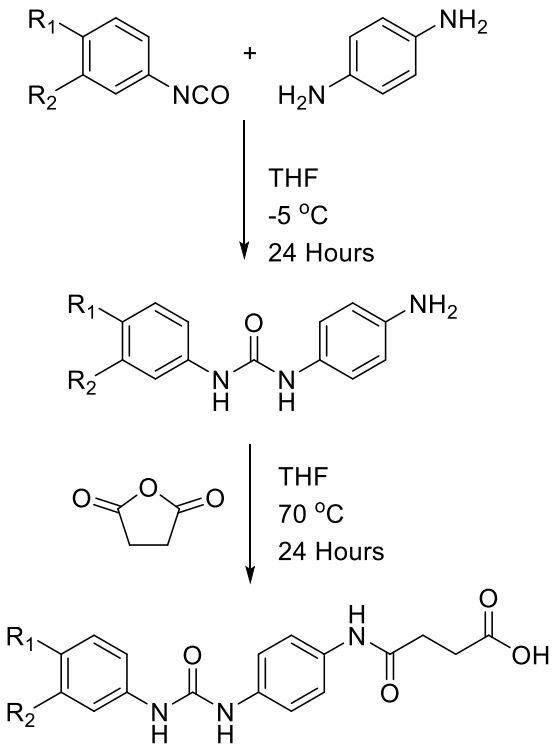
Benjamin C. Baker[a]; I. German[b]; Gary C. Stevens[b]; Howard M. Colquhoun[a]; and Wayne Hayes [a]*

[a] Department of Chemistry, University of Reading, Whiteknights, Reading, RG6 6AD, UK. Email: w.c.hayes@reading.ac.uk, Telephone: +44 118 378 6491, Fax: +44 118 378 6331

[b] Gnosys Global Ltd., 17-18 Frederick Sanger Road, The Surrey Research Park, Guildford, Surrey, GU2 7YD, UK

Supplementary Information

Contents



Scheme S1; Generic synthesis of compounds **3**-**5** (**3**: R_1 = H, R_2 = NO_2. **4**: R_1 = NO_2, R_2 = H. **5**: R_1 = H, R_2 = H).

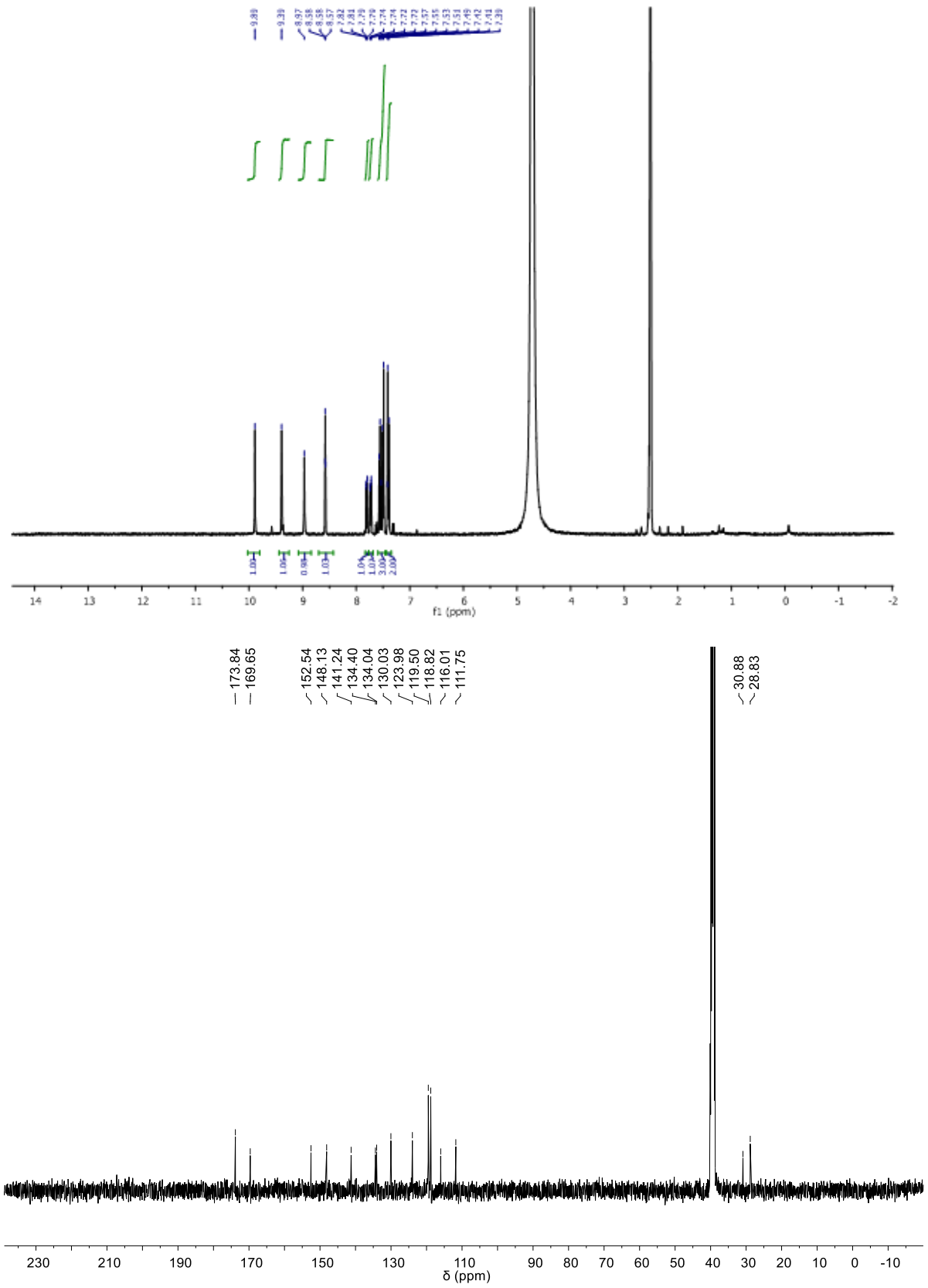


Figure S1; ^{1}H and ^{13}C NMR spectra of **3** in DMSO-d_6

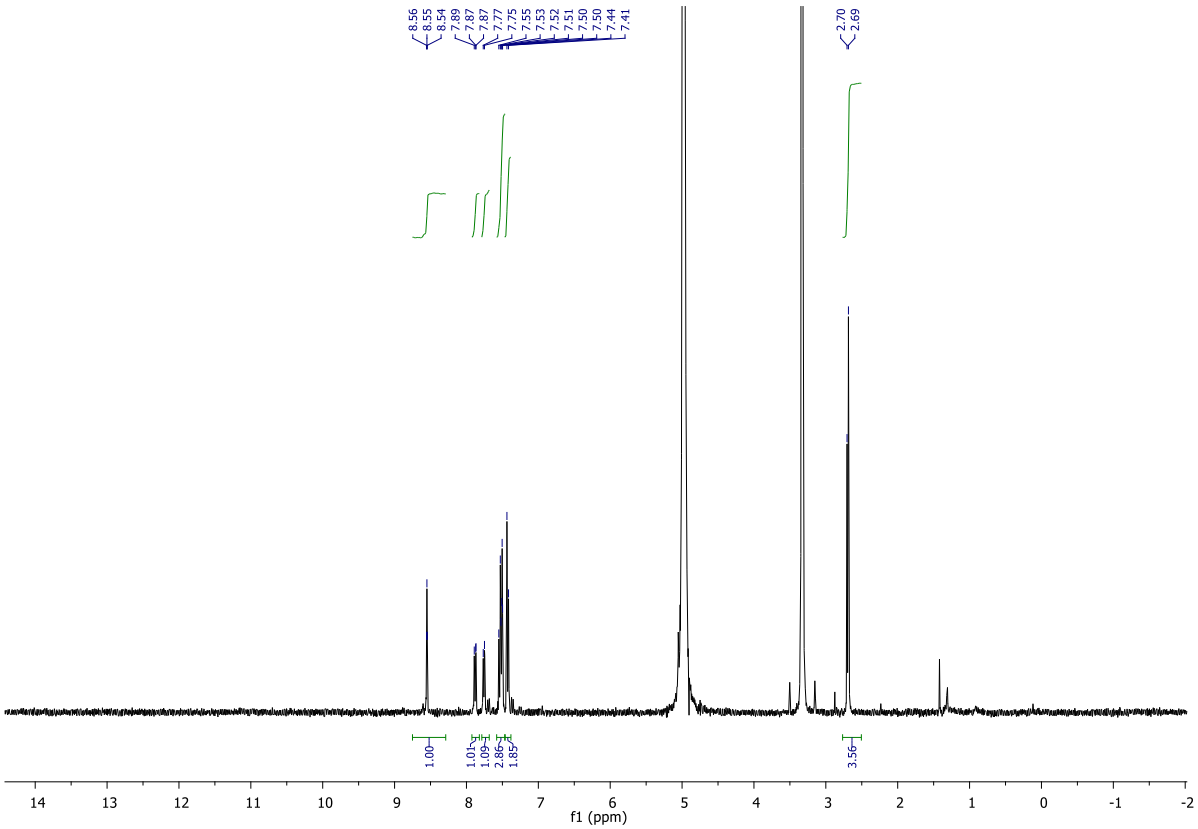


Figure S2; ^{1}H NMR spectrum of **3** in CD_3OD

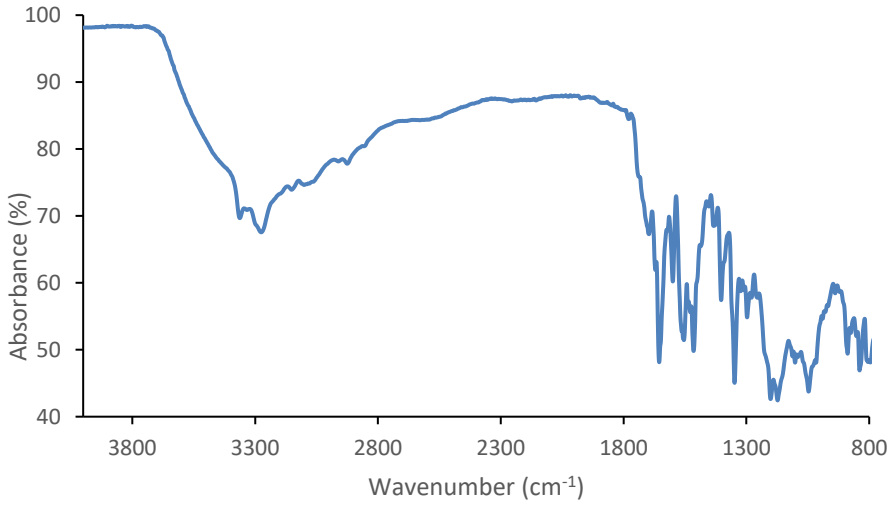


Figure S3; IR spectra of **3**

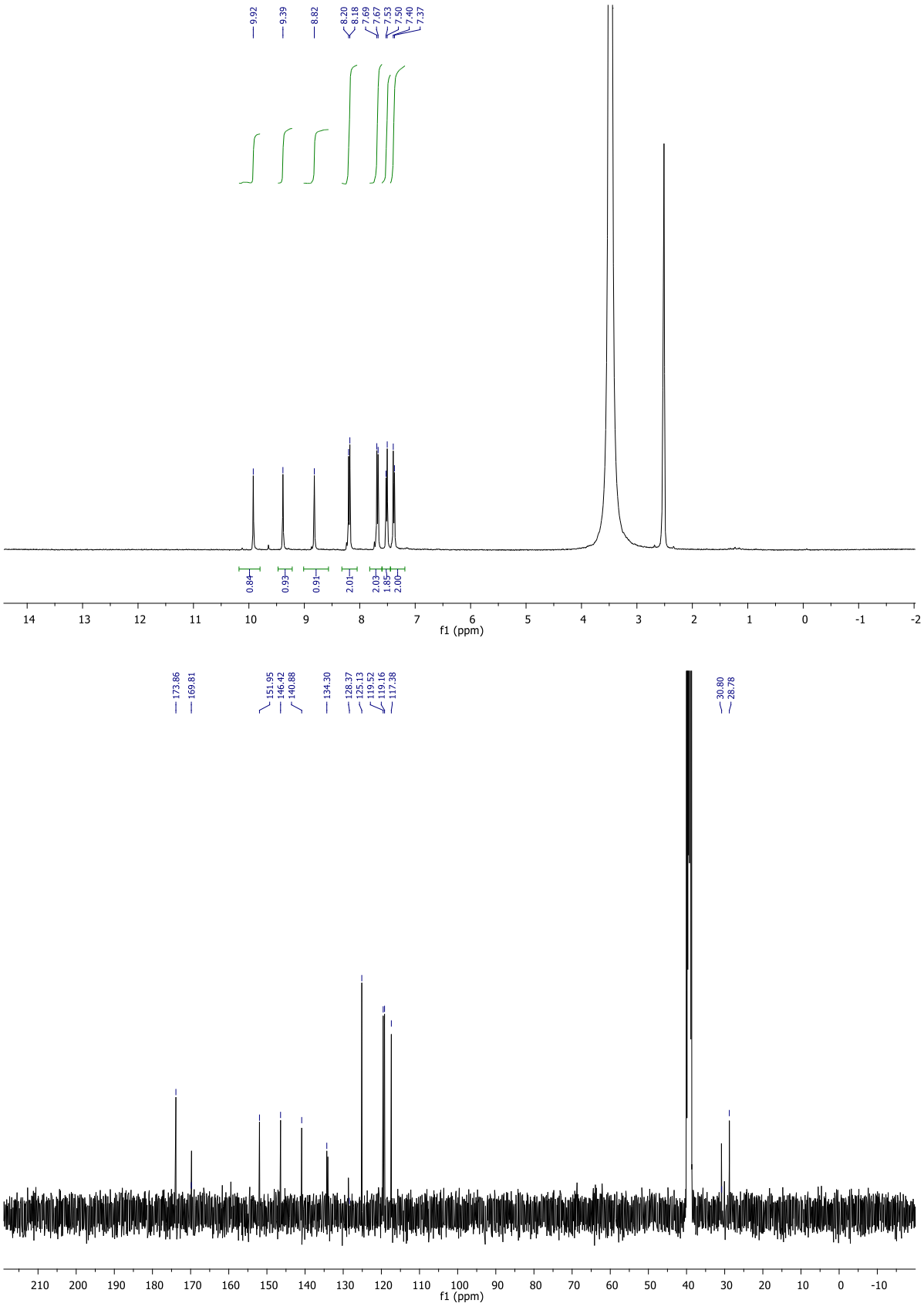


Figure S4; ^{1}H and ^{13}C NMR spectra of **4** in DMSO-d_6

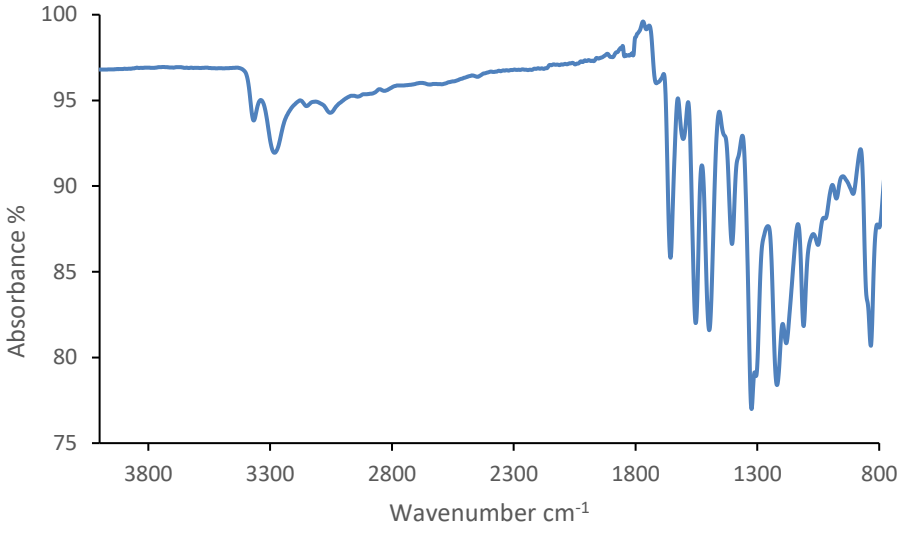


Figure S5; IR spectra of **4**

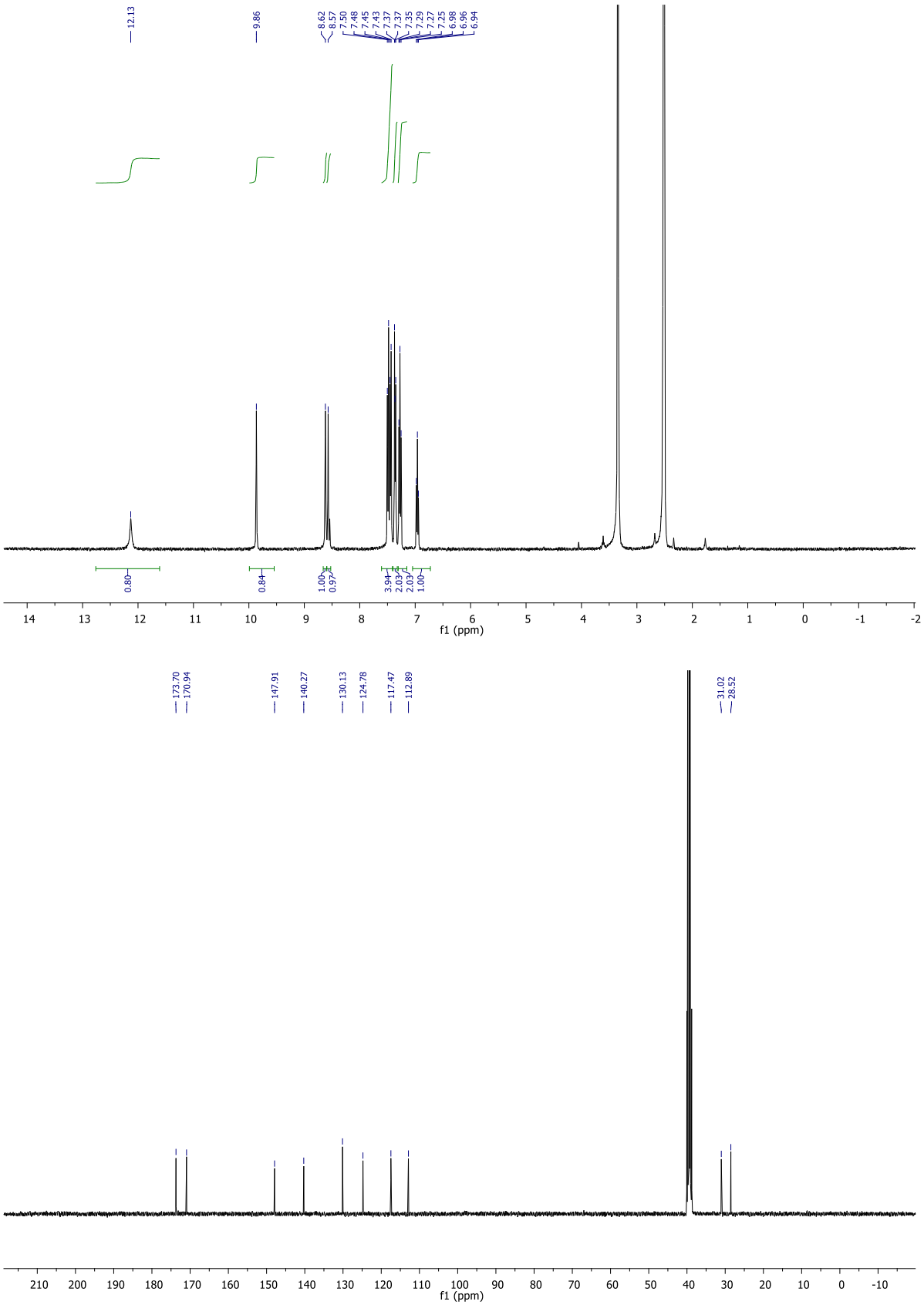


Figure S6; ^{1}H and ^{13}C NMR spectra of **5** in DMSO-d_6

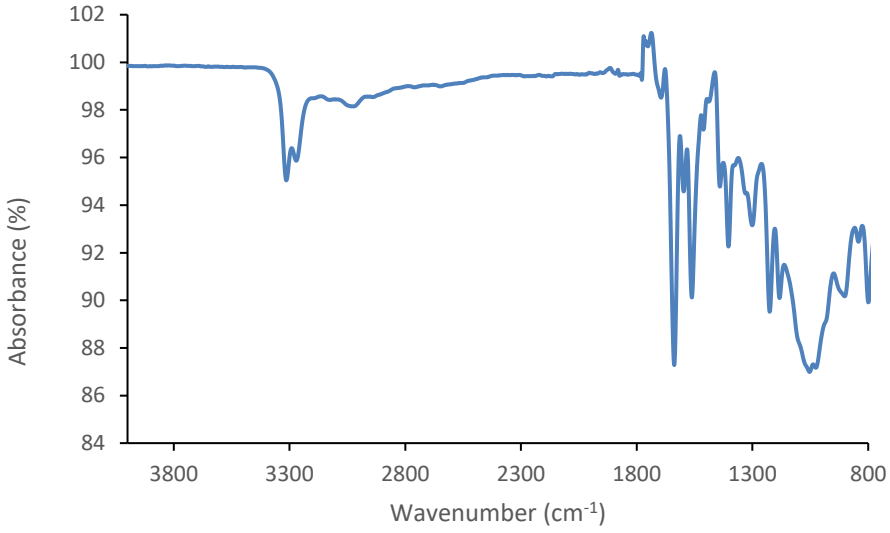


Figure S7; IR spectra of **5**

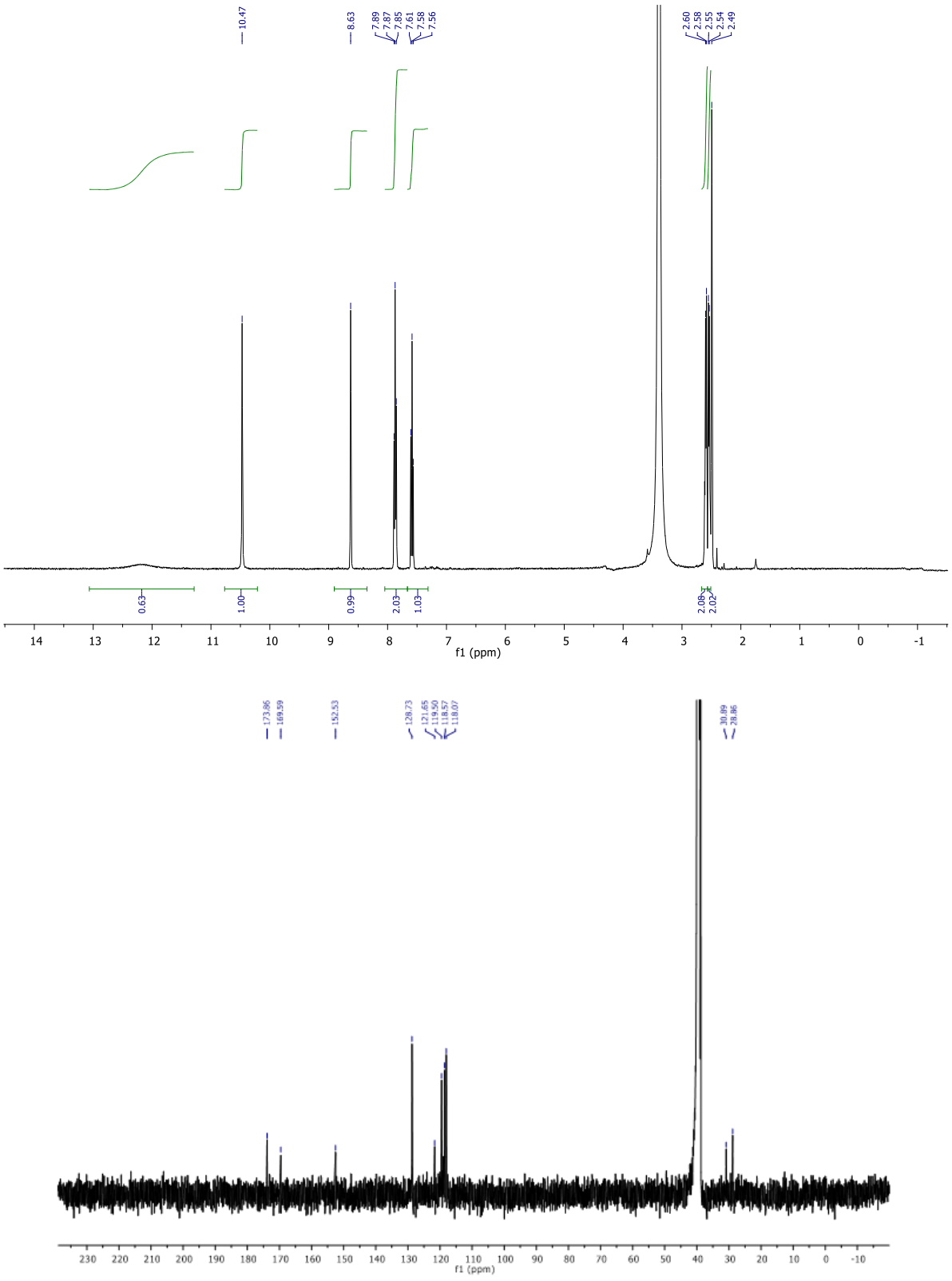


Figure S8; ^{1}H and ^{13}C NMR spectra of **6** in DMSO-d_6

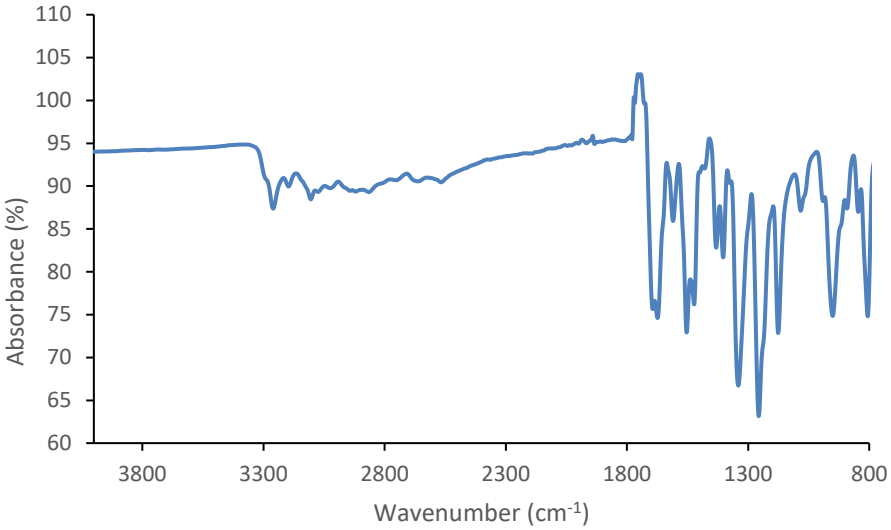


Figure S9; IR spectra of **6**

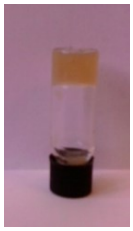


Figure S10; Hydrogelator **3**, CGC 2.7 mM (0.1%wt)

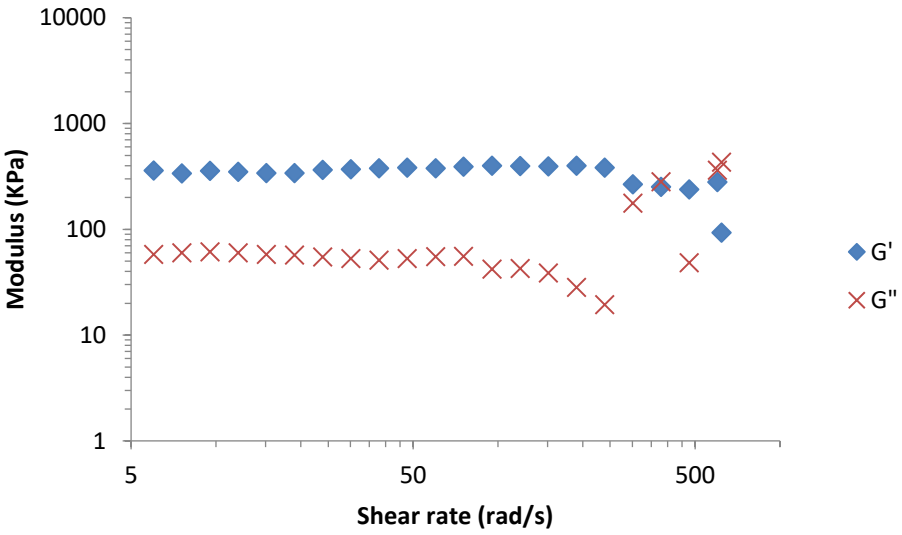


Figure S11; Rheology of aqueous gel of hydrogelator **3** (20 mM).

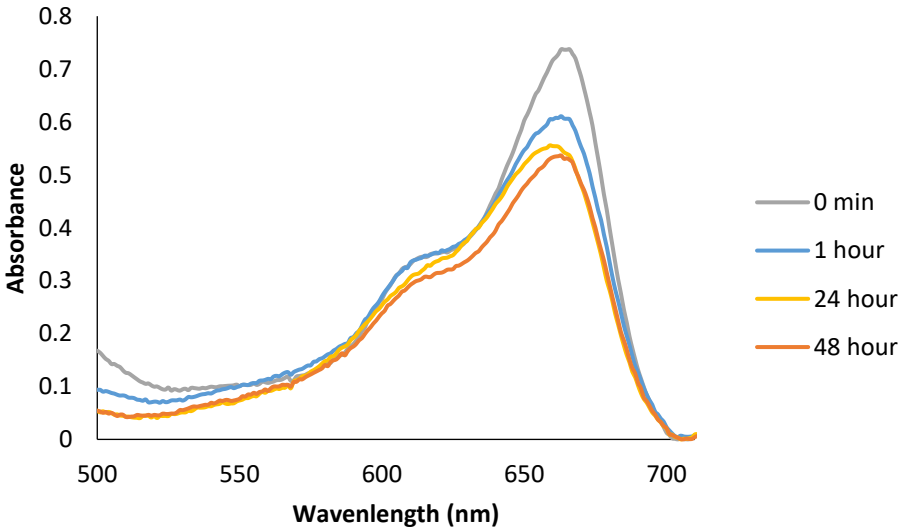


Figure S12; UV/vis absorption spectra of stirred solution of aqueous methylene blue (250 mL, 8 mg L^{-1}) after addition of hydrogelator **3** (1 mL, 80 mM).

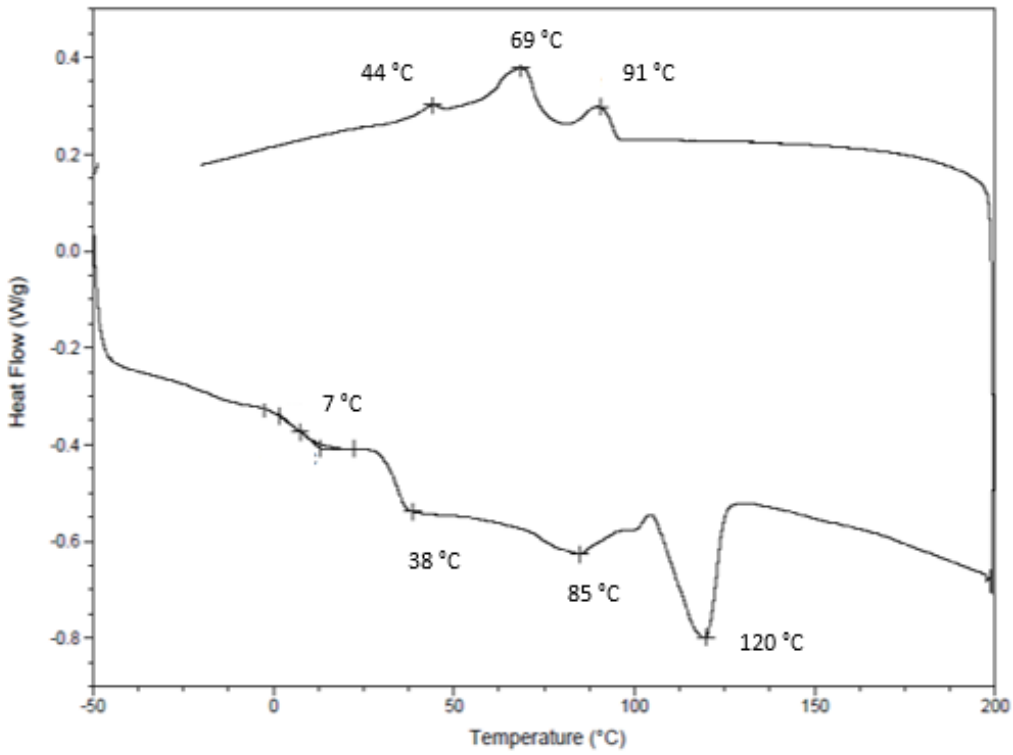


Figure S13; DSC heating (lower) and cooling (upper) curves for **pEAA*15* /1** (10% wt) showing phase separation of polymer and dicarboxylic acid **1** (represented by the melting transition at 120 °C).

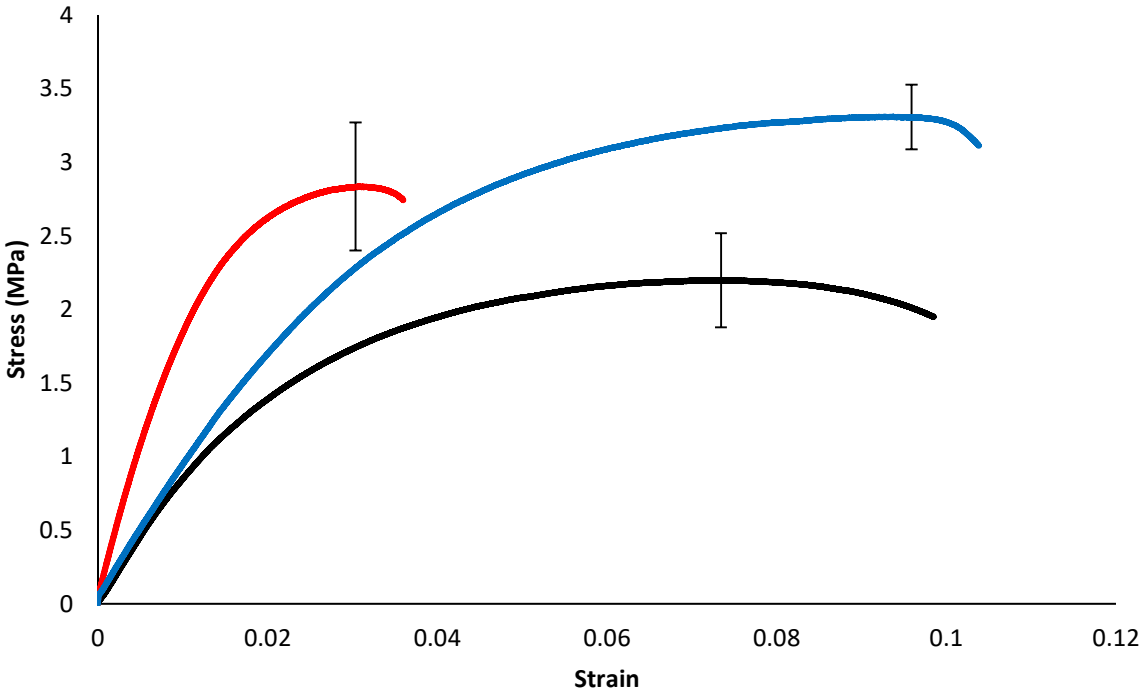


Figure S14; Stress strain curves (average of five samples) for; **pEEA*15*** (black), **pEEA*15*/1** (1% wt.) (red) and **pEEA*15*/1** (5% wt.) (blue).

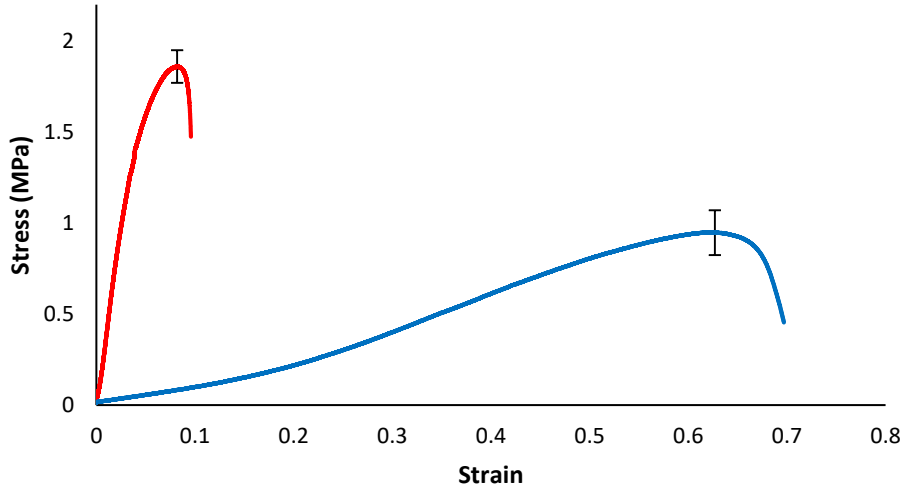


Figure S15; Stress strain curves (average of five samples) for **pEEA*15*/2** (1% wt) (red) and **pEEA*15*/2** (5% wt) (blue).

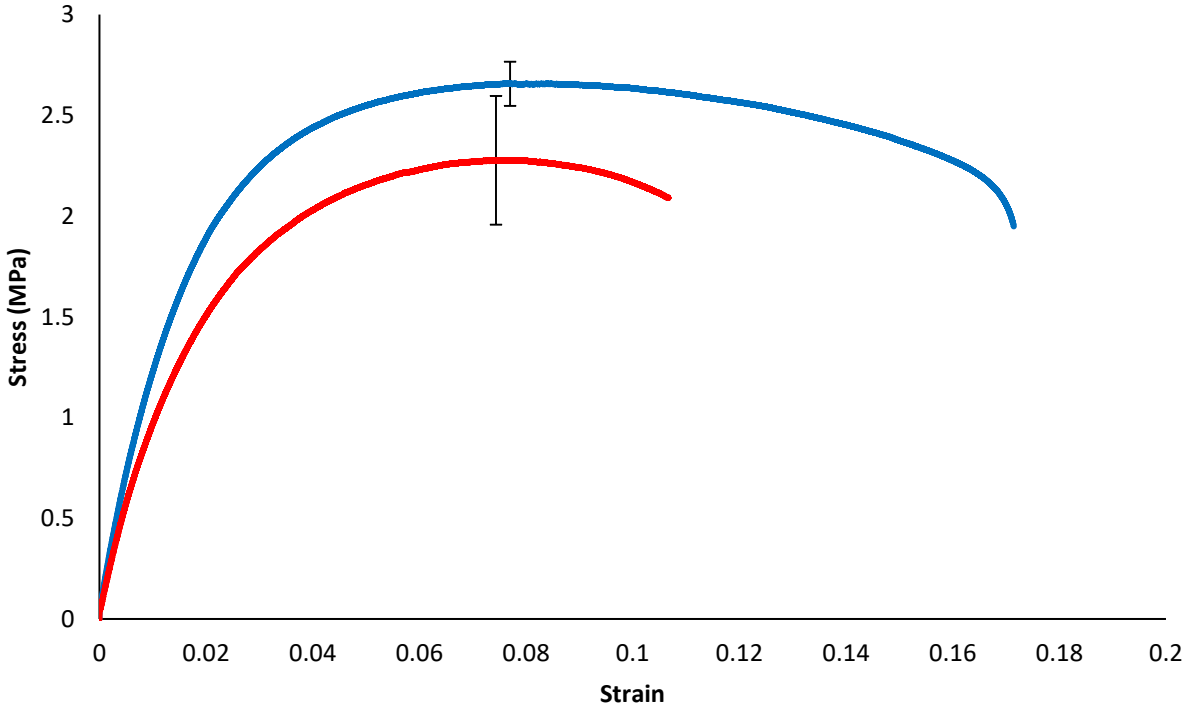


Figure S16; Stress strain curves (average of five samples) for **pEEA*15*/3** (1% wt) (red) and **pEEA*15*/3** (5% wt) (blue).

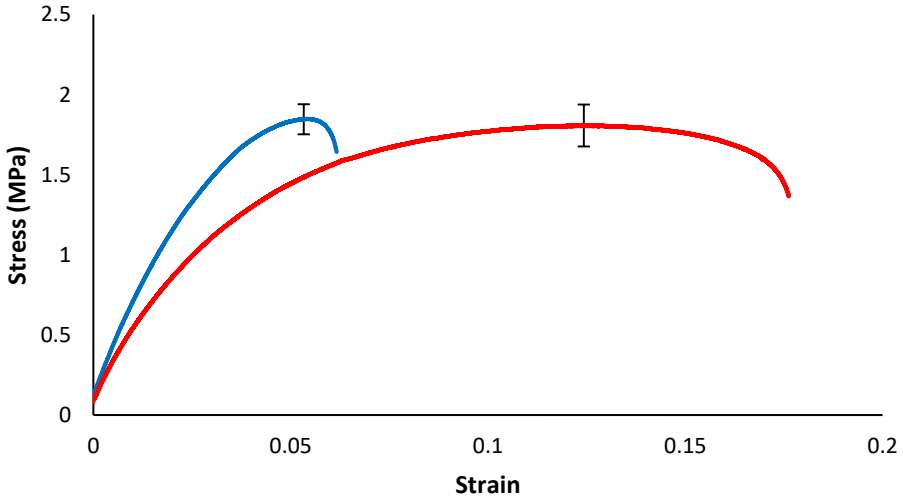


Figure S17; Stress strain curves (average of five samples) for **pEAA*15*** and **4** at 1% (red) and 5% (blue) wt.

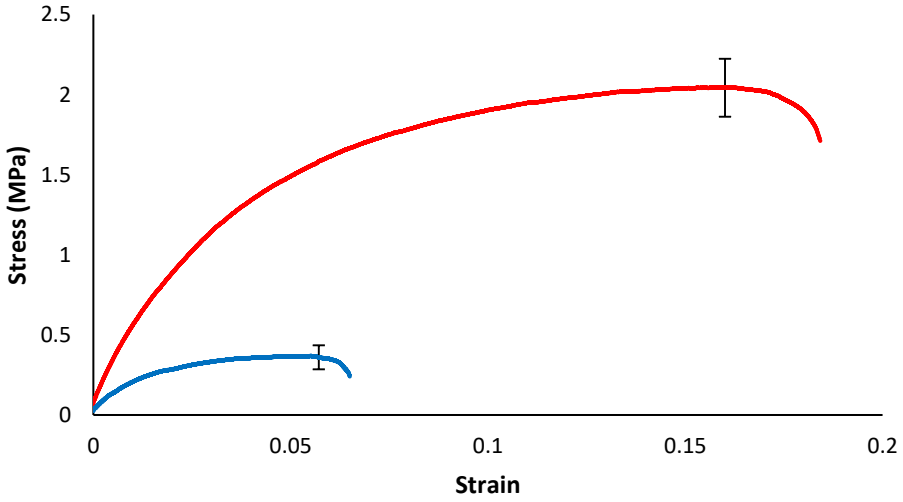


Figure S18; Stress strain curves (average of five samples) for **pEAA*15*** and **5** at 1% (red) and 5% (blue) wt.

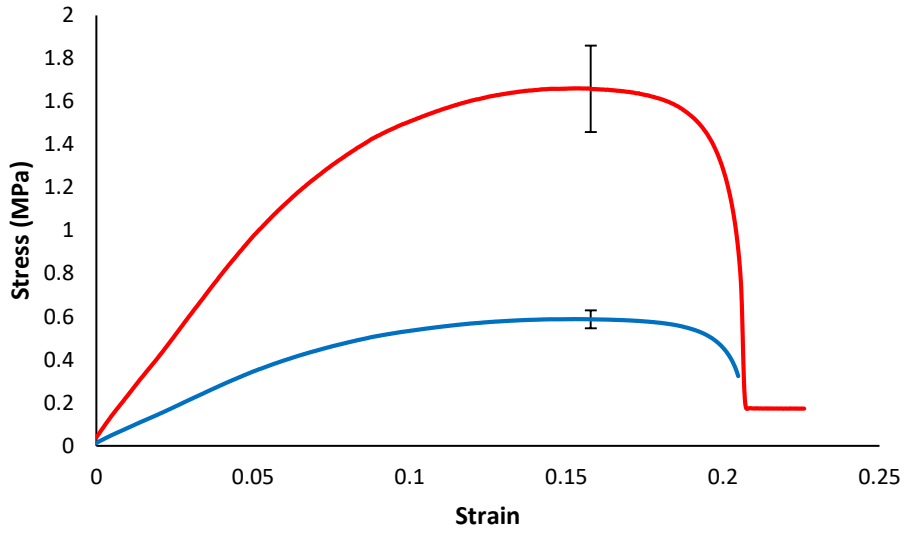


Figure S19; Stress strain curves (average of five samples) for **pEAA*15*** and **6** at 1% (red) and 5% (blue) wt.

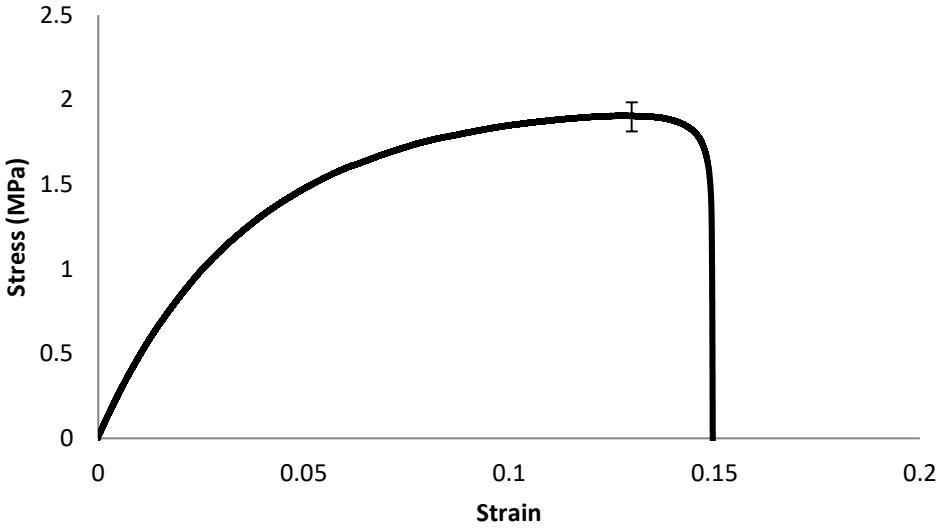


Figure S20; Stress strain curve (average of five samples) for **pEAA*15*** and **7** at 1% wt.

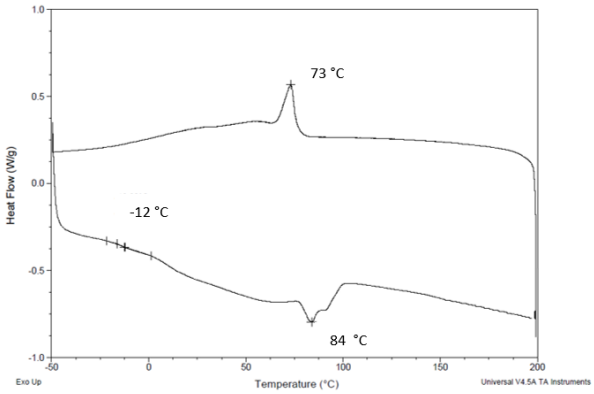


Figure S21; DSC heating scan (below) and subsequent cooling scan (above) of **pEEA*15***.

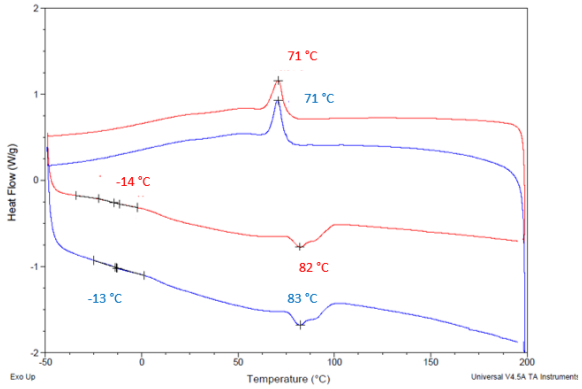


Figure S22; DSC heating/cooling scans of **pEEA*15*/1** at 1% (red) and 5% weight (blue).

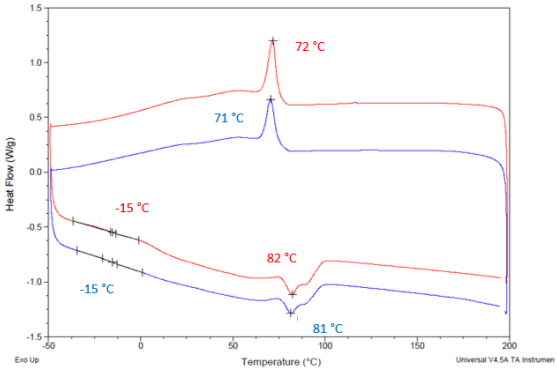


Figure S23; DSC heating/cooling scans of **pEEA*15*/2** at 1% (red) and 5% weight (blue).

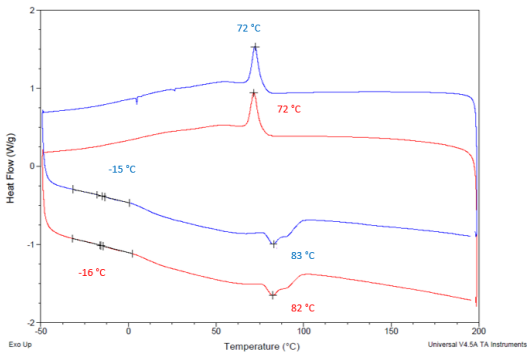


Figure S24; DSC heating/cooling scans of **pEEA*15*/3** at 1% (red) and 5% weight (blue).

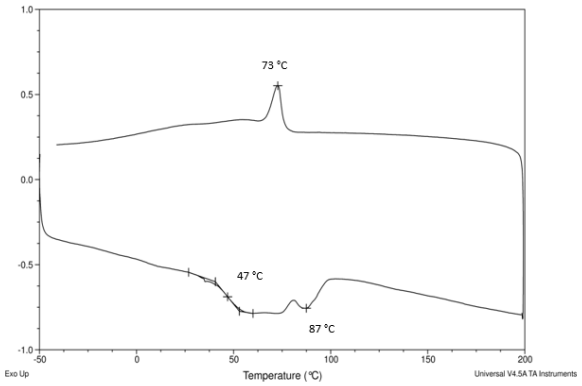


Figure S25; Relaxation DSC scan of **pEEA*15*** (48 hours after scan shown in **Figure S19**).

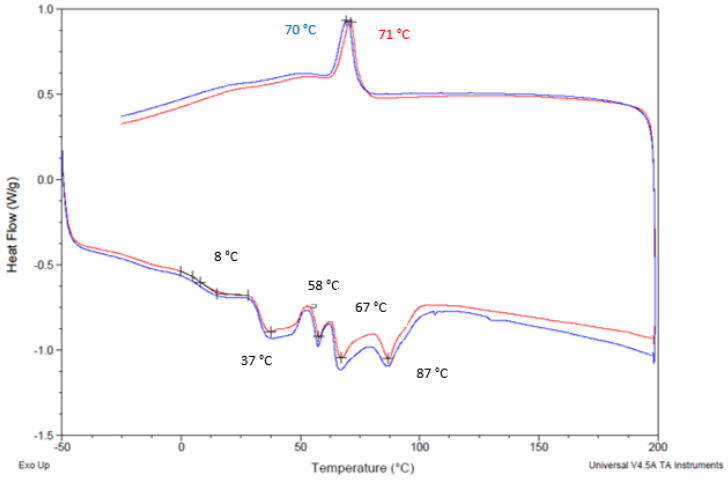


Figure S26; Relaxation DSC scans of **pEEA*15* /1** at 1% (red) and 5% wt. (blue) (taken 48 hours after scan shown in **Figure S20**).

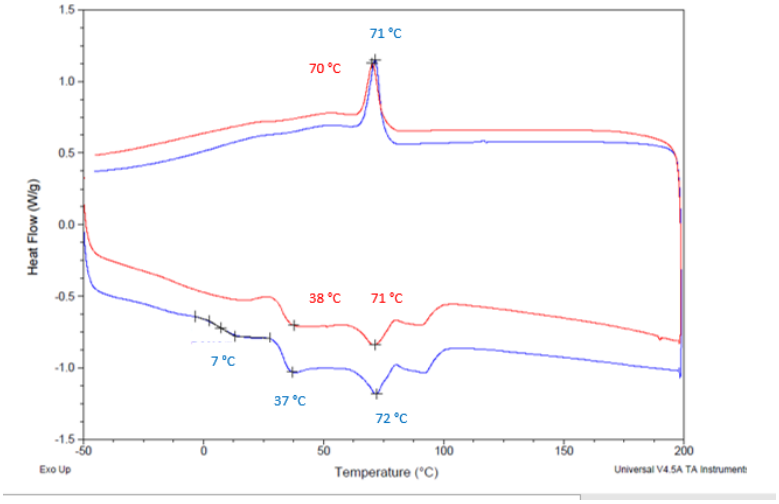


Figure S27; Relaxation DSC scan of **pEEA*15*/2** at 1% (red) and 5% wt. (blue) (taken 48 hours after scan shown in **Figure S21**).

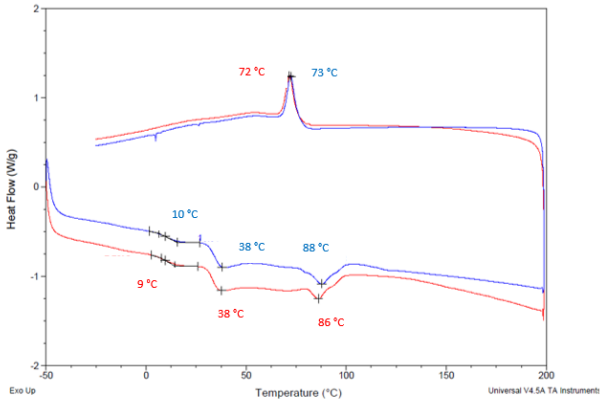


Figure S28; Relaxation DSC scan of **pEEA*15*/3** at 1% (red) and 5% wt. (blue) (taken 48 hours after scan shown in **Figure S22**).

Table S1; Tensile properties after heating fractured films at 50 °C for 8 hours.

Film System	% wt additive	Tensile Strength (MPa)	Fracture Stress (MPa)	Uniform Strain (%)	Strain to Fracture (%)	Energy absorbed (MPa)	Young's Modulus (MPa)
pEEA*15*		0.12	0.12	1.56	1.60	0.002	5.68
pEEA*15*/1	5	0.09	0.09	0.53	0.56	0.001	13.12
pEEA*15*/2	1	0.57	0.57	1.50	1.58	0.013	23.23
pEEA*15*/3	5	0.88	0.88	2.30	2.42	0.013	18.61

Table S2; Tensile properties after heating fractured films at 60 °C for 2 hours.

Film System	% wt additive	Tensile Strength (MPa)	Fracture Stress (MPa)	Uniform Strain (%)	Strain to Fracture (%)	Energy absorbed (MPa)	Young's Modulus (MPa)
pEEA*15*		0.39	0.37	1.67	1.74	0.008	14.22
pEEA*15*/1	5	-	-	-	-	-	-
pEEA*15*/2	1	0.72	0.63	4.43	5.26	0.03	17.97
pEEA*15*/3	5	1.12	1.12	2.29	2.37	0.021	28.53

Table S3; Tensile properties after pressing (0.98 MPa) fractured films for 8 hours.

Film System	% wt additive	Tensile Strength (MPa)	Fracture Stress (MPa)	Uniform Strain (%)	Strain to Fracture (%)	Energy absorbed (MPa)	Young's Modulus (MPa)
pEEA*15*		1.00	0.84	6.15	7.38	0.06	26.31
pEEA*15*/1	5	1.35	0.93	6.75	9.68	0.10	21.83
pEEA*15*/2	1	0.20	0.15	1.07	1.23	0.007	18.60
pEEA*15*/3	5	1.95	0.96	5.62	7.48	0.14	41.43

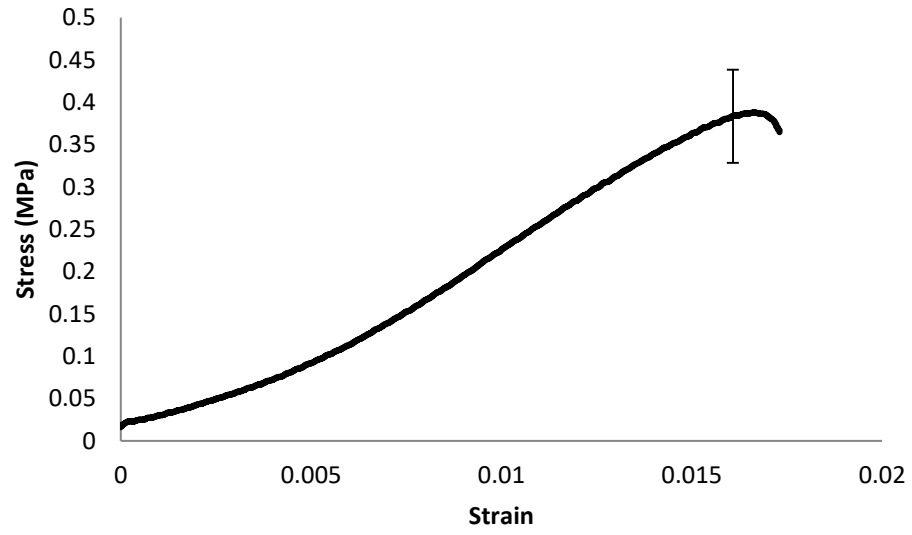


Figure S29; Stress-strain curve (average of five samples) for **pEAA*15*** after healing at 60 ˚C (2 hours)

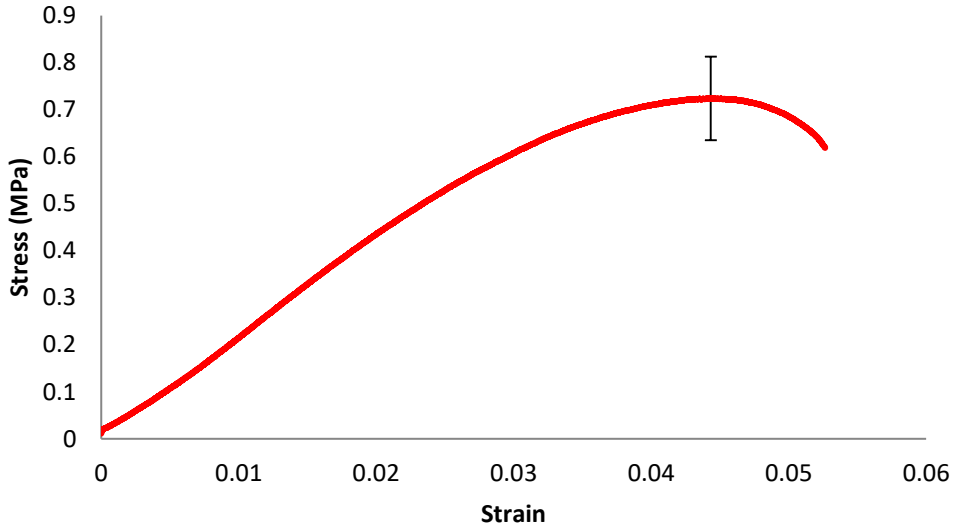


Figure S30; Stress-strain curve (average of five samples) for **pEAA*15*/2** (1% wt) after healing at 60 ˚C (2 hours)

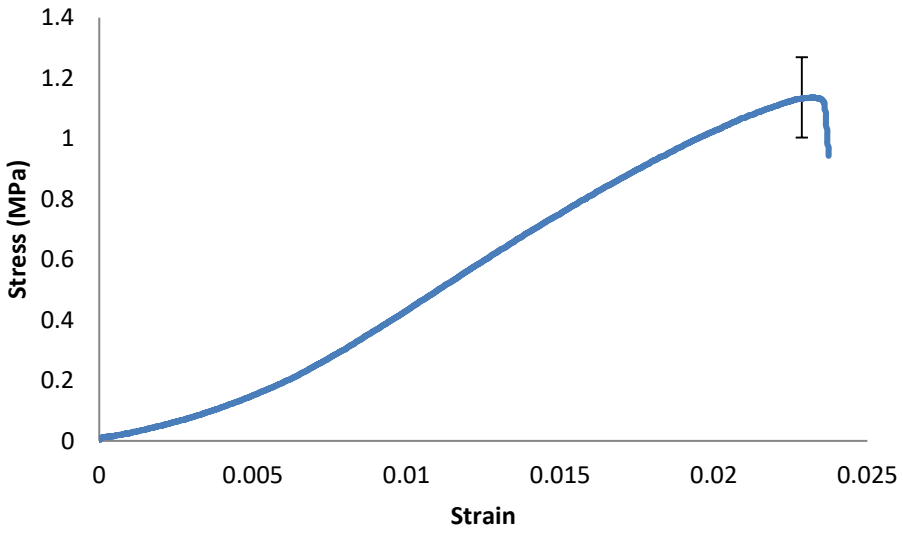


Figure S31; Stress-strain curve (average of five samples) for **pEAA*15*/3** (5% wt) after healing at 60 ˚C (2 hours)

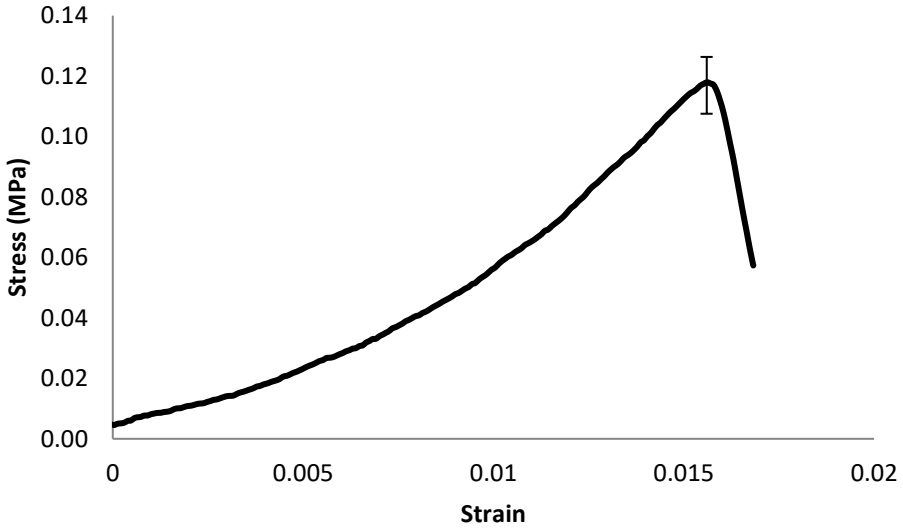


Figure S32; Stress-strain curve (average of five samples) for **pEAA*15*** after healing at 50 ˚C (8 hours).

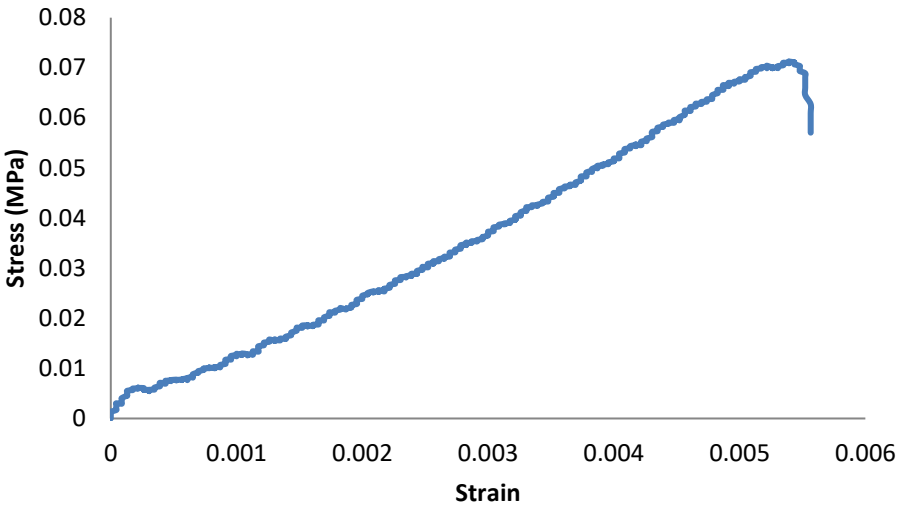


Figure S33; Stress-strain curve for **pEAA*15*/1** (5% wt) after healing at 50 ˚C (8 hours)

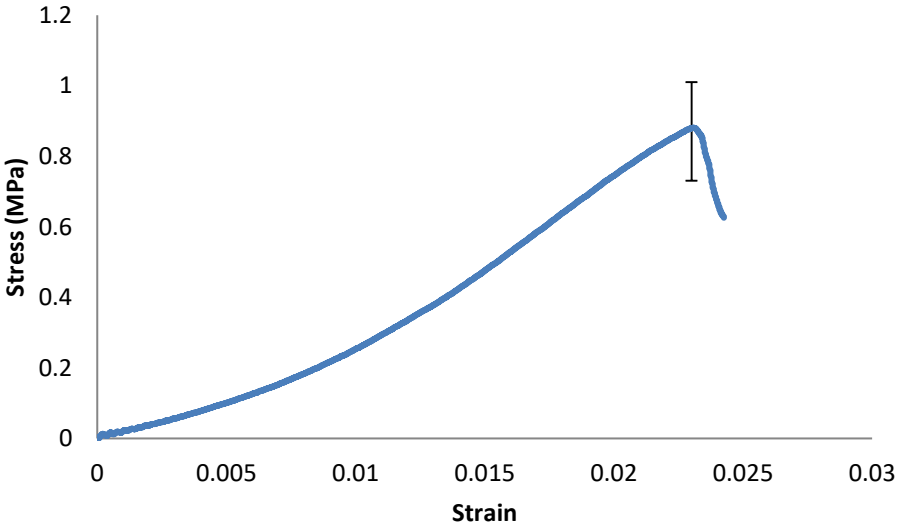


Figure S34; Stress-strain curve (average of five samples) for **pEAA*15*/3** (5% wt) after healing at 50 ˚C (8 hours)

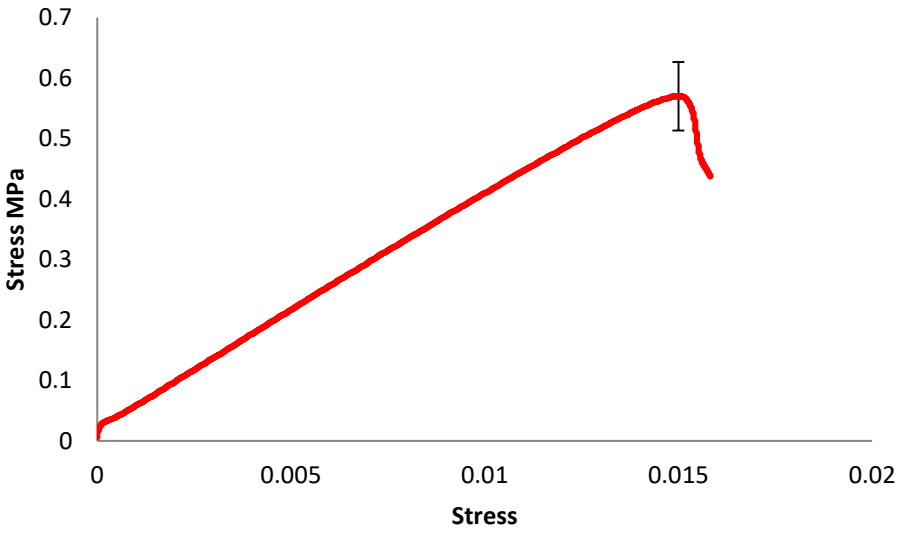


Figure S35; Stress-strain curve (average of five samples) for **pEAA*15*/2** (1% wt) after healing at 50 ˚C (8 hours)

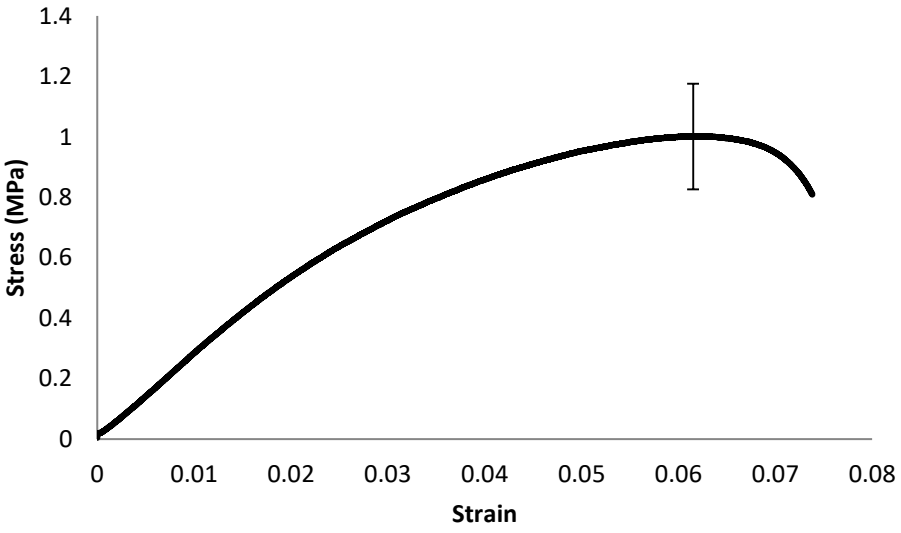


Figure S36; Stress-strain curve (average of five samples) for **pEAA*15*** after healing under pressure (0.98 MPa, 8 hours)

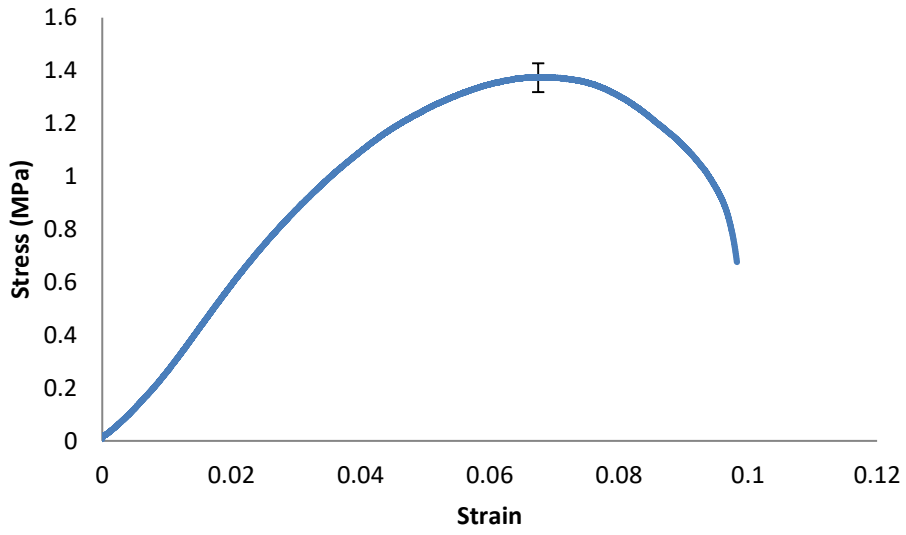


Figure S37; Stress-strain curve (average of five samples) for **pEAA*15*/1** (5% wt) after healing under pressure (0.98 MPa, 8 hours)

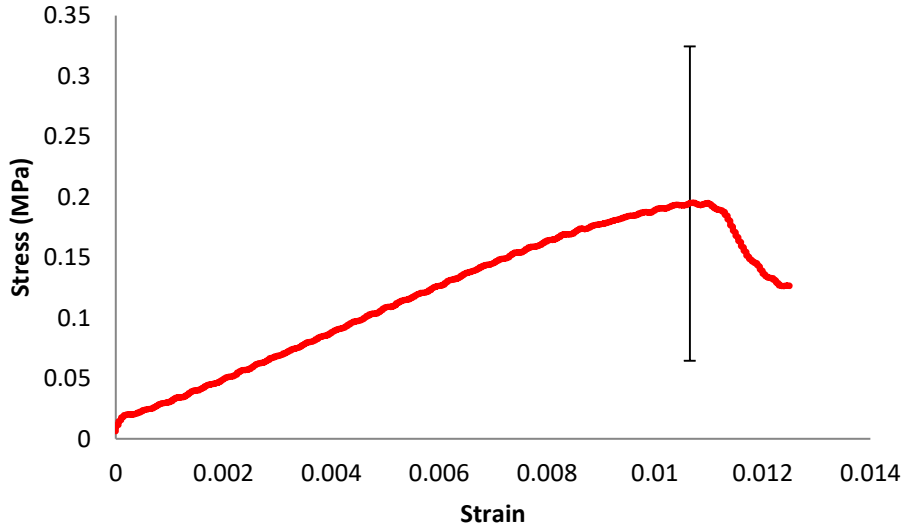


Figure S38; Stress-strain curve (average of five samples) for **pEAA*15/2*** (1% wt) after healing under pressure (0.98 MPa, 8 hours)

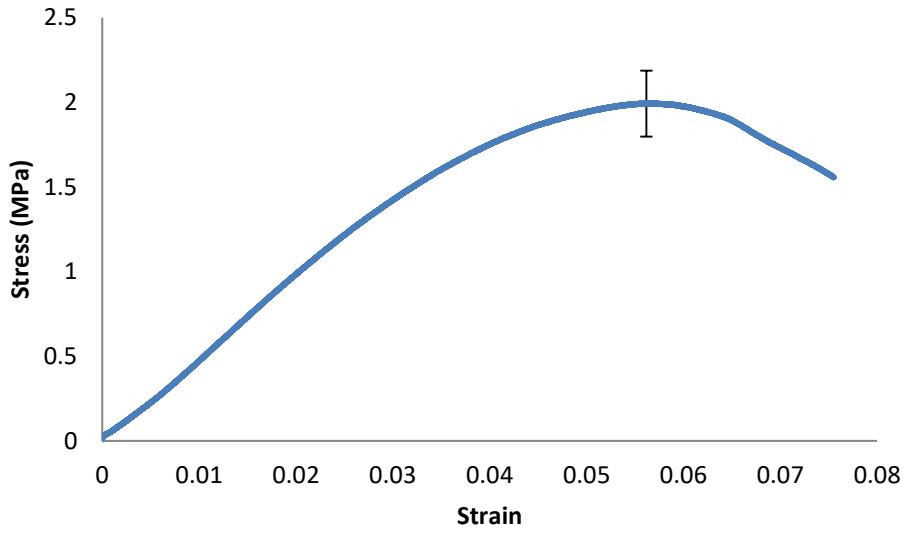


Figure S39; Stress-strain curve (average of five samples) for **pEAA*15*/3** (5% wt) after healing under pressure (0.98 MPa, 8 hours)

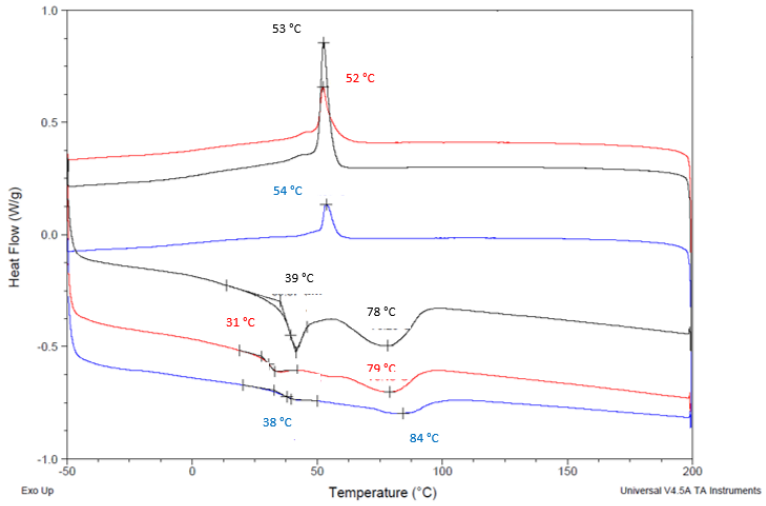


Figure S40; DSC thermograms for **pEAA*20*** (black) and **pEAA*20*/1** (blue) and **3** (red) each at 10% wt. The three lower traces are the heating scans and the three upper traces are the cooling scans.

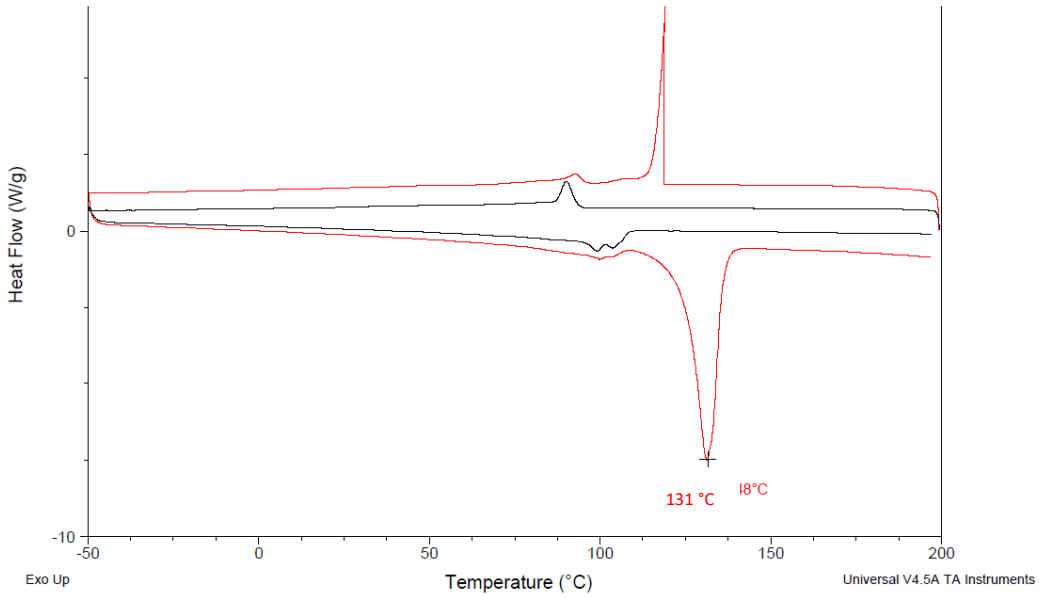


Figure S41; DSC thermograms for **pEAA*5*** (black) and **pEAA*5/1*** (red) at 2% wt.

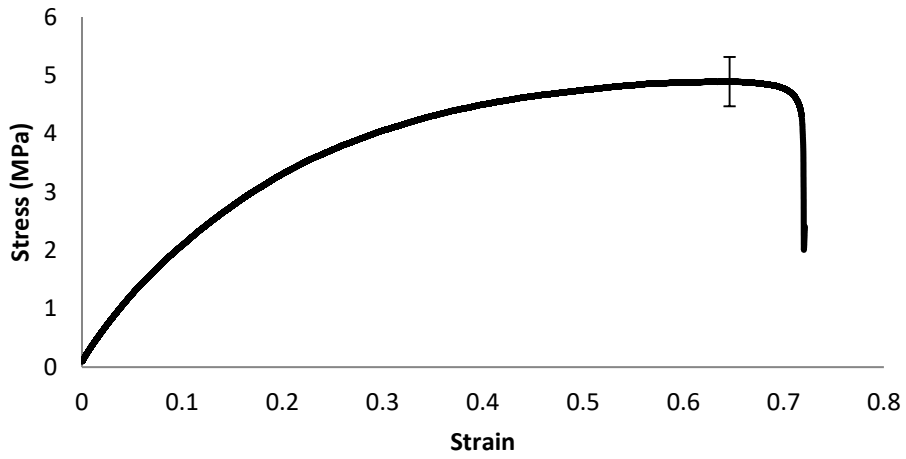


Figure S42; Stress-strain curve (average of five samples) of **pEAA*20***.

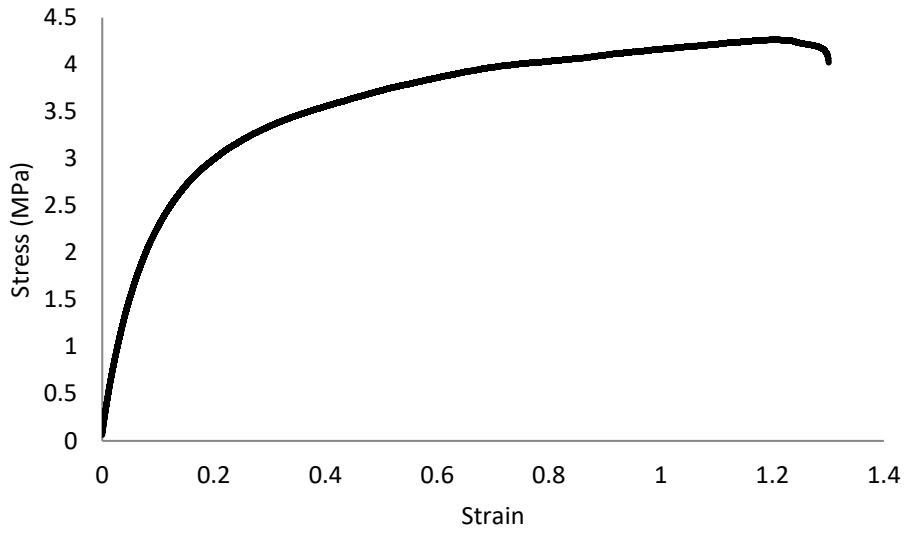


Figure S43; Stress-strain curve of **pEAA*20*/1** (10% wt).

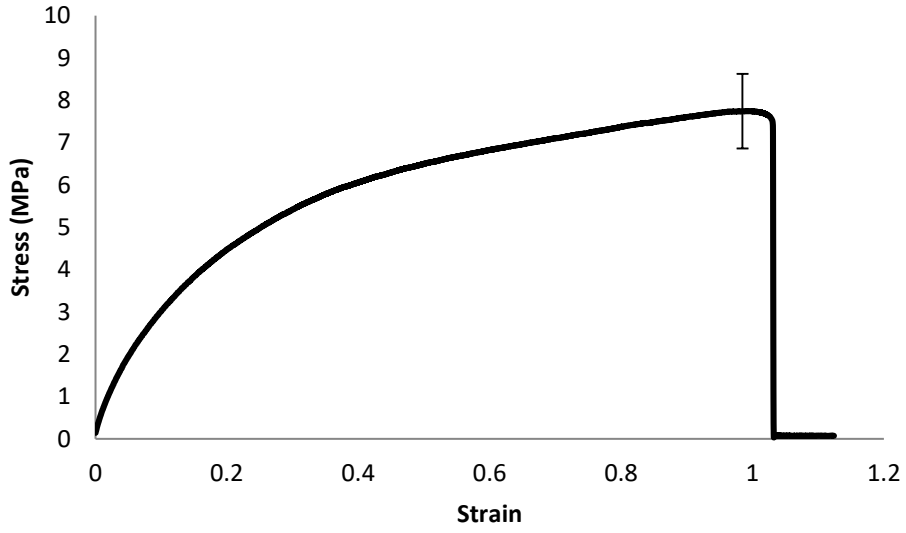


Figure S44; Stress-strain curve (average of five samples) of **pEAA*20*/3** (10% wt).

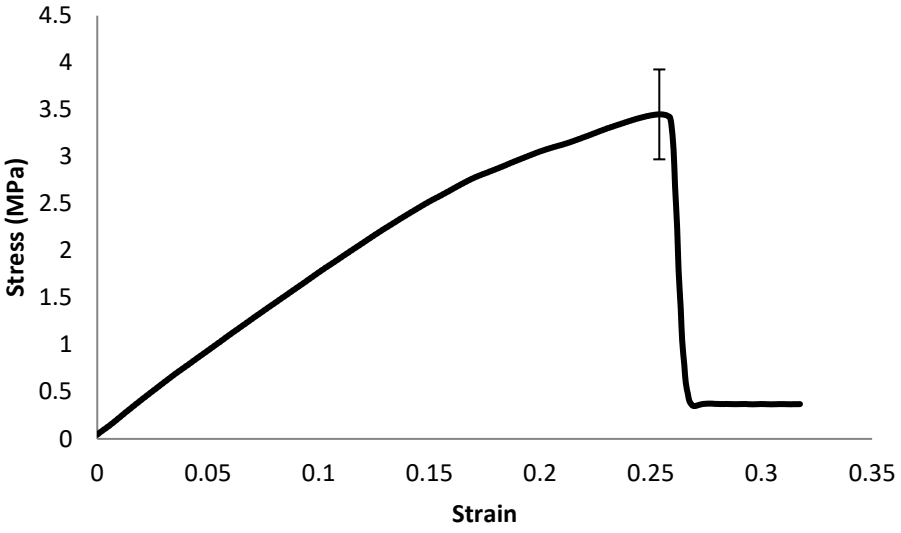


Figure S45; Stress-strain curve (average of five samples) of **pEAA*20*/3** (10% wt) after healing under pressure (0.98 MPa, 8 hours).