

## Supporting Information

for

### **Molecular Insights into the Effect of Graphene Packing on Mechanical Behaviors of Graphene Reinforced cis-1, 4-polybutadiene Polymer Nanocomposites**

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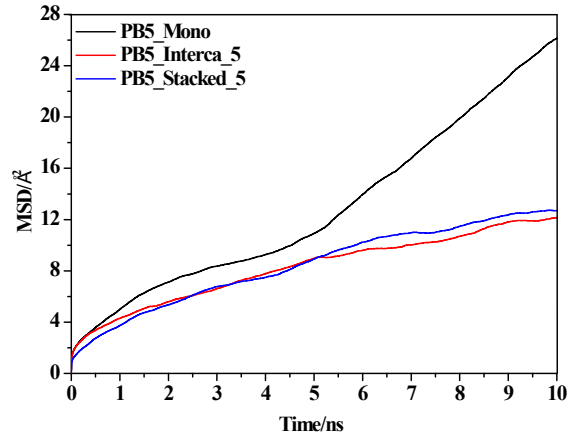
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**Figure S1 The mean-squared displacement (MSD) as a function of simulation time for the center of mass of graphene layers in three different systems at temperature T=298K.**

To have a better understanding on the motion of graphene (GP) layers during relaxation in different systems, we calculated the mean-squared displacement (MSD) for the center of mass of the GP layers in PB5\_Mono, PB5\_Interca\_5 and PB5\_Stacked\_5 systems, which are presented in Figure S1. The MSD is defined as follows:

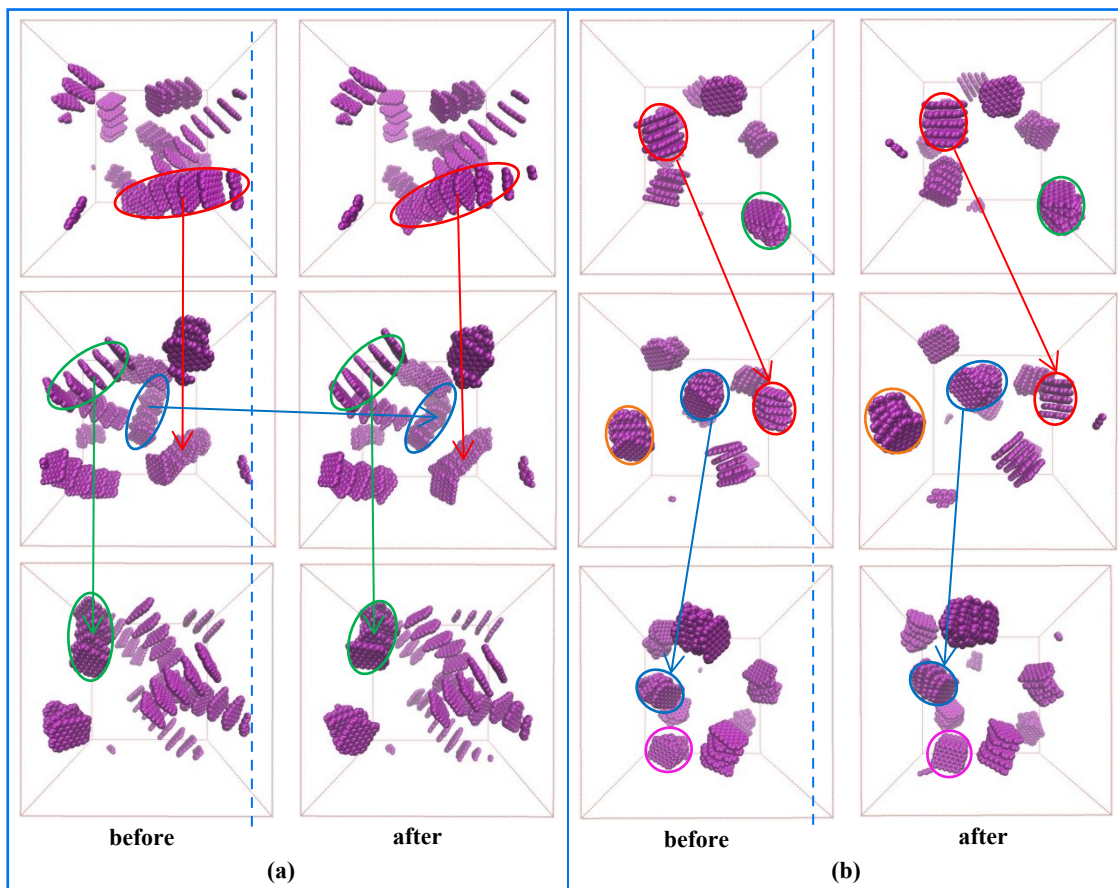
$$MSD = \frac{1}{N} \sum_{i=1}^N \langle |r_i(t) - r_i(0)|^2 \rangle$$

where N is the total number of GP layers,  $r_i(0)$  is the initial center of mass of GP layer i, and  $r_i(t)$  is the center of mass of GP layer i at time t. According to Figure S1, the mobility of GP layers in PB5\_Mono system is the strongest, while in PB5\_Interca\_5 and PB5\_Stacked\_5 systems, the mobility of GP layers is dramatically reduced.

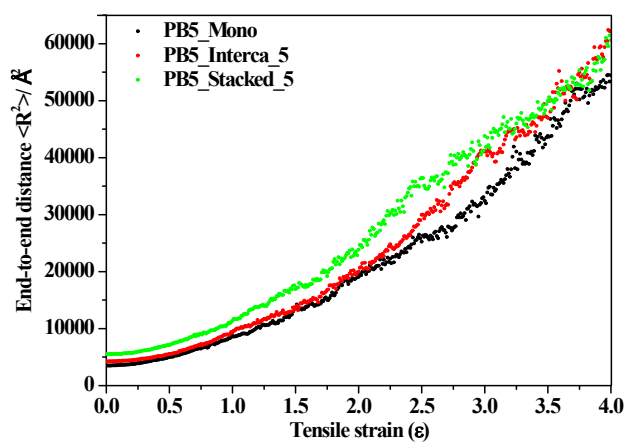
There are two previous works that also calculated the MSD of GP layers. Deepthi Konatham et al<sup>1</sup> evaluated the MSD of alkane functionalized GP sheet (f-GS) in three solvents (n-hexane, n-octane and n-dodecane) at  $T = 300K$ . Their results show that the relatively small f-GS in solvent exhibits strong mobility with a MSD of about  $3000\text{\AA}^2$  at 10ns. While in our rubber/GP hybrid system, GP only demonstrates a MSD of  $26\text{\AA}^2$  at 10ns. And this is easy to understand as follows: in our study, each PB chain contains 256 carbon atoms and then greatly restricts the motion of GPs.

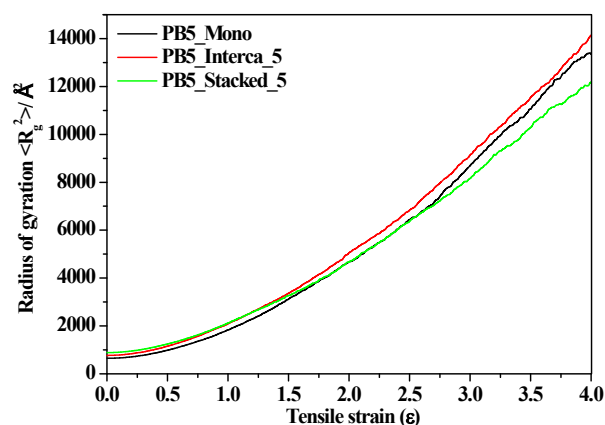
Anastassia N. Rissanou et al<sup>2</sup> built a series of polyethylene (PE)/GP hybrid systems with three different sizes of GPs and investigated the translational dynamic properties of GPs at  $T = 450K$ . Each system only contains one GP layer and each PE chain only consists of 22 carbon atoms. Their simulation results show that GP exhibits a MSD of around 1000  $\text{\AA}^2$  at 10ns. This mobility is much larger than our result, but still easy to understand: the PE chain is rather too short with only 22 carbon atoms, while our PB chain contains 256 carbon atoms, and the simulation temperature is much higher than that of ours. Besides, the mobility of GP decreases with the increment of its layer size.

According to above discussion, our MSD simulation results prove to be reliable. To further understand how the intercalated and stacked structures moved and stabilized during the relaxation process, we took some GP snapshots of GP5\_Interca\_5 and GP5\_Stacked\_5 systems before and after the second relaxation stage, as given in Figure S2. From these snapshots, we find that under the temperature of 298K, GP layers thermodynamically vibrate at their equilibrium positions, and thus leading to a small change of their arrangement within PB matrix and the rotation of whole intercalated/stacked structures. Nevertheless, these intercalated/stacked structures are dynamically stable and cannot be broken up by the thermodynamic vibrations. We believe that the strong GP-GP interactions and GP-PB interactions play important roles in stabilizing the intercalated/stacked GP structures.



**Figure S2 Snapshots of (a) intercalated structures in GP5\_Interca\_5 system and (b) stacked structures in GP5\_Stacked\_5 system before and after the second relaxation stage.**





**Figure S3 (a) Averaged end-to-end distance  $\langle R^2 \rangle$  and (b) radius of gyration  $\langle R_g^2 \rangle$  of PB chains in PB5\_Mono, PB5\_Interca\_5 and PB5\_Stacked\_5 systems during stretching process.**

According to Figure S3, under uniaxial tension process, with the increase of tensile strain, the averaged radius of gyration and end-to-end distance of PB chains increase gradually, which indicates that PB chains stretch out along the direction of uniaxial tensile. Combining with the result in Figure 8 (d) which displays that PB chains orient along the stretch direction, we can conclude that during stretch process, PB chains will extend and orient along the uniaxial tension direction.

## References

1. D. Konatham and A. Striolo, *Nano Letters*, 2008, **8**, 4630-4641.
2. A. N. Rissanou, A. J. Power and V. Harmandaris, *Polymers*, 2015, **7**, 390-417.