Study on Thermal Conductivity of Carbon Fiber / Resin Composite Modified with Graphene Nanoplatelets

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Abstract. A method for calculating thermal conductivity of graphene/carbon fiber reinforced resin composites (GnP-CFRP) was established basing on the Mori-Tanaka program in the DIGIMAT software. The influence of graphene nanoplatelets (GnP) on the thermal conductivity of composites has been simulated and experimentally verified. The results show that the thermal conductivity of GnP-CFRP increased with the increase of GnP content, and when the GnP content is too high, the increasing rate of thermal conductivity decreases gradually. In addition, the maximum prediction error of the simulation calculation method in this paper is within 7.27%, which is in good agreement with the actual situation.

1. Introduction
Carbon fiber reinforced resin composites (CFRP) have excellent properties such as high specific strength, high specific modulus, designable structure and function, which have become one of the important basic raw materials in the fields of national defense, aerospace, mechanical and electronic industries. However, the excellent thermal and mechanical properties of CFRP are mainly reflected in the fiber axial direction, there are some problems of low strength, poor impact resistance and low thermal conductivity in the direction perpendicular to the carbon fiber.

Graphene nanoplatelets (GnP) is a two-dimensional lamellar nanomaterial with good thermal conductivity (5000W/mK), which is considered to be an ideal material for improving the thermal and mechanical properties of composites[1-5]. In this paper, a method for calculating thermal conductivity of graphene/carbon fiber reinforced resin composites (GnP-CFRP) was established basing on the Mori-Tanaka program in the DIGIMAT software. The thermal conductivity of GnP-CFRP was predicted and verified by experiments. The influence of GnP content on the thermal conductivity of GnP-CFRP was studied.

2. Calculation method and experimental process

2.1. Calculation method
All calculations in this paper were carried out by using Mori-Tanaka calculation program of DIGIMAT software. GnP-CFRP was regarded as composition of four different material phases, namely GnP, interface phase between GnP and resin, carbon fiber and resin. The calculation process and assumptions are as follows:

(1) The basic parameters of GnP mass content, geometric size and spatial distribution in the composite were determined. Thermal properties of GnP, carbon fiber and resin are listed in Table 1.
Table 1. Basic thermal performance parameters of materials used in the model.

| materials         | parameters                               | units              | data  |
|------------------|------------------------------------------|--------------------|-------|
| GnP              | Thermal conductivity within the slice    | $\lambda$ W/m·K   | 3000  |
|                  | Thermal conductivity between layers      | $\lambda$ W/m·K   | 20    |
| resin            | Thermal conductivity                     | $\lambda$ W/m·K   | 0.1702|
| carbon fiber     | Axial thermal conductivity                | $\lambda$ W/m·K   | 20    |
|                  | Radial thermal conductivity              | $\lambda$ W/m·K   | 1.5   |

(2) As shown in Figure 1, a model of GnP with a thin coating on the surface is established firstly, which is assumed to be an “equivalent GnP”. The thermal conductivity of the “equivalent GnP” is calculated by using the Mori-Tanaka method. Then “equivalent GnP” / resin is assumed to be an “equivalent resin matrix”, and the thermal conductivity of the “equivalent resin matrix” is also calculated by using the Mori-Tanaka method. The multi-scale model of the resin modified with GnP is shown in Figure 2.

(3) Similarly, the carbon fiber and carbon fiber / resin interface are assumed to be an “equivalent carbon fiber”, and its thermal conductivity is calculated by using the Mori-Tanaka method. At this time, GnP-CFRP can be regarded as composed of “equivalent carbon fiber” and “equivalent resin matrix”, and the thermal conductivity of the composite can be calculated again by using the Mori-Tanaka method. The multi-scale model of GnP-CFRP is shown in Figure 3.

![Figure 1. Schematic diagram of the establishment process of multi-scale model of resin modified with grapheme.](image1)

![Figure 2. Schematic diagram of multi-scale model of resin modified with grapheme.](image2)

![Figure 3. Schematic diagram of the multi-scale model of GnP-CFRP.](image3)

2.2. Experiments

2.2.1. Materials. Commercially prepared GnP were used in the project. The GnP were obtained from Timesnano Inc. and had a purity >95% by weight, a specific surface area 179.7 m$^2$/g and a particle diameter of 2.6-12.6 μm. The brand number of epoxy resin, curing agent and silane coupling agent are TDE-85, T-403 and KH560 respectively. The fabric surface density of T-700 carbon fiber is 300 g/m$^2$. 
2.2.2. Fabrication of composites. Firstly, the epoxy resin was diluted with acetone solvent according to the 1:5 mass ratios. The corresponding ratio of GnP and KH560 were added into the solution. The ultrasonic dispersion with a frequency of 40KHz and a power of 200KW was performed for 2h. Then the resin matrix modified with GnP was obtained by adding the curing agent and stirring evenly.

The resin matrix modified with GnP was brushed onto the surface of carbon fiber fabric. After standing at room temperature for 2 hours, the fabric was treated at 80°C for 15 minutes. Finally, carbon fiber / resin composites modified with GnP were prepared by the molding process. The temperature, time and pressure parameters of the molding process were 120°C, 1hour and 8MPa respectively.

2.2.3. Characterization. The thermal conductivity were tested by the DRH-Ⅲ thermal conductivity tester according to standard GB/T 3139-2005. The thickness of GnP-CFRP was 10mm and the average temperature for testing was 100°C. The microstructure of GnP - CFRP was characterized with a field emission scanning electron microscope with an accelerating voltage of 2 Kv.

3. Results and discussion

3.1. Prediction results

Figure 4 plots the heat flux in the thickness direction of composites with GnP content of 0, 3wt%, 6wt%, 10wt% and 20wt% as a function of temperature gradient. The thermal conductivity was obtained by calculating the slope of each curve, and the relationship between the thermal conductivity of the composite and the content of GnP was formed, as shown in Figure 5.

As can be seen from Figure 5, GnP can significantly improve the thermal conductivity of the composites, and the thermal conductivity of the composites increased with the increase of GnP content. When the GnP content was 20wt%, the thermal conductivity of the composite increased by 306% to 1.5219W/(m•K). However, when the GnP content is too high, the increasing rate of thermal conductivity decreases gradually. It may be due to the consideration of GnP interface factors in this calculation method. When the content of GnP is low, the dispersion of GnP in the composite is uniform, the interfacial thermal resistance is weak, and the thermal conductivity of the composite is significantly improved. With the increase of GnP content, the interface bonding state between GnP and matrix becomes worse, resulting in a decrease in the rate of improvement of composite thermal conductivity.

3.2. Experimental results

Table 2 shows the experimental test results of the thermal conductivity in the thickness direction of the composites with GnP content of 0, 3wt%, 6wt%, 10wt% and 20wt%. The comparison between the
experimental results and the simulation results is shown in Figure 6. The results show that the thermal conductivity of the composites varies with the content of GnP, which is similar to the simulation results. That is, the thermal conductivity of the composite increased with the increase of GnP content, and when the GnP content is too high, the increasing rate of thermal conductivity decreases gradually. In addition, the maximum prediction error of the simulation calculation method in this paper is within 7.27%, which is in good agreement with the actual situation, and can provide effective support for the design of thermal conductivity in the thickness direction of GnP-CFRP.

Table 2. Comparison of prediction results and experimental results of thermal conductivity in the thickness direction of composites.

| Content of GnP (wt%) | Test result of thermal conductivity (W/(mꞏK)) | Calculation result of thermal conductivity (W/(mꞏK)) | Error (%) |
|----------------------|---------------------------------------------|-------------------------------------------------|-----------|
| 1                    | 0.3759                                       | 0.3750                                          | 0.2       |
| 2                    | 0.7520                                       | 0.7527                                          | 0.09      |
| 3                    | 0.9521                                       | 0.9529                                          | 0.08      |
| 4                    | 1.1962                                       | 1.1527                                          | 3.64      |
| 5                    | 1.4187                                       | 1.5219                                          | 7.27      |

3.3. Microstructures of GnP-CFRP
The morphologies of GnP-CFRP with different GnP contents were investigated by SEM (Figure 7). Figure 7 (a) and (b) show the morphology of the composite without GnP. Figure 7 (c) and (d) show the morphology of the composite with 3wt% GnP. Figure 7 (e) shows the morphology of the composite with 10wt% GnP. Notably, from Figure 7 (a) and (b), we can see GnP were uniformly distributed in the resin and bonded to the carbon fiber, which was beneficial to the improvement of thermal conductivity of the composite. When the content of GnP reached to 10wt% (Figure 7 (c) and (d)), the agglomeration of GnP was obvious, and the interface bonding state between GnP and matrix became worse, which led to the decrease in the thermal conductivity improvement rate of the composite.
Figure 7: SEM micrographs of GnP-RFRP with different GnP contents (3wt% (a) and (b), 10wt% (c) and (d), 0 (e)).

References

[1] Novoselov KS, Geim AK, Morozov SV, Jiang D, Zhang Y, Dubonos SV, Grigorieva IV and Firsov A 2004 Science 306 666
[2] Gu J, Xie C, Li H, Dang J, Geng W and Zhang Q 2014 Polym.Compos. 35 1087
[3] Le MT and Huang SC 2015 Materials 8 5526
[4] Wang JY, Yang SY, Huang YL, Tien HW, Chin WK and Ma CCM 2011 J.Mater.Chem. 21 p 13569
[5] Park OK, Kim SG, You BC, Hui D and Lee JH 2014 Compos. B 56 365