An Effective Modulus Predictive Method of Graphene Epoxy Nanocomposites

Huazhen Wei, Danyong Wang, Jianqin Zhang, Haiyun Zhang and Shuhu Li
Shandong Non-metallic Materials Institute, Jinan 250031, China
Email: 13356656553@189.cn

Abstract. Interfacial interaction between flaked graphene and resins was the key element of effecting whether graphene as nanofillers could improve some of the properties of pure resin. Based on really materials and applied manufacturing process, a new kind of an effective modulus predictive method for resins modified with graphene which could compute and analyze modulus of any content ratio of graphene in the resin with only one content ratio was built in order to provide theoretical foundations for design and property of resins modified with graphene. According to practically different materials system and corresponding manufacturing processes, few experiments which only needed elastic modulus of resins modified with one random content-ratio graphene were made to predict effective elastic modulus of any other content ratio of graphene modifying resins under the same manufacturing processes by obtaining experimental constants based on numerical progressive iterative approximation method and compute the above experimental constants as basic materials parameters so as to build the whole analysis model in the next step. An excellent agreement was found between data obtained from this study and the experiment.

1. Introduction

Kinds of modification techniques had been used for epoxy matrix composites in order to improve mechanical properties of epoxy polymers in recent years. Graphene as a new kind of nanofillers with the large scale and mono-atom thick could be added into resins to improve thermal and mechanical properties which has aroused great attentions of numerous scientists[1-7].

The excellent and precise control of graphene content ratio in composites and corresponding surface compatibility during manufacturing graphene reinforced epoxy matrix composites could greatly improve comprehensive properties of composites, modify numerous weakness of composites' properties and solve practical problems in engineering such as weak toughness and hardness required to be improved, simultaneously, so as to push wide applications of new kinds of composites in usages of main-standing parts[8-13].

Design and research development of all-on experiments to research graphene reinforced composites were induced to long research cycle and high cost which could not reach development speed of new-kinds of composites. However, the use of materials-on-computing methods such as molecular mechanical method and molecular dynamic method could achieve well design and development of advanced composites and the research cycle was greatly shortened. These methods have been the key path of researching and developing new materials. However, public literatures of predictive methods of physic and chemical properties of polymers modified with graphene still remained in theoretical phase[14-17], not suitable for corresponding applications in materials research and development. Therefore, a design method convenient to practical engineering applications of epoxy matrix modified with graphene was built in this paper so as to provide technical support for practical applications of equipments.
2. Foundation of Analysis Method
The rational relationships between macro-properties and corresponding properties, macro-properties and micro-structures were built, and the response rules and natures of resins modified with graphene under some certain conditions were revealed. All above could provide necessary theoretical basis and means for modified design, property evaluation of graphene epoxy nanocomposites.

Interfacial interaction between graphene and resins was the key element of effecting whether graphene as nanofillers could improve mechanical properties of resins, therefore, compatibility between graphene and resins could directly make effects on modification results of graphene to resins. Well interfacial interaction between graphene and resins could make stress transmitted effectively during polymerization was formed so that resins system could be greatly improved. However, bad compatibility between graphene and matrix induced into the separation of graphene and resin phases during polymerization, graphene would cluster in some places, materials defects would form, and modification effects would not be so good. Therefore, the modified-resin effects would be totally different with graphene blended into different resins.

Therefore, a new kind of multi-step effective modulus predictive method was built to predict effective modulus of graphene epoxy nanocomposites so as to provide theoretical foundations for materials design and property of composites.

The procedures on predictive method of effective modulus of graphene epoxy nanocomposites were as follows:

First, the following hypotheses were given according to the compatibility of graphene in different resins system for multiple engineering practical conditions.

1. Adding graphene into resins, it was hypothesized that a new kind of interface material which was used to describe compatibility between graphene and resins was formed between graphene and resins.

2. Commonly, the compatibility between graphene and resins was not so perfect in practical conditions, and the interface compatibility was totally connected with manufacturing process. The elastic modulus of interface material was available defined according to practical engineering situations. That was, if compatibility between graphene and resins was well, it was hypothesized that elastic modulus of interface material between graphene and resins was totally close to elastic modulus of graphene, signed as \( E_i \). However, if compatibility between graphene and resins was not so well, \( E_i \) was discounted in ratio to the compatibility degree between graphene and resins.

3. It was hypothesized that the weight ratio of interface material in the whole composite was signed as \( P_{coat} \) and weight percentage of graphene in all composite was signed as \( P_{GP} \), the relationship between \( P_{coat} \) and \( P_{GP} \) was as follows, and \( C \) was experimental constant.

\[
P_{coat} = CP_{GP}
\]

(1)

However, during manufacturing procedure of graphene epoxy nanocomposites, the whole-materials components or manufacturing methods under the same material-system adopted by researchers were different and therefore material-interface properties between graphene and resins were different. Therefore, according to practically different materials system and corresponding manufacturing processes, few experiments which only needed elastic modulus of one random content-ratio graphene epoxy nanocomposites were made to predict effective elastic modulus of any other content ratio of graphene epoxy nanocomposites under the same manufacturing processes by obtaining \( C \) and \( E_i \) based on numerical progressive iterative approximation method and compute the above two values as basic materials parameters so as to build the whole analysis model in the next step.

Computing procedures of effective modulus of graphene epoxy nanocomposites were as follows.

1. By making full use of Mori-Tanaka method[18] computational program in DIGIMAT software and elastic modulus of one random content ratio of graphene epoxy nanocomposites' experimental result, experimental constant \( C \) and interface elastic modulus \( E_i \) by numerical progressive iterative approximation method were obtained as basis materials-input-parameters of this model to build the whole analysis model.
2. Equivalent modulus of two-phase composites composed of graphene and interface material that were considered as one equivalent uniform reinforced material was computed by applying Mori-Tanaka method.

3. The effective modulus of equivalent uniform reinforced resin material was computed by applying Mori-Tanaka method again.

3. Model Validations and Examples Analysis

3.1. Mechanical Property Parameters of graphene
According to the manufacturer of supplying graphene, mechanical property parameters of graphene were that In-plane elastic modulus was 450GPa and In-plane Poisson ratio was 0.3.

3.2. Mechanical Property Parameters of Epoxy
According to experiments, mechanical property parameters of TDE-85 epoxy were that elastic modulus was 2.832GPa and its Poisson ratio was 0.3.

According to literature [19], mechanical property parameters of CYD-128 epoxy were that elastic modulus was 1.817GPa and its Poisson ratio was 0.3.

3.3. Effective Modulus Prediction and Experiment Validation of Graphene TDE-85 Epoxy
Effective modulus of TDE-85 epoxy modified with graphene was computed and analyzed based on method built in this project. Based on 0.29wt% graphene epoxy nanocomposites' elastic modulus experiment value E=2.966GPa, applying Mori-Tanaka computing procedure in DIGIMAT and numerical progressive iterative approximation method, interface material experiment constant C=0.1 in this model and interface material elastic modulus $E_i=0.05GPa$ were obtained. The above as input conditions of interface material's basis mechanical parameters, effective modulus of other content graphene epoxy nanocomposites under the same manufacturing conditions were predicted. Effective modulus of 0.5wt%, 1wt% and 1.5wt% graphene epoxy nanocomposites were predicted and the comparisons were made between computing results and experimental results.

Comparisons between effective modulus predictive results and experimental results of epoxy modified with graphene by making full use of three methods, method built in this project considering interface effect, common Mori-tanaka method without considering interface and traditional mixture model method were made, shown in Table 1.

| graphene content (wt%) | Experimental results of effective modulus (GPa) | Predictive results of effective modulus (GPa) | Error (%) | Predictive results of effective modulus (GPa) | Error (%) | Predictive results of effective modulus (GPa) | Error (%) |
|------------------------|-----------------------------------------------|---------------------------------------------|-----------|---------------------------------------------|-----------|---------------------------------------------|-----------|
|                        |                                               | Method built in this project                | Common Mori-Tanaka Method                   | Traditional Mixture Model               |           |                                             |           |
| 0                      | 2.832                                         | 2.963                                       | 0.10     | 3.190                                       | 7.55      | 3.70                                        | 24.63     |
| 0.29                   | 3.334                                         | 3.057                                       | 8.31     | 3.446                                       | 3.36      | 4.32                                        | 29.65     |
| 0.5                    | 3.380                                         | 3.283                                       | 2.87     | 4.063                                       | 20.21     | 5.81                                        | 71.99     |
| 1.0                    | 3.432                                         | 3.510                                       | 2.27     | 4.683                                       | 36.45     | 7.30                                        | 112.81    |

It was seen from comparison data results, the highest error of effective modulus between predictive result and experimental result by use of Mori-Tanaka without considering interface was up to 36.45% (predictive conformability was 63.55% and predictive error was huge while with high content graphene epoxy nanocomposites). The highest error of effective modulus between predictive results...
and experimental results by use of traditional mixture model was up to 112.81%, predictive error was huge while with the same content graphene epoxy nanocomposites. However, the highest error of effective modulus between predictive results and experimental results by use of method built in this project was up to 8.31%, that means, predictive conformability was 91.69%, greatly improved by Mori-Tanaka without considering interface and traditional mixture model.

3.4. Effective Modulus Prediction and Experiment Validation of Graphene CYD-128 Epoxy [19]

Effective modulus of CYD-128 epoxy modified with graphene was computed and analyzed based on method built in this project. Based on 0.5wt% graphene epoxy nanocomposites' elastic modulus experiment value $E=2.301\text{GPa}$, applying Mori-Tanaka computing procedure in DIGIMAT and numerical progressive iterative approximation method, interface material experiment constant $C=0.05$ in this model and interface material elastic modulus $E_i=0.2\text{GPa}$ were found. The above as input conditions of interface material basis mechanical parameters, effective modulus of other content graphene epoxy nanocomposites under the same manufacturing situations were predicted. Effective modulus of 0.1wt%, 0.3wt% and 1wt% graphene epoxy nanocomposites were predicted and the comparisons were made between computing results and experimental results.

Comparisons of effective modulus predictive results and experimental results of CYD-128 Epoxy Modified with Graphene by making full use of three methods, method built in this project considering interface effect, common Mori-tanaka method without considering interface and traditional mixture model method were made, shown in Table 2.

| graphene content (wt%) | Experimental results of effective modulus (GPa)[19] | Method built in this project | Common Mori-Tanaka Method | Traditional Mixture Model |
|------------------------|------------------------------------------------------|----------------------------|---------------------------|-------------------------|
|                        | Predictive results of effective modulus (GPa) | Error (%)                  | Predictive results of effective modulus (GPa) | Error (%)                  | Predictive results of effective modulus (GPa) | Error (%)                  |
| 0                      | 1.817                                               | -                          | 1.930                     | 3.82                     | 2.116                     | 13.81                      |
| 0.1                    | 1.864                                               | 1.913                      | 2.63                      | 1.930                     | 3.82                     | 2.116                     | 13.81                      |
| 0.3                    | 1.946                                               | 2.107                      | 8.27                      | 2.151                     | 11.80                     | 2.713                     | 41.03                      |
| 0.5                    | 2.301                                               | 2.300                      | 0.04                      | 2.380                     | 6.49                      | 3.311                     | 48.14                      |
| 1                      | 2.098                                               | 2.070                      | 1.33                      | 2.931                     | 43.61                     | 4.805                     | 135.42                     |

It was seen from comparison data results, the highest error of effective modulus between predictive result and experimental result by use of Mori-Tanaka without considering interface was up to 43.61%. The highest error of effective modulus between predictive results and experimental results by use of traditional mixture model was up to 135.42%, predictive error was huge while with the same content graphene epoxy nanocomposites. However, the highest error of effective modulus between predictive results and experimental results by use of method built in this project was up to 8.27%, greatly improved by Mori-Tanaka method and traditional mixture model method without considering interface's effect.

4. Conclusions

A new multi-step effective modulus predictive method of graphene epoxy nanocomposites was built according to practical engineering conditions.

The effective modulus predictive results and experimental results for TDE-85 epoxy modified with graphene and CYD-128 epoxy modified with graphene with different content ratios of graphene in resin systems by making use of effective modulus predictive method built in this project were compared and analyzed. The results showed that the maximal error of predictive result was up to
8.31%, and that means, the predictive precision was above 91.69%. The predictive results were well and it could provide theoretical basis for material design and property evaluation of graphene epoxy nanocomposites. However, the currency of Common Mori-Tanaka Method and traditional mixture model was not well, and predictive results were just well for latter while large error for materials' system.

5. References
[1] Novoselov K S, Geim A K, Morozov S V, Jiang D, Zhang Y, Dubonos S V, Grigorieva I V and Firsov A A 2004 Science 306 666
[2] Lee C, Wei X, Kysar J W and Hone J 2008 Science 321 385
[3] Ranjbartoreh A R, Wang B, Shen X and Wang G 2011 J. Applied Physics 109 14306
[4] Kalaitzidou K, Fukushima H and Drzal L T 2007 Carbon 45 1446
[5] Kalaitzidou K, Fukushima H and Drzal L T 2007 Composites: Part A 38 1675
[6] Sanada K, Tada Y and Shindo Y 2009 Composites Part A: Applied Science and Manufacturing 40 724
[7] Salavagione H J, Martinez G and Gomez M A 2009 J. Materials Chemistry 19 5027
[8] Yin Y and Tu S T 2002 J. Reinforced Plastics and Composites 21 1619
[9] Tu S T 2005 Journal of Composite Materials 39 617
[10] Cai W, Tu S and Tao G 2005 J. Thermoplastic Composite Materials 18 241
[11] Kim H and Jeong Y G 2010 J. Polymer Science Part B: Polymer Physics 48 850
[12] Kim H, Miura Y and Macosko C W 2010 Chemistry of Materials 22 3441
[13] Shahil K M F and Balandin A A 2012 Solid State Communications 152 1331
[14] Mortazavi B, Baniassadi M, Bardon J and Ahzi S 2013 Compos Part B: Eng 45 1117
[15] Chivrac F, Gueguen O, Pollet E, Ahzi S, Makradi A and Averous L 2008 Acta Biomater 4 1707
[16] Sheng N, Boyce M C, Parks D M, Rutledge G C, Abes J I and Cohen R E 2004 Polymer 45 487
[17] Zeng Q H, Yu A B and Lu G Q 2008 Prog Polym Sci 33 191
[18] Mori T and Tanaka K 1973 Act. Metall. 21 571
[19] Wang Y K 2013 Dissertation, Zhengzhou University China 29