

Supporting Online Material for

**Influence of Stoichiometry on the Glass Transition and Bond Exchange Reactions in Epoxy  
Thermoset Polymers**

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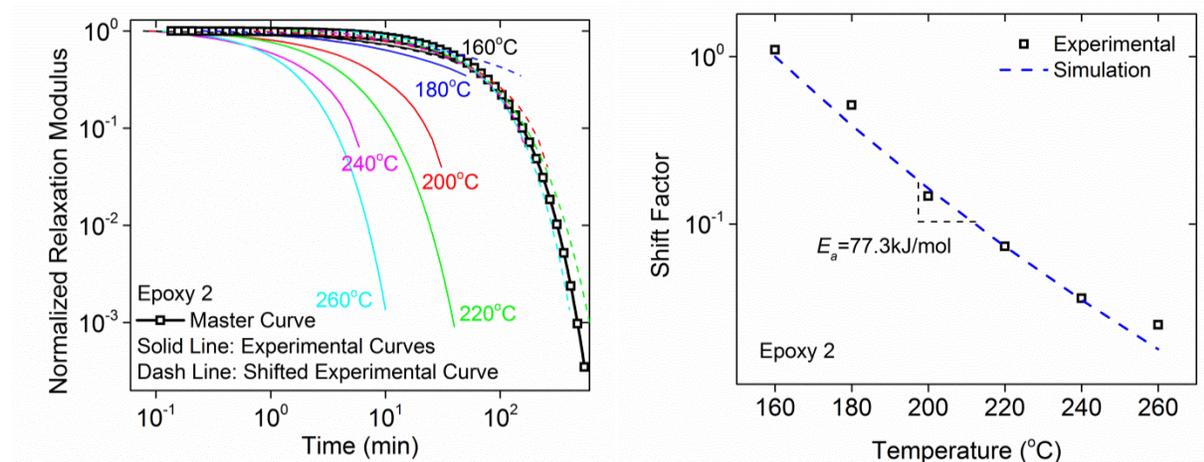
S1. Time and temperature dependent stress relaxation of Epoxy 2-5

S2. Thermal stability of Epoxy 1-5

## S1. Time and temperature dependent stress relaxation of Epoxy 2-5

The time and temperature dependent stress relaxation behavior of Epoxy 2-5 is shown in Fig. S1. The experimental procedure is the same as mentioned in the main text: all the epoxy samples with the same dimensions (10mm × 5mm × 1mm) were first preloaded by  $1 \times 10^{-3}$  N force to ensure straightness. After reaching the testing temperature, it was allowed 30 min for the thermal equilibrium. The specimen was then stretched by 1% on the DMA machine and the deformation was maintained during the test. The decrease of stress was recorded and the stress relaxation modulus was calculated.

Fig. S1a, S1c, S1e and S1g firstly show the normalized relaxation modulus of Epoxy 2-5 at different temperatures. Then by shifting each curves horizontally into the reference temperature (160 °C), a master relaxation curve was constructed for each epoxy sample, which can be further captured by using an exponentially decay function. Both the simulation and the estimated relaxation times are presented in Fig. 4a. During shifting the relaxation curves, the associated shift factors are then plotted in Fig. S1b, S1d, S1f and S1h. It is seen the stress relaxation behavior of all the epoxy samples is following the Arrhenius type temperature-time superposition (TTSP). The different curve slopes of each sample indicate different energy barrier for the bond exchange reactions.



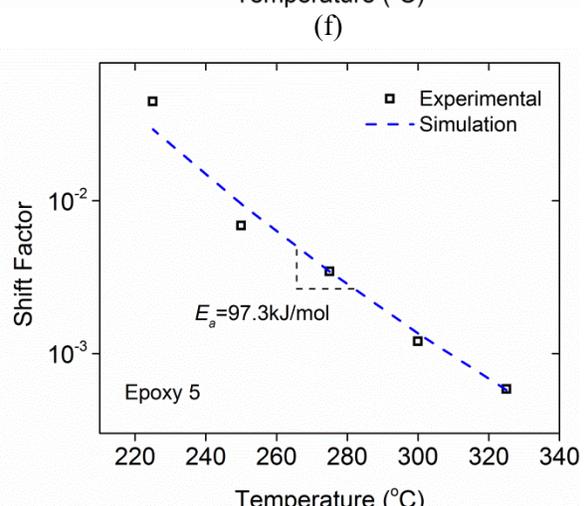
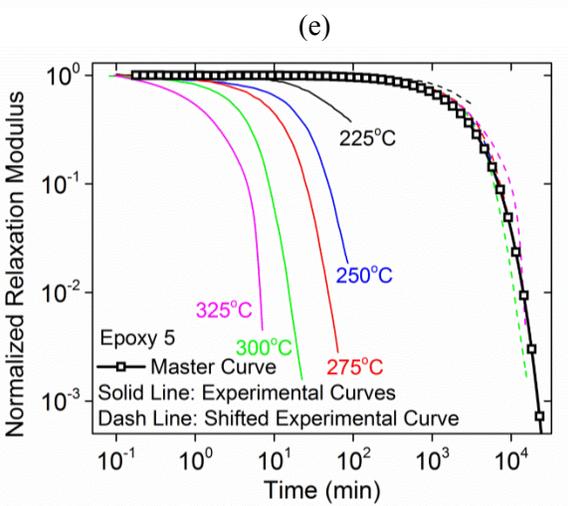
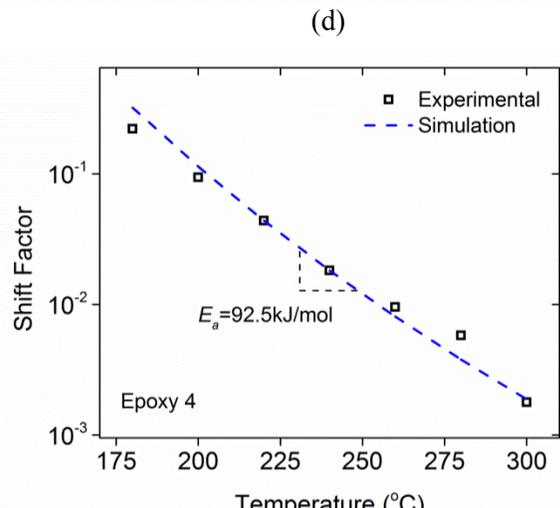
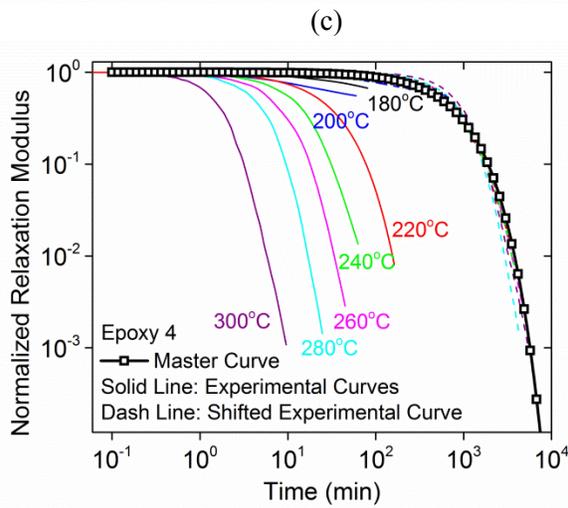
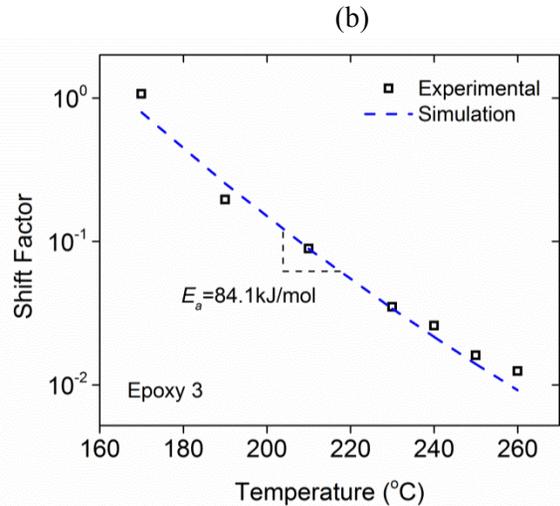
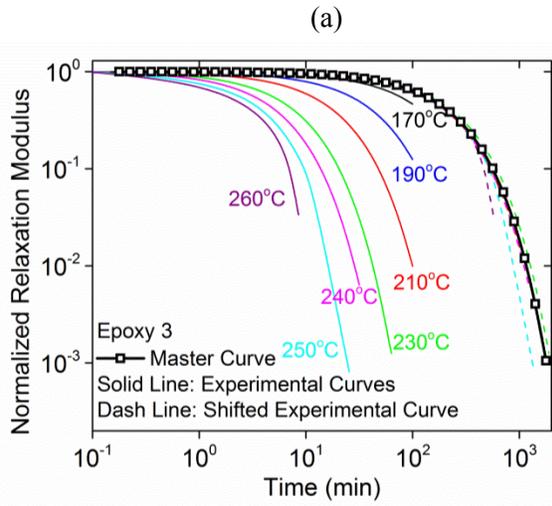


Figure S1. The stress relaxation curves, master relaxation curves and associated shift factors plots of (a) Epoxy 2, (b) Epoxy 3, (c) Epoxy 4 and (d) Epoxy 5. The stress relaxation behavior of Epoxy 1 is shown in Figure 1

## S2. Thermal stability of Epoxy 1-5

Comment [K]: In response to Reviewer 3, Comment 6

The thermal stability of epoxy materials was tested by using the thermogravimetric analysis (TGA) tester (Model, STA 6000, Perkin Elmer, Waltham, MA, USA). The samples weighing 20-25 mg were heated from 35 °C at a constant rate of 10 °C min<sup>-1</sup> in the presence of air. Weight loss due to the thermal degradation of Epoxy 1-5 was shown in Fig S2. It is shown that with the increment of crosslinking density of epoxy sample, the onset of decomposition temperature increases slightly. But these onset temperatures (~350 °C - ~390 °C) are much higher than the temperature used for stress relaxation, which suggest that no thermally induced degradation occurred during the relaxation tests.

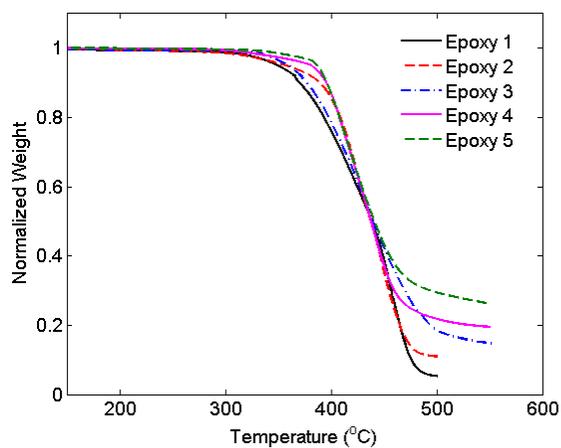


Figure S2. Normalized weight as a function of temperature during the TGA test.

In addition to the TGA tests, we further conducted uniaxial tension tests on Epoxy 1-5 after being heated for 30min. The temperatures are taken to be the highest one in the corresponding stress relaxation test (i.e. 200 °C for Epoxy 1, 260 °C for Epoxy 2, 260 °C for Epoxy 3, 300 °C for Epoxy 4 and 325 °C for Epoxy 5). Meanwhile, fresh epoxy samples without heat treatment were also tested and their stress-strain curves are shown in Fig. S3.

All the tension tests were carried out on the DMA machine at room temperature (23°C). The loading stress rate was chosen to be 3MPa/min, and at least three samples were tested for each epoxy material. Then the average modulus (measured over the initial 10% stretch), stretch ability (maximum strain before break) and strength (maximum stress before break) are summarized in Table 1.

As shown in Fig. S3, after being heated for 30min, all the epoxy materials exhibit thermally induced hardening effect [1, 2] with increased elastic modulus and decreased stretch ability. Such hardening effect is more obvious in epoxy material with higher  $T_g$  (see the relative change of mechanical property in Table 1). However, the material strength is seen to be stable without significant changes, which also indicates no obvious heat decomposition or network damage occurred within the epoxy samples at high temperature. Since in this paper, we are focusing on the revealing of relationship between glass transition and BERs, this difference in mechanical properties after heat treatment can be ignored in the current study.

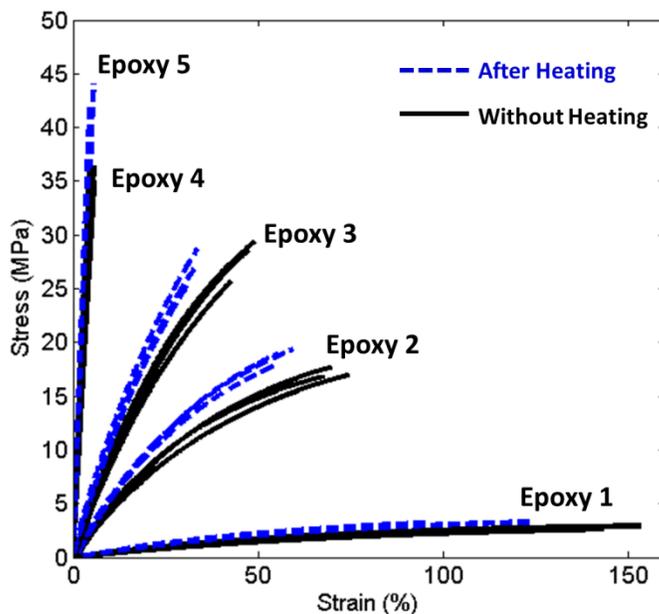


Figure S3. Stress-strain curves of Epoxy 1-5 before and heat treatment.

Table S1. Summary of mechanical properties of Epoxy 1-5 before and after heat treatment

<b>Elastic Modulus (MPa)</b>	<b>Before Heating</b>	<b>After Heating</b>	<b>Relative Change</b>
Epoxy 1	3.8	3.9	2.6%
Epoxy 2	59.1	66.2	11.9%
Epoxy 3	150.8	172.6	14.5%
Epoxy 4	659.0	745.1	13.1%
Epoxy 5	728.3	862.7	18.5%
<b>Stretch Ability</b>	<b>Before Heating</b>	<b>After Heating</b>	<b>Relative Change</b>
Epoxy 1	144.9%	124.6%	-14.0%
Epoxy 2	70.8%	59.6%	-15.8%
Epoxy 3	46.5%	32.4%	-30.3%
Epoxy 4	5.8%	5.0%	-16.0%
Epoxy 5	4.6%	4.3%	-6.5%
<b>Strength (MPa)</b>	<b>Before Heating</b>	<b>After Heating</b>	<b>Relative Change</b>
Epoxy 1	3.0	3.1	3.3%
Epoxy 2	17.5	17.9	2.3%
Epoxy 3	28.7	27.0	-5.9%
Epoxy 4	35.4	34.4	-2.8%
Epoxy 5	37.7	41.3	5.2%

**Reference:**

1. L.I. Komarova, et al., *A Study of the Infrared Absorption Spectra of Polymers based on Bisphenols and Formaldehyde during Hardening and Thermal Degradation*. Zhurnal Prikladnoi Spektroskopii, 1967. 7(4): p. 611-614.
2. Beyler, C.L. and M.M. Hirschler, *Thermal Decomposition of Polymers*, in *SFPE Handbook of Fire Protection Engineering (3rd Edn)*, P.J. DiNenno, Editor. 2001, NFPA: Quincy