Properties of modified epoxy matrix composites reinforced by glass fiber

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Abstract. The glass fiber reinforced epoxy resin matrix composites were prepared by press molding. Experiments show that the bending strength and flexural modulus of the composite are increased by 16.2% and 21.2%, and the interlaminar shear strength is increased by 28%. The fibers of modified resin matrix composites were uniformly arranged and adhesion of the interface was decent through the scanning electron microscope.

1. Introduction
At present, glass fiber reinforced composite has been widely applied to fairing, radome, movable wing surface and other aircraft secondary load-carrying structure because of its outstanding performances such as high specific strength and stiffness, good fatigue resistance, high temperature resistance and designable characteristic, etc. Epoxy resin is a common matrix material, which has the advantages of high tensile strength, low curing shrinkage, chemical resistance and so on, but the brittleness of cured pure epoxy resin needs to be toughened. Carbon nanotubes (CNTs) are one-dimensional structural materials with unique physical properties, excellent mechanical and electrical properties, as well as relatively low manufacturing cost, which are considered as promising materials to improve the shortcomings of epoxy resin in the application.

In this research, Fe3O4 functionalized amino CNTs modified epoxy resin and glass fiber were respectively used as the matrix and reinforced material to prepare the composite. The room-temperature mechanical properties and the interlaminar shear (ILSS) failure mechanism of the composite were studied.

2. Experimental
2.1. Materials and instruments
The materials and instruments used in this study are listed in Table 1 and Table 2.

Table 1 Experimental material.

| Experimental materials        | Specifications     |
|------------------------------|--------------------|
| Epoxy resin                  | Industrial reagent |
| Fe3O4 functionalized CNTs    | Self-made          |
| (F/CNTs)                     |                    |
| 4,4’-diamino-diphenyl sulfone| Analytical purity  |
| Alkali-free glass fiber cloth| --                 |
| Absolute ethanol             | Analytical purity  |
Table 2 Experimental instruments

| Experimental instruments | Models          |
|--------------------------|-----------------|
| Weighing balance         | MP2002          |
| Collector type constant temperature heating magnetic stirrer | DF-101S |
| Ultrasonic cleaner       | KQ2200          |
| Electric blast drying oven | 101-0AB   |
| Vacuum drying oven       | DZF-6050        |
| Microcomputer controlled electronic universal testing machine | CMT7204 |
| Scanning electron microscope | VEGA3LMH |

2.2. Preparation of materials and composites
The modified resin solution was prepared with epoxy resin system (0.1wt.% of F) as matrix and ethanol as solvent. The prepreg was made by wet hand paste method using aromatic diamine epoxy curing agent and alkali-free glass fiber cloth reinforced material. Finally, composite laminates were fabricated by molding. Fig. 1 shows the molding process of the composite.

![Fig. 1 The molding process of composite material.](image)

2.3. Characterization
Characterization methods used in this study are as follows:

- **Bending strength test**: According to ASTM D 7264 test standard, the ratio of support span to standard specimen thickness was 32:1. The thickness and the width of the specimen was 4 mm × 13 mm. The loading speed was kept as 1 mm/min until the specimen failed, and at least 5 samples should be tested for each case.

- **ILSS test**: According to ASTM 2344 test standard, the specimen with dimensions 24 mm × 8 mm × 4 mm was examined on a SANS CMT7204 universal testing machine with a span to thickness ratio of 4:1. The diameter of the loading head and the support were 6 mm and 3 mm respectively. The load was applied at 1 mm/min until the specimen fracture, conduct at least 5 samples for each case and calculate the average of them.

- **Scanning electron microscopy (SEM) test**: The interlaminar shear fracture surface sample was fixed on the conductive adhesive sample stage. The fracture morphology was investigated with VEGA3LMH SEM at 20kV.
3. Result and discussion

3.1. Room-temperature mechanical properties
Table 3 compares the mechanical properties of glass fiber reinforced pure epoxy and modified epoxy composites at ambient temperature.

| Properties       | Pure epoxy | Modified epoxy | Increment (%) |
|------------------|------------|----------------|---------------|
| Bending strength, MPa | 370.51     | 430.54         | 16.2          |
| Bending modulus, GPa  | 20.98      | 25.42          | 21.2          |
| ILSS, MPa         | 35.86      | 45.87          | 28.2          |

According to the results, the room temperature mechanical properties of the modified epoxy group are significantly improved. The bending strength and modulus could reach 430.54MPa and 25.42GPa, with an increment of 16.2% and 21.2% compared to pure epoxy composite, and ILSS (45.87MPa) is also 28% higher after being modified. Bending performance depends on tensile, compression, shear failure and so on. The failure mode is not only related to the performance of matrix, fiber and interface, but also affected by the relative content of fiber and void and test conditions with the failure mechanisms including delamination, fiber matrix peeling and interlaminar matrix cracking. Meanwhile, ILSS is determined by the strength of the composite matrix and the strength of the interface. The introduction of F/CNTs on the fiber surface enhances the wettability of the epoxy matrix to the glass fiber, and there is no formation of volatile small molecule during curing, which improves the interface shear strength between the matrix and the fiber. The ductility of F/CNTs-modified epoxy matrix increases the energy dissipation during the fracture process and improve the interlaminar fracture toughness. Besides, the toughness and cohesion between the middle layer and the adjacent composite layer are enhanced by F/CNTs through the "fiber bridging mechanism" in the resin rich interface area. Additive F/CNTs plays the role of rigid filler, which can prevent microcrack propagation and provide direct reinforcement for the resin. The "fiber bridging effect" is more significant in toughened composites, because as the load of F/CNTs increases, more energy can be absorbed to overcome the delamination. Moreover, F/CNTs serves as a supplementary reinforcement material with the sizes of nanometer, which is several orders of magnitude smaller than glass fiber, so as to reduce the stress concentration and improve the adhesion between fiber and matrix.

3.2. Fracture surface morphology of composite ILSS
The mainly mechanism responsible for typical glass fiber/epoxy composite laminate shearing fracture is interface failure between fiber and resin, so fracture morphology is one of the important means to characterize the interface bonding properties of composite materials. As shown in Fig. 2 (a) and (b), the interlaminar shear section of the pure epoxy matrix is typical of brittle fracture, which shows exposed fiber, small deformation, fiber pulling out and holes or gaps between the matrix and fiber. This is due to the weak adhesion of smooth and clean fibers, which leads to the limited combination of fibers and matrix. In contrast, Fig. 2 (c) and (d) shows the interlaminar shear section of modified epoxy resin, with irregular and uneven wavy structure fracture, large resin deformation and a large number of dimple structures on the glass fiber section with tight and unsmooth bonding, which increases the fracture surface area and microcracks. The fiber gap is filled with resin, which means a high fiber volume fraction. There is no obvious resin starvation area or resin-rich area between the fiber and the matrix, indicating that the modified epoxy resin matrix and the fiber interface have good bonding strength. However, some glass fibers will inevitably pull out form the resin. In conclusion, F/CNTs absorbs energy by its highly flexible elasticity in the process of deformation, at the same time, the good wettability of the resin to the fiber results in the good interface adhesion, which increases the mechanical properties of the composite.
Fig. 2 The fracture surface morphology of glass fiber reinforced composite: (a) Pure epoxy (250 times). (b) Pure epoxy (2500 times). (c) Modified epoxy (500 times). (d) Modified epoxy (2500 times).

4. Conclusion
In this paper, the glass fiber reinforced modified epoxy composite was prepared and its performance was investigated. The main conclusions are drawn as follows:

- After modified by Fe3O4 functionalized amino CNTs, the bending strength, bending modulus and ILSS of epoxy composites reinforced by glass fiber can be significantly improved.
- The micro morphology of interlaminar shear section further proves that the epoxy resin modified by Fe3O4 functionalized amino CNTs absorbs energy by highly flexible elastic behavior during deformation. Furthermore, the modified resin with good wettability creates a strong fiber/matrix interface, which is more conducive to stress transfer and crack energy absorption, resulting in an improvement in mechanical properties.

References
[1] Liu Z.L., Li H.F., Gu J.Y. (2017) Research progress of functional epoxy resin. Engineering Plastics Application, 45:126-131.
[2] Wu L.Y. (2002) Development status of new epoxy resin adhesive in foreign countries. Adhesion, 23: 6-12.
[3] Zhang J.X., Zheng Y.P., Xu L.(2006) Research progress of toughening modification of epoxy resin. Adhesion., 27: 35-38.

[4] Zhao Y, Barrera E V. (2010) Asymmetric Diamino Functionalization of Nanotubes Assisted by BOC Protection and Their Epoxy Nanocomposites. Advanced Functional Materials., 20: 3039-3044.

[5] Li Z.D.(2008) Surface modification of carbon nanotubes. Adhesion., 29: 49-49.

[6] Luan J.F., Zhang A.B., Zhao C.Y., etc. (2011) Application of carbon nanotube in dye-sensitized solar cell. Adhesion., 32: 85-89.

[7] Li, B., Lian Y.F., Shi Z.J., etc. (2000) Chemical modification of single-wall carbon nanotube. Chemical Research in Chinese Universities., 21: 1633-1635.

[8] Hu R., Wang R.M. (2016) Preparation and characterization of bismaleimide resin-composite modified by new allyl compound. China Adhesives., 25: 4-7.