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SUPPLEMENTARY MATERIAL TO

The influence of interlayer interactions on the mechanical properties of polymeric nanocomposites

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CONSIDERED MODELS, THEIR THEORETICAL BACKGROUND AND THE METHOD OF CALCULATIONS

In the MM method, which was introduced for the first time by Li and Chou,[1] CNTs and GSs were simulated using mechanical elements, *i.e*., beams, rods and springs.

In this method, the use each element has some benefits or problems. For example, a linear beam element requires the cross section area be defined, which causes some errors but defining such elements is simple and the amount of computations is very low. Using a linear spring element decreases the errors, is simply defined and the amount of computation for this step is the same as for linear beam elements. The only probable error in this step is the linear behavior of the elements. Using nonlinear spring elements increases the accuracy of the computations but increases drastically the amount of computations necessary and defining such elements is problematic.

In this study, all three elements were initially used and the most suitable element with minimum amount of computations and errors was introduced.

Therefore, paying attention to the location and arrangement of carbon atoms in GSs, a program was prepared using MATLAB software to calculate the location of the nodes (carbon atoms) and then between each two neighboring atoms, a mechanical element was introduced. For defining, a model based on linear beam elements, the same model as introduced by Li and Chou[1] was employed. The cross section area of the elements was 0.147 nm, the elastic module was 5.49 TPa and the shear module was 0.871 TPa with a length of 0.1421 nm (Fig. S-1). To define a linear spring, the same strategy as employed by Giannopoulos *et al.*[2] was used, which includes two types of elements A and B responsible for the stretching and bending of bonds (Fig. S-1). The stiffness of spring type A was equal to $K_{r\mathrm{A}} = 6.52\times10^{7}\ \mathrm{N\ nm^{-1}}$ and of type B, it was $K_{r\mathrm{B}} = 1.735\times10^{7}\ \mathrm{N\ nm^{-1}}$. In the third model, which was the same model as used previously[3-5] and by Rafiee and Heidarhaei[6] and Shariati *et al.*,[7] two types of nonlinear spring elements (types A and B, Fig. S-1) were used. The nonlinear behavior of spring group A obeyed the following equation:[8]

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$$F(\Delta r) = 2\beta D_e(1 - e^{\beta\Delta r})e^{\beta\Delta r} \quad (1)$$

where $D_e = 6.03105\times10^{10}$ Nn m, β= 26.26 nm^{-1} and Δr is the amount of deviation of the length of the bond length from its equilibrium distance (r_0 = 0.1421 nm). The nonlinear behavior of spring type "B" was defined using the following equation:

$$F(\Delta R) = \frac{4}{r_0^2}k_\theta \Delta R[1 + \frac{48}{r_0^4}k_{\text{sextic}}(\Delta R)^4] \quad (2)$$

with K_θ=0.9×10^{-18}N m rad^{-2}, K_{sextic}=0.754 rad^{-4} and ΔR is the deviation of bond's length from its equilibrium value ($R_0 = \sqrt{3}\ r_0$).

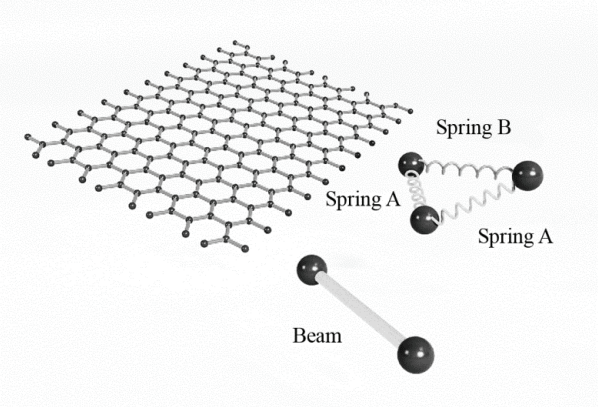

Fig. S-1. Definition of the mechanical elements.

To continue, after defining the mentioned elements, the model was imported into ABAQUS software, one side of the model was restricted and a stretching force was applied to the other side. In this study, initially, two sheets with dimension of 2.21 nm×2 nm (model I) and 3.69 nm×3.26 nm (model II) in the armchair direction were stretched and the related elastic module was calculated. The polymeric base employed in this study had an elastic module equal to 3.5 GPa and the volume fraction of the reinforcement agent in all cases was 5 %. The dimension of the polymeric base was calculated with attention being paid to the volume fraction of the reinforcement agent.

Models

Generalities. To define weak Van der Waals interlayer interactions in multilayers and nanocomposites, usually nonlinear spring elements defined by Leonard–Jones (L–J) potential are used,[6,9,10] although using these elements, especially in the models with large dimensions, increases the amount of computations intensively. On the other hand, stronger interlayer interactions are needed in nanocomposites. Therefore, some researchers presented the idea of functionalization or chemical changes in the GSs,[11-16] which induces them to make covalent bond with other layers (or the composite base) or using other stronger chains of molecules as a link between them.

In this study, an attempt was made to investigate the effect of different types of interlayer interactions for both double layer GSs and nanocomposites reinforced with mono and multilayer GSs.

Interlayer interaction: type I. Initially using nonlinear spring elements defined by the Leonard–Jones potential, the same as was employed by other researchers,[6,9,10] the interlayer interactions were simulated and the following equation shows their nonlinear behavior:

$$F(r) = 24\frac{\varepsilon}{\sigma}\left(2\left(\frac{\sigma}{r}\right)^{13} - \left(\frac{\sigma}{r}\right)^{7}\right) \tag{3}$$

where r is the distance between interacting atoms and ε and σ are the L–J parameters, which are $\varepsilon = 0.38655\times10^{-3}$ nN nm and $\sigma = 0.34$ nm for carbon atoms. In this step, the results related to the elastic module could be compared with the results of other studies to validate the models. It should be mentioned that in this step, each atom makes a bond with an atom from another layer or the composite base, the distance of which from each other is less than 0.85 nm (cut-off distance, Fig. S-2). In this study, the thickness of the GSs was assumed 0.34 nm and the distance between the graphene layers or GS and the composite base was 0.17 nm. To reduce the amount of computations, the cut-off distance was assumed 0.38 nm. The chirality of all models is armchair and Fig. S-3 shows the model created for double layer GS and Fig. S-4 is a schematic view of a nanocomposite reinforced by a monolayer GS.

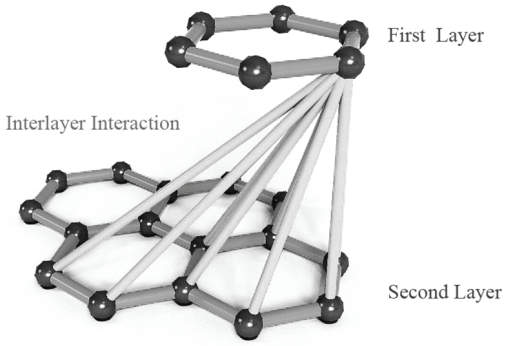

Fig. S-2. Definition of interlayer interactions by nonlinear spring elements.

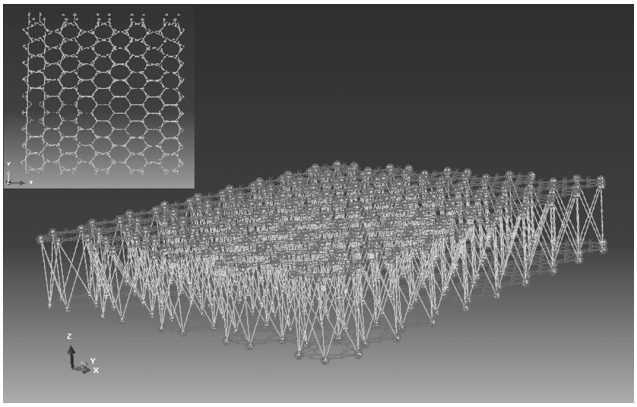

Fig. S-3. Two views of double-layer GSs coupled by Van der Waals forces.

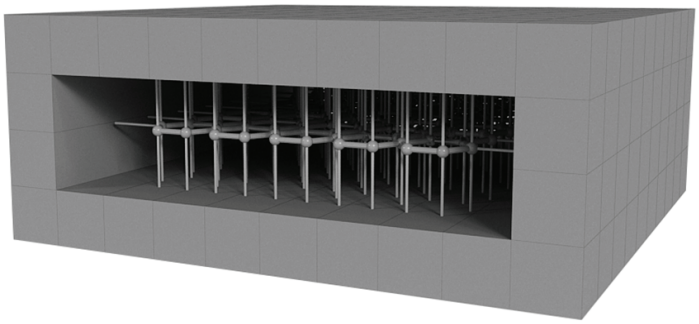

Fig. S-4. Graphic view of a nanocomposite reinforced by a monolayer GS coupled by Van der Waals forces.

Interlayer interaction: type II. In this step using a linear spring element (Fig. S-5) and change in its stiffness, an attempt was made to calculate the ultimate force-translating ratio from the reinforcement agent to the polymeric base. For this purpose, initially a spring with zero stiffness was located between two atoms from different layers and then its stiffness was increased systematically.

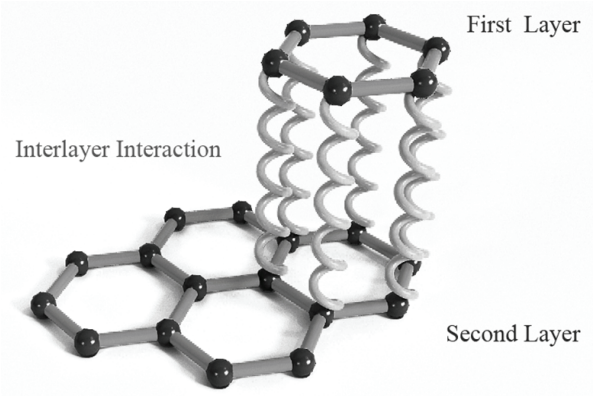

Fig. S-5. Definition of interlayer interactions by linear spring elements**.**

Interlayer interaction: type III. All the van der Waals forces were eliminated in this step and a vacancy defect was introduced into each layer (one atom is diminished), so three atoms obtain one empty orbital and they can make covalent atoms by three atoms from another layer or the polymeric base (Fig. S-6). For this step, the interlayer thickness was assumed to be 0.1421 nm and the interlayer covalent bonds were made using a linear spring element type A ($K_{r\mathrm{A}} = 6.52\times10^{7}\,\mathrm{N\,nm^{-1}}$).[6] Here, initially, van der Waals forces with a cut-off distance of 0.38 nm and the next time, a combination of covalent and van der Waals interlayer interactions were used to have a better comparison between the base and the functionalized level. To better understanding the effect of functionalization, atoms that should make a covalent bond with each other were chosen from different layers an are not *vis-à-vis* (Figs. S-7 and S-8).

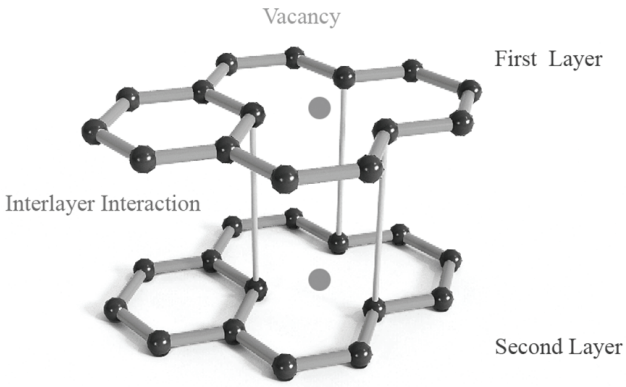

Fig. S-6. Definition of covalent interlayer interactions.

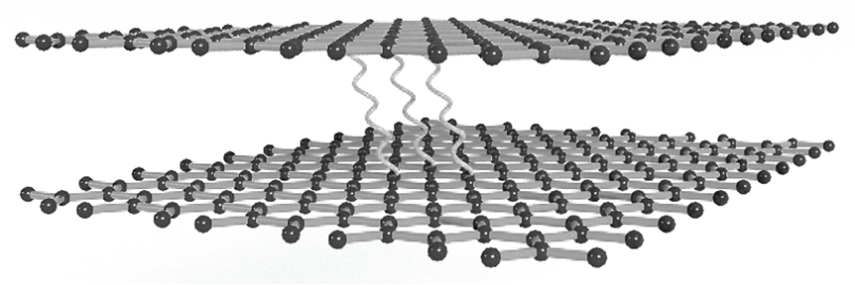

Fig. S-7. Graphic view of GSs coupled by covalent bonds.

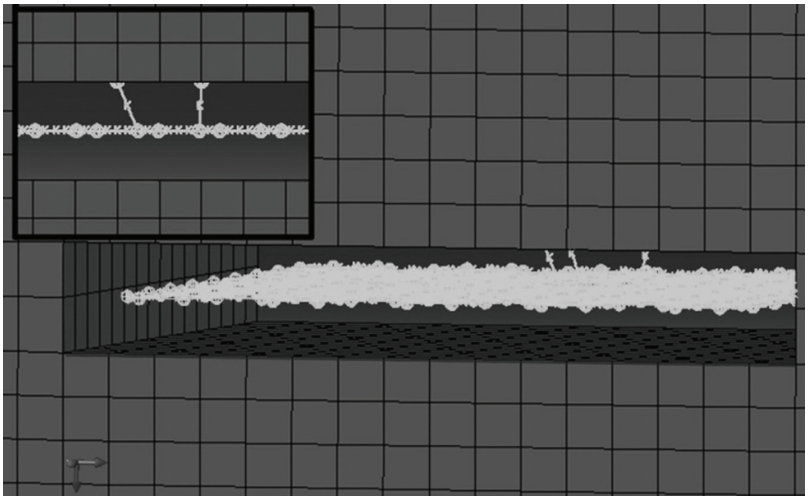

Fig. S-8. Nanocomposite reinforced by a monolayer GS and covalent bonds as interlayer interactions.

In addition, to study further the effect of covalent interlayer bonds, second defects, bidirectional covalent interlayer interactions are created (Fig. S-9). All the mentioned steps were repeated for importing monolayer and double-layer GS into the polymeric base (Fig. S-10).

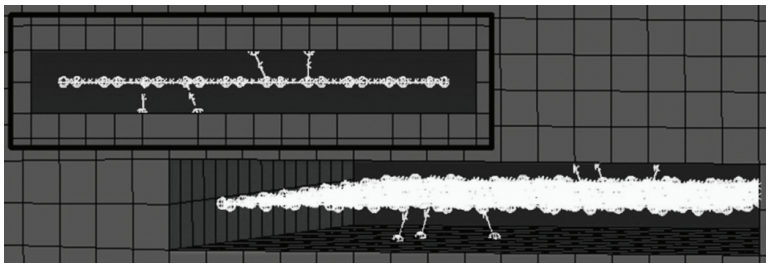

Fig. S-9. Nanocomposite reinforced by a monolayer GS and bidirectional covalent bonds as interlayer interactions.

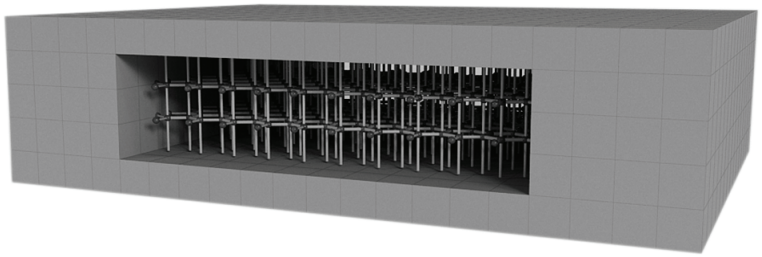

Fig. S-10. Graphic view of a nanocomposite reinforced by double-layer GSs.

To validate the results in the case of nanocomposites, the rule of mixture (ROM) was employed:

$$E_t = \upsilon_G E_G + \upsilon_z E_z \tag{4}$$

where E_t is the total elastic module of a nanocomposite, E_G is the GS elastic module, E_Z is the polymeric base elastic module, υ_G is the GS volume fractions and υ_Z is the polymeric base volume fraction.

REFERENCES

1. C. Li, T.-W. Chou, *Int. J. Solids Struct*. **40** (2003) 2487
2. G. I. Giannopoulos, P. A. Kakavas, N. K. Anifantis, *Comp. Mater. Sci.* **41** (2008) 561
3. A. R. Golkarian, M. Jabbarzadeh, *Comp. Mater. Sci.* **74** (2013) 138
4. A. R. Golkarian, M. Jabbarzadeh, *Journal of Solid Mechanics* **4** (2012) 106
5. A. A. Shariati, A. R. Golkarian, M. Jabbarzadeh, *Journal of Solid Mechanics* **6** (2014) 255
6. A. Montazeri, H. Rafii-Tabar, *Phys. Lett.* A **375** (2011) 4034
7. V. Parvaneh, M. Shariati, H. Torabi, *Comp. Mater. Sci.* **50** (2011) 2051
8. K. Machida, Principles of molecular mechanics, Wiley and Kodansha, 1999
9. M. M. Shokrieh, R. Rafiee, *Compos. Struct.* **92** (2010) 2415
10. K. I. Tserpes, A. Chanteli, *Compos. Struct.* **99** (2013) 366
11. J. L. Bahr, J. M. Tour, *J. Mater. Chem.* **12** (2002) 1952

12. S. J. V. Frankland, A. Caglar, D. W. Brenner, M. Griebel, *J. Phys. Chem.* **106** (2002) 3046
13. M. L. Shofner, V. N. Khabashesku, E. V. Barrera, *Chem. Mater.* **18** (2006) 906
14. F. Buffa, G. A. Abraham, B. P. Grady, D. Resasco, *J. Polym. Sci. B Polym. Phys.* **45** (2007) 490
15. C. A. Cooper, S. R. Cohen, A. H. Barber, H. D. Wagner, *Appl. Phys. Lett.* **81** (2002) 3873
16. A. H. Barber, S. R. Cohen, H. D. Wagner, *Appl. Phys. Lett.* **82** (2003) 4140.