Study on preparation and properties of graphene reinforced epoxy resin composites

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Abstract. In order to study the preparation methods of graphene reinforced epoxy resin composites and analyze the influence of graphene content on the viscosity and mechanical properties of the resin, the surface of graphene oxide was modified to make graphene oxide disperse uniformly in the matrix resin, and then composite the modified graphite oxide and resin. Three groups of graphene oxide reinforced epoxy resin composites with graphene oxide content of 0.3wt%, 0.5wt% and 0.8wt% were prepared. The results show that the modified graphene oxide keeps good dispersion uniformity in the resin matrix. With the increase of graphene oxide content, the viscosity of the composite decreases gradually. The strength of the composite is better than that of the pure resin after adding graphene oxide. When the graphene content is 0.3%, the tensile strength is the highest, which is about 16% higher than that of pure resin. With the increase of graphene content, the tensile strength decreases.

1. Background introduction

Polymer resin matrix composite is a kind of composite material which combines macromolecule resin and surface modified reinforced phase according to a certain proportion and process method to obtain excellent performance, anti-corrosion, wear resistance and other properties. It is mainly used in functional structural parts or further extended to downstream products, and can serve aviation industry, aerospace, electronics, transportation, ocean and other fields.

Graphene is a two-dimensional material with hexagonal honeycomb structure, which is composed of carbon atoms and SP2 hybrid orbital. Graphene's special monoatomic layer structure determines its rich and excellent physical properties, such as excellent barrier, anti-corrosion and wear resistance. Graphene with flexible lamellar structure can obstruct erosion, penetration and spread of corrosive media effectively [1-5]. Compound resin matrix as additive phase can improve the strength and corrosion resistance of matrix [6-8]. Compared with graphene, graphene oxide has a large number of hydroxyl, carboxyl and epoxy functional groups on its surface, which show strong hydrophilicity. On the other hand, these functional groups also provide an active structural basis for surface modification. After organic modification, graphene oxide can be stably dispersed in organic solvents and macromolecule resins [9-11].

Graphene oxide was used in this paper, using the active hydroxyl, carboxyl and epoxy groups on the surface and edge of graphene oxide, There will be a covalent reaction between graphene oxide and organic modifiers. The novelty and significance of this paper are that the mechanical properties of resin materials can be significantly improved by choosing suitable raw materials and preparation technology. In addition, this paper provides an important basic rule for the study of graphene reinforced resin matrix composites.
2. Test scheme
Three groups of graphene reinforced resin composites were prepared. The ratio of graphene oxide to resin was 0.3 wt%, 0.5 wt% and 0.8 wt%, respectively. They were recorded as 0.3GO, 0.5 GO and 0.8 GO. By comparing the viscosities and mechanical properties of three groups of samples with those of pure resin, the mechanism of graphene oxide affecting the properties of resin was summarized.

3. Material preparation

3.1. Raw material
The raw materials used in this paper include graphene oxide powder, E51 epoxy resin, amino long chain modifier, alcohol, and curing agent. Among them, graphene oxide is an important raw material. Its specifications are as follows: thickness is about 1 nm, sheet diameter is about 0.2-10 micron, carbon content is about 45 wt.%.

3.2. Preparation of composite materials
Firstly, graphene oxide and amino long chain modifiers were dissolved in alcohol solution in a certain proportion, the modifier is excessive. The reaction temperature was raised 60°C for 1-2 hours. After the reaction, the reaction products were washed with alcohol and centrifugally collected to obtain modified graphene oxide. Then, modified graphene oxide was added to the resin, and mechanical stirring for 2-3 hours to obtain modified graphene oxide reinforced epoxy.

Because graphene oxide has nano-size and can play a nano-effect, a small amount of graphene oxide added to the resin can play a significant role in improving the performance, the premise is that graphene oxide must maintain good dispersion uniformity. According to the requirement of 0.3GO, 0.5GO and 0.8GO groups of samples, modified graphene oxide was added into epoxy resin, heated to 60-80 degrees Celsius, stirred for 3-5 hours, then graphene reinforced epoxy resin composite was obtained. Amine curing agent was selected. The curing temperature was room temperature and the curing time was 48 h.

4. Result analysis

4.1. Structural analysis of modified graphene oxide
Infrared spectrum analysis of graphene oxide is shown in figure 1 and infrared spectrum analysis of modified graphene oxide, prepared by our group, is shown in figure 2. It can be seen that modified graphene oxide has more functional groups. The stretching vibration absorption peaks of -CH3 and -CH2 were found at 2955 cm⁻¹ and 2892 cm⁻¹, indicating that the organic modifiers reacted successfully with graphene oxide and grafted onto the surface of graphene oxide.

![Figure 1. Infrared spectrum analysis of graphene oxide.](image)
**Figure 2.** Infrared spectrum analysis of modified graphene oxide.

**Figure 3.** Distribution of modified graphene oxide in resin matrix (0.3GO).

**Figure 4.** Distribution of modified graphene oxide in resin matrix (0.5GO).

**Figure 5.** Distribution of modified graphene oxide in resin matrix (0.8GO).
4.2. Uniformity analysis
The uniformity of graphene reinforced epoxy resin composites with 0.3GO, 0.5GO and 0.8GO was analyzed. The distribution of graphene in epoxy resin was observed 100 times larger in three groups of composites under optical microscope. As shown in the figures 3-5, it can be seen that the distribution uniformity of modified graphene oxide in epoxy resin was good in three groups of samples. Macroscopic segregation is due to the structural changes of graphene oxide after organic modification, which has good similarity and compatibility with resins.

4.3. Viscosity analysis
The viscosities of epoxy resin, 0.3GO, 0.5GO and 0.8GO modified graphene oxide reinforced epoxy resin composites were tested by rotational rheometer. The effects of graphene content on the matrix viscosities were compared at 20 ~80℃, as shown in figure 6.

![Figure 6. Viscosity analysis.](image)

As can be seen from figure 6, with the increase of graphene content, the viscosity of resin materials tends to decrease at 20 ~30℃. The viscosity of 0.3GO and 0.5GO curves is close to each other, and the viscosity of 0.8GO decreases obviously. This is because the small size of graphene and the very thin lamellar structure of graphene play a lubricating role. When the temperature rises to about 30 ~80℃, the viscosity of the four groups of samples tends to be the same, because in the high temperature stage, the effect of temperature on the resin viscosity becomes more and more obvious, and finally the viscosity of each sample tends to be the same.

4.4. Mechanical properties analysis
Tensile specimens were prepared according to GB/T2567-2008 “Test methods for properties of resin casting body”, the mechanical properties of epoxy resin, 0.3GO, 0.5GO and 0.8GO graphene reinforced epoxy resin composites were analyzed. The tensile strength was shown in table 1 and figure 7.

| Sample   | Tensile Strength /MPa |
|----------|------------------------|
| epoxy resin | 65.7                   |
| 0.3GO      | 76.1                   |
| 0.5GO      | 69.6                   |
| 0.8GO      | 66.7                   |
From table 1 and figure 7, it can be seen that the properties of the composites with modified graphene oxide are better than those of epoxy resin. When the content of graphene is 0.3, the tensile strength reaches the highest, increasing by about 16%. With the increase of the content of graphene, the tensile strength decreases. When the content of graphene is 0.8, the tensile strength and epoxy resin are matched. This may be due to the excellent compatibility and interface structure between modified graphene oxide and resin matrix, which play a role as reinforcing phase in continuous phase resin and promote the improvement of mechanical properties [12,13]. The decrease of mechanical properties with the increase of graphene content may be attributed to the excessive introduction of modified graphite. The functional groups of olefins have an effect on the curing process of resins, resulting in changes in curing crosslinking parameters. On the other hand, with the increase of graphene oxide content, a small amount of local agglomeration will inevitably occur, which will also affect the performance [14].

5. Conclusion

- Infrared analysis showed that the surface-modified graphite oxide had more active organic functional groups.
- Microscopic optical analysis showed that the modified graphene oxide maintained good dispersion uniformity in the matrix.
- With the addition of modified graphene oxide, the viscosity of resin matrix decreases, and with the increase of graphene content, the viscosity decreases gradually.
- The tensile strength of modified graphene oxide reinforced epoxy resin composites is better than that of epoxy resin. When the content of graphene is 0.3, the tensile strength reaches the highest, increasing by about 16%. With the increase of graphene content, the tensile strength decreases.

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