Supporting Information

Molecular Dynamics Investigation of the Structural and Mechanical Properties of Off-Stoichiometric Epoxy Resins

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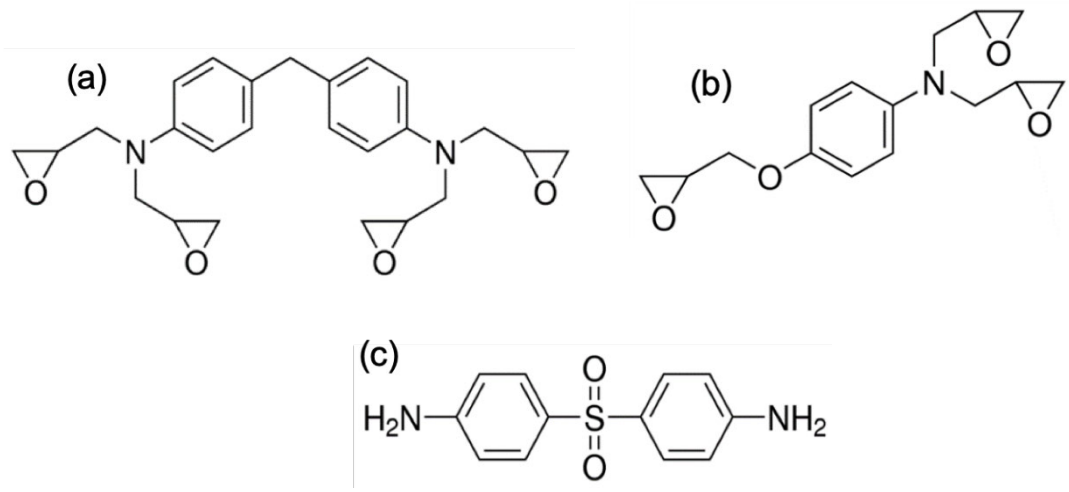

Figure *S1*. Chemical structures of components in the API-60 resin: (a) the tetrafunctional epoxy (E_4), 4,4'-methylenebis(N,N-diglycidylaniline) (TGDDM), (b) the trifunctional epoxy (E_3), N,N-diglycidyl-4-glycidyloxyaniline (TGAP), and (c) the tetrafunctional hardener (H_4), 4-4'-diaminodiphenyl sulfone (DDS).

Table *S1*. Number of molecules and molecular weight fractions (wt %) as a function of the offset ratio *r*. The subscription represents the number of functionalities.

r	# of E_4	# of E_3	# of H_4	# of atoms	wt% of E_4	wt % of E_3	wt % of H_4
0.3	319	121	123	31023	67.8	16.8	15.4
0.5			205	33401	61.8	15.4	22.9
0.8			327	36939	54.3	13.6	32.1
1.0			410	39346	50.2	12.5	37.3
1.5			614	45262	42.2	10.6	47.0
2.0			819	51207	36.6	9.1	54.3
2.5			1024	57152	32.2	8.1	59.7
3.0			1229	63097	28.5	7.1	64.4

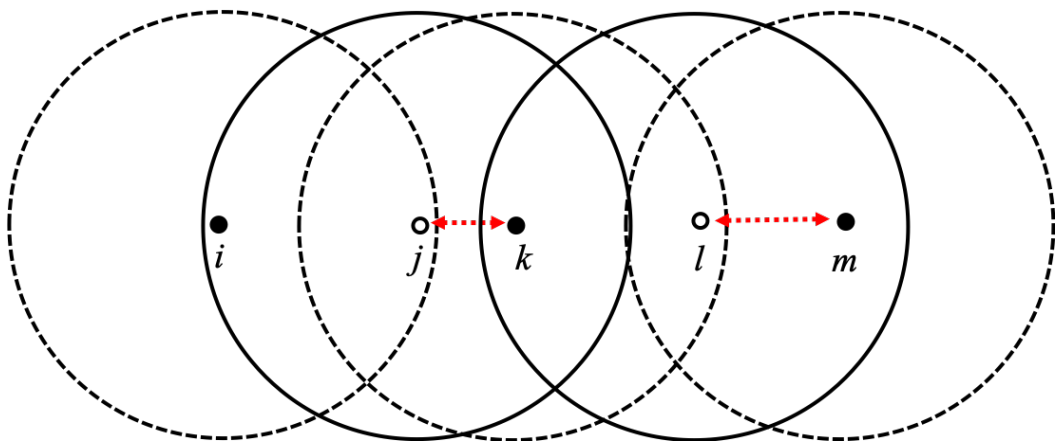

Figure *S2*. The 1-D schematic figure of the search criterion in which atoms are reacted with their counter pairs. All atoms have the same search radii. Although atoms *j* and *k* are involved in multiple possible bond partners *i*-*j*, *j*-*k*, and *k*-*l*, only the *j*-*k* pair is eligible to be reacted.

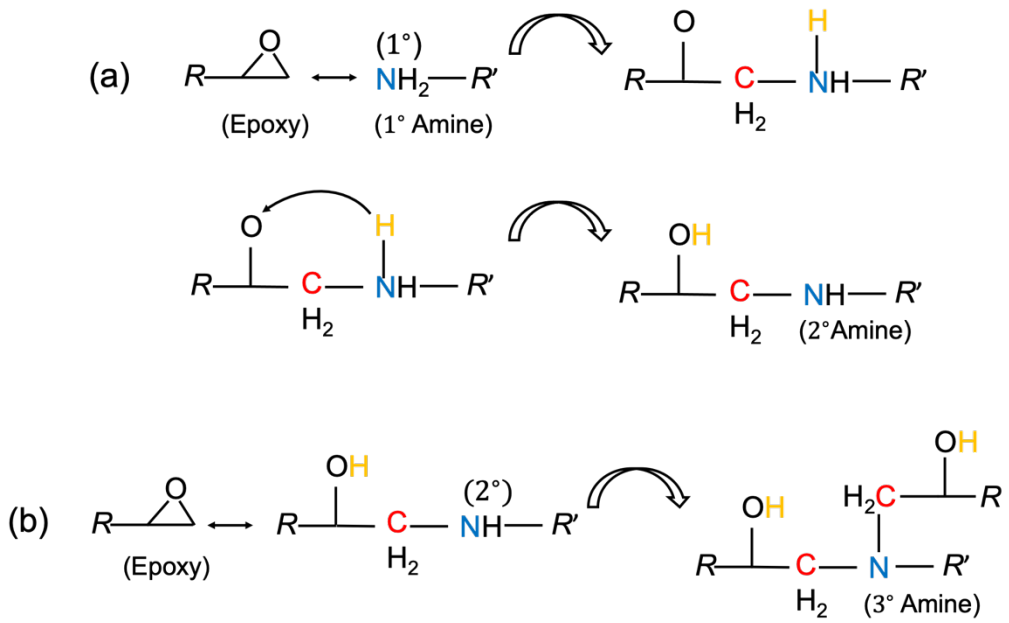

Figure *S3*. The crosslinking algorithm for (a) primary amine to epoxy reaction turning into secondary amine and (b) secondary amine to epoxy reaction turning into tertiary amine.

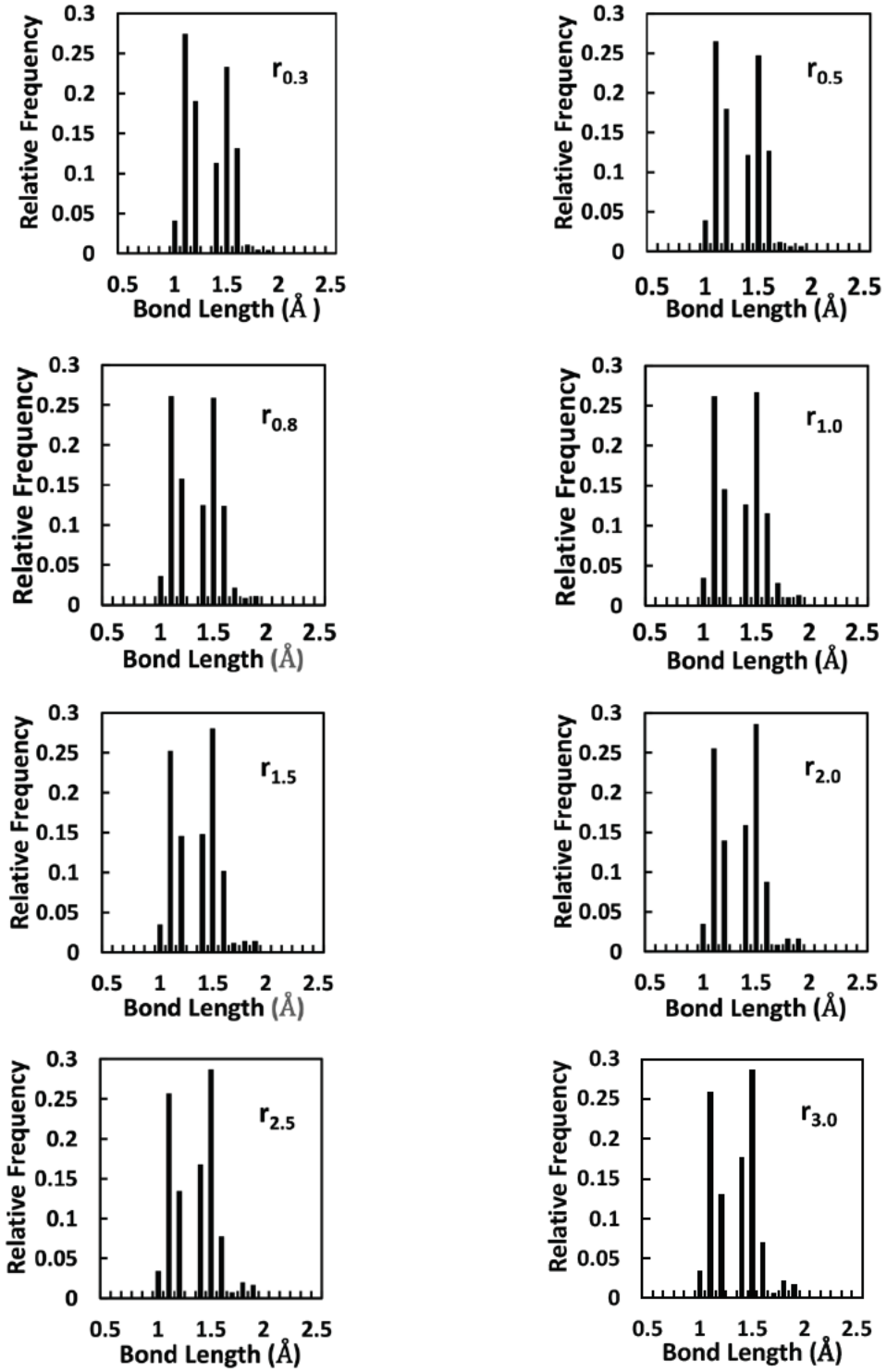

FIG. *S4*. Bond length distributions after cure and equilibration.

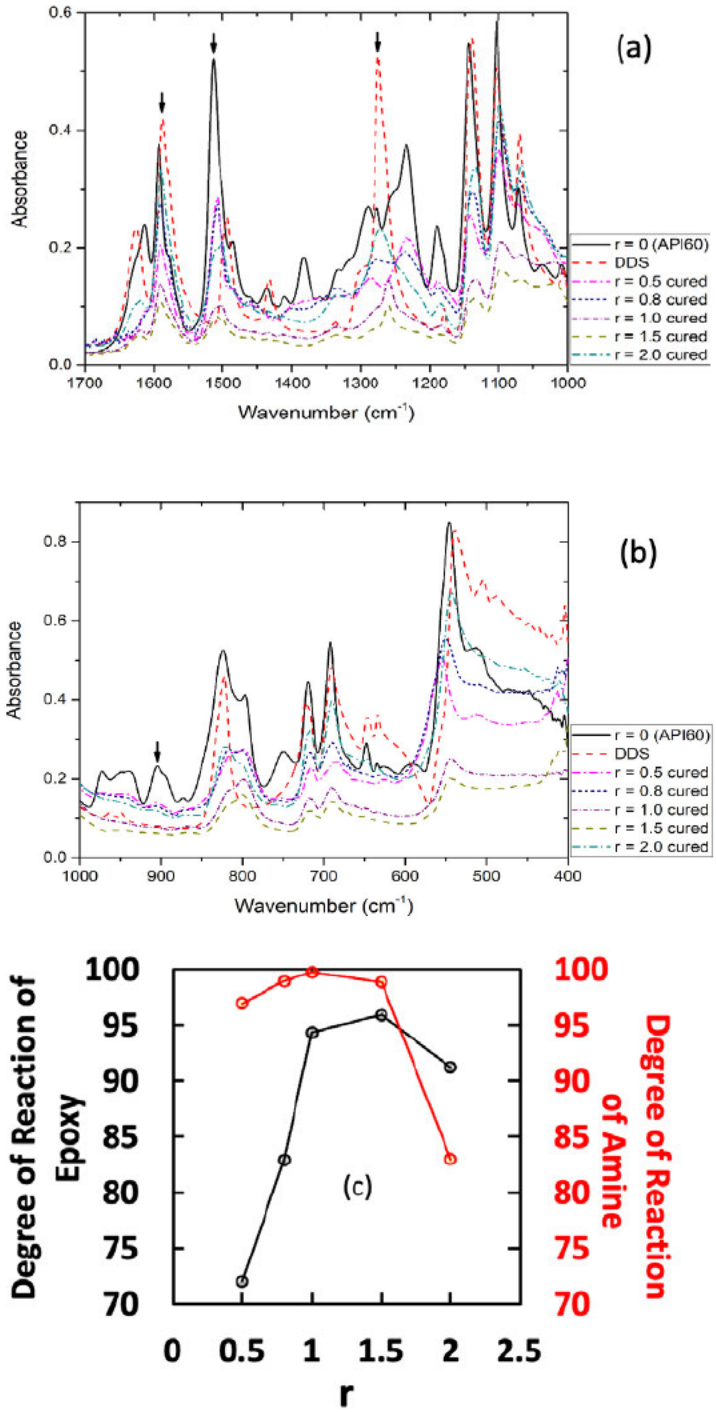

FIG. *S5*. FT-IR spectra of API60 epoxy resin, DDS and cured resin with various ratio of *r*. Experimental degree of reaction of epoxy and degree of reaction of amine hardener analyzed by a FT-IR spectroscopy.

Table *S2*. Average calculated mass density and volume contraction as a function of the offset ratio *r*.

r	Uncured Liquid Resin Density, g/cm^3	Cured Solid Resin Density, g/cm^3	Volume Shrinkage, %
0.3	1.1227±0.0012	1.1554±0.0020	3.2750
0.5	1.1416±0.0015	1.1851±0.0029	4.3538
0.8	1.1623±0.0013	1.2469±0.0355	8.4634
1.0	1.1780±0.0010	1.2607±0.0282	8.2665
1.5	1.2024±0.0009	1.2586±0.0066	5.6254
2.0	1.2233±0.0019	1.2768±0.0024	5.5942
2.5	1.2346±0.0014	1.2868±0.0012	5.2210
3.0	1.2473±0.0012	1.2959±0.0030	4.8625

Table *S3*. Measured experimental mass density of uncured and cured resin as a function of the various ratio of *r*.

r	Uncured Liquid Resin Density, g/cm^3	Cured Solid Resin Density, g/cm^3	Volume Shrinkage, %
0.5	1.229±0.007	1.284±0.001	4.302
0.8	1.228±0.003	1.290±0.001	4.796
1.0	1.230±0.004	1.292±0.001	4.841
1.5	1.244±0.011	1.305±0.002	4.614
2.0	-	1.310±0.001	-

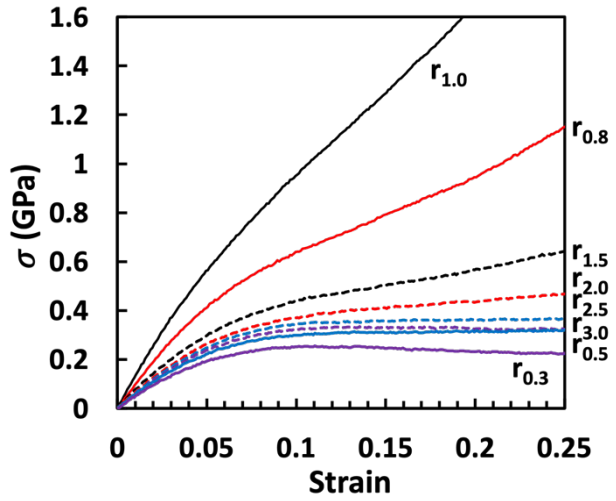

Figure *S6*. Stress-strain curves computed from uniaxial tension simulation at the strain rate of 10^9 s^{-1} at 300 K. The stress response varied with the r values.

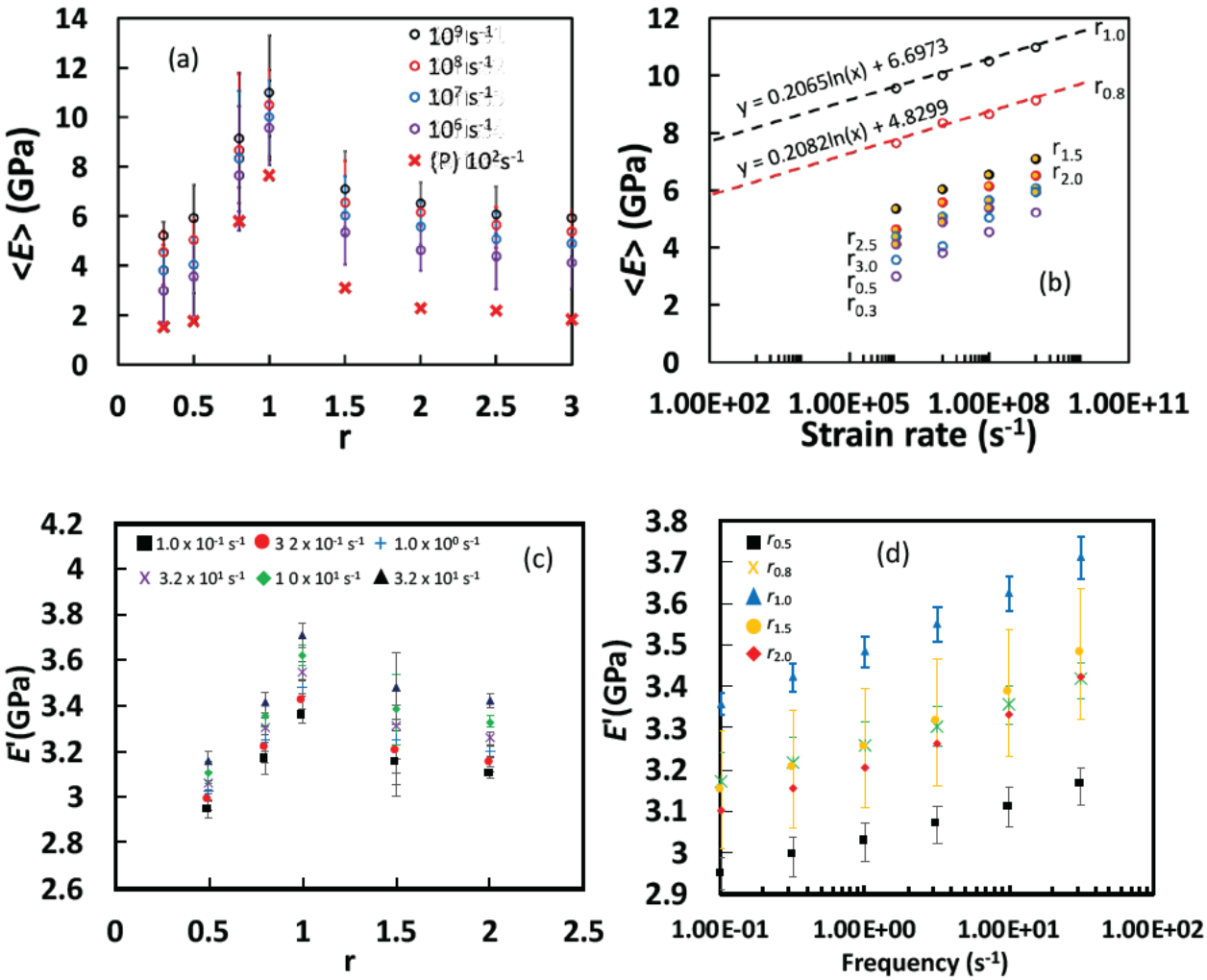

FIG. *S7*. (a-b) MD calculation of average Young's modulus as a function of mixing ratio r and strain rate. (c-d) Measured elastic modulus as a function of mixing ratio r and frequency.

Table *S4*. Computed Young's modulus as a function of the strain rate in the offset ratio *r*. The predictive *E* values at 10^2 s^{-1} are calculated from fitting the simulation results.

	<*E*> (GPa)				
r	10^9 s^{-1}	10^8 s^{-1}	10^7 s^{-1}	10^6 s^{-1}	***(p)10^2 s^{-1}***
0.3	5.21±0.46	4.55±1.08	3.81±0.87	2.99±1.12	***1.54***
0.5	5.92±0.51	5.04±1.16	4.03±0.79	3.57±0.95	***1.76***
0.8	9.13±2.34	8.65±2.54	8.33±2.41	7.63±2.43	***5.79***
1.0	10.98±2.13	10.49±1.52	10.01±1.53	9.55±1.24	***7.64***
1.5	7.08±0.77	6.53±1.19	6.03±1.45	5.35±1.19	***3.11***
2.0	6.51±0.53	6.14±0.84	5.57±1.38	4.63±0.91	***2.29***
2.5	6.07±0.41	5.64±0.36	5.07±0.54	4.38±0.46	***2.18***
3.0	5.92±0.47	5.38±0.69	4.89±0.75	4.11±0.62	***1.82***

Table *S5*. Measured experimental elastic modulus as a function of the frequency in the offset ratio *r*.

	<*E'*> (GPa)					
r	1.0×10^{-1} s^{-1}	3.2×10^{-1} s^{-1}	1.0×10^{0} s^{-1}	3.2×10^{0} s^{-1}	1.0×10^{1} s^{-1}	3.2×10^{1} s^{-1}
0.5	2.95±0.04	3.00±0.05	3.00±0.05	3.07±0.05	3.11±0.05	3.16±0.04
0.8	3.17±0.07	3.22±0.06	3.26±0.06	3.30±0.05	3.35±0.05	3.42±0.04
1.0	3.34±0.03	3.42±0.03	3.48±0.04	3.55±0.04	3.62±0.04	3.71±0.05
1.5	3.15±0.14	3.20±0.14	3.25±0.14	3.31±0.15	3.39±0.15	3.48±0.16
2.0	3.10±0.02	3.15±0.02	3.20±0.02	3.26±0.03	3.33±0.03	3.42±0.03

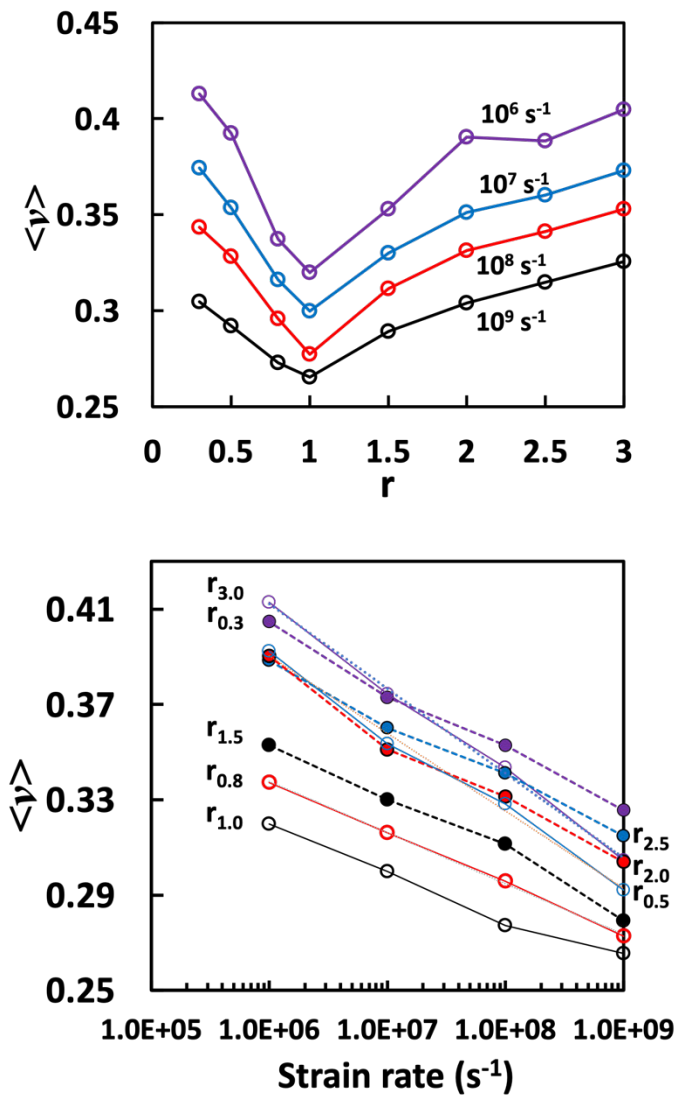

FIG. *S8*. Poisson's ratio as a function of strain rate and mixing ratio r.

Table *S6*. Experimental degree of reaction and crosslinking density in the various ratio of *r*. The values were calculated from FT-IR analysis.

r	Degree of reaction of epoxy	Degree of reaction of amine	Crosslinking density
0.5	0.73	0.97	0.85
0.8	0.83	0.99	0.91
1.0	0.94	1.00	0.97
1.5	0.96	0.99	0.97
2.0	0.91	0.83	0.87

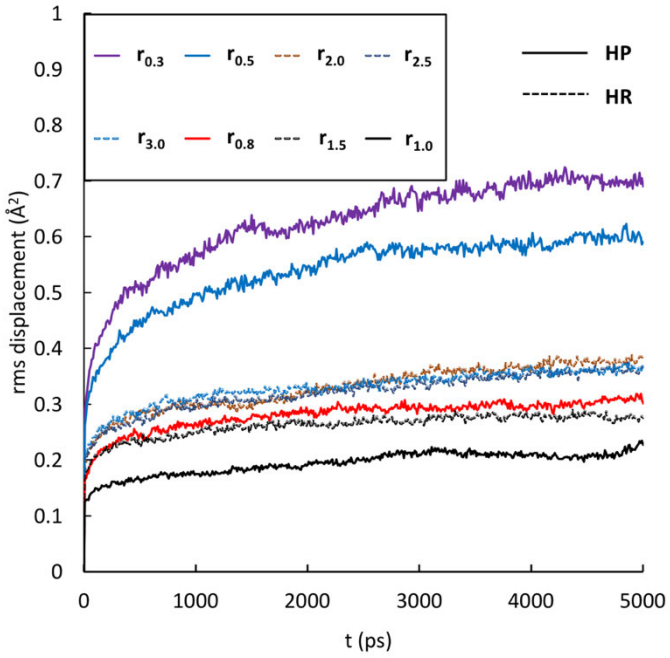

FIG. *S9*. Root mean square displacement of off-stoichiometric systems. All systems reached plateau around 5000 ps.