*Supplementary Material for*

**The nonequilibrium behaviors of covalent adaptable network polymers during**

**the topology transition**

Xiaojuan Shi[1,2], Qi Ge[3], Haibao Lu[2, *], Kai Yu[1, *]

*1. Department of Mechanical Engineering, University of Colorado Denver, Denver, CO 80217, USA*

*2. National Key Laboratory of Science and Technology on Advanced Composites in Special Environments, Harbin Institute of Technology, Harbin, 150080, PR China*

*3. Department of Mechanical and Energy Engineering, Southern University of Science and Technology, Shenzhen, Guangdong, China*

*\* Corresponding author HBL: luhb@hit.edu.cn; KY: kai.2.yu@ucdenver.edu*

## S1. $T_g$ of vitrimer samples with different catalyst contents

The $T_g$ of vitrimer samples with different catalyst contents (0%, 5%, and 10%) was characterized. During the tests, the sample was first stabilized at 0°C for 10 mins, then the temperature was increased from 0 to 80°C at 2 °C/min. The testing frequency was 2 Hz. As shown in the following figure, there is no notable difference when the catalyst content is different in the epoxy sample.
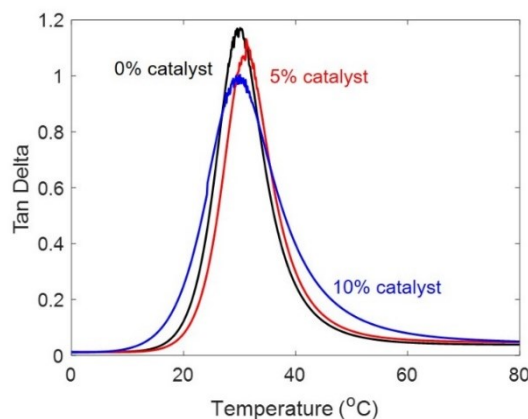


**Figure S1.** Tan $\delta$ of epoxy samples with different catalyst contents.

## S2. Hypothesis with extremely low heating rate

To further explore the hypothesis during the heating/cooling cycle of epoxy vitrimers, we performed thermal expansion tests with extremely low heating rate. During the tests, the vitrimer sample with 10% catalyst was first equilibrated at 160°C for one hour, a period that was long enough to reach the network equilibrium state. Then the temperature was increased to 180°C at 0.1°C/min, followed by cooling at the same rate to 160°C. As shown in the following figure, the hysteresis between the heating and cooling curves is negligible.
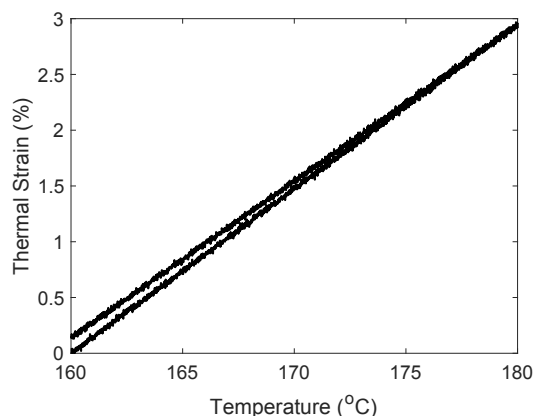


*Figure S2. Evolution of thermal strain during the heating/cooling cycle of vitrimer sample with extremely low heating rate.*

**S3. Parameters identification and evolution of fictive temperature**

As shown in Fig. S3a, by fitting with the thermal strain evolution of the control sample with 0.5°C/min heating rate, the coefficient of thermal expansion, $\alpha_n$ (in Eq. 5b), is determined to be 0.00023 °C⁻¹. The fitting parameters in the WLF equation, $C_1$ and $C_2$ (in Eq. 4a), are determined to be 0.07 and 18°C, respectively. The structural relaxation time, $\tau_0$ (in Eq. 3a), is 0.15s. With these parameters, the model is able to capture the difference in thermal strain evolution between 0.5°C/min and 5°C/min (Fig. S3b). Fig. S3c presents the evolution of $\tau_{BR}$ and $\tau_{TR}$ of epoxy vitrimer with 10% catalyst. It is observed to decrease with temperature and be 2-3 orders of magnitude higher than $\tau_{TR}$. Because of this, the fictive temperature for BER-induced structural relaxation, $T_{Bf}$, shows a higher rate-dependency compared to that for intrinsic network thermal expansion, $T_{Tf}$.
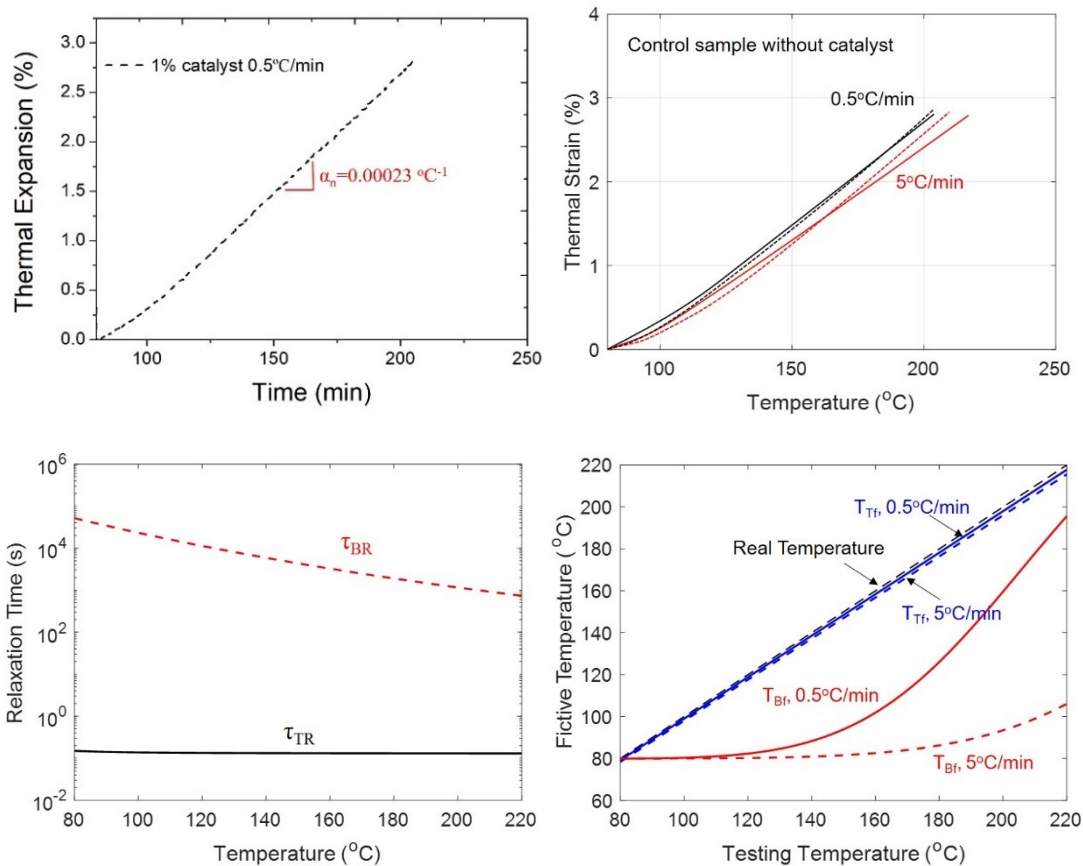
***Figure S3.*** *(a) Determining the thermal expansion coefficient α_n. (b) Evolution of thermal strain of control sample without catalyst. Solid lines: experiment. Dashed line: model prediction. (c) Evolution of relaxation time $\tau_{BR}$ and $\tau_{TR}$ of vitrimer sample with 10% catalyst as a function of temperature. (d) Evolution of fictive temperatures of vitrimer sample with 10% catalyst as a function of temperature.*

## S4. Thermal expansion with extended isothermal stabilization time

We performed additional tests on vitrimer samples with extended isothermal stabilization time. The samples contain 10% and 5% catalyst, respectively. During the tests, the sample was first stabilized at 180°C for 1 hour, then the temperature was increased to 200°C at 10°C/min. After isothermal stabilization for 120 mins, the temperature was further increased to 220°C at 10°C/min followed by 120 min stabilization. The experimental results are shown below as solid lines, and the model predictions are shown as dashed lines. It is observed that with the same model parameters, the model can closely capture the plateau behavior at 220 and 200 °C.
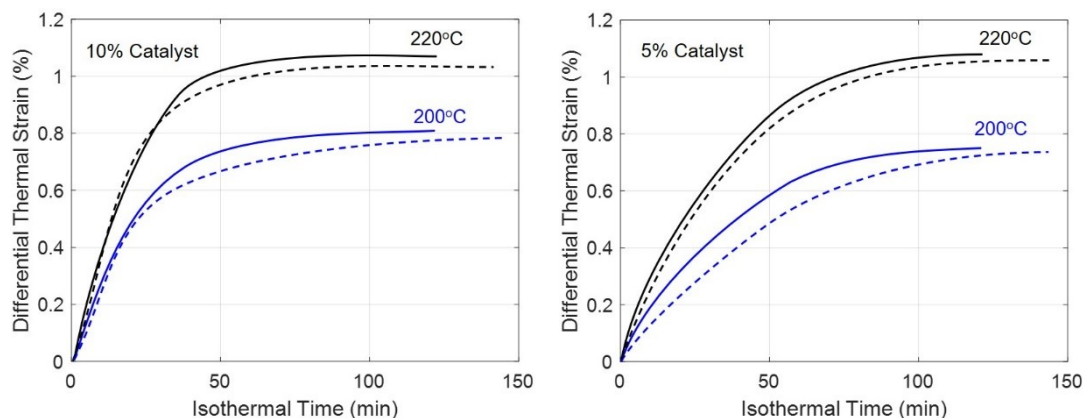
***Figure S4.*** *Evolution of the differential thermal strain during the isothermal stabilization. Solid lines: experiment. Dashed line: model prediction.*

## S5. Defining $T_{vi}$ based on intersection of the linear regressions

If $T\_vi$ is defined as the intersection of the linear regressions for the pre- and post-transition regions, we still observe the same trends change in terms of heating rate and catalyst content. For example, the following two figures show the experimental data of thermal strain evolutions of vitrimer samples with 10 % and 5 % catalyst. For the 10 % catalyst, the newly defined $T\_vi$ increases from ~161°C to 207°C when the heating rate is increased from 0.5°C/min to 5°C/min. With the same heating rate of 0.5°C/min, the $\_vi$ increases from ~161°C to 169°C when the catalyst content is decreased from 10 % to 5 %.
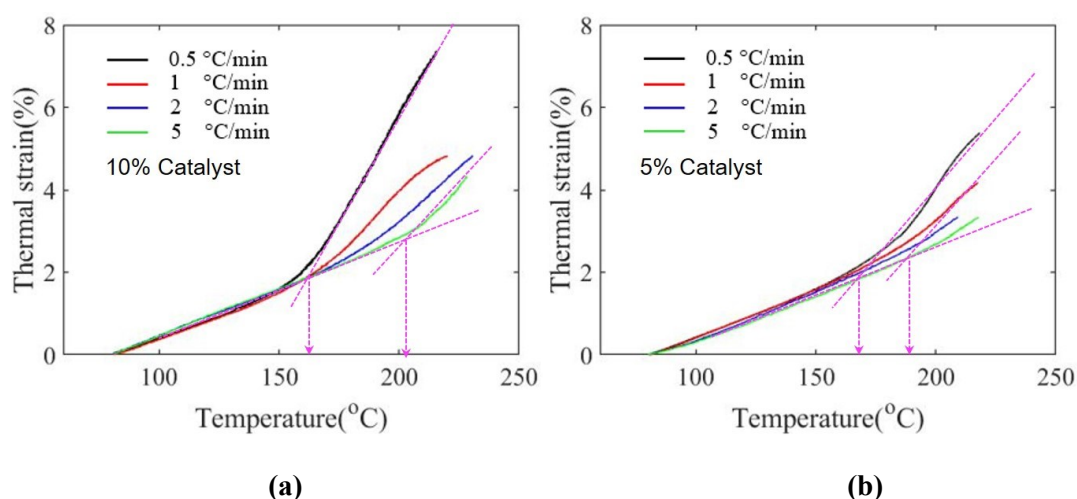


(a)  (b)

***Figure S5.*** *Defining $T_{vi}$ as the intersection of the linear regressions for the pre- and post-transition regions for vitrimer samples with (a) 10% catalyst and (b) 5% catalyst.*

## S6. Stress relaxation of vitrimer and control network in tension and compression
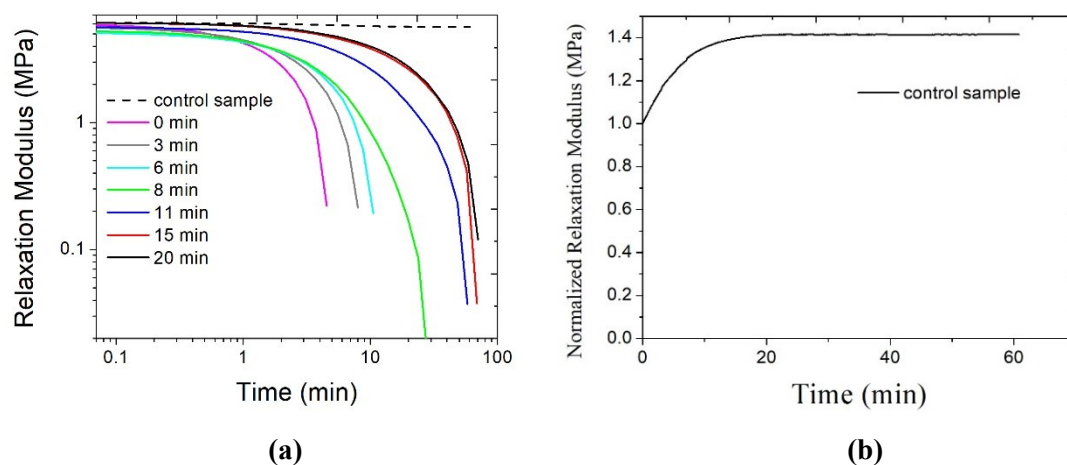


|     |     |
| --- | --- |
| (a) | (b) |

**Figure S6.** *(a) Evolution of relaxation modulus of vitrimer and control networks during the stress relaxation in tension state. (b) Evolution of normalized relaxation modulus of control network during the stress relaxation in compression state*

## S7. Comparison of time to peak stress in compression and relaxation time in tension

**Table S1.** *Comparison of time to peak stress in compression and relaxation time in tension*

| Temperature | Time to peak stress in compression | Relaxation time in tension |
| --- | --- | --- |
| **10% catalyst** | | |
| 140 °C | 4.1 min | 4.7 min |
| 160 °C | 10.3 min | 7.1 min |
| 180 °C | 11.3 min | 13.9 min |
| 200 °C | 29.6 min | 31.4 min |
| **5% catalyst** | | |
| 160 °C | 25.0 min | 22.7 min |
| 180 °C | 12.9 min | 11.1 min |
| 200 °C | 9.9 min | 9.1 min |
| 220 °C | 5.4 min | 5.5 min |
| **1% catalyst** | | |
| 160 °C | 43.3 min | 181.1 min |
| 180 °C | 30.3 min | 99.2 min |
| 200 °C | 25.8 min | 62.0 min |
| 220 °C | 23.7 min | 30.3 min |

## S8. BER relaxation contribution map with $E_a$=9 kJ/mol
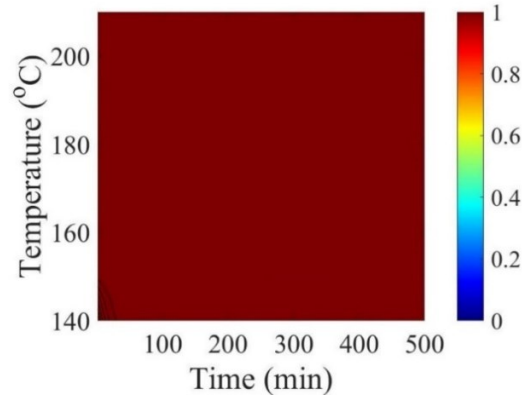
**Figure S6.** *The BER relaxation contribution map during the relaxation of epoxy vitrimer with $E_a=9$ kJ/mol*

## S9. The effect of isothermal time on the BER contribution ratio of epoxy containing 5% and 1% catalyst

Fig. S7 and Fig. S8 respectively shows the predicted BER contribution ratio for CANs containing 5% and 1% catalyst. Before applying the strain, the temperature was increased from room temperature to the target temperature at 20°C/min and then followed by isothermal stabilization for different times (0-600 min). The evolutions of BER contribution ratio are similar to that of epoxy containing 10% catalyst, expect for the case that a lower catalyst content reduces the BER contribution ratio due to the slow reaction rate.
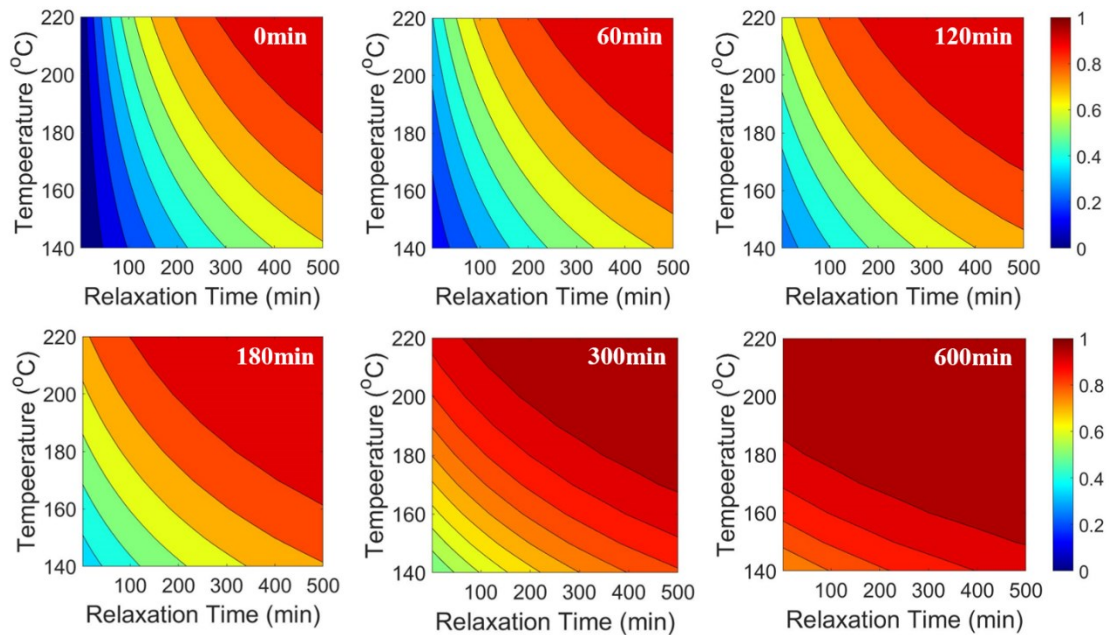


**Figure S7** *The BER contribution ratio during the stress relaxation of epoxy CAN containing 5%*

*catalyst. In each figure, the BER contribution ratio is predicted with different isothermal holding times before stress relaxation.*
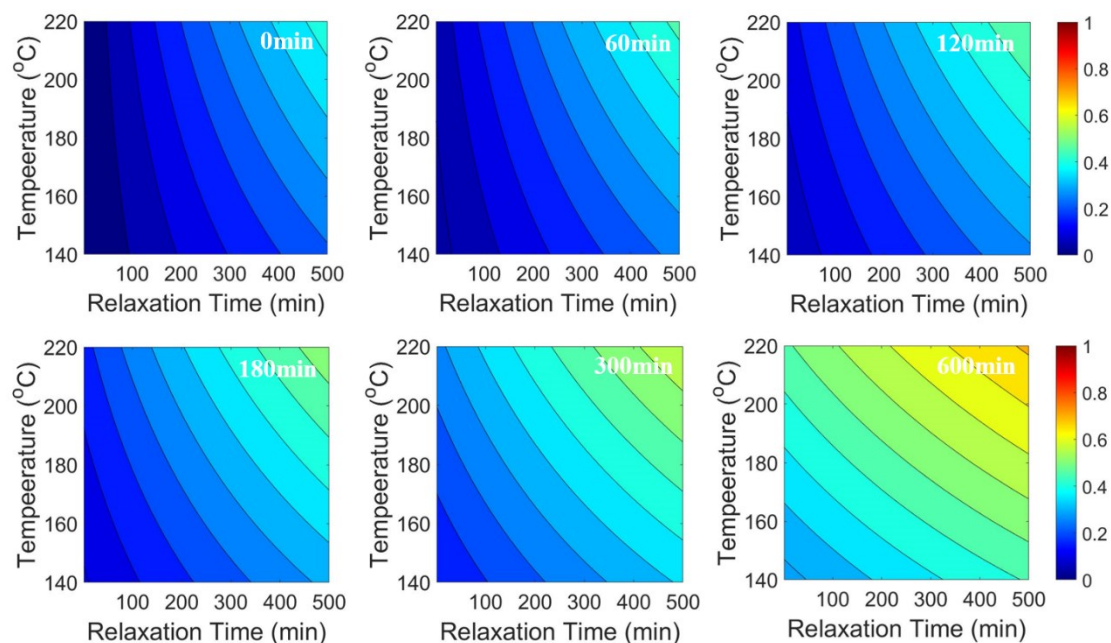


***Figure S8*** *The BER contribution ratio during the stress relaxation of epoxy CAN containing 1% catalyst. In each figure, the BER contribution ratio is predicted with different isothermal holding times before stress relaxation.*

## S10. The effect of heating rate on BER contribution ratio of epoxy containing 5% and 1% catalyst

Fig. S9 and Fig. S10 respectively shows the BER contribution ratio during the stress relaxation of epoxy CANs containing 5% and 1% catalyst. Before applying the strain, the temperature was increased from room temperature to the target temperature at different heating rates (0.01, 0.05, 0.1, 0.5, 1, 20 °C/min, respectively). No isothermal holding step was applied before the stress relaxation. It is also observed that evolutions of BER contribution ratio are similar to that of epoxy containing 10% catalyst, expect for the case that a lower catalyst content reduces the BER contribution ratio.
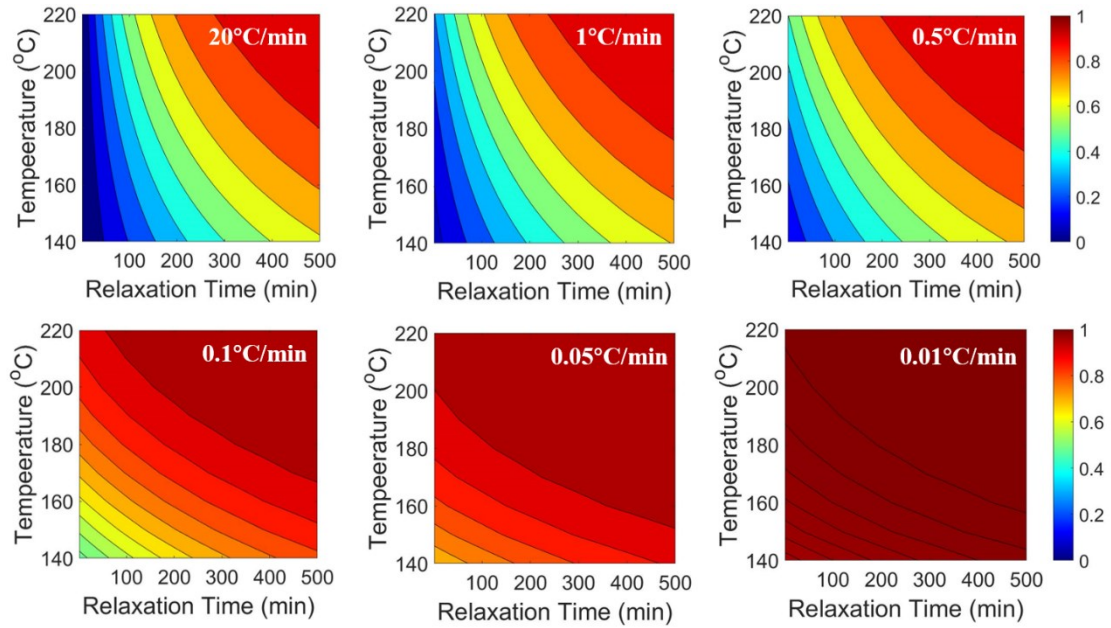
***Figure S9*** *The BER contribution ratio during the stress relaxation of epoxy CAN containing 5% catalyst. In each figure, the BER contribution ratio is predicted with different heating rates before stress relaxation (0.01, 0.05, 0.1, 0.5, 1, 20 °C/min, respectively).*
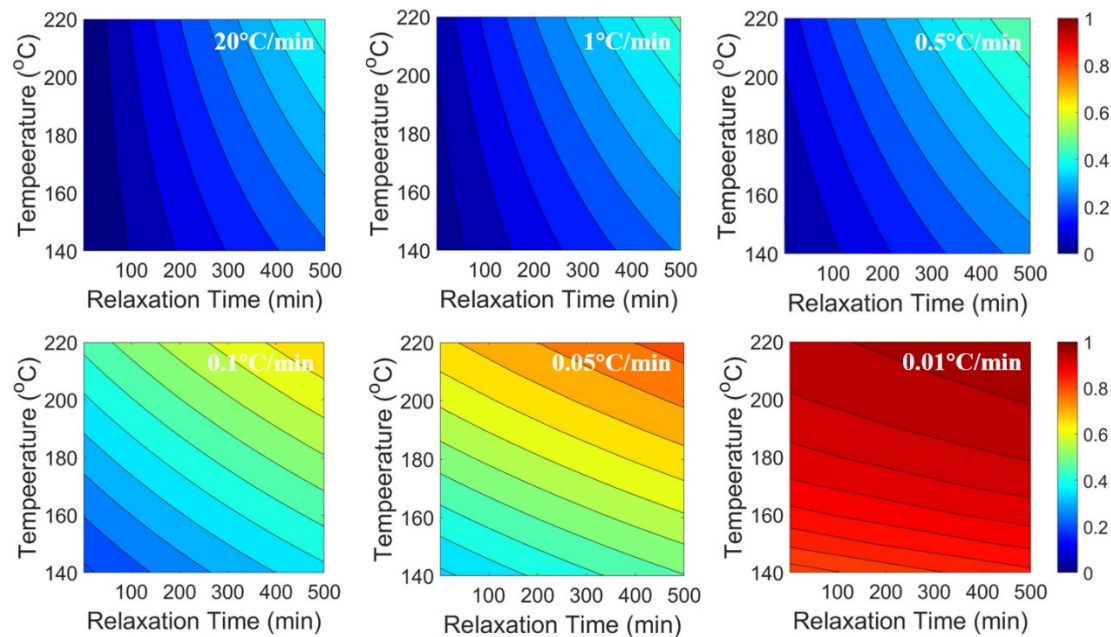


***Figure S10*** *The BER contribution ratio during the stress relaxation of epoxy CAN containing 1% catalyst. In each figure, the BER contribution ratio is predicted with different heating rates before stress relaxation (0.01, 0.05, 0.1, 0.5, 1, 20 °C/min, respectively).*