Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting information: Tuning Thermoresponsive Network Materials through Macromolecular Architecture and Dynamic Thiol-Michael Chemistry

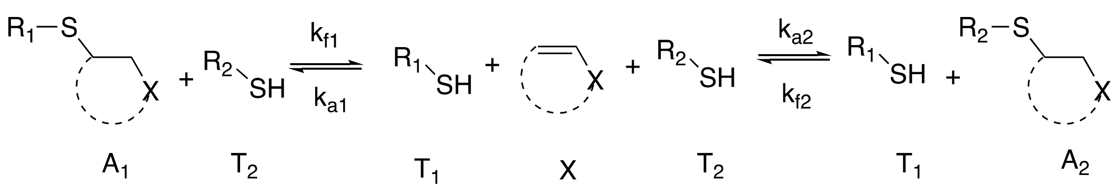
Progyateg Chakma,[a] Zachary A. Digby,[a] Jeremy Via, [a] Max P. Shulman[a] Jessica L. Sparks,[b] Dominik Konkolewicz[a]*

a. Department of Chemistry and Biochemistry, Miami University, 651 E High St. Oxford, OH 45056

b. Department of Chemical, Paper and Biomedical Engineering, Miami University, 650 E High St. Oxford, OH 45056

Kinetic Model of Small Molecule Exchange

The thiol-Michael dynamic equilibrium was modeled using the following scheme, which was described in an earlier publication,[1] which was adapted to a series of coupled differential equations:



The species X represents the free unreacted Michael acceptor in this case a Maleimide, A_1 and A_2 are the thiol-Michael adducts of X with thiol-1 (T_1) and thiol-2 (T_2). k_{a1} and k_{a2} are the Michael addition rate coefficients of thiol-1 and thiol-2 to X, respectively. k_{f1} and k_{f2} are the fragmentation, or retro Michael reaction, rate coefficients of adduct-1 and adduct-2, respectively. Note that in these systems negligible free Michael acceptor (X) is observed.

Equilibrium constant between the A_1, T_1, A_2 and T_2 is given below, accounting for the non-measurable nature of the intermediate X:

$$K_{\mathrm{overall}} = \frac{k_{\mathrm{f1}}}{k_{\mathrm{f2}}}\frac{k_{\mathrm{a2}}}{k_{\mathrm{a1}}} = \frac{[A_2][T_1]}{[A_1][T_2]}$$

Since the intermediate free Michael acceptor, X, is below the detection limit of the NMR experiments, it is not included in the overall equilibrium constant, but it is included in the simulations. This dynamic system can be represented using the following series of coupled differential equations. All equations were coded and solved using MATLAB_R2017a.

$$\frac{d[A_1]}{dt} = k_{\mathrm{a1}}[X][T_1] - k_{\mathrm{f1}}[A_1] \qquad (1)$$

$$\frac{d[T_1]}{dt} = -k_{\mathrm{a1}}[X][T_1] + k_{\mathrm{f1}}[A_1] \qquad (2)$$

$$\frac{d[A_2]}{dt} = k_{\mathrm{a2}}[X][T_2] - k_{\mathrm{f2}}[A_2] \qquad (3)$$

$$\frac{d[T_2]}{dt} = -k_{\mathrm{a2}}[X][T_2] + k_{\mathrm{f2}}[A_2] \qquad (4)$$

$$\frac{d[X]}{dt} = -k_{\mathrm{a1}}[X][T_1] - k_{\mathrm{a2}}[X][T_2] + k_{\mathrm{f1}}[A_1] + k_{\mathrm{f2}}[A_2] \qquad (5)$$

Supplementary Figures and Table

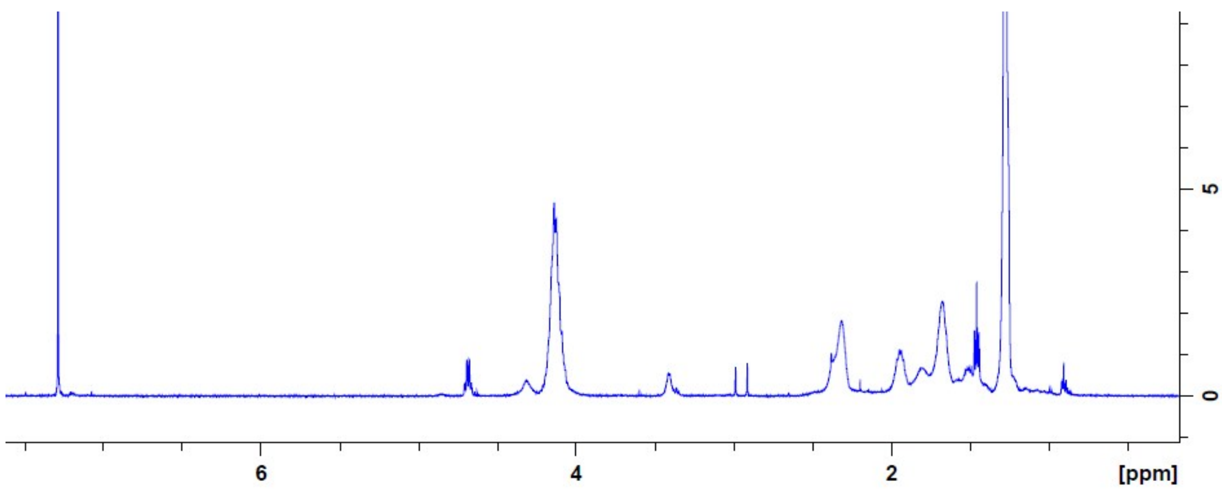


Figure S1: ^{1}H-NMR data of PEA_{50}-TM_3-$EGDMA_0$.

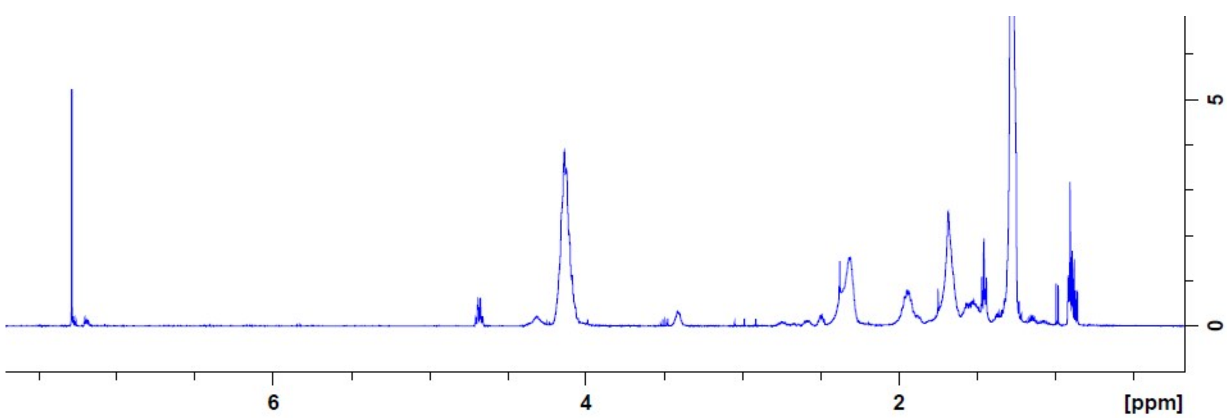


Figure S2: ^{1}H-NMR data of FRP-PEA-7%TM.

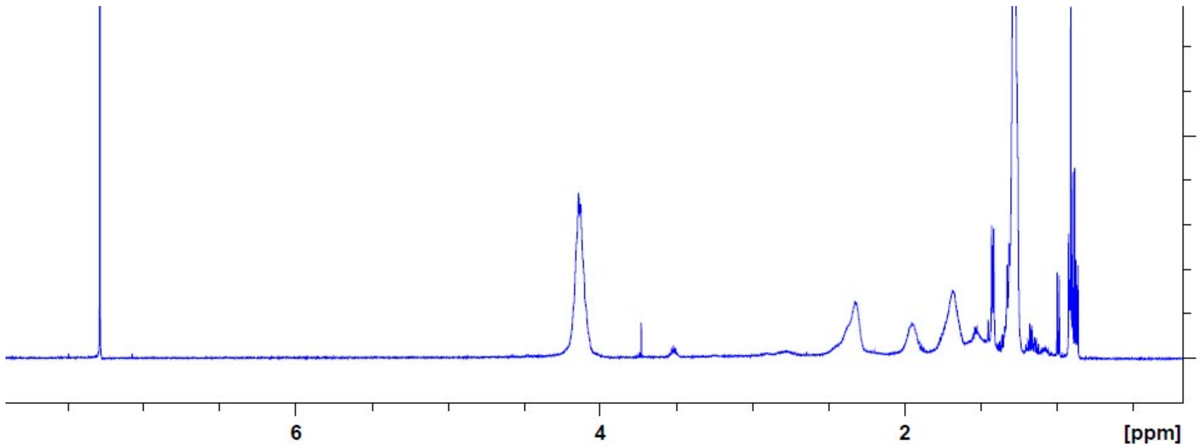


Figure S3: ^{1}H-NMR data of deprotected PEA_{50}-TM_3-$EGDMA_0$.

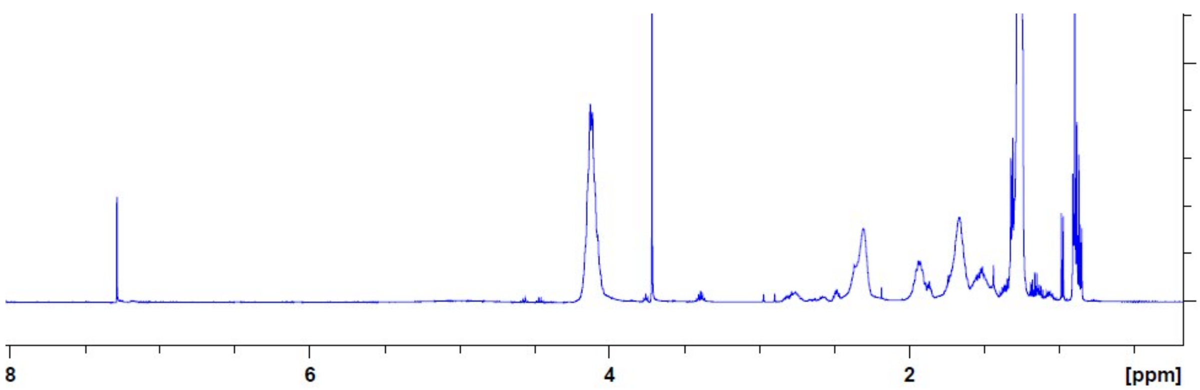


Figure S4: ^{1}H-NMR data of deprotected FRP-PEA-7%TM.

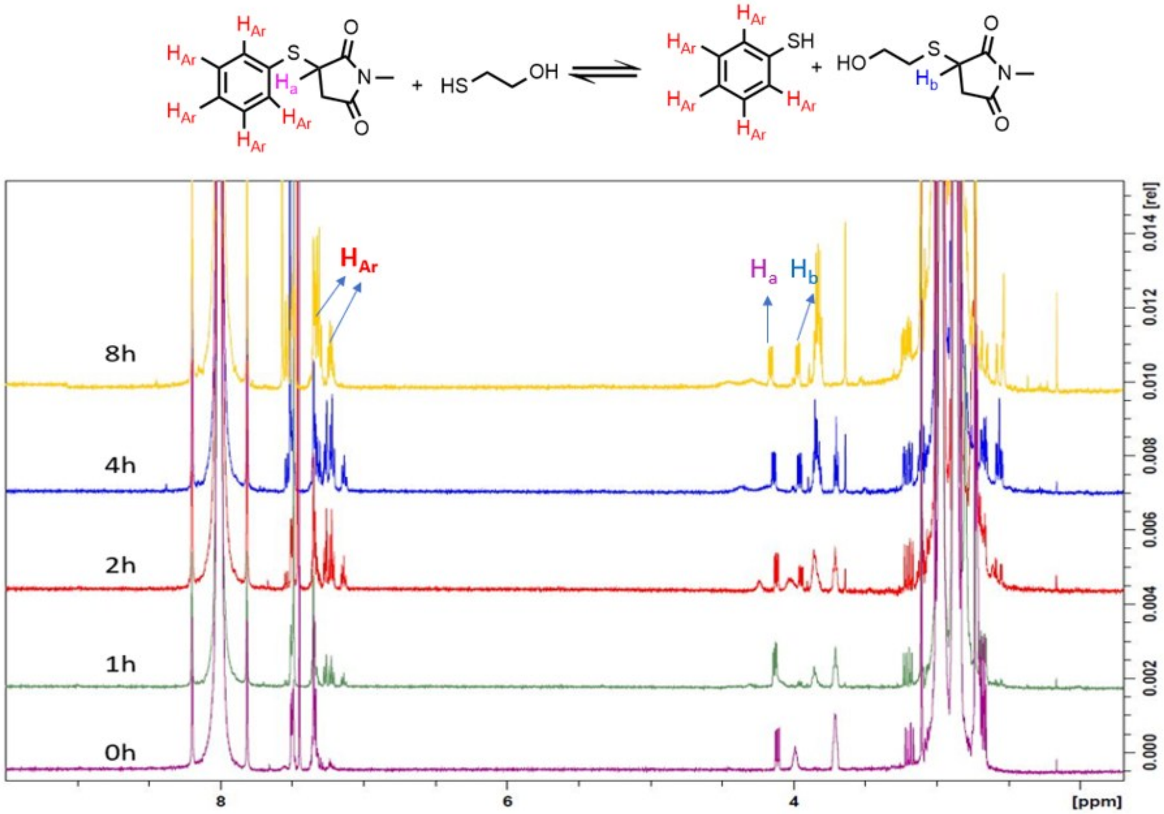


Figure S5: Stacked NMR plot of dynamic exchange starting with ME and MM-TP adduct

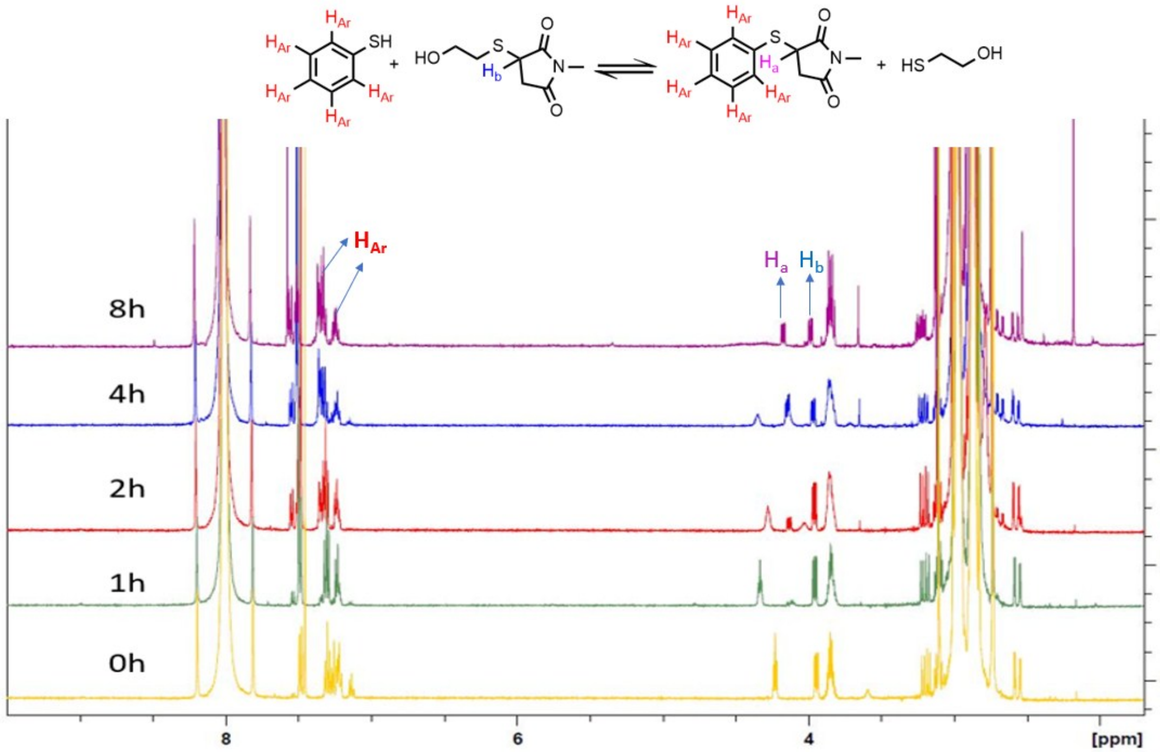


Figure S6: Stacked NMR plot of dynamic exchange starting with TP and MM-ME adduct

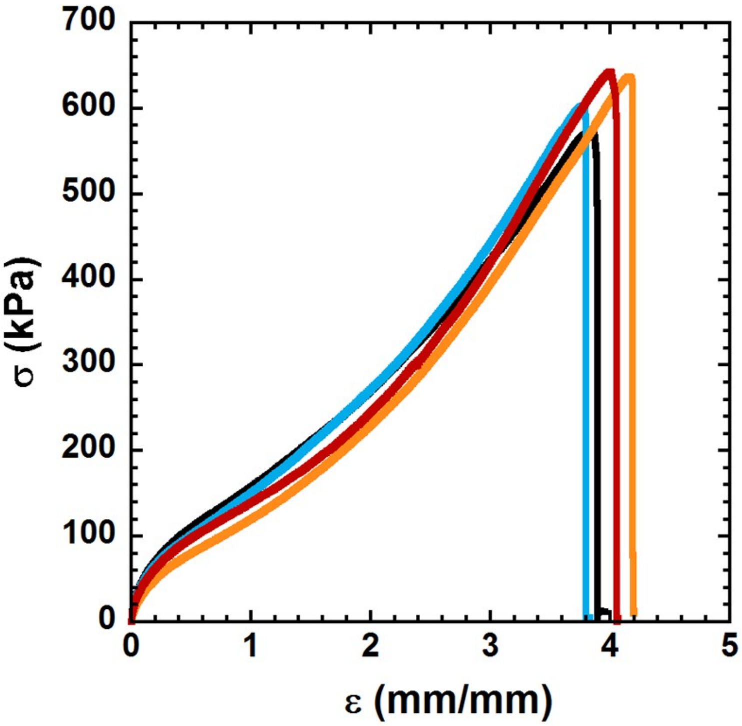


Figure S7: Stress-strain curves for uncut PEA_{100}-TM_3-$EGDMA_1$ materials

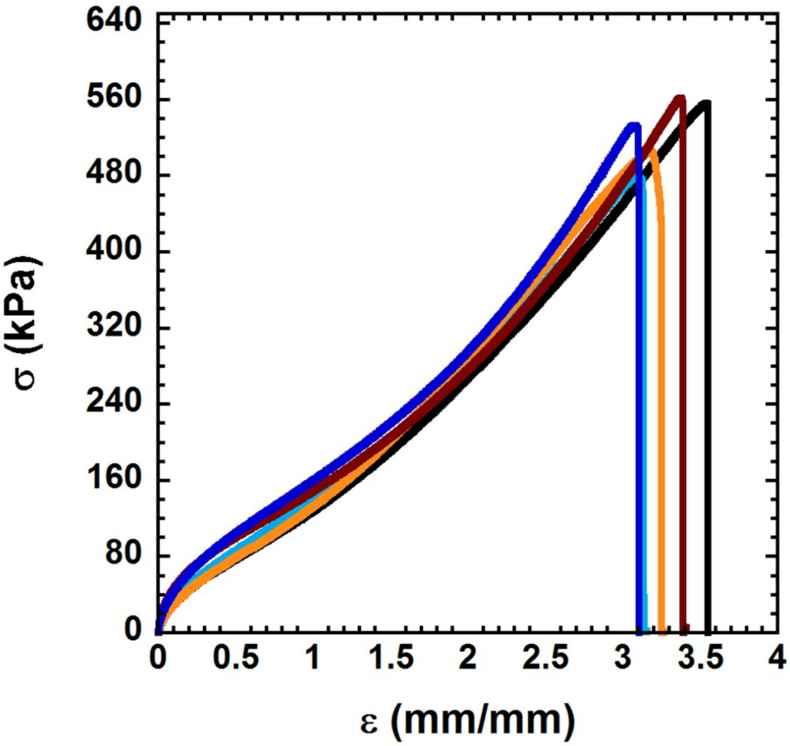


Figure S8: Stress-strain curves of uncut PEA_{50}-$TM_{1.5}$-$EGDMA_1$ materials

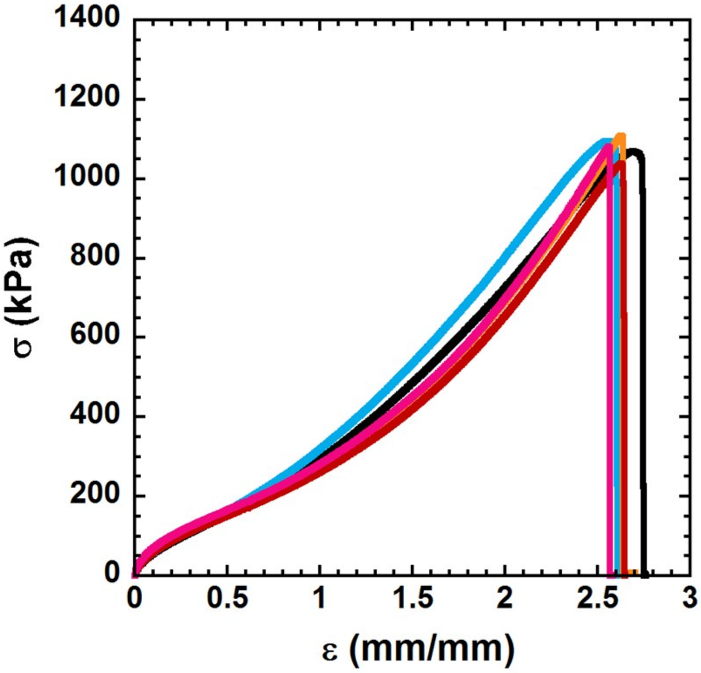


Figure S9: Stress-strain curves of uncut PEA_{100}-TM_6-$EGDMA_1$ materials

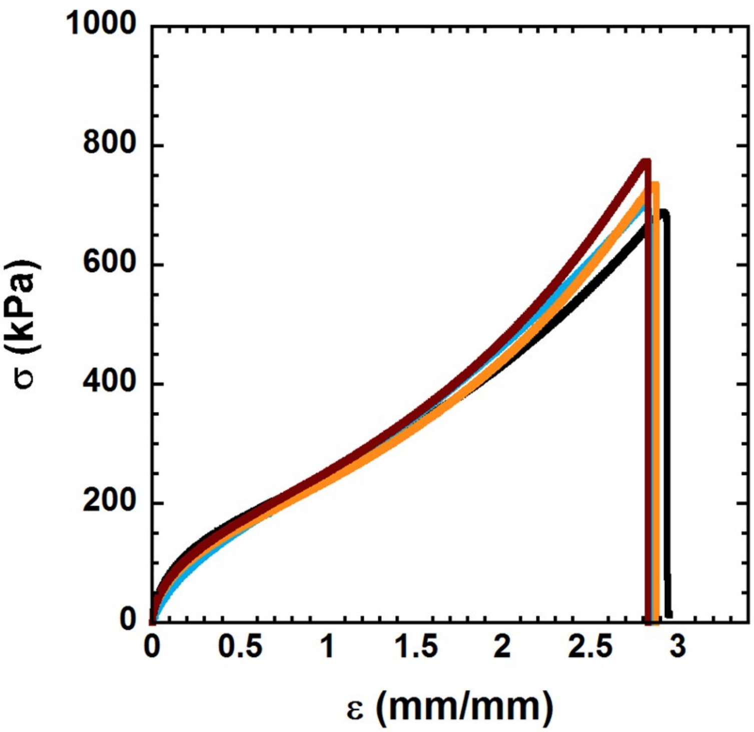


Figure S10: Stress-strain curves of uncut PEA_{50}-TM_{3}-$EGDMA_{0}$ materials

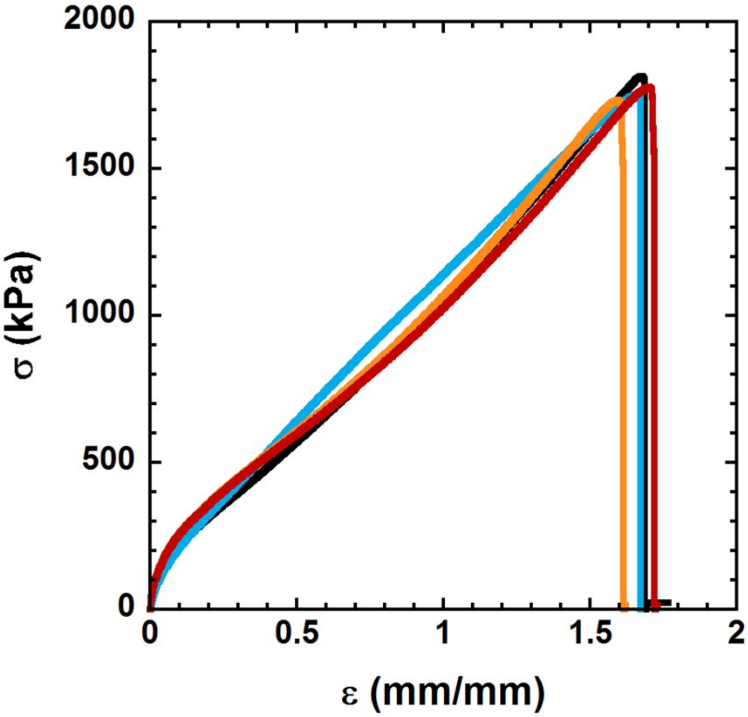


Figure S11: Stress-strain curves of uncut PEA_{50}-TM_5-$EGDMA_1$ materials

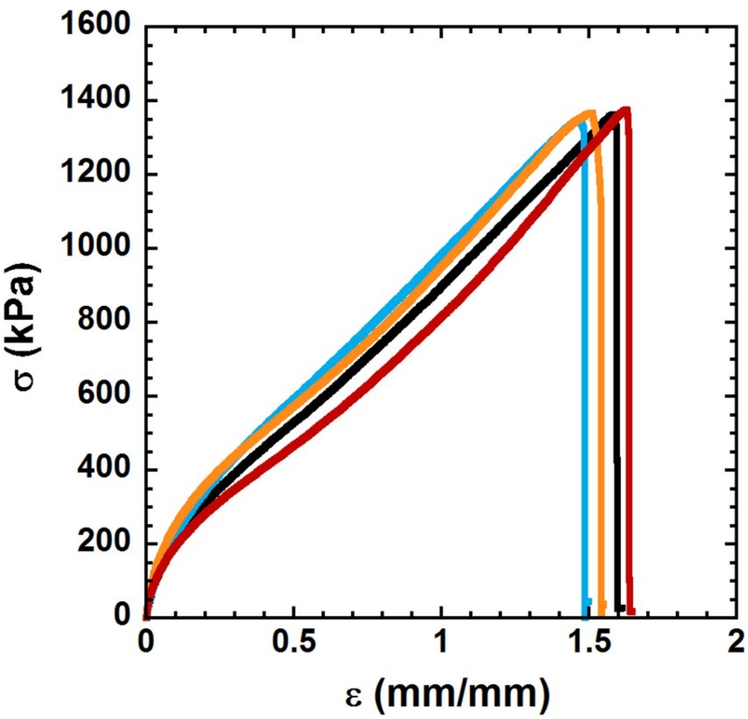


Figure S12: Stress-strain curves of uncut PEA_{50}-TM_{5}-$EGDMA_{0}$ materials

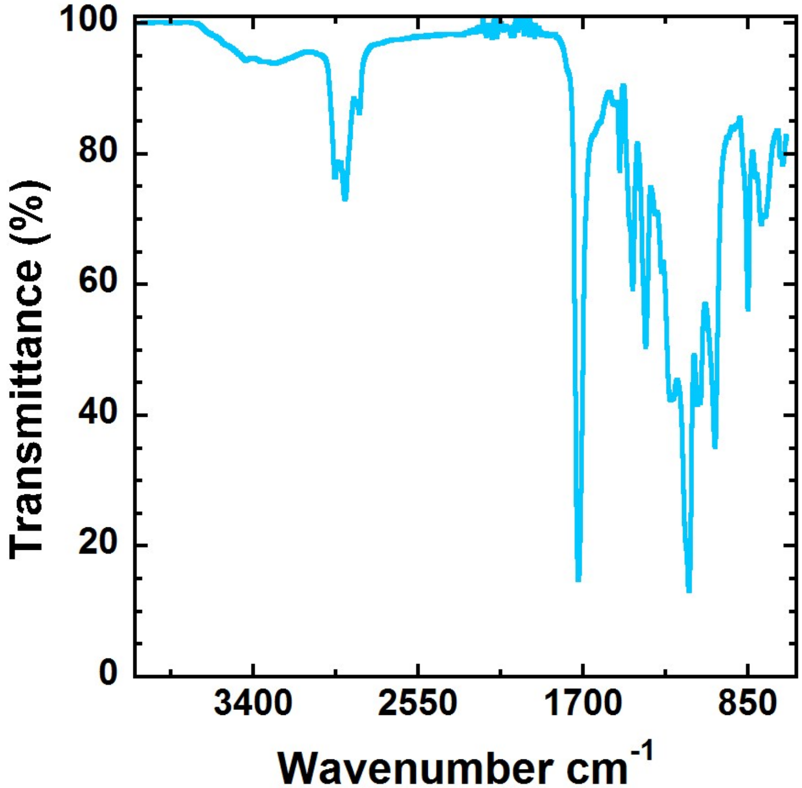


Figure S13: IR spectrum of PEA_{100}-TM_3-$EGDMA_1$ material

Table S1: IR assignment of PEA_{100}-TM_3-$EGDMA_1$ material.

Peak (cm^{-1})	Proposed Assignment	Reference
3275	O-H carboxylic acid stretch	[2]
2940	C-H stretch	[3,4]
1730	C=O ester stretch	[4]
1600	C=C stretch of phenyl ring	[2]
1410	CH_2 bending adjacent to carbonyl group	[2]
1251	C-O antisymmetric stretching	[4]
1171	C-O symmetric stretching	[4]
1020	C-N stretch	[2]
850	C-H out of plane bending	[2]

Table S2: Swelling ratio of PEA-TM (RAFT) materials

Entry	Materials	Swelling Ratio (DCM)	Swelling Ratio (H_2O)	Swelling Ratio (Acetone)	Swelling Ratio (Hexane)
1	PEA_{100}-TM_3-$EGDMA_1$	9.8± 0.1	1.0	6.2±0.1	1.0
2	PEA_{50}-$TM_{1.5}$-$EGDMA_1$	9.2 ±0.1	1.0	5.8±0.1	1.0
3	PEA_{100}-TM_6-$EGDMA_1$	8.3 ±0.1	1.0	4.2±0.1	1.0
4	PEA_{50}-TM_3-$EGDMA_0$	8.2±0.1	1.0	3.7±0.1	1.0
5	PEA_{50}-TM_5-$EGDMA_1$	6.4±0.1	1.0	3.0±0.1	1.0
6	PEA_{50}-TM_5-$EGDMA_0$	6.8±0.1	1.0	3.1±0.1	1.0

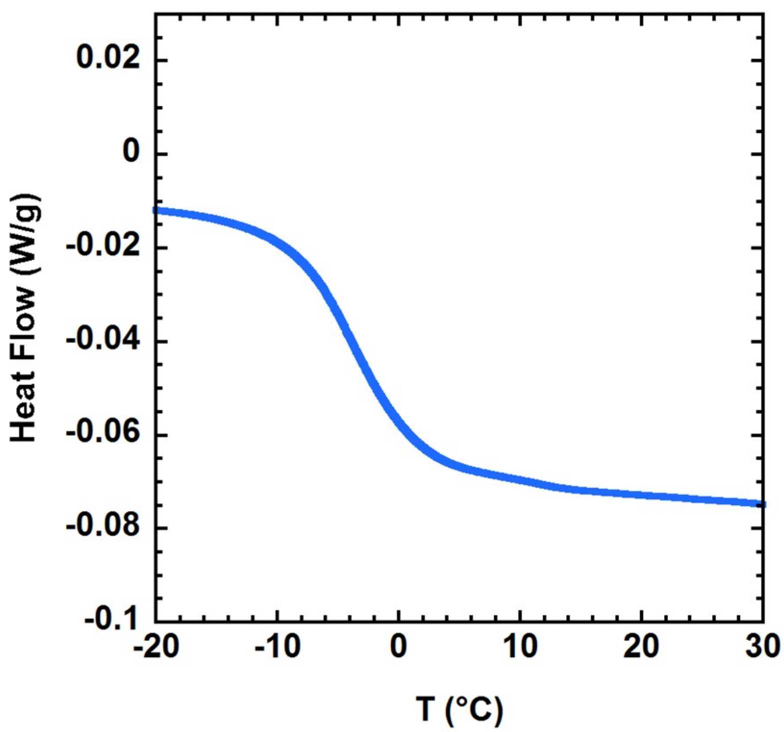


Figure S14: DSC curve for PEA_{100}-TM_3-$EGDMA_1$ material measured from the second heating cycle.

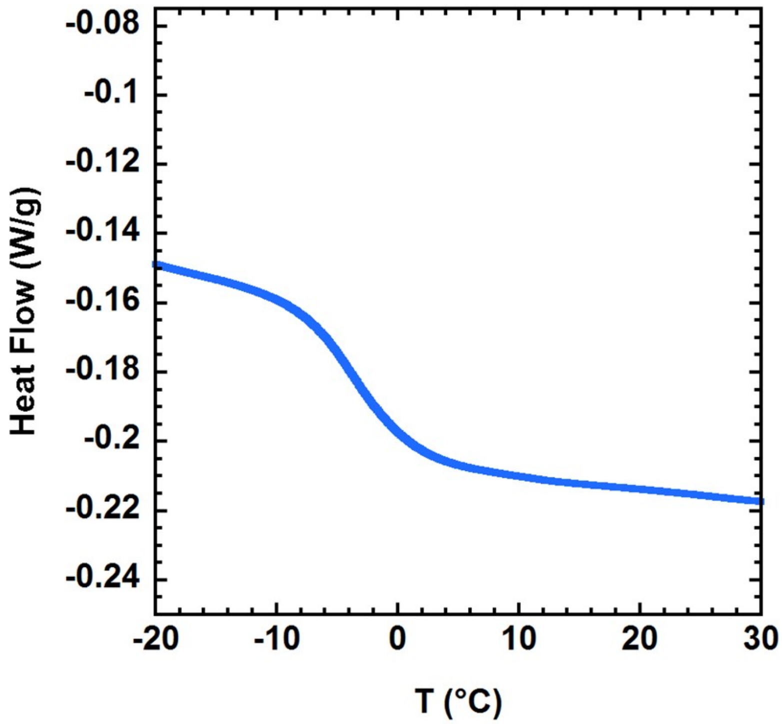


Figure S15: DSC curve for PEA_{50}-$TM_{1.5}$-$EGDMA_{1}$ material measured from the second heating cycle.

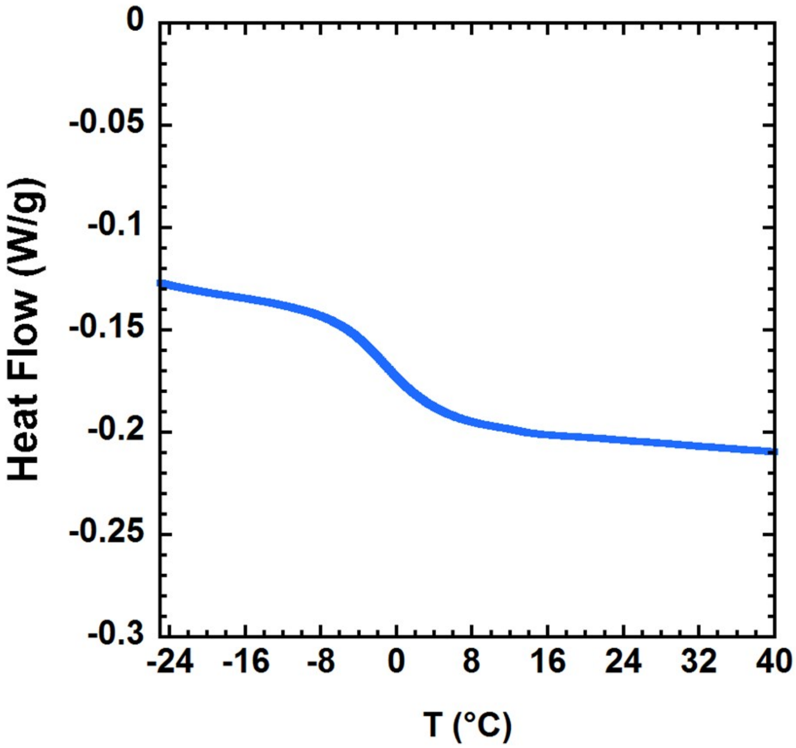


Figure S16: DSC curve for PEA_{100}-TM_6-$EGDMA_1$ material measured from the second heating cycle.

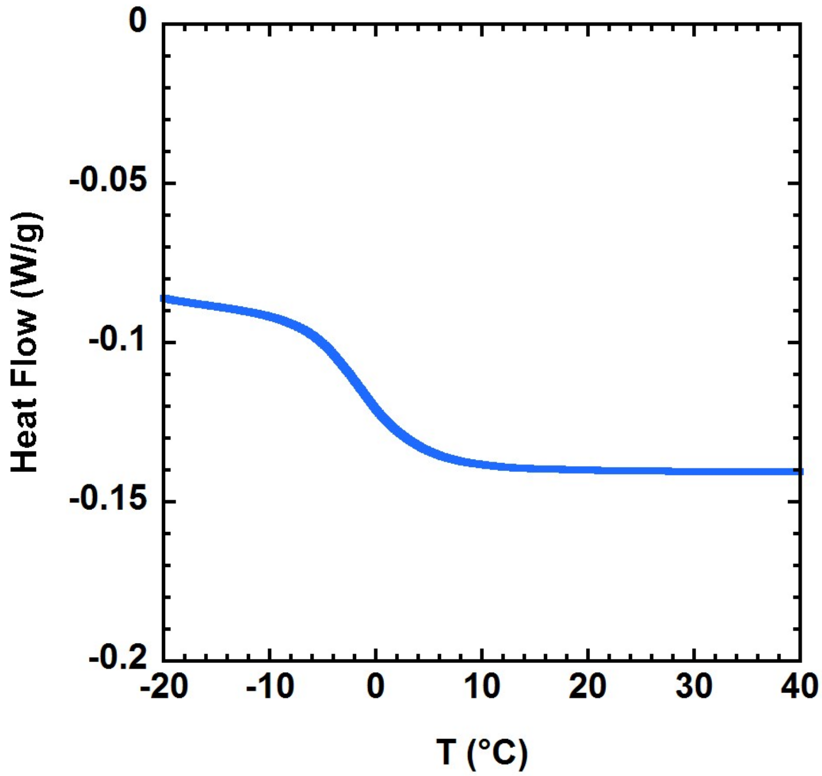


Figure S17: DSC curve for PEA_{50}-TM_3-$EGDMA_0$ material measured from the second heating cycle.

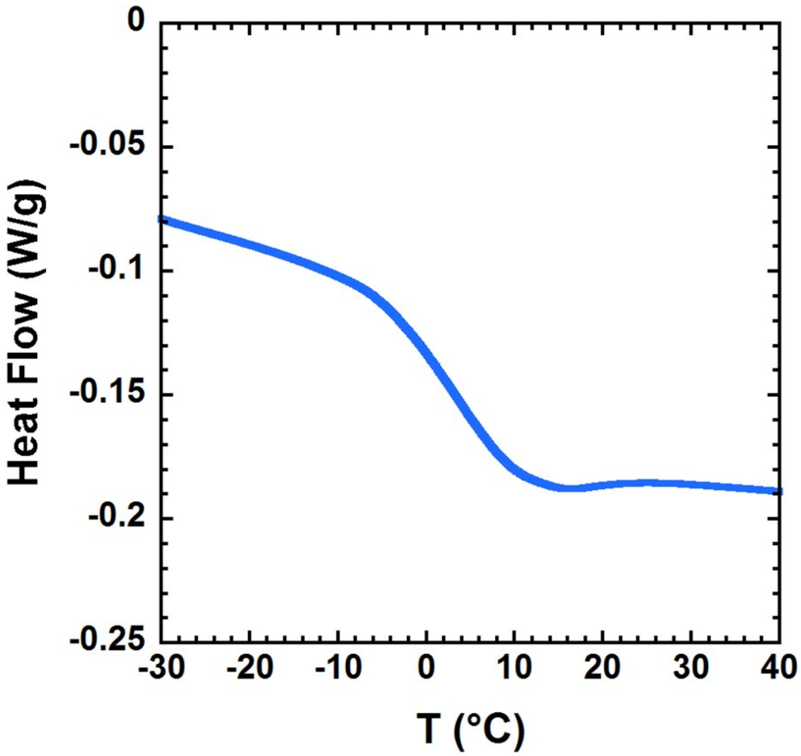


Figure S18: DSC curve for PEA_{50}-TM_{5}-$EGDMA_{1}$ material measured from the second heating cycle.

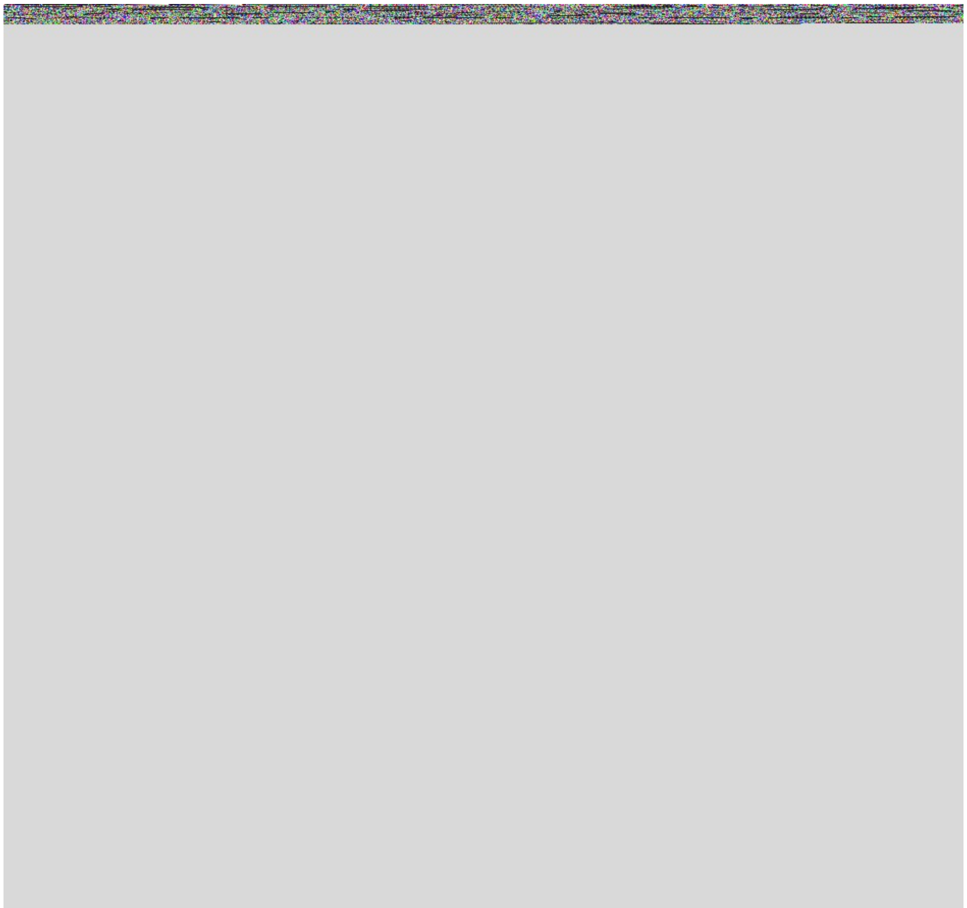


Figure S19: DSC curve for PEA_{50}-TM_5-$EGDMA_0$ material measured from the second heating cycle.

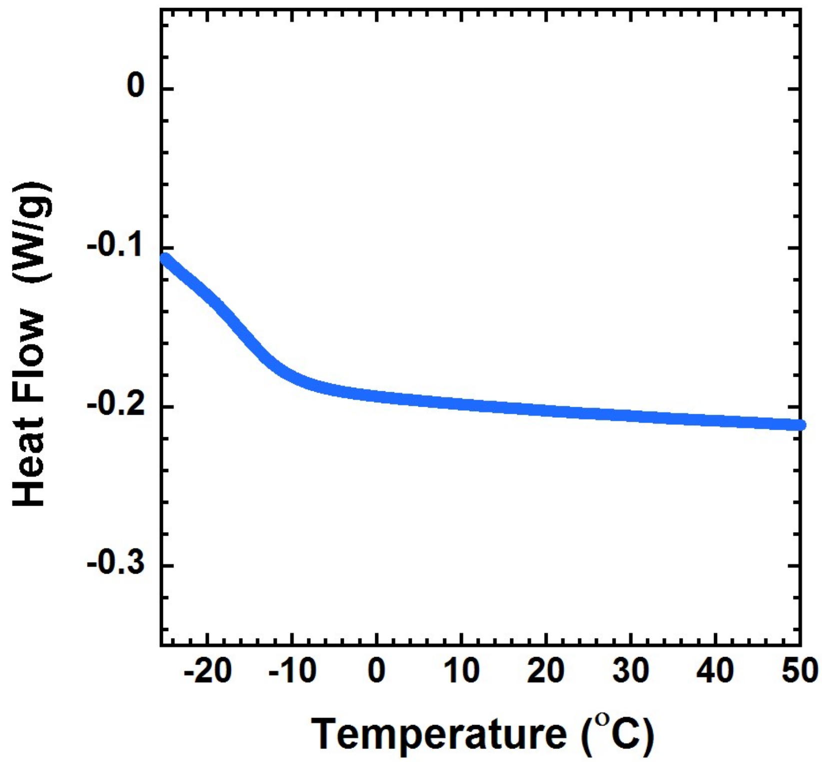


Figure S20: DSC curve for FRP-PEA-7%TM material measured from the second heating cycle.

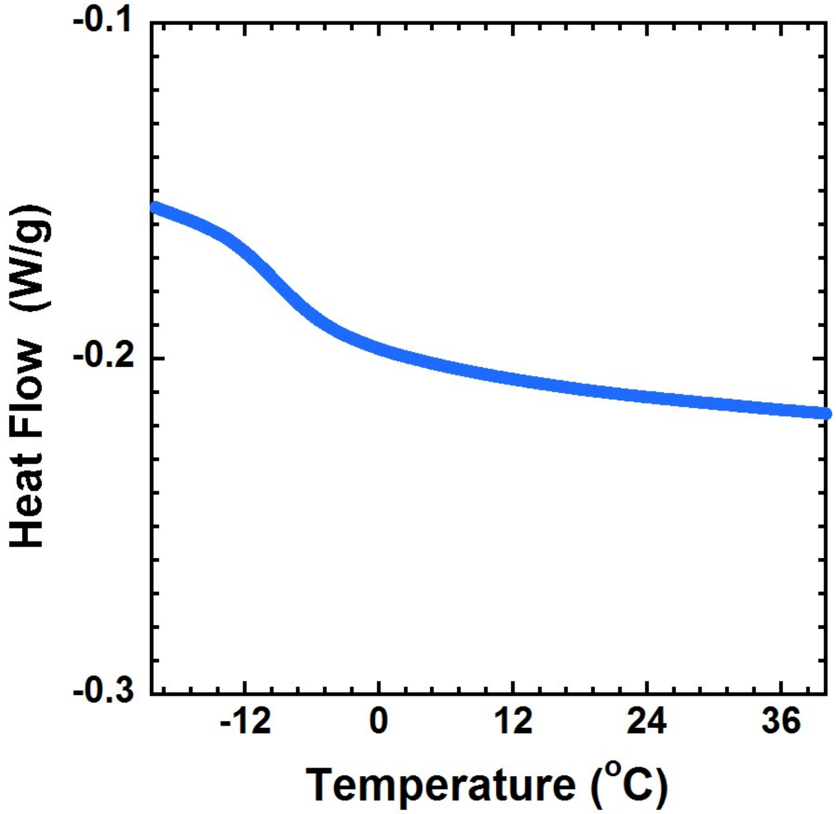


Figure S21: DSC curve for FRP-PEA-4%DVB material measured from the second heating cycle.

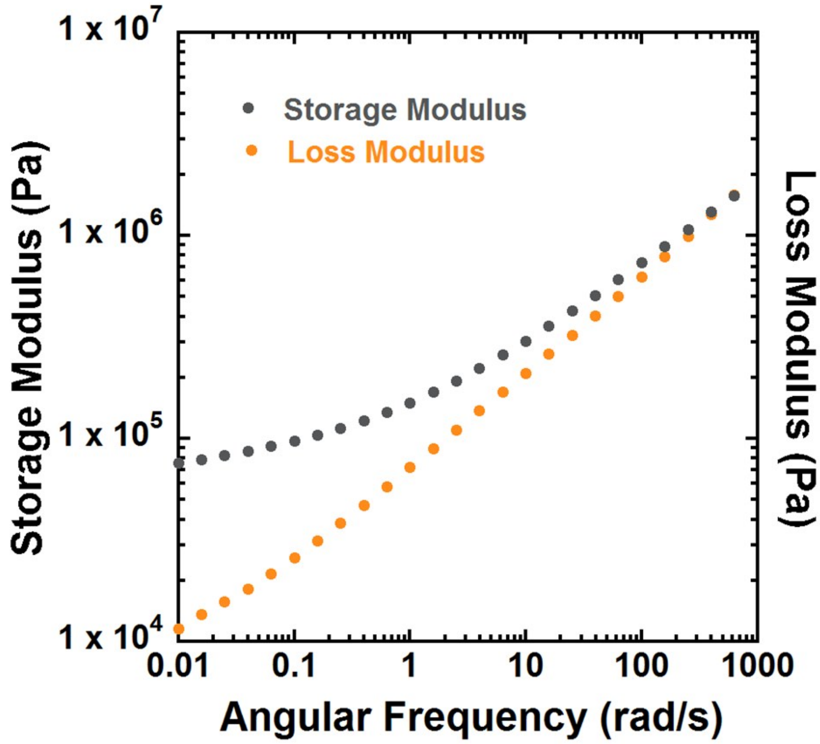


Figure S22: Rheology of PEA_{50}-TM_5-$EGDMA_1$ material

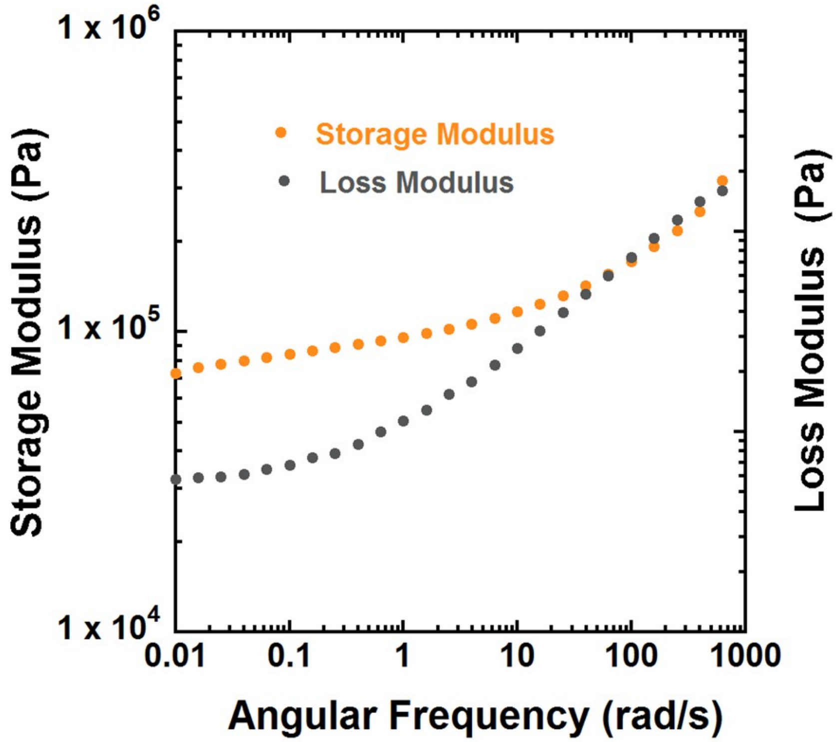


Figure S23: Rheology of PEA_{50}-TM_5-$EGDMA_0$ material

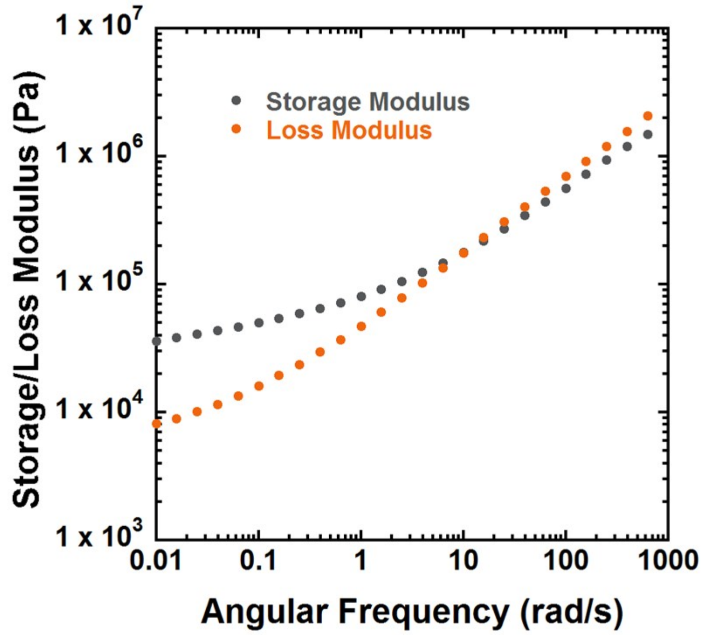


Figure S24: Rheology of FRP-PEA-7%TM material

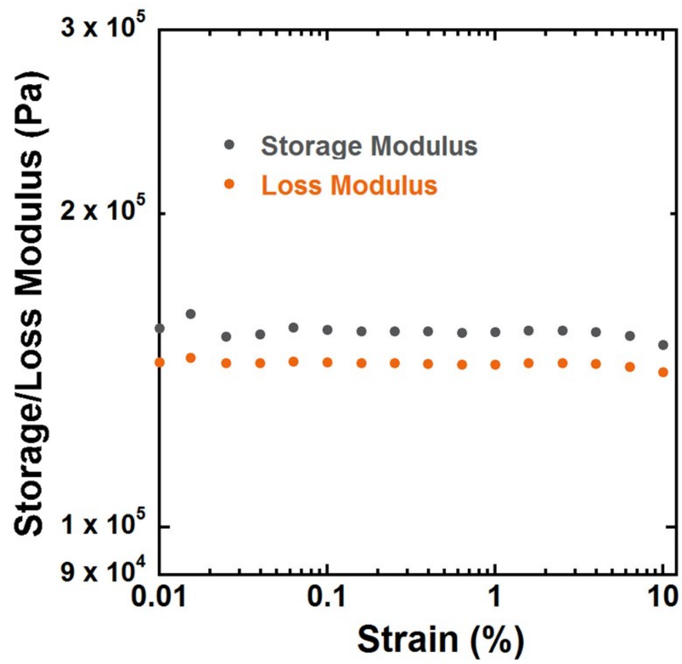


Figure S25: Rheology Strain sweep data of FRP-PEA-7%TM material at angular frequency of 6.28 rad/s

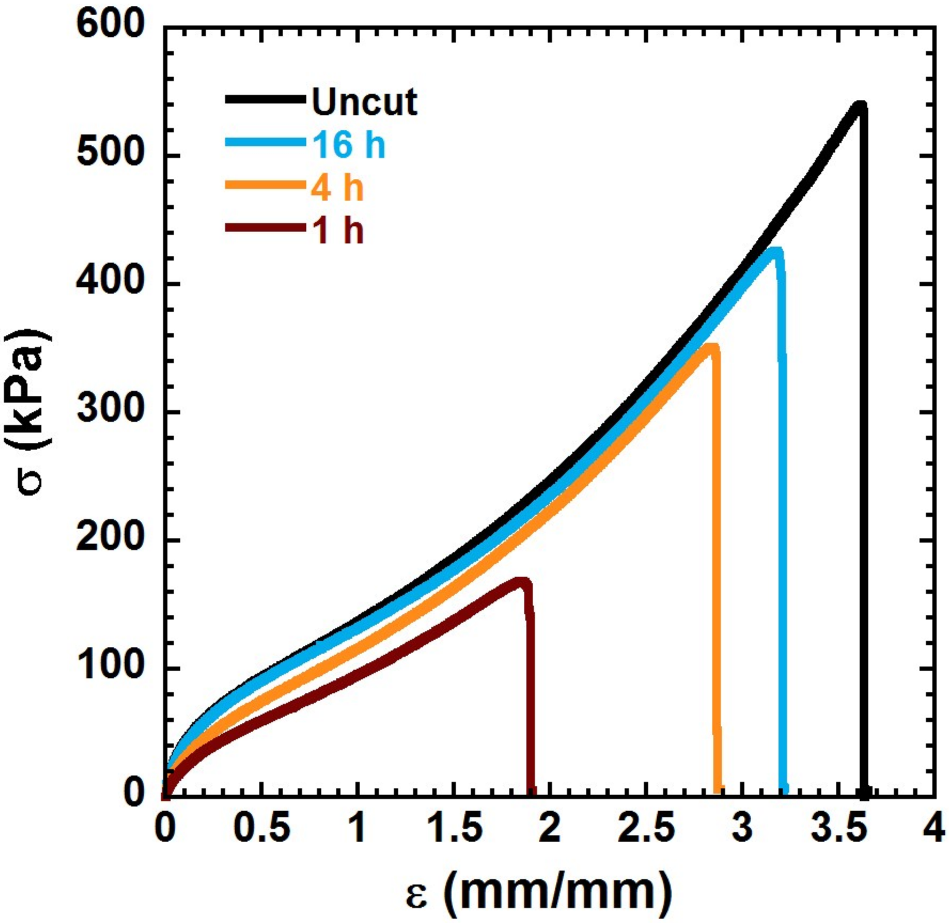


Figure S26: Self-healing properties of PEA_{50}-$TM_{1.5}$-$EGDMA_1$ material after healing at different times at 90 °C.

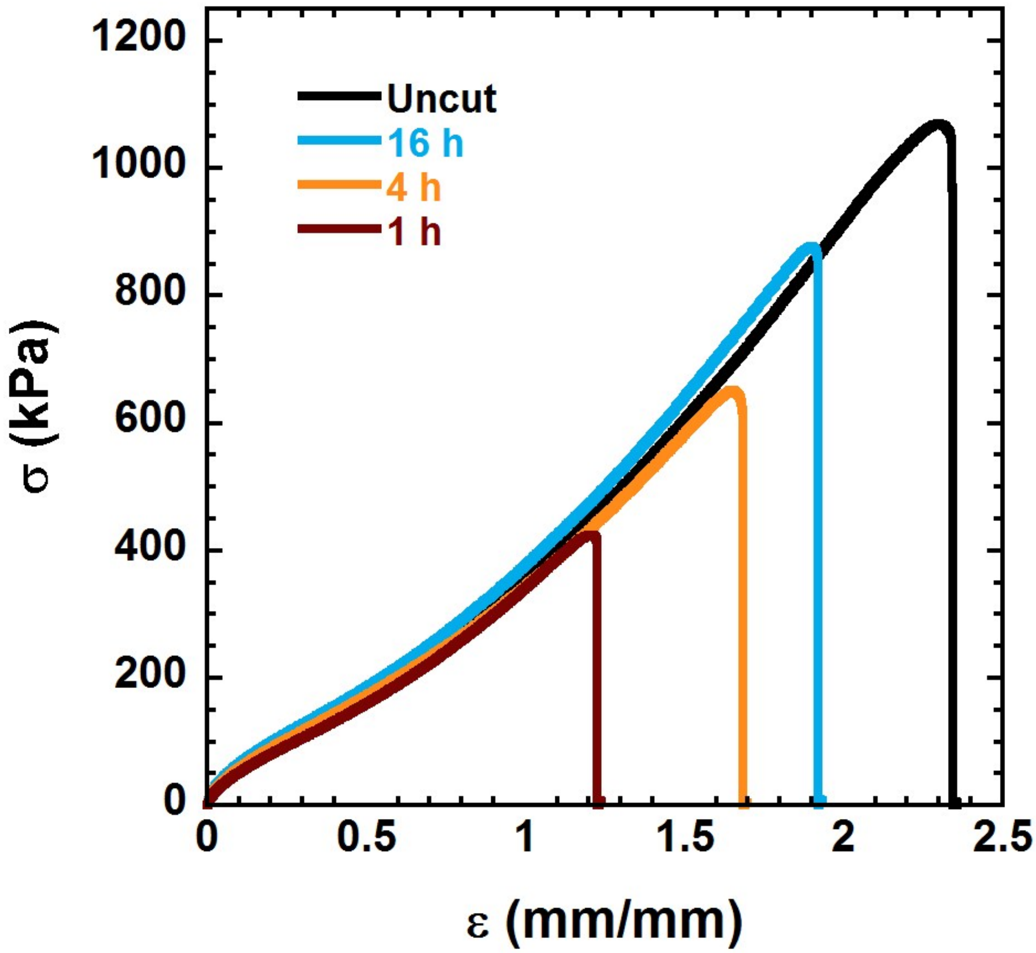


Figure S27: Self-healing properties of PEA_{100}-TM_6-$EGDMA_1$ material after healing at different times at 90 °C.

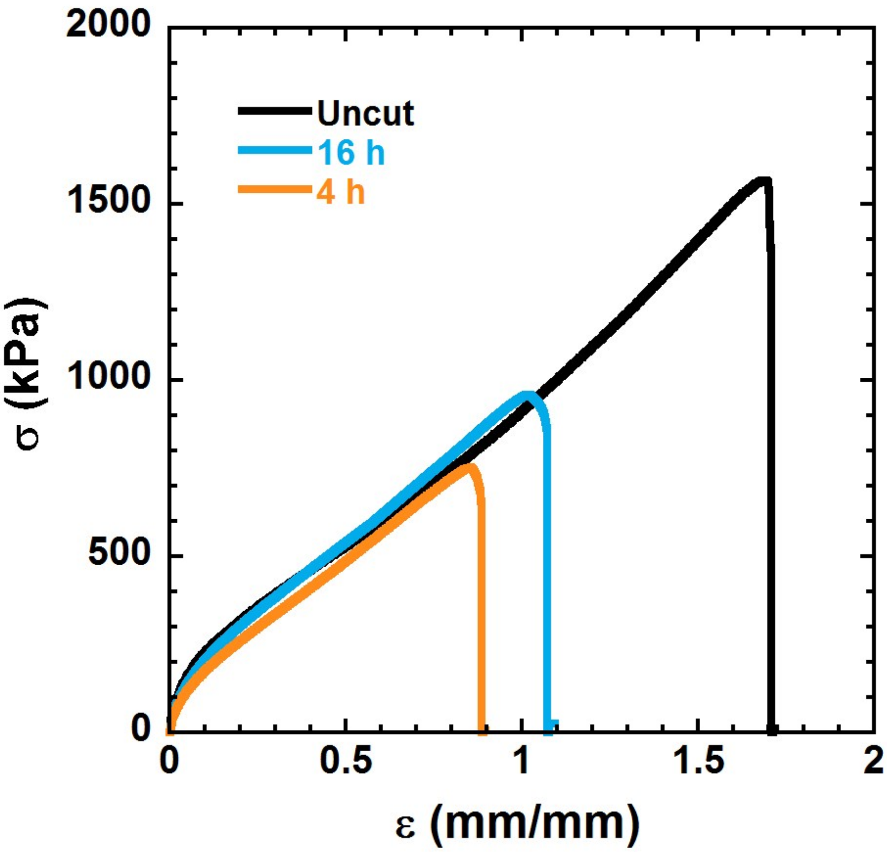


Figure S28: Self-healing properties of PEA_{50}-TM_5-$EGDMA_1$ material after healing at different times at 90 °C.

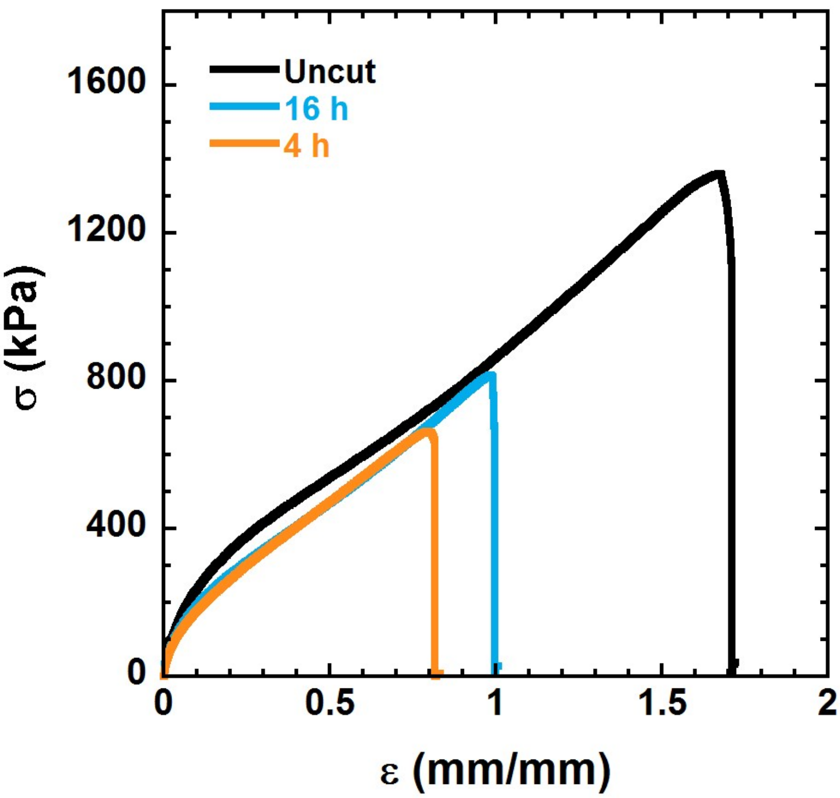


Figure S29: Self-healing properties of PEA_{50}-TM_5-$EGDMA_0$ material after healing at different times at 90 °C.

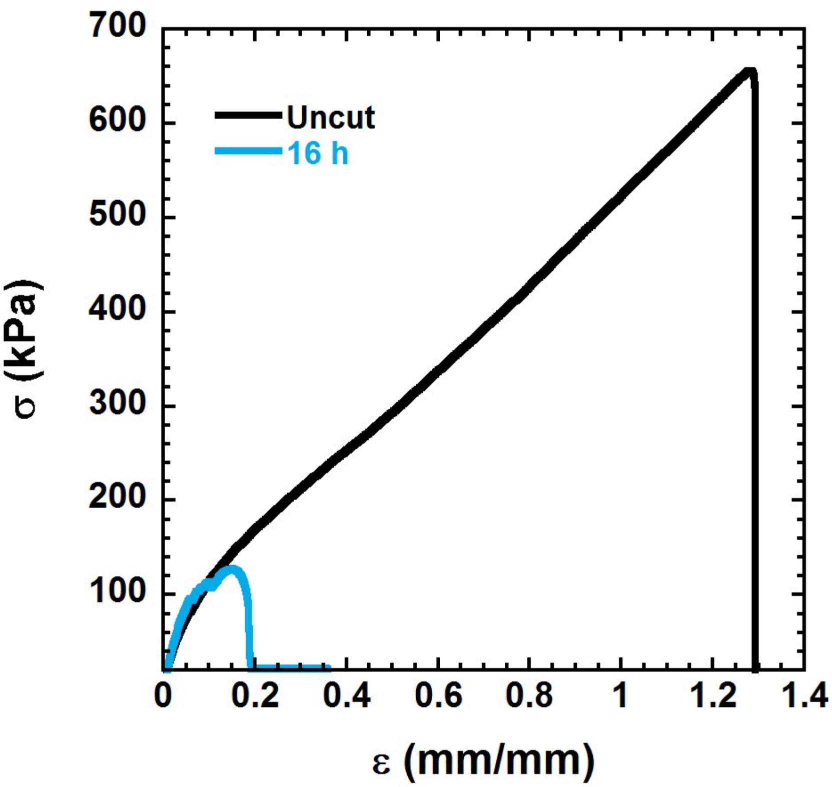


Figure S30: Self-healing properties of FRP-PEA-4%DVB material after healing at 90 °C

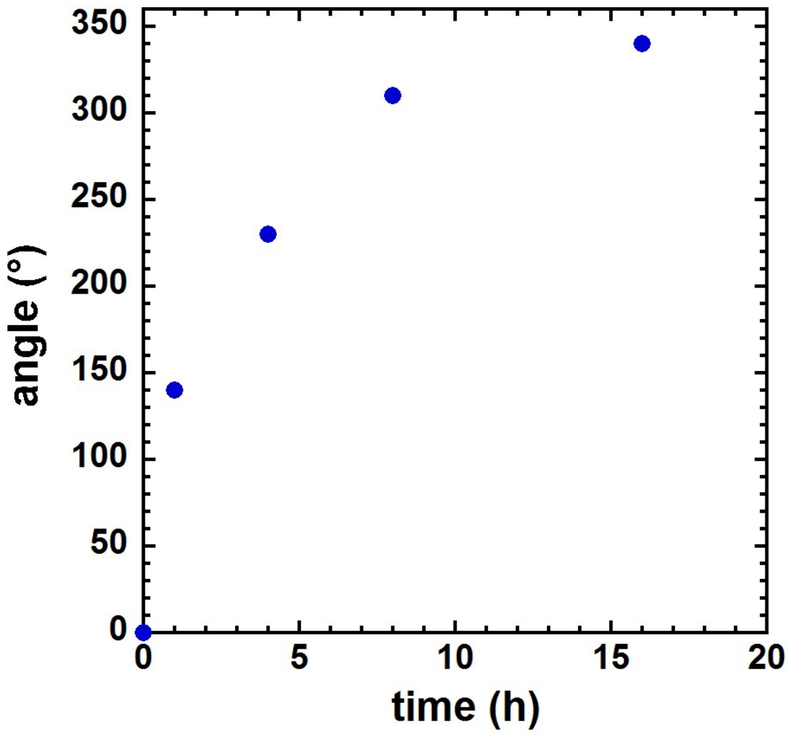


Figure S31: Malleability of PEA_{50}-$TM_{1.5}$-$EGDMA_1$ materials at different time periods, performed in 90 °C.

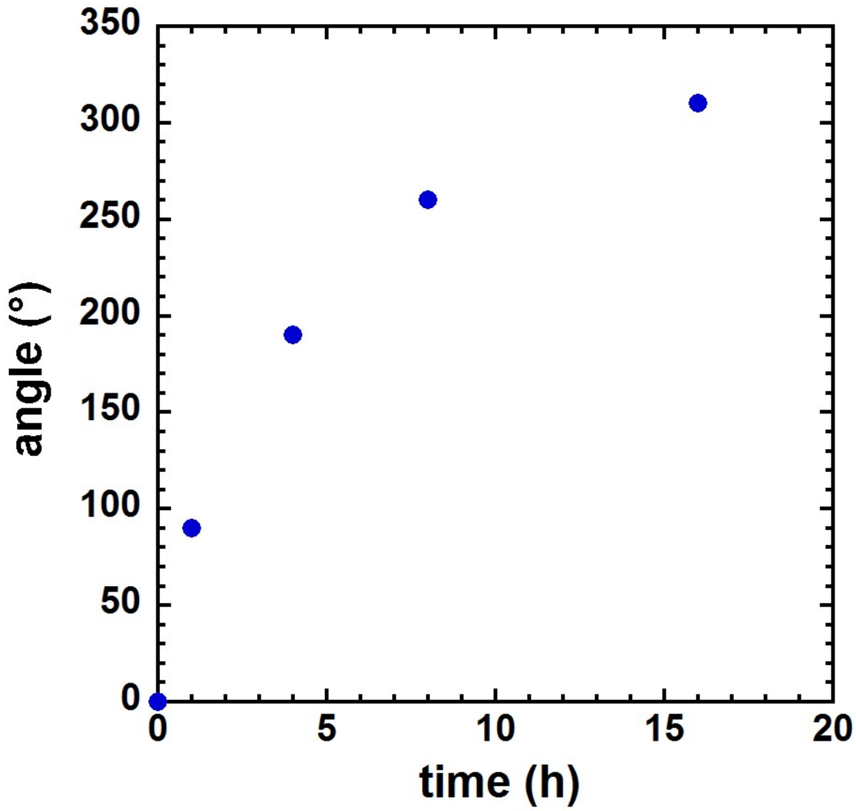


Figure S32: Malleability of PEA_{100}-TM_6-$EGDMA_1$ materials at different time periods, performed in 90 °C.

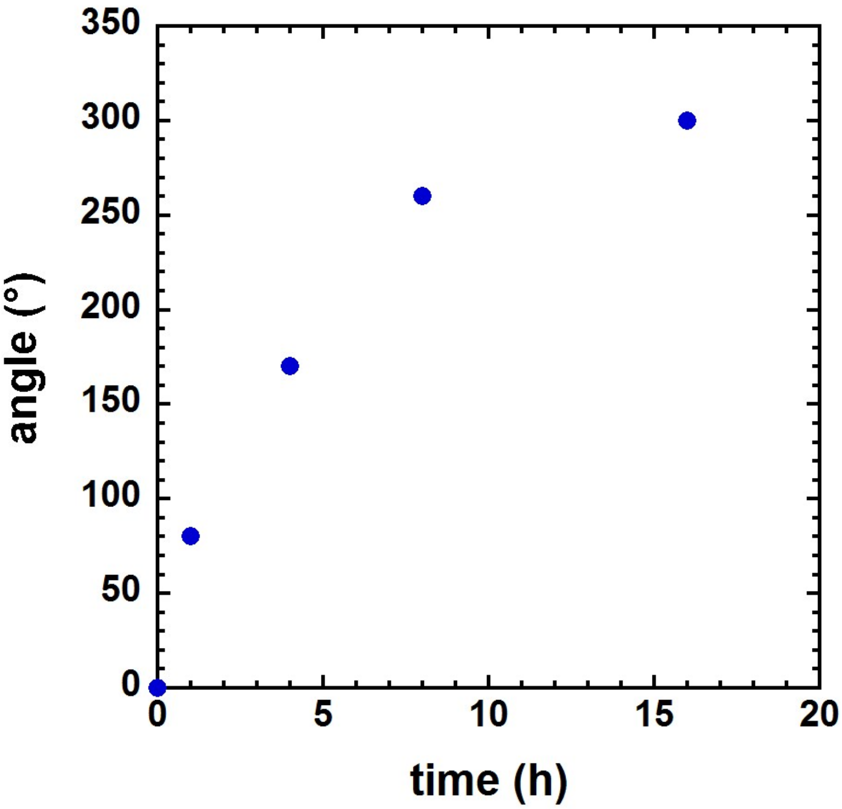


Figure S33: Malleability of PEA_{50}-TM_3-$EGDMA_0$ materials at different time periods, performed in 90 °C.

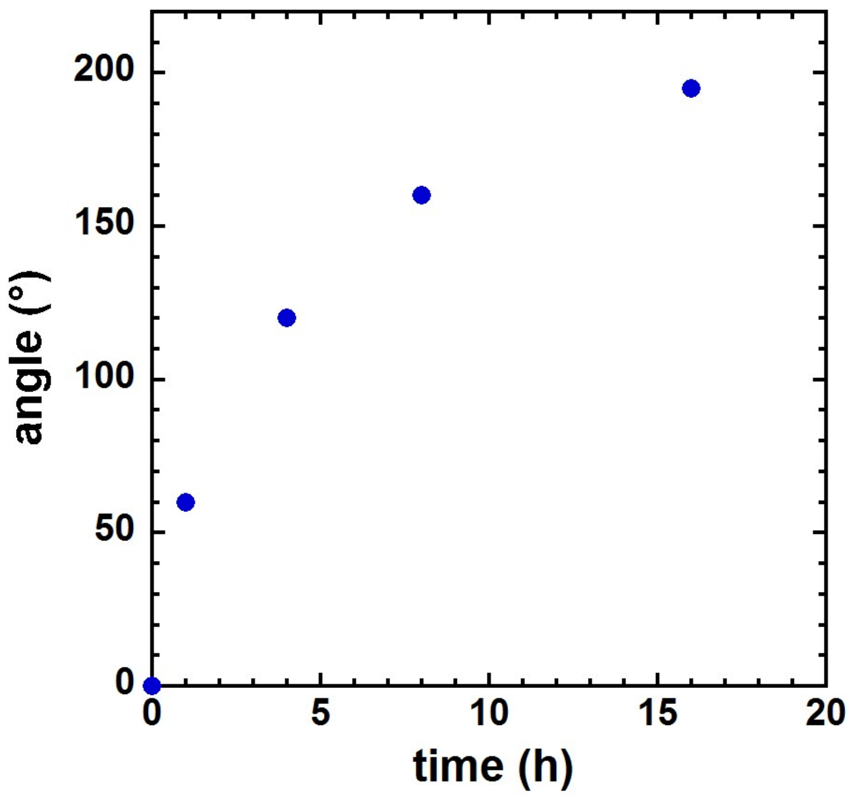


Figure S34: Malleability of PEA_{50}-TM_5-$EGDMA_1$ materials at different time periods, performed in 90 °C.

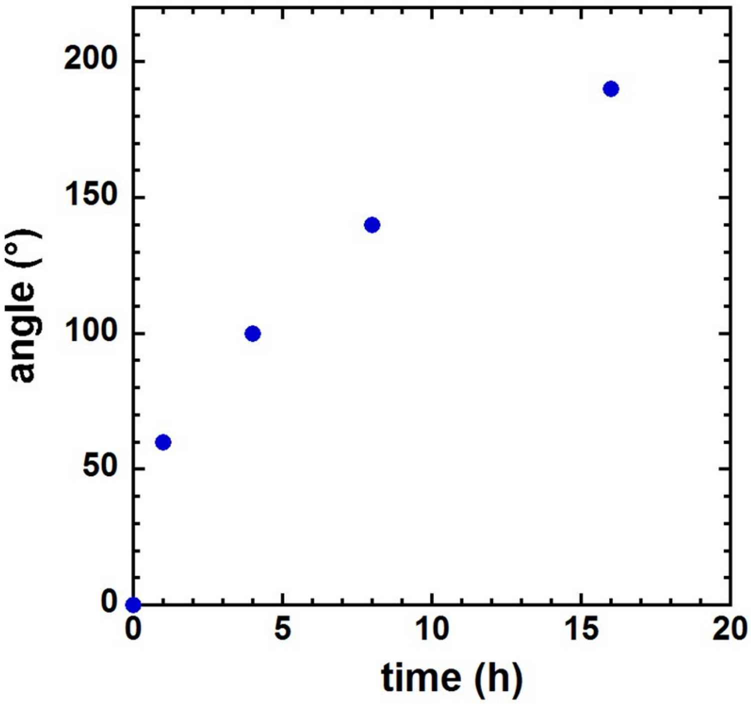


Figure S35: Malleability of PEA_{50}-TM_5-$EGDMA_0$ materials at different time periods, performed in 90 °C.

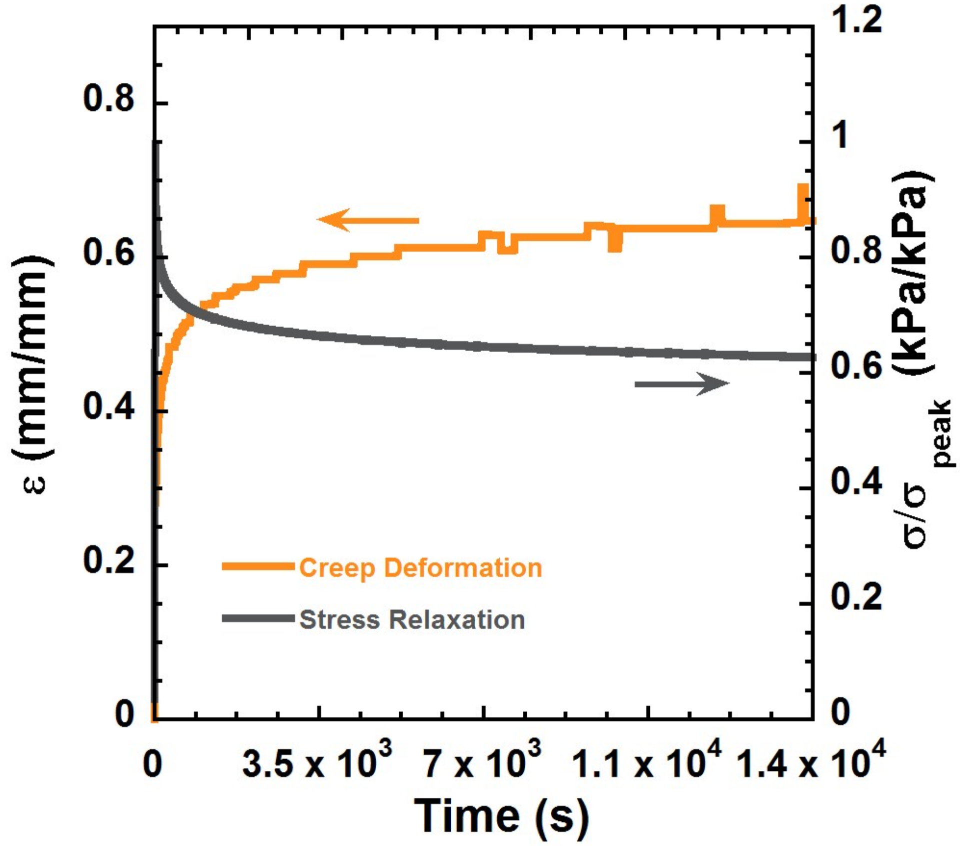


Figure S36: Stress relaxation and creep deformation of PEA_{50}-$TM_{1.5}$-$EGDMA_1$ material as a function time

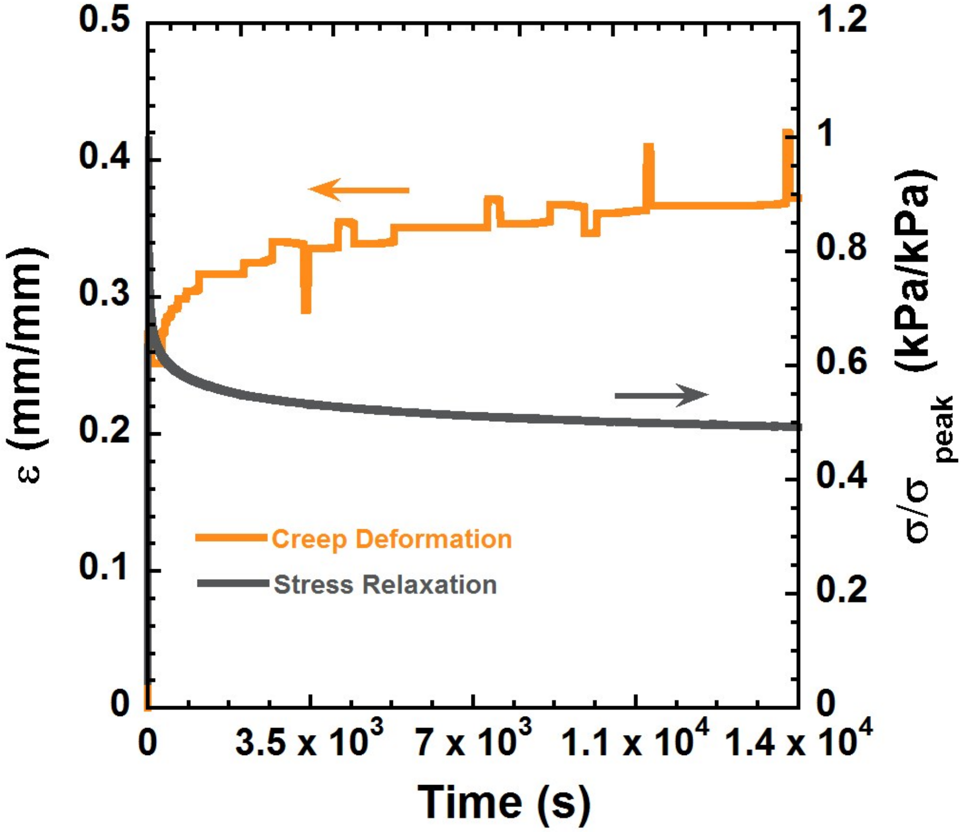


Figure S37: Stress relaxation and creep deformation of PEA_{100}-TM_{6}-$EGDMA_{1}$ material as a function time

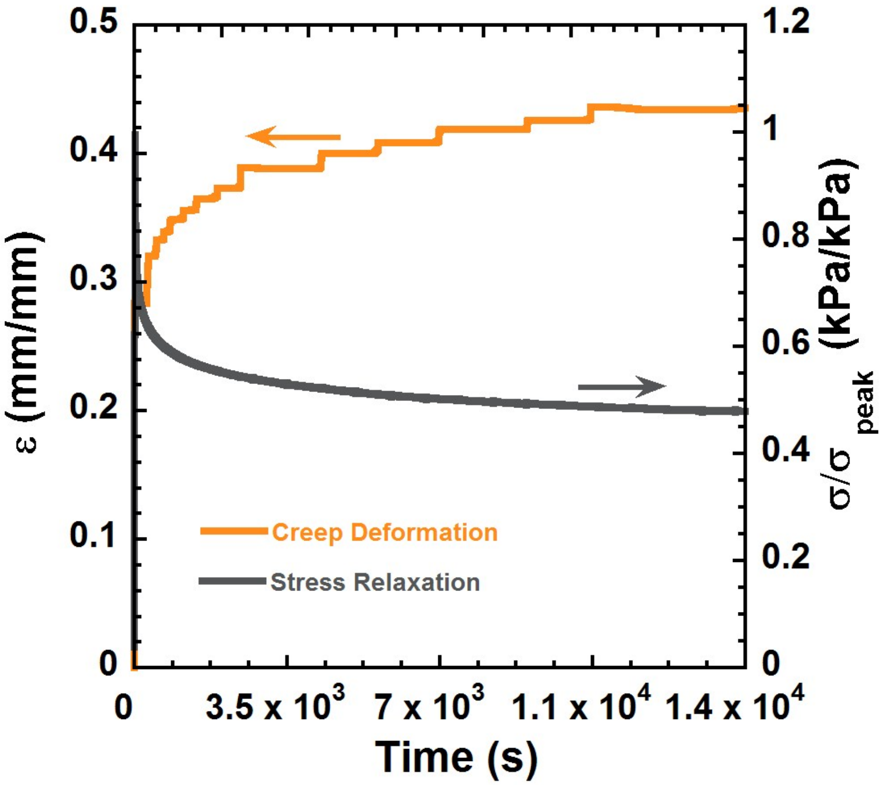


Figure S38: Stress relaxation and creep deformation of PEA_{50}-TM_3-$EGDMA_0$ material as a function time

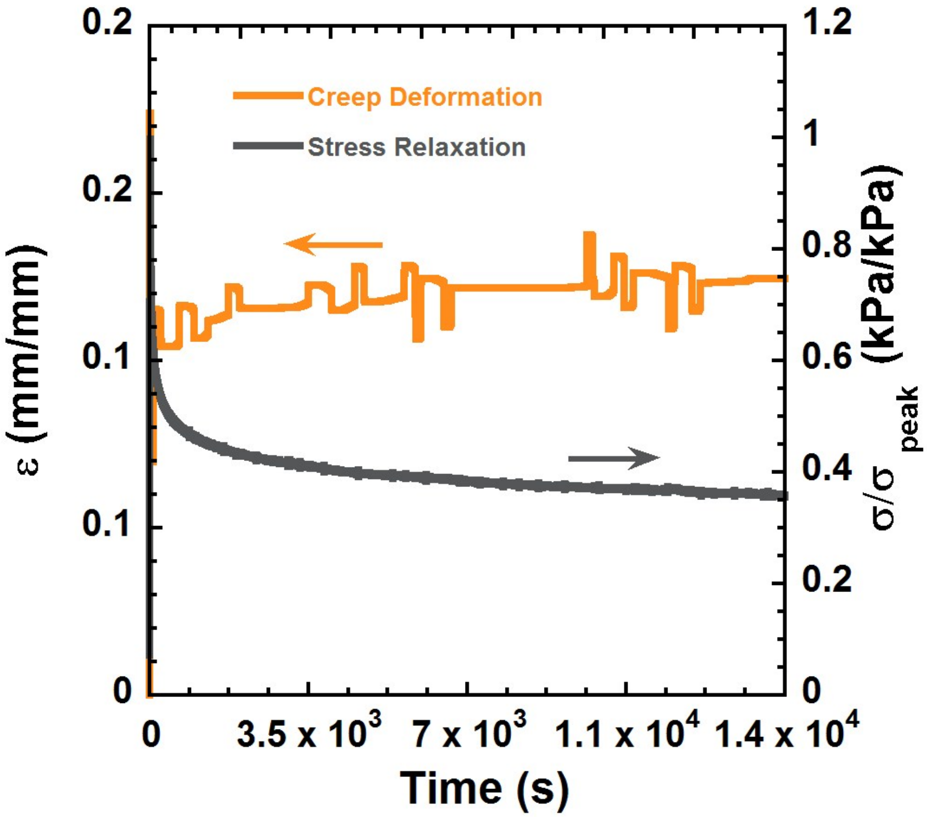


Figure S39: Stress relaxation and creep deformation of PEA_{50}-TM_5-$EGDMA_1$ material as a function time

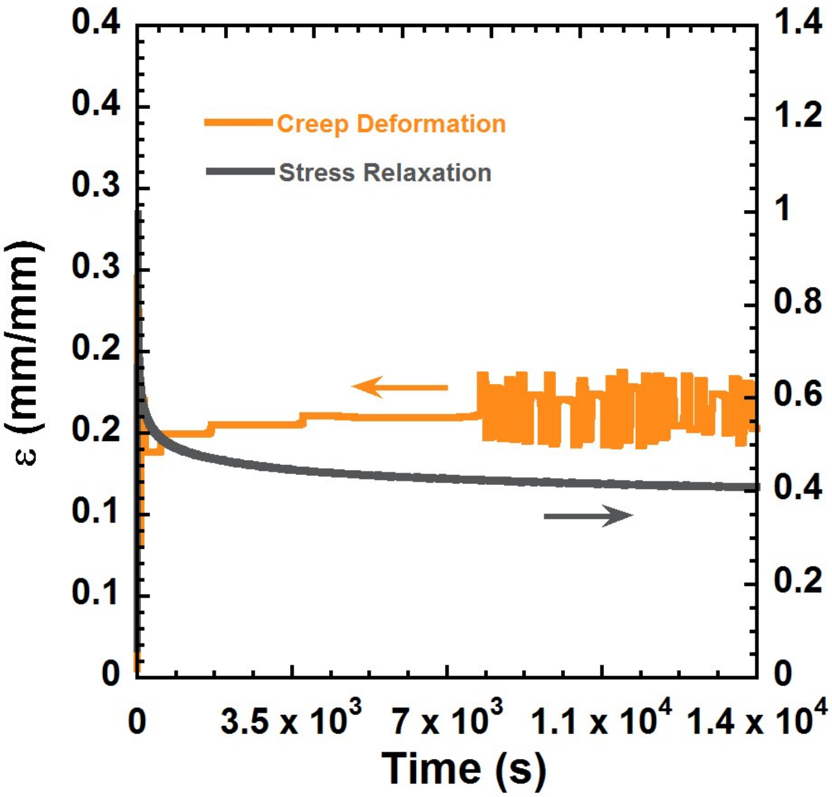


Figure S40: Stress relaxation and creep deformation of PEA_{50}-TM_5-$EGDMA_0$ material as a function time

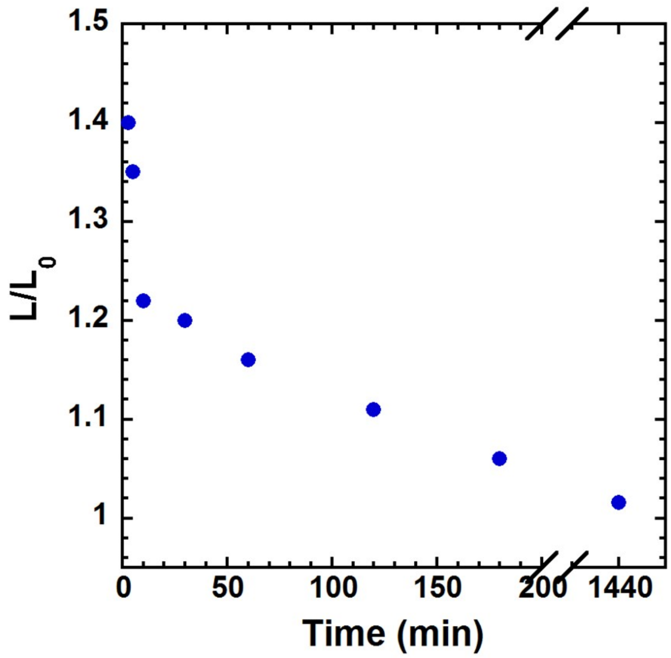


Figure S41: Creep recovery of PEA_{50}-$TM_{1.5}$-$EGDMA_1$ material as a function of time after releasing from 100% strain for 2 days.

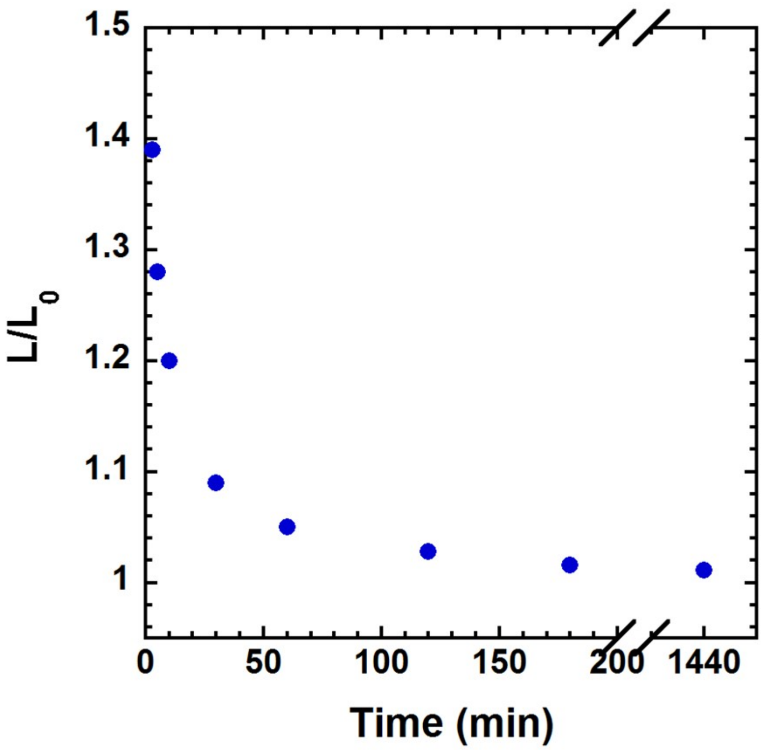


Figure S42: Creep recovery of PEA_{100}-TM_6-$EGDMA_1$ material as a function of time after releasing from 100% strain for 2 days.

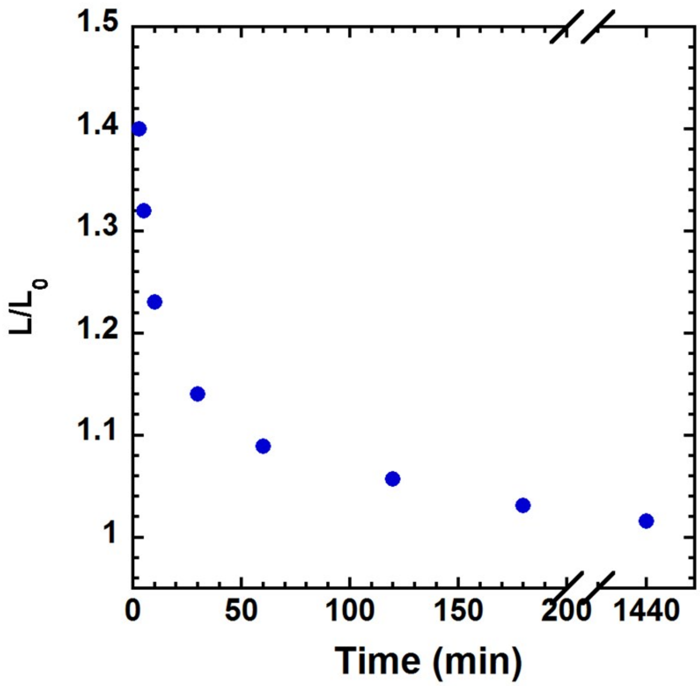


Figure S43: Creep recovery of PEA_{50}-TM_3-$EGDMA_0$ material as a function of time after releasing from 100% strain for 2 days.

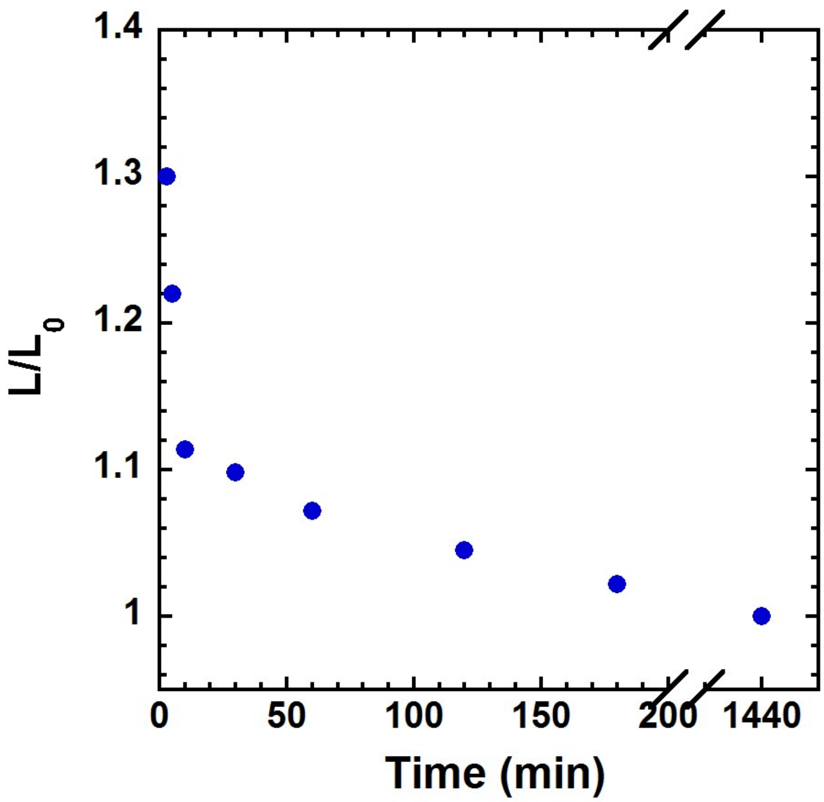


Figure S44: Creep recovery of PEA_{50}-TM_5-$EGDMA_1$ material as a function of time after releasing from 100% strain for 2 days.

Figure S45: Creep recovery of PEA_{50}-TM_{5}-$EGDMA_{0}$ material as a function of time after releasing from 100% strain for 2 days.

References

1. B. Zhang, P. Chakma, M. P. Shulman, J. Ke, Z. A. Digby and D. Konkolewicz, *Org. Biomol. Chem.*, 2018, **16**, 2725-2734
2. D. R. Palleros, *Experimental organic chemistry*, Wiley & Sons, 2000.
3. E. Vargün and A. Usanmaz, *J. Polym. Sci., Part A: Polym. Chem.*, 2005, **43**, 3957-3965.
4. L. Wang, W. Dong and Y. Xu, *Carbohydrate Polymers*, 2007, **68**, 626-636.