## **Supporting Information**

## Uniaxial deformation of nanorod filled polymer nanocomposites: A coarse-

## grained molecular dynamics simulation

Yangyang Gao<sup>1, 2</sup>, Jun Liu<sup>1, 2</sup>, Jianxiang Shen<sup>1</sup>, Dapeng Cao<sup>2\*</sup>, Liqun Zhang <sup>2\*</sup> and Zhanhu Guo<sup>3\*</sup>

<sup>1</sup>Key Laboratory of Beijing City on Preparation and Processing of Novel Polymer Materials

<sup>2</sup> State Key Laboratory of Organic-Inorganic Composites, Beijing University of Chemical Technology, Beijing 100029, People's Republic of China.

3 Integrated Composites Laboratory (ICL), Dan F. Smith Department of Chemical Engineering, Lamar University, Beaumont, TX 77710 USA

\* Corresponding author: <u>caodp@mail.buct.edu.cn</u>, <u>zhanglq@mail.buct.edu.cn</u> or <u>zhanhu.guo@lamar.edu</u>



Fig. S1(a) The snapshots for a bridging cluster of nanorods via one polymer layer. The red beads denote one polymer chain and other color beads denote nanorods. (b) The inter-agent radial distribution function g(r) for different polymer-nanorod interaction strengths and ranges.



Fig. S2 The stress at small strain for filler volume fraction V=1.20% and 2.46% respectively with polymer-nanorod interaction strength  $\varepsilon_{np} = 12.0$ .



Fig. S3 The snapshots for four typical aspect ratios of nanorods: (2) 5:1, (4) 10:1; (5) 15:1, (6) 10:2 respectively. Note that the polymer chains are represented by green points to avoid obscuring the nanorods with yellow spheres, and the purple spheres represent the cross-linking agents.

## 3.8 Further discussion

By tuning polymer-nanorod interaction strength, aspect ratio of nanorod, nanorod functionalization, chemical couplings and the nanorod volume fraction, we have systematically investigated their effects on the macroscopic stress-strain curves. For better interpretation, here the thermodynamic equation of rubber elasticity is shown as follows:

$$f = \left(\frac{\partial U}{\partial l}\right)_{T,V} - T\left(\frac{\partial S}{\partial l}\right)_{l,V} \tag{7}$$

where U stands for the internal energy of the system, S stands for the entropy, and 1 is the initial length of the rubbery sample. The formula tells us if we want to improve stress at some strain, there are two aspects that we could consider: (1) chain slippage and orientation; and (2) the finite chain extensibility. The nanorods can help to increase chain orientation and alignment, which will lead to a reduced chain entropy. On the other hand, the formation of chain bridges induced by the nanorods will exhibit finite chain extensibility at large deformation, which can increase the change of bond energy. It is also very difficult to break chain bonds due to the consistent alignment and parallel-arraying for all chains. This is the reason to account for the molecular origin of polymer reinforcement.

Then we will explore which factors will influence the chain slippage and orientation under deformation. As shown in Fig. S4(a), in the case of purely repulsive interaction, the bond orientation is the lowest. Furthermore, the bond orientation of the system with  $\varepsilon_{np} = 1.0$  is nearly the same with the unfilled system. However, when

the strong affinity further increases, the bond orientation ceases to increase, and the change slope of the bond energy as a function of strain increases with  $\varepsilon_{np} = 2.0$  in Fig. S4(b). It is very interesting to find that the nanorod orientation gets to the maximum when the  $\varepsilon_{np} = 2.0$  in Fig, S4(c). It is very hard to achieve efficient interfacial stress transfer to the nanorods network when interaction strength is weak, while the nanorods are very hard to slip for strong interaction strength. Meanwhile, the modulus increases with the increase of interfacial interaction, which is related to the change of Van der waals pairwise energy in Fig. S4(d). Here we can conclude that although the orientation does not increase with the polymer-nanorod interaction, greater finite chain extensibility contributes to the enhanced mechanical behavior. Similarly, the bond orientation is nearly unchanged for the high aspect ratio of nanorod in Fig. S5(a). Combined with the bond energy in Fig. S5(b), the increase of stress at large strain comes from bond energy. As mentioned above, in order to further explain the high reinforcing efficiency observed in the nanorods functionalization, we still studied the bond orientation and the bond energy. From the simulated results in Fig. S6(a), the bond orientation does not change with the extent of nanorods functionalization. Furthermore, from the Fig. S6(b) we found that the change of bond energy is consistent with the stress-strain curves.







Fig. S4(a) The bond orientation  $\langle P_2 \rangle$ . (b) The change of bond energy  $E_t - E_{initial}$  of the system. (c)The nanorod orientation  $\langle P_2 \rangle$ . (d) The change of Van der Waals pairwise energy  $E_t - E_{initial}$  of the system with respect to the strain for systems with different polymer-nanorod interfacial interactions.



Fig. S5(a) The bond orientation  $\langle P_2 \rangle$ . (b) The change of bond energy  $E_t - E_{initial}$  of the system with respect to the strain for systems filled with nanorods with different aspect ratios.



Fig. S6(a) The bond orientation  $\langle P_2 \rangle$ . (b) The change of bond energy  $E_t - E_{initial}$  of the system with respect to the strain for systems filled with functionalized nanorods. The unfilled system and filled non-functionalized nanods system are also added for better comparison.