Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.


# Optimizing the fracture toughness of the dual cross-linked hydrogel via molecular dynamics simulation

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## 1. The definition and calculation method of voids

First, the periodic box is divided into the cubic sub-cells of size $\Delta$. Then, whether the polymer beads are within these small sub-cells are checked according to their positions. The sub-cells will be considered to be voids if there are no beads within these sub-cells. Thus, the position of voids can be obtained. Following it, the unoccupied sub-cells will be assigned to the same void if they share a common face (namely they are neighbors). As a result, the number of voids can be calculated. It is noted that the $\Delta$ of the sub-cell is chosen to be $1.6\sigma$ in this work, which can ensure no voids at strain=0.0.

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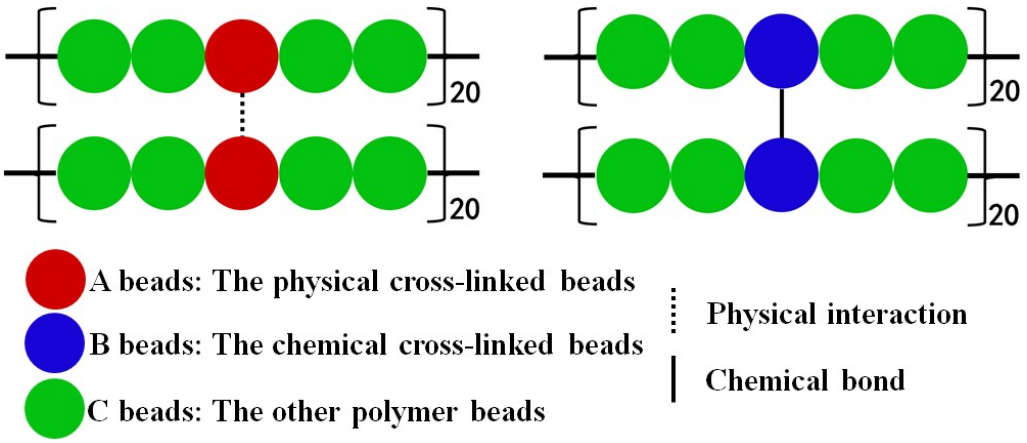


**Fig. S1 Schematic diagram of the polymer chain which contains three kinds of beads: (1) The red beads which form the physical network; (2) The blue beads which form the chemical network; (3) The green beads which are the other polymer beads.**

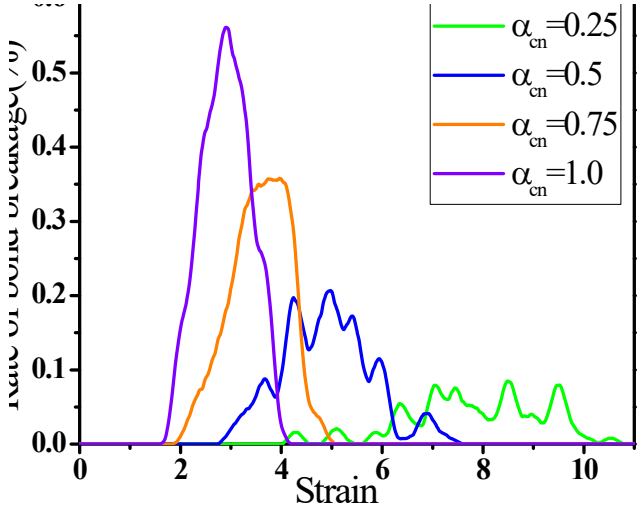


**Fig. S2 Rate of bond breakage with respect to the strain for different ratios ($\alpha_{cn}$) of the chemical network to the total networks.**

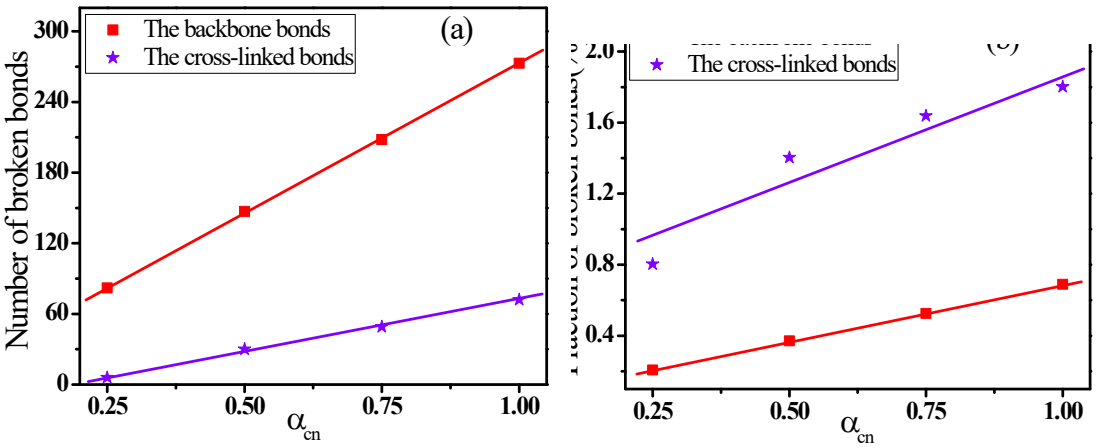


**Fig. S3 (a) Number and (b) fraction of broken backbone bonds or cross-linked bonds for different ratios ($\alpha_{cn}$) of the chemical network to the total networks. ($T^*$=1.0)**

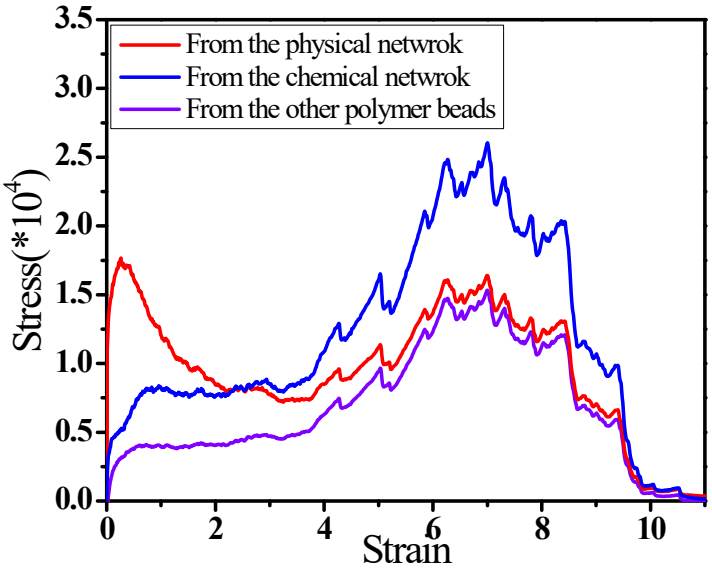


**Fig. S4 The stress borne by one bead from physical network, chemical network or other polymer beads as a function of strain. ($\alpha_{cn}$=0.25)**

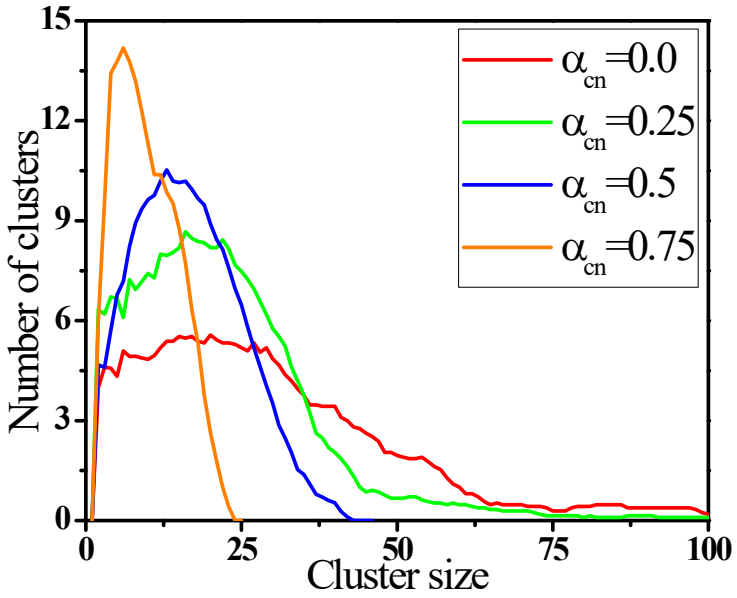


**Fig. S5 The number distribution of clusters with the cluster size for different ratios ($\alpha_{cn}$) of the chemical network to the total networks. ($T^*$=1.0)**

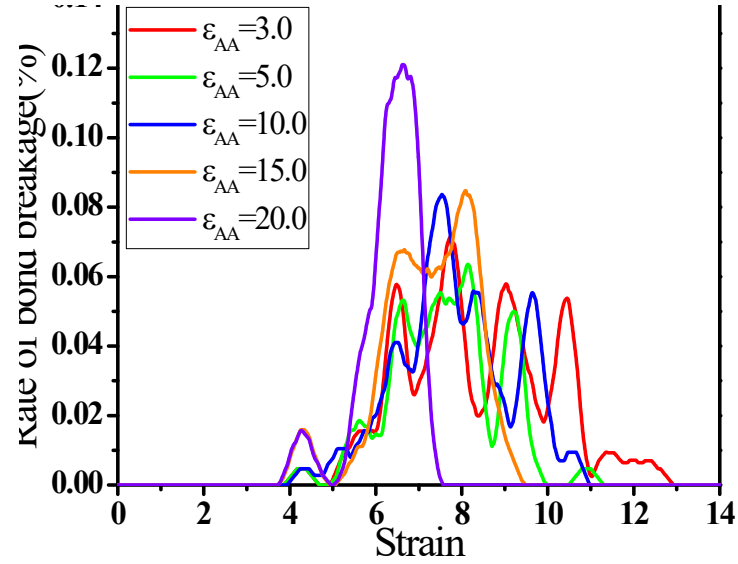


**Fig. S6 Rate of bond breakage with respect to strain for different A bead-A bead interactions ($\varepsilon_{AA}$). ($\alpha_{cn}$=0.25)**

**Table SI Parameters of each simulated system**

| System | Chain length | Number of chains | $\alpha_{cn}$ | $N_A$ | $N_B$ | $\varepsilon_{AA}$ | $K_{CB}$ |
|---|---|---|---|---|---|---|---|
| 1 | 100 | 400 | 0.0 | 8000 | 0 | 10.0 | 1000 |
| 2 | 100 | 400 | 0.25 | 6000 | 2000 | 10.0 | 1000 |
| 3 | 100 | 400 | 0.5 | 4000 | 4000 | 10.0 | 1000 |
| 4 | 100 | 400 | 0.75 | 2000 | 6000 | 10.0 | 1000 |
| 5 | 100 | 400 | 1.0 | 0 | 8000 | 10.0 | 1000 |
| 6 | 100 | 400 | 0.25 | 6000 | 2000 | 10.0 | 250 |
| 7 | 100 | 400 | 0.25 | 6000 | 2000 | 10.0 | 500 |
| 8 | 100 | 400 | 0.25 | 6000 | 2000 | 10.0 | 750 |
| 9 | 100 | 400 | 0.25 | 6000 | 2000 | 10.0 | 1500 |
| 10 | 100 | 400 | 0.25 | 6000 | 2000 | 10.0 | 2000 |
| 11 | 100 | 400 | 0.25 | 6000 | 2000 | 10.0 | 3000 |
| 12 | 100 | 400 | 0.25 | 6000 | 2000 | 3.0 | 1000 |
| 13 | 100 | 400 | 0.25 | 6000 | 2000 | 5.0 | 1000 |
| 14 | 100 | 400 | 0.25 | 6000 | 2000 | 15.0 | 1000 |
| 15 | 100 | 400 | 0.25 | 6000 | 2000 | 20.0 | 1000 |

**$\alpha_{cn}$ : Ratio of the chemical network to the total networks; $N_A$: Number of the physical cross-linked beads (A) in Fig. S1; $N_B$: Number of the chemical cross-linked beads (B) in Fig. S1; $\varepsilon_{AA}$ : The A bead-A bead interaction parameter; $K_{CB}$: The coefficient for the cross-linked bond potential.**