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

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Abstract: In this study, the influence of the type of interlayer interactions on the elastic modules of multilayer graphene sheets (GS) and nanocomposites was investigated. The modeling and investigation of mechanical properties of graphite layers were performed using the molecular mechanics (MM) method. Initially, for improving the model and decreasing the amount of computations, three types of elements, *i.e.*, a beam, a linear spring and a nonlinear spring, were used. Continuing, the mechanical properties of multilayers and nanocomposites were compared using three types of interlayer interactions. Initially, a nonlinear spring defined by the Leonard Jones potential was used to define the interlayer interactions (ordinary case). Then, a linear spring with a certain stiffness, to obtain an equal linear spring and to investigate the ultimate capacity of interlayer interactions in the translation of force, by increasing the stiffness of linear springs, was employed (chemical change). Then, by omitting all Van der Waals interactions and the creation of defects in the graphite layers, covalent interlayer interactions (using the Morse potential) were created. Finally, Van der Waals and covalent interlayer interactions were created spontaneously to study the properties of multilayers and nanocomposites (functionalization). The results were compared with other available literature data in order to validate the modeling.

Keywords: structural mechanics approach; graphene sheet; elastic modules; vacancy defect; functionalization.

INTRODUCTION

Graphene sheets (GS) and carbon nanotubes (CNT) have attracted the attention of many researchers and scientists due to their wonderful properties and abundant applications in industry, medicine, martial science and other fields.[1–6] Besides their unique mechanical, thermal and electrical properties, their significant capabilities in other fields have attracted further attention. Among these

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properties, their potential to be used as a reinforcement agent in polymeric composites and producing nanocomposites with exclusive properties could be mentioned. High tensile strength beside the lightening and high flexibility of these products is one of their extraordinary mechanical properties that make them unique. Besides the mentioned benefits, weak interlayer interactions, which persuade researchers to demonstrate the functionalization idea or chemical changes,[7–12] should be noticed.

Modeling approaches for these nanomaterials are needed, due to their small scales and expensive equipment in this field. One of the most attractive methods in this field is the molecular mechanic (MM) method, which was introduced for the first time by Li and Chou[13] who used linear beam elements to simulate CNTs. Subsequently, many researchers devoted their time to improving this field by working on the type and quality of the employed elements. Among the studies performed in this field, one by Meo and Rossi,[14] who introduced spring elements as a suitable replacement for beam elements, could be mentioned. Afterwards, Georgantzinos *et al.*[15] presented the idea of using fully nonlinear spring-based models, which were then improved further by other researchers.[16–20]

To date, nonlinear spring elements were commonly used to simulate interlayer interactions in nanocomposites.[21–23] Rafiee *et al.*[24] studied the idea of functionalization of CNT nanocomposites using linear beam elements (introduced by the AMBER potential) as covalent interlayer interactions and reported that this action decreased the elastic modulus of CNTs and reinforced nanocomposites. The focus of this study was the important problem that the connector between the base material and the reinforcement (CNT) agent are weak Van der Waals interactions, which cannot translate the maximum power of the reinforcement to the base.

Therefore, in this study, the effect of using different types of interlayer interactions was investigated. The most important goals were the calculation of the maximum limit of load transferring and the study of the influence of different types of functionalization (introduced by many researchers).[7–12] The most important objectives investigated were:

– The influence of different types of mechanical elements used to simulate monolayer GS.

– The influence of four different types of interlayer interactions on the mechanical properties of multilayer GSs and nanocomposites, *i.e.*: a) van der Waals interlayer interactions using nonlinear spring elements defined by the Leonard–Jones potential (ordinary case), b) linear spring elements, whose the stiffness of which increased at each step to obtain the ultimate value of translating force (chemical change), c) covalent interlayer interaction using a linear spring element defined by the Morse potential energy and d) a combination of Van der Waals and covalent bonds.

– A comparison between the reinforcing effect of monolayer and multilayer GSs in nanocomposites.

CONSIDERED MODELS

Considered models, theoretical background and calculations are described in Supplementary material to this paper.

RESULTS AND DISCUSSION

Monolayer GS

The results related to the elastic module of a monolayer GS for different types of mechanical elements are given in Table I. With change in the mechanical element from linear beam to linear spring, the influence of the defined cross section area could be obtained. By replacing a nonlinear spring with a linear spring, the influence of the definition of the nonlinear behavior for the employed elements could be computed. It was observed that by a replacing a linear beam with a linear spring, the elastic module in model I increased by 11 % and in model II increased by 17 %. This shows that by assuming a cross section area for the element, a significant change was observed in the elastic module. In addition, in this step, the time of the computations for both cases was the same. To continue, by replacing a nonlinear spring with a linear spring, the elastic module of both models increased by about 3 %. This showed that by defining nonlinear behavior for the elements, the results did not show significant changes but the time of the computations was very long, which further increased on increasing the dimensions of the sheets. Therefore, a linear spring element could be introduced as a suitable element to simulate interatomic interactions of GSs, because they make less error and require shorter computation times.

TABLE I. Variation of the elastic module of a GS in dependence on the type of the mechanical element

Type of the mechanical element	Elastic module, TPa	
Linear beam	Model I:	1.096
	Model II:	1.078
	Lit.[25]:	1.025
Linear spring	Model I:	1.217
	Model II:	1.269
	Lit.[26]:	1.367
Nonlinear spring	Model I:	1.255
	Model II:	1.308
	Lit.[18]:	1.245

Double-layer GSs

Interlayer interaction: type I. GS used at this step is perfect and its elastic module is about 1.2175 TPa. By defining a second layer at a distance of 0.34 nm from the first one and the creation of Van der Waals interaction between the layers with a cut-off distance of 0.38 nm, the elastic module increased to 1.2275 TPa. This result is in good agreement with the results reported by other researchers (Table II).

TABLE II. A comparison of the results related to the elastic module of double-layer GSs with Van der Waals interlayer interactions

Study	Elastic module of a monolayer, TPa	Elastic module of a double-layer, TPa
Present study	1.2175	1.2275
Golkarian and Jabbarzadeh[18]	1.2447	1.2537
Li and Chou[13]	1.025	1.035
Bao *et al.*[27]	1.030	1.032

Interlayer interaction: type II. The results obtained at this step (Table III) showed that at a stiffness of 300 nN nm^{-1}, the elastic module is about 1.2263 TPa, which is in good agreement with the value 1.2257 TPa related to the previous step and showed that this stiffness is a good replacement for nonlinear Van der Waals interactions. It was observed that at a stiffness of about 10^8 nN nm^{-1} (330000 times stronger than 300 nN nm^{-1} equal to the van der Waals forces), the elastic module of double-layer GS increased to 1.59 TPa, showing a 30 % increase. It could be deduced that if the maximum increase of 30 % was satisfactory and the complication of working on the power of interlayer interactions was possible, chemical work on the interlayer interactions could be helpful.

TABLE III. Variation of the elastic module of double-layer GSs from the stiffness of linear springs as interlayer interactions

Stiffness, nN nm^{-1}	Elastic module, TPa
0	1.2175
1	1.2176
10	1.2178
100	1.2205
300	1.2263
10^3	1.2452
10^4	1.5513
10^6	1.5905
10^8	1.5954
10^{10}	1.5955
10^{12}	1.5955

Interlayer interaction: type III. In the third step, by defining a defect in each layer, the elastic module of each layer was reduced to 1.1979 TPa; this negligible decrease is in the range of results reported by other researchers (Table IV). By defining van der Waals forces between two layers, the elastic module of the layers increased to 1.2060 TPa. If the layers were linked together by covalent bonds, the elastic module increased to 1.1988 TPa and when a combination of van der Waals and covalent bonds was used, the elastic module increased to 1.2067 TPa, which shows a 0.7 % increase in comparison to defective monolayers and 0.9 % reduction if compared to the perfect ones.

TABLE IV. Variation of elastic module of a monolayer GS caused by defining a defect

Study	Perfect elastic module, TPa	Defective elastic module, TPa
Present study	1.2175	1.1979
Rafiee & Pourazizi[24]	1.032	0.990
Ansari *et al.*[28]	0.79	0.77
Scalante *et al.*[29]	1.042	1.036

The results showed that by defining a defect in the layers, the elastic module showed a 1.6 % reduction and that the reduction after functionalization by defining covalent and van der Waals forces was 1.5 %, which is a negligible difference. From these results, it could be deduced that functionalization in order to repair existing defects or after defining the defects in the model, to form covalent interlayer interactions cannot improve the mechanical properties of the model. Therefore, other ways, such as a change in the type of interlayer interaction, should be considered.

Nanocomposite

Monolayer reinforcement. Interlayer interaction: type I. In this step, a GS with an elastic module of 1.2175 TPa was imported into a polymeric base with an elastic module of 3.5 GPa and they were coupled with Van der Waals forces. The elastic module of nanocomposite at this step was 63.7 GPa, which is in good agreement with the result of 64.2 GPa obtained from ROM. In a same research performed by Rafii-Tabar and Montazeri[21] for a polymeric base with an elastic module of 3.5 GPa, the elastic module of nanocomposite was reported to be about 59.536 GPa, which is in suitable agreement with the results obtained in this study. Moreover, the elastic module of the polymeric base (3.5 GPa) in this step was found to be 3.67 GPa, which was a 4.8 % increase.

Interlayer interaction: type II. By using linear springs instead of Van der Waals forces and increasing its stiffness, no significant change was observed in the translate ratio from reinforced to polymeric base (Table V). It could be seen that the maximum elastic module of the nanocomposite in a stiffness of 300 nN nm^{-1} (the same as when van der Waals forces existed) was obtained, which was equal to the 63.68 GPa. The maximum value for the elastic module of polymeric base was about 3.678 GPa, *i.e.*, a 1.5 % increase.

Interlayer interaction: type III. By omitting all van der Waals forces, defining a defect and creating three covalent bonds, the elastic module of the nanocomposite and the polymeric base were about 62.69 GPa and 3.5 GPa, respectively. By defining, a second defect and the next three covalent bonds (bidirectional), the elastic module of the nanocomposite and of the polymeric base were 61.69 and 3.5 GPa, respectively. By defining van der Waals forces (together with bidirectional covalent bonds), the elastic modules reached 61.71 and 3.6 GPa, respectively. From these results, it can be deduced that the functionalization of nanocomposites reinforced by monolayer GS does not lead to an improvement of the elastic module of the nanocomposite.

TABLE V. Variation of elastic module of polymeric base according to the stiffness of a linear spring as an interlayer interaction (monolayer reinforcement)

Stiffness, nN nm^{-1}	Elastic module of polymeric base, GPa
0	3.5
0.1	3.557
10	3.67
300	3.677
1000	3.678
10^4	3.678

Double-layer reinforcement. Interlayer interaction: type I. By importing a double-layer GS in polymeric base, the elastic module of nanocomposite increased to 64.11 GPa, which is a 0.7 % increase. In this step, the elastic module of polymeric base decreased to 3.6 from 3.67 GPa for a monolayer reinforcement. This showed that increasing the number of layers in the presence of van der Waals forces as interlayer interactions was inefficient.

From the results of this step and the previous steps (related to the functionalization by using monolayer reinforcement), it can be deduced that the functionalization of double-layer GS would be inefficient, because the increase in the number of layers did not improve the elastic module of the nanocomposite and also defect creation (in order to make covalent bonds) decreased the elastic module of the nanocomposite.

Interlayer interaction: type II. By increasing the stiffness of all interlayer interactions including the interactions GS–GS and GS–polymeric base, the elastic module of the nanocomposite increased to 82.5 GPa, *i.e.*, a 30 % increase (in a stiffness of 1 nN nm^{-1}) (Table VI), which is equal to the time that the elastic module of double-layer GS reached its maximum value. In addition, the elastic module of the polymeric base decreased to 3.605 GPa (in stiffness of 100 nN nm^{-1}) from 3.67 GPa related to the use of monolayer reinforcement (Table VII). This shows that increasing the number of layers and the stiffness of interlayer interactions cannot improve the elastic module of the polymeric base.

Some of the important points that can be deduced from the results are:

1. Making a defect in the graphene layer for replacing three carbon–carbon covalent bonds instead of three weak van der Waals interlayer interactions to inc-

TABLE VI. Variation of elastic module of nanocomposite according to the stiffness of the linear spring element as an interlayer interaction (double layer reinforcement)

Stiffness, nN nm^{-1}	Elastic module of nanocomposite, GPa
0	63.7
1	63.68
10	63.69
100	63.74
1000	64.18
10^4	67.39
10^5	76.72
10^6	81.68
10^7	82.41
10^8	82.48
10^9	82.5

rease the elastic module of nanocomposite or multilayers is a useless operation. This is because the decreasing effect of making a defect in a layer on the elastic module more than decreases the effect of this type of functionalization.

TABLE VII. Variation of the elastic module of the polymeric base in dependence on the stiffness of the linear spring elements as interlayer interaction (double-layer reinforcement)

Stiffness, nN nm^{-1}	Elastic module of the polymeric base, GPa
0	3.5
1	3.585
10	3.602
100	3.605
1000	3.605

2. By increasing the strength of interlayer interactions (which includes each type of functionalization or chemical changes), a maximum increasing effect of 30 % in the elastic module of nanocomposites reinforced by multilayer graphene sheets is estimated. Of course, this results may have some changes in experimental studies because, in this case, the influence of many graphene layers as a multilayer GS was only investigated and the influence of some important parameters, such as the contribution, dispersion, local density, direction of the layers and some other parameters that could not be considered in the atomic mechanical modeling and appear only in real, experimental investigations.

3. This increasing effect is when the employment of multilayer graphene layers (in the experimental works most of the employed graphene layers are also multilayers, because monolayers are rarely available) and increasing the strength of interlayer interactions between a monolayer graphene sheet and a polymeric base does not lead to a significant increasing effect in the elastic module of the nanocomposite.

Among theoretical studies performed in this case, the study performed recently by Rafiee and Rourazizi[24] could be mentioned, in which they used the molecular mechanic modeling method and reinforced a polymeric cylindrical matrix with monolayer carbon nanotube and investigated the influence of this type of functionalization (making defect and replacing C–C covalent bonds instead of van der Waals interlayer interactions) and reported the same results.

They reported the decreasing effect of this type of functionalization on the elastic module of a cylindrical polymeric base reinforced by single layer carbon nanotube and they explained that the effect of functionalization cannot be observed on the micro scale but its improving effect may appear on the meso or macro scale.

Therefore, in the present study, time was devoted to investigate the effect of each type of functionalization (by increasing the strength of interlayer interactions up to its highest level) for both mono and multilayer graphene sheets. It was found that in the case of multilayers, an up to 30 % increase in the elastic module of the nanocomposite was possible by increasing the effect but in the case of monolayer reinforcements, no increase was observed in the case of graphene sheet, but not with carbon nanotubes

As a general result, it could be deduced that, maybe, more attention should be paid to the interactions between the graphene layers than those between the graphene layer and the polymeric base. However, this objective cannot be strongly emphasized because, as explained previously, there are some crucial parameters that cannot be considered using this modeling approach.

CONCLUSIONS

In this paper the influences of three types of interlayer interactions on the elastic module of multilayer GSs and nanocomposites reinforced by monolayer and double-layer GS were studied. The following important cases were considered in this investigation:

The influence of type of element used for simulating of GSs on the elastic module and the amount of computations.

The influence of type of element used for simulating interlayer interactions in double-layer GSs and nanocomposites reinforced by monolayer and double--layer GS.

Using four types of interlayer interactions:

– van der Waals interlayer interaction using nonlinear spring element defined by the Leonard–Jones potential to validate the modeling method,

– linear spring elements, the stiffness of which was increased at each step to find the ultimate value of the possible force translation ratio,

– omitting all van der Waals forces, defining defects in the layers and make three covalent interlayer interactions by defining each defect and

– combination of van der Waals and covalent interlayer interactions.

The influence of an increase in the number of layers on the reinforcement of the nanocomposites.

The maximum amount of possible force translation ratio from reinforcement to polymeric base (chemical changes).

Some of the important results are:

– The linear spring element is in best agreement with other results and requires the lowest computations time.

– Making defects and replacing van der Waals interlayer interactions with C–C covalent bonds cannot improve the elastic module of multilayer GSs and nanocomposites. This means that the decreasing effect of making defects is more than the increasing effect of the replacement by covalent interlayer interactions.

– Chemical changes (functionalization) in interlayer interactions under the best conditions can lead to an increase of about 30 % in the elastic module of multilayer GSs and nanocomposites reinforced by multilayer GSs.

– Improving the elastic modules of nanocomposites due to the functionalization (reported by experimental works) is the consequence of functionalization of interlayer interactions between graphene layers not between graphene layer and polymeric base.

– Improving the quality of interlayer interactions cannot help to improve the elastic module of polymeric base.

Consequently, it could be deduced that by using multilayer GSs and improving the strength of the interlayer interactions, significant increases in the elastic module of double-layer GSs and also nanocomposites reinforced by multilayer GSs of up to 30 % could be expected. In addition, improving the strength of the interlayer interactions or increasing the number of layers does not lead to an improvement in the elastic module of the polymeric base.

SUPPLEMENTARY MATERIAL

Details of the considered models, their theoretical background and method of calculations are available electronically from http://www.shd.org.rs/JSCS/, or from the corresponding author on request.

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ИЗВОД

УТИЦАЈ ИНТЕРАКЦИЈА МЕЂУСЛОЈА НА МЕХАНИЧКА СВОЈСТВА ПОЛИМЕРНИХ НАНОКОМПОЗИТА

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Проучаван је утицај типова интеракције међуслоја на еластичне модуле вишеслојног графена (GS) и нанокомпозита. Моделовање и испитивање механичких својстава графитних слојева изведено је методом молекулске механике (MM). Најпре су, због побољшања модела и смањења обима израчунавања, коришћена три елемента: зрак, линеарна и нелинеарна опруга, а у наставку су упоређена механичка својства вишеструких слојева и нанокомпозита применом три типа интеракције међуслоја. Прво је коришћена нелинеарна опруга дефинисана Leonard–Jones потенцијалом да би се дефинисале интеракције међуслоја (ординарни случај). Затим је примењена донекле пригушена линеарна опруга (еквивалентна линеарна опруга) и повећавањем пригушености линеарних опруга испитао крајњи капацитет интеракције међуслоја у транслацији силе (хемијска промена). Уз то су, у једном случају занемарене све van der Waals интеракције и настајање дефеката у графитним слојевима, те је оно доводило до ковалентних интеракција међуслоја (Morse потенцијал), а у другом , van der Waals и ковалентне интеракције међуслоја креиране су спонтано да би се проучила својства вишеструких слојева и нанокомпозита (функционализација). Резултати су поређени са подацима из литературе ради валидизације моделовања.

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REFERENCES

1. M. Paradise, T. Goswami, *Mater. Design* **28** (2007) 1477
2. C. P. Firme, P. R. Bandaru, *Nanomedicine* **6** (2010) 245
3. D. A. Gomez-Gualdron, J. C. Burgos, J. Yu, P. B. Balbuena, *Prog. Mol. Biol. Transl. Sci.* **104** (2011) 175
4. R. Orinakova, A. Orinak, *Fuel* **90** (2011) 3123
5. V. K. K. Upadhyayula, S. Deng, M. C. Mitchell, G. B. Smith, *Sci. Total Environ.* **408** (2009) 1
6. V. N. Popov, *Mater. Sci. Eng. R* **43** (2004) 61
7. J. L. Bahr, J. M. Tour, *J. Mater. Chem.* **12** (2002) 1952
8. S. J. V. Frankland, A. Caglar, D. W. Brenner, M. Griebel, *J. Phys. Chem.* **106** (2002) 3046
9. M. L. Shofner, V. N. Khabashesku, E. V. Barrera, *Chem. Mater.* **18** (2006) 906
10. F. Buffa, G. A. Abraham, B. P. Grady, D. Resasco, *J. Polym. Sci. B Polym. Phys.* **45** (2007) 490
11. C. A. Cooper, S. R. Cohen, A. H. Barber, H. D. Wagner, *Appl. Phys. Lett.* **81** (2002) 3873
12. A. H. Barber, S. R. Cohen, H. D. Wagner, *Appl. Phys. Lett.* **82** (2003) 4140
13. C. Li, T.-W. Chou, *Int. J. Solids Struct*. **40** (2003) 2487
14. M. Meo, M. Rossi, *Compos. Sci. Technol.* **66** (2006) 1597
15. S. K. Georgantzinos, D. E. Katsareas, *Physica E* **43** (2011) 1833
16. V. Parvaneh, M. Shariati, H. Torabi, *Comp. Mater. Sci.* **50** (2011) 2051
17. R. Rafiee, M. Heidarhaei, *Compos. Struct.* **94** (2012) 2460
18. A. R. Golkarian, M. Jabbarzadeh, *Comp. Mater. Sci.* **74** (2013) 138
19. A. R. Golkarian, M. Jabbarzadeh, *J. Solid Mechanics* **4** (2012) 106

20. A. A. Shariati, A. R. Golkarian, M. Jabbarzadeh, *J. Solid Mechanics* **6** (2014) 255
21. A. Montazeri, H. Rafii-Tabar, *Phys. Lett.* A **375** (2011) 4034
22. M. M. Shokrieh, R. Rafiee, *Compos. Struct.* **92** (2010) 2415
23. K. I. Tserpes, A. Chanteli, *Compos. Struct.* **99** (2013) 366
24. R. Rafiee, R. Pourazizi, *Comp. Mater. Sci.* **93** (2015) 576
25. C. Li, T. W. Chou, *Int. J. Solids Struct.* **40** (2003) 2487
26. S. K. Georgantzinos, G. I. Giannopoulos, N. K. Anifantis, *Mater. Design* **31** (2010) 4646
27. B. Wen Xing, Z. Chang Chun, C. Wan Zhao, *Physica, B* **352** (2004) 156
28. R. Ansari, S. Ajori, B. Motevalli, *Superlattice. Microst.* **51** (2012) 274
29. A. Tapia, R. Peon-Escalante, C. Villanueva, F. Avilés, *Comp. Mater. Sci*. **55** (2012) 255.