Supporting Information

Combing Experimental Methods and Molecular Simulations to Study Self-Healing Behaviors of Polyurethane Elastomers Containing Multiple Hydrogen Bond Networks and Flexible Blocks

Guangwei Xu[1], Zhaopeng Liang[1], Sumin Li[1], Yinmao Wang[2], Juan Yang[1], Yijing Nie[1,*]

[1] Research School of Polymeric Materials, School of Materials Science and Engineering, Jiangsu University, Zhenjiang, China

[2] Key Laboratory for High Performance Transparent Protective Materials of Jiangsu Province, Jiangsu Tiemao Glass Co., Ltd., Nantong, 226600, China

Lattice model

In the lattice space, one lattice site has 26 the nearest-neighbor sites (that is, 6 lattice sides, 8 body diagonals and 12 face diagonals), as shown in Fig. S1.
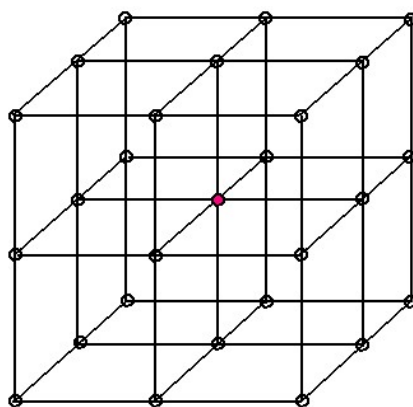

Fig. S1. The lattice space model used in the current simulation.

Chain movement mode

(1) We first numbered vacancy sites in the whole system and recorded their positions.

(2) Then, we selected one vacancy site, and randomly chose one lattice site in its nearest

* Corresponding Authors. E-mail: nieyijing@ujs.edu.cn (Y.J. Nie)

neighboring regions. If this lattice site was occupied by one polymer bead, we tried to

swap the vacancy site with the polymer bead. (3) If no chain break occurred during the

exchange (the length of the newly formed bonds on the both sides of this bead after the

exchange is no more than $\sqrt{3}$), this jumping would be accepted, as shown in Fig. S2(a)

of the Supporting Information. (4) If the jumping caused the newly formed bonds on

the both sides to break (the length of the newly formed bonds on the both sides of this

bead after the exchange is more than $\sqrt{3}$), the jumping would be rejected, as shown in

Fig. S2(b) of the Supporting Information. (5) If only one newly formed bond would be

broken due to the jumping (the length of this newly formed bond on one side of this

bead after the jumping is more than $\sqrt{3}$), we would try to find the nearest "kink" along

the chain to this side, and then sliding diffusion of beads from the selected bead to that

next to the "kind' was carried out, as shown in Fig. S2(c) of the Supporting Information.

During simulations, the information about the above motion process of each bead could

be recorded, and then the event of bead moving along the sliding path could be checked.

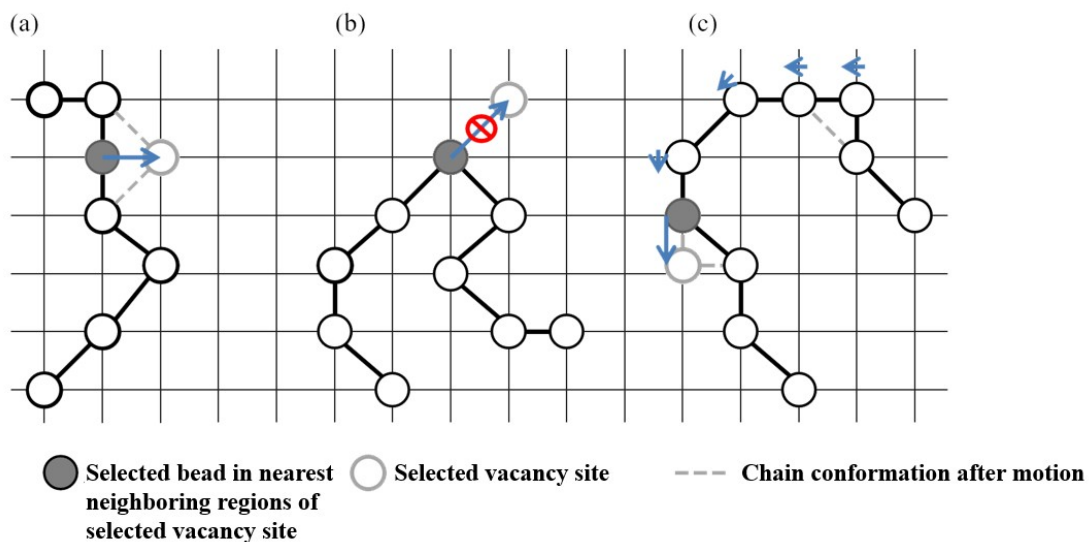We observed that both the jumping and the sliding occur during simulation.

Fig. S2. Schematic diagram of the micro-relaxation model. (a) Jumping mode of one bead that can

be accepted. (b) Jumping mode of one bead that cannot be accepted (the forbidden symbol suggests

that the jumping is rejected in this condition); (c) Sliding mode of local chain segments in lattice space. The arrows indicate the directions of bead jumping or sliding.

Setting of simulation parameters

In the current simulation, B_1 was the mixing-interaction energy for one nearest-neighbor pair of interaction sites of the first kind, and B_2 was the mixing-interaction energy for one nearest-neighbor pair of interaction sites of the second kind. The value of B_1/E_c was set to -0.1, reflecting weak attractive interaction existing between the interaction sites of the first kind. In order to explore the effect of the interaction strength of between the interaction sites of the second kind, the values of B_2/E_2 were set as 0, -0.1, -0.2, -0.3, -0.4, -0.5, -0.6, -0.8 and -1.0, respectively (the higher absolute value of B_2/E_c reflects the higher interaction strength). If we assume $B_1/E_c = s$, we can obtain $B_1 = sE_c$. According to the corresponding literature,[1] E_c of *trans*- and *cis*-conformers of carbamic acid is around 10 kJ/mol. Then, $B_1 = 0.1 \times 10$ kJ/mol = 1 kJ/mol. Then, further considering the effect of coordination number ($q = 26$) in the lattice space, the total strength of one interaction site of the first kind interacting with other interaction sites of the first kind should be $B_1 \times (q\text{-}2) = 24$ kJ/mol. In experiments, it was measured that the hydrogen bonding energy of carbamate groups is 22.42 kJ/mol,[2] the value of which is close to the above value in the simulation (24 kJ/mol).

E_{f1} and E_{f2} were introduced in the current simulations to control chain diffusion ability in the two systems, corresponding to the frictional barrier for sliding diffusion of the beads imposed by other neighboring beads. If the value of is set to 0, this means that the local slip process of segments is not restricted. If the value of E_{f1}/E_c or E_{f2}/E_c is set larger, the slippage process of the segments in the corresponding system becomes more difficult. In the system with E_{f1}/E_c or $E_{f2}/E_c = 0.5$, almost all chain segments are unable to slip. Thus, for the system 1, the segments in which exhibit relatively strong

diffusion ability, the value of E_{f1}/E_c is set to 0.02, while the value of E_{f1}/E_c is set to 0.2 for the system 2, reflecting that the corresponding segments have low diffusion ability. Then, in order to study the effect of segment diffusion ability on self-healing, the values of E_{f1}/E_c were set as 0, 0.01, 0.02, 0.1, 0.2 and 0.5, respectively (the higher values of E_{f1}/E_c reflect the weaker segment diffusion ability). But it is difficult to correlate E_{f1} and E_{f2} directly with the relevant physical quantities in experiments.

We defined the diffusion ability as the average number of beads involved in the sliding diffusion process in a single MC cycle over the 100 MC cycles in the systems with the same bead density but without the crack. If more beads participate in the sliding diffusion in a single MC cycle, this means the system will have stronger diffusion ability. Then, the effect of the sliding friction parameters E_{f1} and E_{f2} can be revealed by calculating the dependence of the diffusion ability on the values of the sliding friction parameters. Fig. S3 in the Supporting Information displayed the diffusion ability as a function of E_{f1} in the system 1 and as a function of E_{f2} in the system 2 at $T^* = 0.5$, respectively. It can be seen that the diffusion ability in both of the two systems decreases with the increase of the values of E_{f1} or E_{f2}, demonstrating that the diffusion ability of polymer chains can be controlled by setting different values of the sliding friction parameters E_{f1} and E_{f2}.
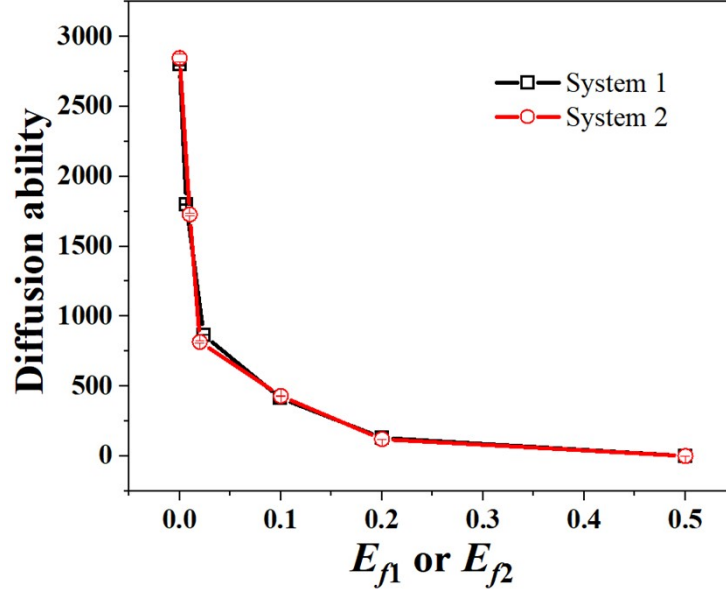
Fig. S3. The diffusion ability as a function of E_{f1} in the corresponding system 1 and as a function of E_{f2} in the system 2 at $T^* = 0.5$, respectively.

The procedure of dynamic MC simulations

The MC acceptance ratio in our simulation is calculated as follows:

$$p = \min\{1, \exp(-\Delta E/kT)\}, \Delta E = E_2 - E_1$$

where ΔE represents the total energy difference of molecular configuration before and after the movement of chain segment, E_1 represents the total energy of the molecular configuration before the movement of chain segment, E_2 represents the total energy of the new molecular configuration after the movement of chain segment, k represents the Boltzmann constant, $\exp(-\Delta E/kT)$ represents the Boltzmann factor, T represents the temperature. If $\Delta E \leq 0$, the segment motion is accepted, and the new state participates in the statistics. If $\Delta E > 0$, a random number between [0, 1] is generated, and if the random number is less than the Boltzmann factor, the motion is accepted. The increase of temperature can lead to the decrease of the values of $\dfrac{\Delta E}{kT}$, then resulting in increase of the acceptability, that is, the bead mobility.
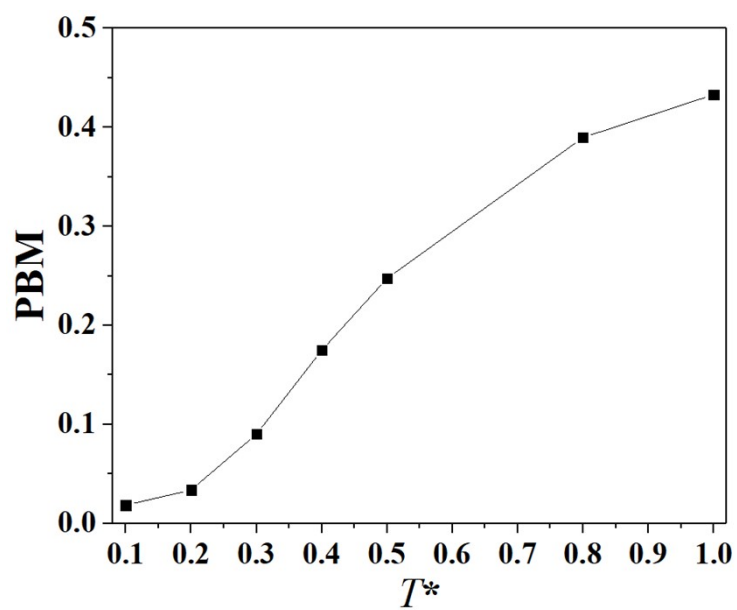
Simulation results

Fig. S4. The PBM values as a function of simulation temperature.

References

1   H. Sun, *Macromolecules*, 1993, **26**, 5924-5936.

2   Q. Li, H. Zhou, D. A. Wicks, C. E. Hoyle, D. H. Magers and H. R. McAlexander, *Macromolecules*, 2009, **42**, 1824-1833.