Electronic Supplementary Information for: A robust and reproducible procedure for cross-linking thermoset polymers using molecular simulation

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Methodological Details

Partial Atomic Charge Calculation

First, we generated a structure for each of the two monomers, EPON-862 and DETDA, in isolation. Note that for EPON-862 we model the 'activated' form of the structure, following Li and Strachan[1]. The activation of EPON-862 was captured by breaking the epoxide bonds (C-O) at both ends of the molecule, with subsequent hydrogenation of these exposed atomic sites. Herein, we denoted the activated form of EPON-862 merely as EPON. These two initial molecular structures (EPON and DETDA) were built from scratch using the freely-available Avogadro[2] software package, and then subjected to geometry optimization using the generalised Amber FF (GAFF)[3] (chosen because of its availability in Avogadro). The convergence criterion at this step was met when the potential energy difference between two successive steps dropped to below 10^{-8} kJ mol^{-1}. Structures of these two molecules are provided in Figure 2 of the main text. The resulting molecular structures of the EPON and DETDA molecules were used to calculate the atomic partial charges, as outlined below.

Unreacted molecules

For the calculation of the partial atomic charges of the unreacted molecules, we tested two procedures: calculation of charges for a single (effectively isolated) molecule *in vacuo*, and, calculation of charges for a molecule in the condensed phase. Note that both sets of conditions involved 3-D periodic boundary conditions in the calculation of the charges. In the former case, the single geometry-optimised molecule (either EPON or DETDA) was placed in the centre of a cubic simulation cell of dimensions $200 \times 200 \times 200$ Å^3. In the latter case, by the term 'condensed phase', we refer to a system that contains 16 EPON and 8 DETDA molecules placed in a simulation cell with dimensions $40 \times 40 \times 40$ Å^3. We used the PACKMOL software package[4] to randomly place these geometry-optimized molecules in the cell prior to the charge calculation. For the QEq calculation, the partial charges were calculated to a tolerance of 10^{-6}, with taper radius high and low values of 10.0 and 0.0 Å respectively, using the "*fix qeq/reax*" command in LAMMPS . For each element (C, H, O, N) we specified values of the atomic electronegativity (χ, eV), the self-Coulomb potential (η, eV) and the valence orbital exponent (γ, dimensionless). These parameters for our epoxy system were taken from Refs.[5–8]. These values are provided in Table S1 of the ESI†.

For the calculation of the partial atomic charges in each case, we averaged the partial charges for each unique type of atomic environment. The labelling system that illustrates each unique atomic environment is provided in Figure S1 of the ESI†. In the case of the 'condensed phase' calculation, we first averaged over all unique sites in each molecule, and then averaged these over all instances of the same molecule type (either EPON or DETDA).

Reacted molecules

Since the chemical environment of the atoms in the immediate (and possibly more distant) vicinity of the cross-link bond changes after the cross-link bond is formed, the partial atomic charge distribution for the reacted EPON/DETDA molecule may be different to their counterparts for the unreacted molecules. To account for this, the partial atomic charges after cross-linking were also calculated. The EPON molecules were bonded with one DETDA molecule by cross-linking them manually using Avogadro[2]. For the primary amine reaction, one DETDA molecule was reacted with two EPON molecules (see Figure 3 in the main text), one located on each nitrogen site of the DETDA. For the secondary amine reaction, we bonded four

EPON molecules to a single DETDA molecule (see Figure S2 in the ESI[†]). In each case (primary and secondary amine reaction) the resulting structure was geometry-optimised following the same optimisation procedure as described above for the individual EPON and DETDA molecules.

Partial atomic charges were calculated over the reacted EPON/DETDA model as described above for the individual molecules. Based on our results for the unreacted molecules, we chose to use the 'isolated' *in vacuo* configuration, again placing the molecule in the centre of a $200 \times 200 \times 200$ Å^3 periodic cubic cell. The same settings for the charge equilibration calculation were used as described above. Again, we averaged the atomic partial charges over all unique atomic environments, following the same labelling scheme as shown in Figure S1 in the ESI[†].

vdW Potentials for Pure Liquid Simulations

vdW interactions can be captured using different analytical forms; *e.g.* Lennard-Jones (LJ) and Buckingham (X6) potentials. Equations 1 and 2 show the LJ and X6 potentials, respectively. The main difference between LJ and X6 potentials is found in the repulsive term. To investigate the performance of these two forms, we conducted MD simulations on our pure liquid samples using both forms of the vdW interaction.

$$E_{LJ} = 4\varepsilon \left[(\frac{\sigma}{r})^{12} - (\frac{\sigma}{r})^6 \right] \tag{1}$$

$$E_{Buckingham} = \left[A \exp(\frac{-r}{\rho}) - \frac{B}{r^6} \right] \tag{2}$$

In Equations 1 and 2, σ is the inter-atomic distance at which the LJ potential between a given atom pair is zero and r is the distance between the atom pair. ε is the minimum energy as a function of atom pair separation, which is also called the well depth. A, B, and ρ are constants of the Buckingham potential. The A and B parameters are a function of ξ, which is a dimensionless scaling parameter. There are two options for the implementation of the Buckingham potential, based on the value of the ξ parameter: 1) $\xi = 12$ (denoted here as $X6_{const}$) for all atoms, and 2) $\xi = 12$ to 14.444 (denoted here as $X6_{var}$)[9], depending on the atom type. In the case of $X6_{var.}$, each different atom has a different ξ value within the range stated above. These were H: 12.382, C: 14.034, N: 13.843 and O: 13.483.

Table S1: Atomic parameters, electronegativity (χ, eV), the self-Coulomb potential (η, eV) and the valence orbital exponent (γ, dimensionless), used in our QEq partial charge calculations.

Element	χ	η	γ
C	5.7254	13.8470	0.8712
H	3.8446	20.1678	0.8910
O	8.5000	14.2824	0.8712
N	6.7768	13.6070	1.0512

Table S2: Ideal bond-lengths (Å) and bond force constants (kcal mol^{-1} Å^{-1}) for the C–N cross-link bond, as a function of the relaxation protocol used in our cross-linking procedure.

Relaxation Step	Force constant	Ideal bond length
step 1	1	3
step 2	10	2.75
step 3	50	2.5
step 4	100	2.25
step 5	200	2
step 6	250	1.75
step 7	300	1.5
step 8	350	1.462

Table S3: Partial atomic charges calculated using the 'vacuum' (isolated) systems, for both EPON and DETDA. The labels refer to those shown in Figure S1 of the ESI.

| Atom type	Charge (esu)
C1	-0.1429
C2	-0.0307
C3	0.2454
C4	-0.0728
C5	-0.3161
C6	-0.1832
C7	-0.3306
C8	-0.3576
C9	0.1388
C10	-0.0400
C11	0.2704
C12	-0.1339
C13	0.0439
C14	-0.2600
H1	0.1133
H2	0.2734
H3	0.1087
H4	0.1342
H5	0.3573
H6	0.1208
O1	-0.5994
O2	-0.5168
N1	-0.7496
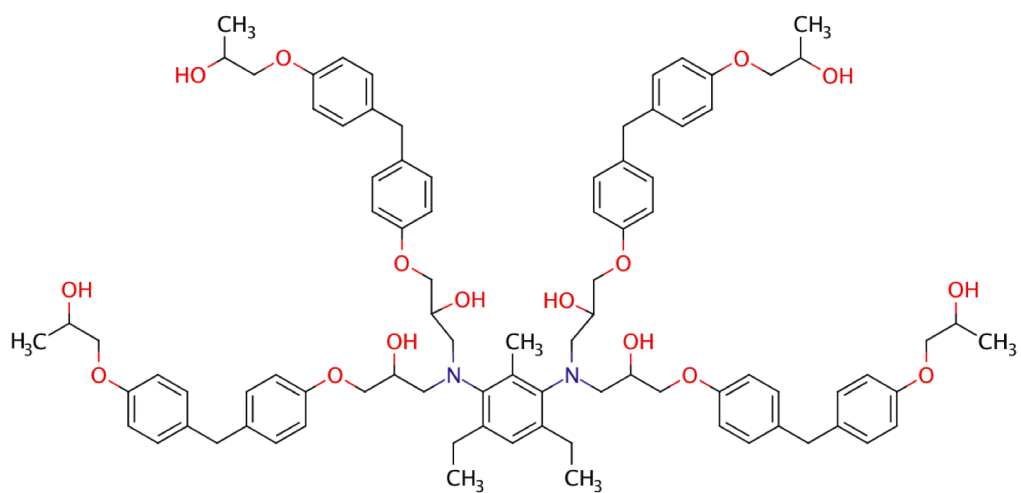
Figure S1: Product of the reaction between four EPON molecules and the secondary amine of the DETDA molecule.
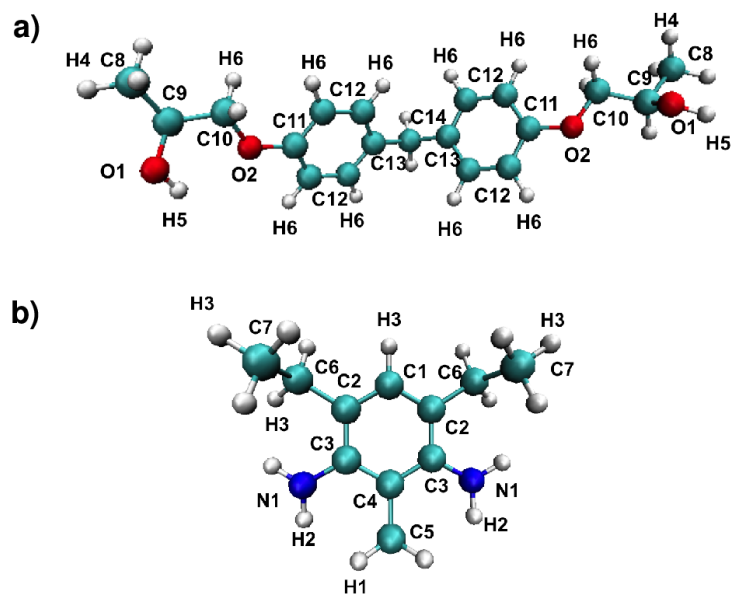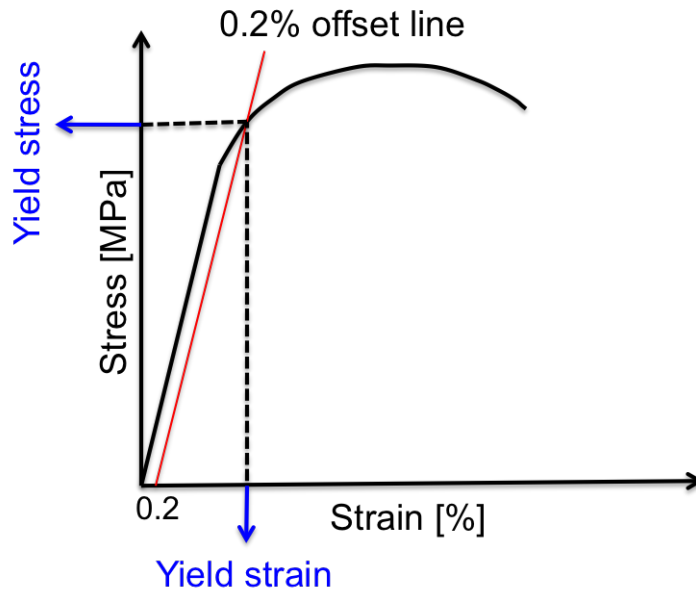
Figure S2: Labels for unique atomic environments in a) the EPON molecule and b) the DETDA molecule.
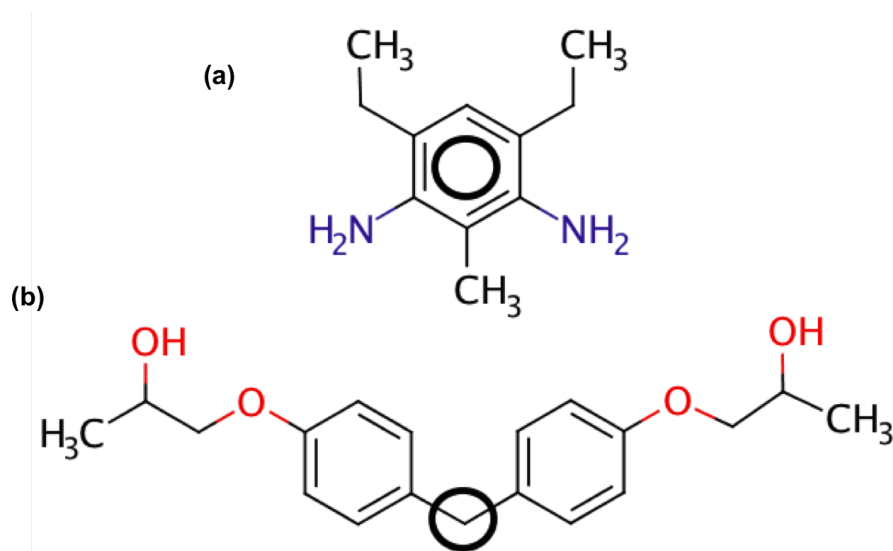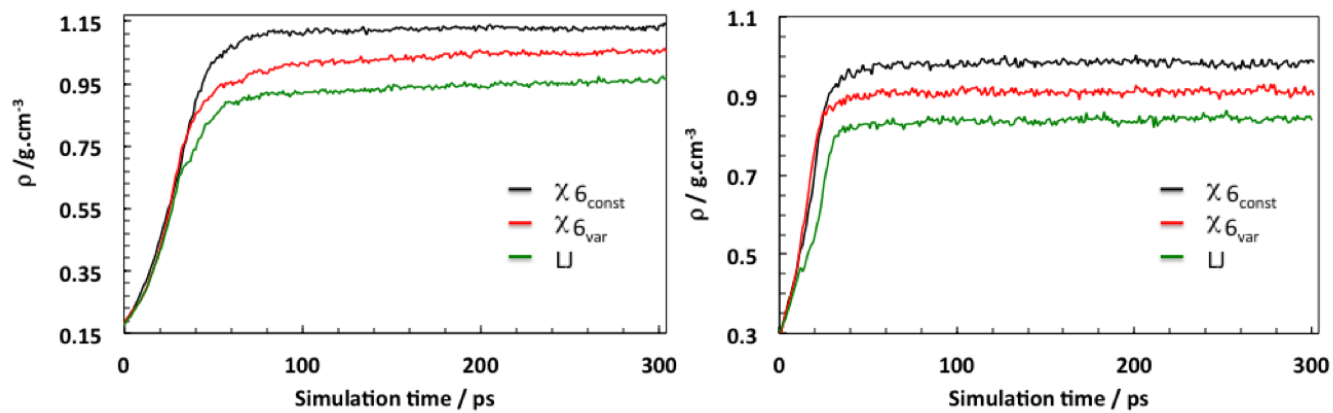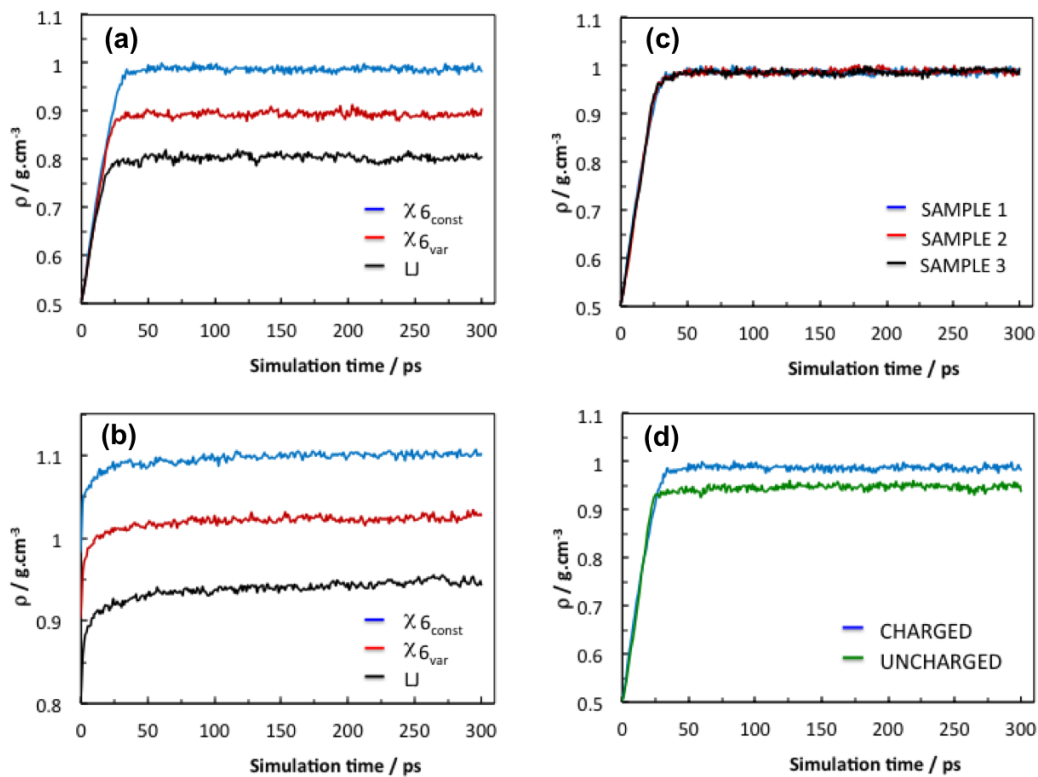
Figure S3: Reference sites on EPON and DETDA used for calculation of radial distribution functions (RDFs).

Figure S4: Illustration of the yield strength and strain calculated using the convention of the 0.2% offset line.

Figure S5: Density of (a) pure EPON and (b) pure DETDA, at 300 K and 1 atm.

Figure S6: Density of the liquid precursor mixture at (a) 500 K and 1 atm (b) 300 K and 1 atm. Densities at (c) 500 K and 1 atm for three independently-generated samples. (d) Densities of systems with and without partial atomic charges at 500 K and 1 atm.
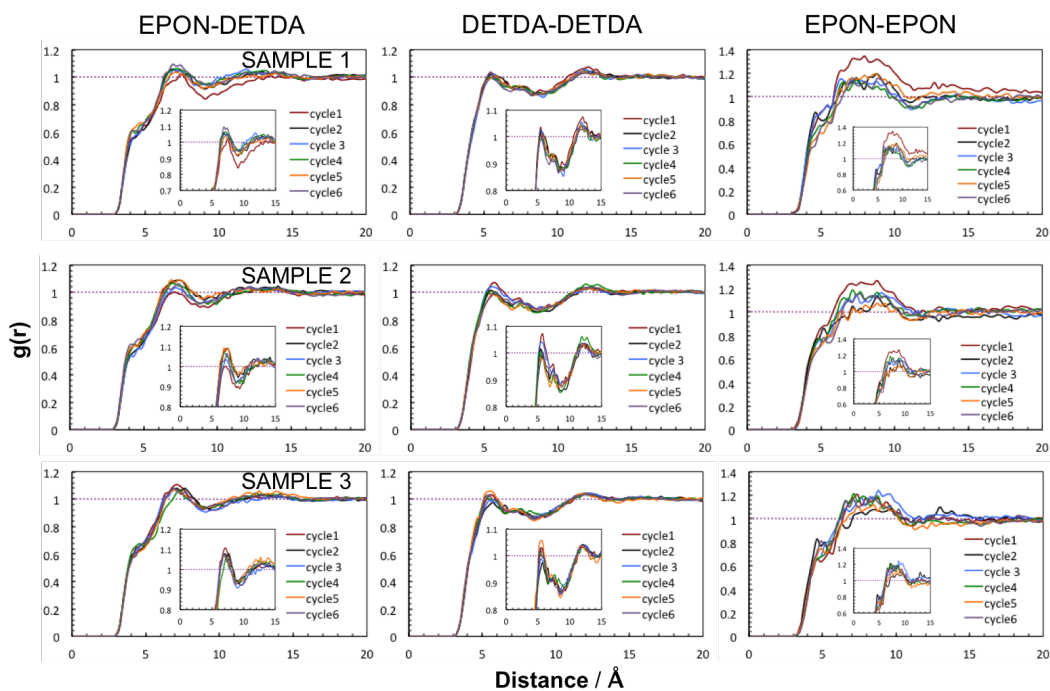
Figure S7: Evolution of the RDFs calculated for the liquid precursor mixture at 500 K, as a function of the six simulated annealing cycles: from left to right show the RDFs between EPON-DETDA, DETDA-DETDA and EPON-EPON, for our three independently-generated samples.
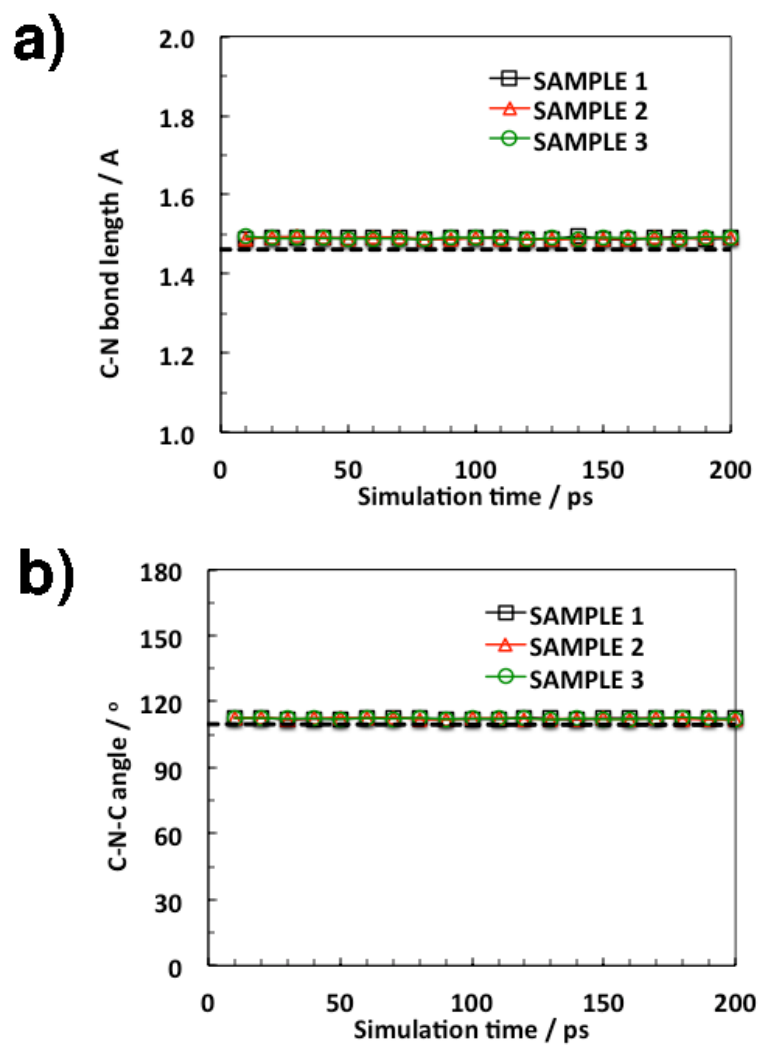
Figure S8: (a) Bond lengths of the epoxy polymer cross-link bonds, and (b) bond angles between the C-N-C atoms of the cross-link bonds for the relaxed cross-linked samples at 78% degree of cross-linking.
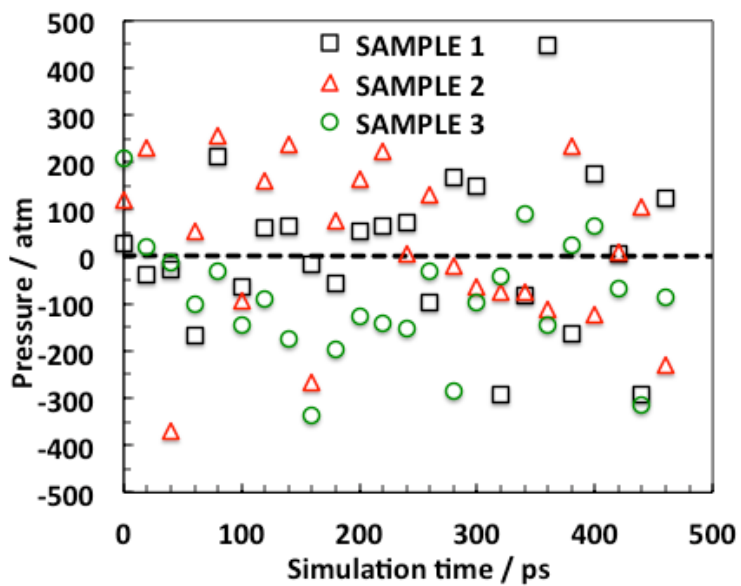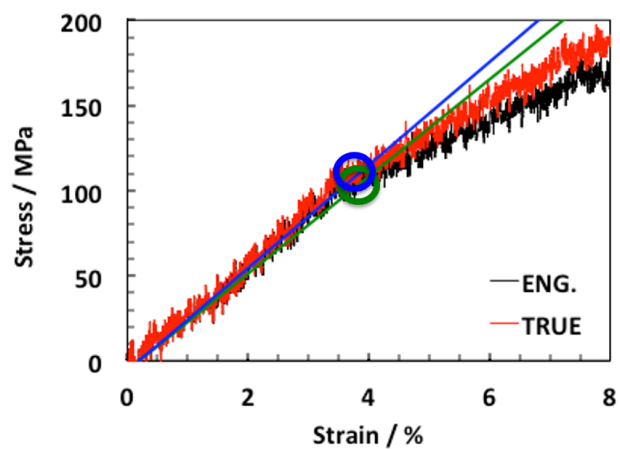
Figure S9: Calculated pressure of the sample after the cross-linking process. Dashed line indicates the target pressure, 1 *atm*.
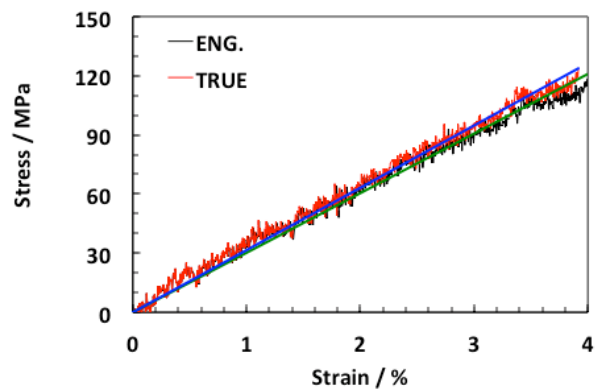
Figure S10: Predicted mechanical properties of the epoxy polymer with a 78% cross-linking degree showing Young's modulus plot.

Figure S11: Predicted mechanical properties of the epoxy polymer with a 78% cross-linking degree showing yield strength and yield strain calculated via the 0.2% offset line.

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