A Thermal Conductivity Predictive Method of Graphene Epoxy Nanocomposites

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Abstract. Interfacial interaction between flaked graphene and epoxy was the key element of whether graphene as nanofillers could improve some of the properties of epoxy. Based on really materials and applied manufacturing process, a new kind of a thermal conductivity predictive method for graphene epoxy nanocomposites which could compute and analyze thermal conductivity of any content ratio of graphene in the epoxy with only one content ratio was built in order to provide theoretical foundations for design and property of graphene epoxy nanocomposites. According to practically different materials system and corresponding manufacturing processes, few experiments which only needed thermal conductivity of one random content-ratio graphene epoxy nanocomposites were made to predict effective thermal conductivity of any other content ratio of graphene epoxy nanocomposites 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 thermal and 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 thermal conductivity 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 thermal 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 graphene epoxy nanocomposites 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 epoxy was the key element of effecting whether graphene as nanofillers could improve thermal properties of epoxy, therefore, compatibility between graphene and epoxy could directly make effects on modification results of graphene to epoxy. Well interfacial interaction between graphene and epoxy could make heat transmitted effectively during polymerization was formed so that matrix system could be greatly improved. However, bad compatibility between graphene and epoxy induced into the separation of graphene and epoxy phases during polymerization, graphene would cluster in some places, materials defects would form, and modification effects would not be so good. Therefore, the modified-matrix effects would be totally different with graphene blended into different resins.

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

The procedures on predictive method of thermal conductivity 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 epoxy, it was hypothesized that a new kind of interface material which was used to describe compatibility between graphene and epoxy was formed between graphene and epoxy.

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

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

$$M_{coat} = CM_{GP}$$

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 epoxy were different. Therefore, according to practically different materials system and corresponding manufacturing processes, few experiments which only needed thermal conductivity of one random content-ratio graphene epoxy nanocomposites were made to predict effective thermal conductivity 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 thermal conductivity of graphene epoxy nanocomposites were as follows.

1. By making full use of Mori-Tanaka method[18] computational program in DIGIMAT software and thermal conductivity of one random content ratio of graphene epoxy nanocomposites'
experimental result, experimental constant $C$ and interface thermal conductivity $\lambda_i$ by numerical progressive iterative approximation method were obtained as basis materials-input-parameters of this model to build the whole analysis model.

② Equivalent thermal conductivity 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 thermal conductivity of equivalent uniform reinforced resin material was computed by applying Mori-Tanaka method again.

3. Model Validations and Examples Analysis

3.1. Thermal Property Parameters of graphene

According to the manufacturer of supplying graphene, thermal property parameters of graphene were that In-plane thermal conductivity was 3000W/(m•K), Out-plane thermal conductivity was 20W/(m•K) and Aspect ratio was 200 according to the manufacturer.

3.2. Thermal Property Parameters of Epoxy

According to experiments, thermal property parameters of TDE-85 epoxy were that thermal conductivity was 0.1702W/(m•K).

3.3. Thermal Conductivity Prediction and Experiment Validation of Surface Unmodified Graphene TDE-85 Epoxy

Thermal conductivity of surface unmodified graphene TDE-85 epoxy was computed and analyzed based on method built in this project. Based on 3wt% surface unmodified graphene epoxy nanocomposites' thermal conductivity experiment value $\lambda=0.1907$W/(m•K), 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 thermal conductivity $\lambda_i=0.00115$W/(m•K) were obtained. The above as input conditions of interface material's basis thermal parameters, thermal conductivity of other content graphene epoxy nanocomposites under the same manufacturing conditions were predicted. Thermal conductivity of 1wt% and 2wt% graphene epoxy nanocomposites were predicted and the comparisons were made between computing results and experimental results.

Comparisons between thermal conductivity predictive results and experimental results of surface unmodified graphene TDE-85 epoxy by making full use of two methods, method built in this project considering interface effect and common Mori-tanaka method without considering interface were made, shown in Table 1.

| Graphene content (wt%) | Experimental results of thermal conductivity (W/(m•K)) | Method built in this project Predictive results of thermal conductivity (W/(m•K)) | Error (%) | Common Mori-Tanaka method Predictive results of thermal conductivity (W/(m•K)) | Error (%) |
|------------------------|----------------------------------|----------------------------------|-----------|----------------------------------|-----------|
| 0                      | 0.1702                           | -                                | -         | -                                | -         |
| 1                      | 0.1734                           | 0.1755                           | 1.21      | 0.3920                           | 126.07    |
| 2                      | 0.1798                           | 0.1822                           | 1.33      | 0.6183                           | 243.88    |
| 3                      | 0.1907                           | 0.1901                           | 0.31      | 0.8492                           | 345.31    |

It was seen from comparison data results, the highest error of thermal conductivity between predictive result and experimental result by use of Mori-Tanaka without considering interface was up
to 345.31%, predictive error was huge while with high content graphene epoxy nanocomposites. However, the highest error of thermal conductivity between predictive results and experimental results by use of method built in this project was up to 1.33%, that means, predictive conformability was 98.67%, greatly improved by Mori-Tanaka without considering interface.

3.4. Thermal Conductivity Prediction and Experiment Validation of Surface Modified Graphene TDE-85 Epoxy

Thermal conductivity of surface modified graphene TDE-85 epoxy was computed and analyzed based on method built in this project. Based on 1wt% surface modified graphene epoxy nanocomposites' thermal conductivity experiment value $\lambda = 0.2313 \text{W/(m}\cdot\text{K})$, 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 thermal conductivity $\lambda_i = 0.0075 \text{W/(m}\cdot\text{K})$ were found. The above as input conditions of interface material basis thermal parameters, thermal conductivity of other content surface modified graphene epoxy nanocomposites under the same manufacturing situations were predicted. Thermal conductivity of 2wt%, 3wt% and 5wt% surface modified graphene epoxy nanocomposites were predicted and the comparisons were made between computing results and experimental results.

Comparisons of thermal conductivity predictive results and experimental results of surface modified graphene TDE-85 epoxy by making full use of two methods, method built in this project considering interface effect and common Mori-Tanaka method without considering interface were made, shown in Table 2.

| Graphene content (wt%) | Experimental results of thermal conductivity (W/(m•K)) | Predictive results of thermal conductivity (W/(m•K)) | Error (%) | Predictive results of thermal conductivity (W/(m•K)) | Error (%) |
|------------------------|--------------------------------------------------------|-----------------------------------------------------|-----------|-----------------------------------------------------|-----------|
|                        | 1                                                        | 0.2313                                              | 0.2324    | 0.3920                                              | 69.48     |
|                        | 2                                                        | 0.2995                                              | 0.2955    | 0.6183                                              | 106.44    |
|                        | 3                                                        | 0.3572                                              | 0.3595    | 0.8492                                              | 137.74    |
|                        | 5                                                        | 0.4843                                              | 0.4903    | 1.3254                                              | 174.64    |

It was seen from comparison data results, the highest error of thermal conductivity between predictive result and experimental result by use of Mori-Tanaka without considering interface was up to 174.64%, predictive error was huge while with the high content surface modified graphene epoxy nanocomposites. However, the highest error of thermal conductivity between predictive results and experimental results by use of method built in this project was up to 1.34%, greatly improved by Mori-Tanaka method without considering interface's effect.

4. Conclusions

A new multi-step thermal conductivity predictive method of graphene epoxy nanocomposites was built according to practical engineering conditions. The thermal conductivity predictive results and experimental results for surface unmodified graphene TDE-85 epoxy and surface modified graphene TDE-85 epoxy with different content ratios of graphene in matrix systems by making use of thermal conductivity predictive method built in this project were compared and analyzed. The results showed that the maximal error of predictive result was up to 1.34%, and which means, the predictive precision was above 98.66%. 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 was not well and predictive results were just well for latter while large error for materials' system.

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