Research on Aging Resistance of Three Phase Composites for Anti-collision Intelligent Control of Bridge Engineering

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Abstract. Aminated Carbon Nanotubes (CNTs) and Carbon Fiber (CF) materials for anti-collision intelligent control of Bridge Engineering were used to enhance the properties of Bismaleimide Resin (BMI) matrix resin and then tested the moist heat aging, salt spray aging and erosion resistance in this study. The result showed that when the aging time was 168h, after wet heat and salt spray, the flexural strength and impact strength of three-phase composites with 1.5wt% MWNTs-NH₂ content can reach maximum, and the wet heat aging bending performance is 45% better than that of non-added carbon nanotubes, the impact performance is 41% higher, the salt spray aging bending performance is 43% higher and the salt spray aging impact performance is 32% higher.

Keywords: Carbon Nanotubes; Carbon Fiber; Bismaleimide Resin; Aging resistance.

1. Introduction
Carbon fiber polymer matrix composites have been widely used in the anti-collision intelligent control of Bridge Engineering field, gradually replacing the traditional metal materials. However, due to the shortcomings of carbon fiber / polymer matrix composites, such as easy delamination, low interfacial adhesion and shear strength, the properties of the composites are affected[1-6]. In order to improve the mechanical properties of carbon fiber (CF) and polymer matrix materials, some researchers prepared three-phase composites by adding a certain amount of carbon nanotubes (CNTs) into the carbon fiber / polymer matrix composites. The added CNTs will improve the toughness of the matrix, prevent microcracks, and improve the interlaminar shear strength of the composites through bridging effect[7-10]. In his research, Zhang Lin[11] compounded carbon nanotubes and carbon fibers (fabrics) to make carbon fiber and carbon nanotube hybrid fiber reinforced bismaleimide resin composites (MWNTs/CF/BMI). Due to the characteristics of high strength and toughness, CNTs can share the axial stress and play the role of strengthening composites.

In the actual use process, the aging resistance of materials is very important. Hygrothermal aging test can be used to evaluate and study whether materials have good hygrothermal resistance under certain environmental conditions. Composite materials always contact with water molecules in the air when they are used, while high-performance resin matrix requires a lower moisture absorption rate, which depends on the free volume of matrix resin, the type and concentration of polar groups and the number of interfaces[12-16]. Salt spray aging is to evaluate and study the salt spray corrosion resistance of
materials in salt spray atmosphere. Sometimes, it is also necessary to evaluate the performance of materials in the presence of highly corrosive electrolyte solution. Because the materials in this study may be used in marine environment, sodium chloride solution salt spray is the main corrosive agent in marine environment, which is particularly important for the application of this material in this field\cite{17-19}. As we all know, sodium chloride solution has no significant corrosion effect on polymer itself, and due to the high osmotic pressure of salt solution, the absorption of polymer to salt solution is generally less than that of pure water, but it cannot be inferred that salt solution has no corrosion effect on composite materials or interface containing filler. Therefore, this work will mainly study the properties of MWNTs/CF/BMI three-phase composites, such as wet heat aging resistance, salt spray aging resistance and erosion resistance.

2. Design and Preparation of Three Phase Composites

2.1. Design of Carbon Nanotubes / Carbon Fibres / Bismaleimide Resin Three Phase Composites

Bismaleimide (BMI) is n, n’- 4,4’- diphenylmethane bismaleimide (BDM), industrial grade, Hubei Honghu bismaleimide resin factory. o. O’- diallyl bisphenol A (DBA) is an excellent product (purity > 96%), which is the production base of Hubei Institute of chemistry. Multi walled carbon nanotubes (p-MWNTs), diameter < 8nm, purity > 95 wt%, cheaptubes, USA. Aminated carbon nanotubes (MWNTs-NH2) were prepared as described\cite{20}. Carbon fiber cloth, model (h3k-cp5), t300-3000 carbon fiber braided by Toray company, Jiangsu Zhongxin composite products Co., Ltd. Ethylenediamine (EDA), N, n’- dimethylformamide (DMF), acetone, anhydrous ethanol, nitric acid (concentration 65 ~ 68%) and N, n’- Dicyclohexylcarbodiimide (DCC) are analytically pure, provided by Sinopharm Chemical Reagent Co., Ltd; Polyimide film, Shanghai Jinshan Qianfeng insulation material Co., Ltd; Release agent, model: 744, Shanghai Hailian lubricating material technology Co., Ltd; Cellulose microporous membrane, pore size 0.22 \( \mu \) m. Shanghai Xingya purification material factory; PP microporous membrane, pore size 0.45 \( \mu \) m. Shanghai Xingya purification material factory; Model: zyp-100, Shanghai Xima Weili Rubber & Plastic Machinery Co., Ltd.

2.2. Preparation of Carbon Nanotubes / Carbon Fibres / Bismaleimide Resin Three Phase Composites

Carbon nanotubes with different contents were dispersed in 100 ml acetone solution by ultrasonic wave for 30 min, and then evenly dispersed by mechanical stirring. Ba solution with carbon nanotube modifier was obtained by dropping BA at the same time. Acetone was volatilized completely after standing in the fume hood for 48 h, and then heated to 130 \( ^\circ \)C, BMI was added and dispersed by magnetic stirring for 30 min, so that BMI was completely melted and the glue was prepared for use; The carbon fiber cloth was dried at 80 \( ^\circ \)C for 1 h, then weighed. The glue solution was evenly brushed on the carbon cloth at 130 \( ^\circ \)C, and the glue content was controlled to be about 50wt%. Then the prepreg was dried at 130 \( ^\circ \)C for 90 min to remove the water and solvent; The 18 pieces of prepreg cut according to the size of the mold were laid in the mold, and then the mold was put into the 140 \( ^\circ \)C vacuum molding machine. The pressure was increased to 8MPa after 30min and 15MPa after 90min, and then cured according to the process of 150 \( ^\circ \)C / 2H + L60 \( ^\circ \)C / 2H + L80 \( ^\circ \)C / 2H + 210 \( ^\circ \)C / 2H. After curing, the composite profiles were randomly cooled to room temperature and demolded. The samples were cut to the required size according to the experimental requirements.

3. Study on Aging Resistance of Carbon Nanotubes / Carbon Fiber / Bismaleimide Resin Composites

According to GB 2573-2008, the aging time is 72 h and 168 h respectively. The mechanical properties of aged samples were tested. If the materials are damaged by high temperature, humidity and other environmental factors in the actual use process, it will cause the hygrothermal aging of materials, and the existence of water molecules will have a great impact on the heat resistance and mechanical properties of polymers. Salt spray aging is to evaluate and study the salt spray corrosion resistance of materials in salt spray atmosphere. Because of the high osmotic pressure of salt solution, the absorption of polymer matrix to salt solution is generally less than that of pure water.
3.1. Effect of Modifier Content and Aging Time of Carbon Nanotubes on Hygrothermal Aging Resistance of Composites

The hygrothermal aging test can be used to evaluate and study whether MWNTs / CF / BMI three-phase composites have better hygrothermal resistance under certain environmental conditions. Fig.1 shows the mechanical properties of MWNTs / CF / BMI three-phase composites after 0 h, 72 h and 168 h wet heat aging. Group (1) shows the CF / BMI two-phase composites without carbon nanotube modifier, which are treated by 0 h, 72 h and 168 h wet heat aging respectively; Group (2) MWNTs / CF / BMI three-phase composites with MWNTs modifier content of 1wt% were subjected to hydrothermal aging treatment for 0h, 72h and 168h, respectively; Group (3) MWNTs / CF / BMI three-phase composites with 2.5wt% carbon nanotube modifier were subjected to hydrothermal aging treatment for 0h, 72h and 168h, respectively.

Figure 1. Moisture and heat ageing on the mechanical properties of three-phase composites.

From the experimental results of hygrothermal aging in Fig.1, it can be seen that the bending and impact strength of the composites decrease after hygrothermal aging, and the longer the hygrothermal aging time is, the greater the decrease is. In addition, the interfacial bonding between resin matrix and carbon fiber or carbon nanotube is weakened, resulting in the decrease of fiber pull-out work and the overall performance of the material. When the content of carbon nanotubes exceeds a certain content, the dispersion of carbon nanotubes will become worse, which will cause a large number of microcracks. After a long time of hydrothermal aging treatment, water molecules can first enter the microcracks, attack the defects, and produce cracking. In addition, with the increase of CNTs content, the number of interfaces increases, the bonding strength of some interface layers is not enough, and the internal defects of the system increase, thus the mechanical strength decreases.

From the analysis of the above results, it can be seen that the bending strength of three-phase composites decreases after hygrothermal aging, and the longer the hygrothermal aging time is, the greater the decrease range is. In order to further study the influence of hygrothermal aging on the mechanical properties of the composites, the MWNTs-NH2/CF/BMI three-phase composites after 168 h hygrothermal aging were taken for comparison.

3.2. Effects of Modifier Content and Aging Time of Carbon Nanotubes on Salt Spray Aging Resistance of Composites

Salt spray aging is to evaluate and study the salt spray corrosion resistance of materials in salt spray atmosphere. Because the composite materials in this study may be used in marine environment, sodium chloride solution (salt spray) is the main corrosive agent in marine environment, which is particularly important for the application of this material in this aspect. Fig.2 shows the mechanical properties of MWNTs-NH2 / CF / BMI three-phase composites after 0 h, 72 h and 168 h salt spray aging, Among them, (1) the carbon nanotube free CF / BMI two-phase composites were treated with 0
h, 72 h and 168 h salt spray aging, respectively (2) In the group, MWNTs-NH2 / CF / BMI three-phase composites with MWNTs modifier content of 1wt% were subjected to salt spray aging for 0h, 72h and 168h, respectively (3) MWNTs-NH2 / CF / BMI three-phase composites with 2.5wt% carbon nanotube modifier were treated with 0 h, 72 h and 168 h salt spray aging respectively.

Figure 2. Salt spray ageing on the mechanical properties of three-phase composite materials.

From the experimental results of salt spray aging in Fig.2, it can be seen that the bending strength of the composites increases after salt spray aging, and the longer the salt spray aging time is, the greater the increase range is; But the impact test results show that the impact strength of the composites decreases after salt spray aging. The longer the salt spray aging time is, the greater the impact strength decreases. Salt spray aging is to evaluate and study the salt spray corrosion resistance of materials in salt spray atmosphere. The salt spray aging mechanism is more complicated due to the addition of sodium chloride in the aging system. Sodium chloride ions precipitate to form sodium chloride micro nano particles, which can fill the micro cracks of the composite, prevent water molecules from invading into the composite to a certain extent, and improve the strength of the composite in a relatively short time. It is confirmed that the bending strength of the composites increases after salt spray aging. The longer the salt spray aging time is, the greater the rising range is. At the same time, the more the content of carbon nanotubes is and the greater the defect probability is, the greater the improvement range of the bending strength of the composites is. But on the other hand, after salt spray aging, the water molecules enter into the microcrack zone and attack the defect area, resulting in the decrease of interfacial bonding strength and cracking of the composite, which affects the mechanical properties of the composite. The impact strength of the composite decreases after salt spray aging. The longer the salt spray aging time is, the greater the decrease of impact strength is.

4. Conclusions
In this work, MWNTs/CF/BMI three-phase composites were subjected to hydrothermal and salt spray aging at 80 °C. The longer the aging time is, the greater the decrease is; After salt spray aging, the bending properties of the composites increase, the longer the salt spray aging time is, the greater the increase range is, while the impact properties decrease, and the longer the salt spray aging time is, the greater the decrease range is. When the aging time is 168 h, the bending strength and impact strength of the three-phase composites with MWNTs-NH2 content of 1.5 wt% reach the maximum after hydrothermal and salt spray aging. The bending strength and impact strength of the composites with MWNTs-NH2 content of 1.5 wt% are 45% and 41% higher than those without carbon nanotubes; the bending property and impact property of the composites aged in salt spray are 43% and 32% higher than those of the composites without carbon nanotubes.
SEM images of impact section of CF / BMI two-phase composites after salt spray aging for 168 h showed that the carbon fiber braid was separated, and the carbon fiber and matrix resin were debonded, which indicated that the salt spray aging had a great influence on the mechanical properties of the composites. The addition of 1.5wt% amino carbon nanotubes can effectively improve the interfacial adhesion between carbon fiber and matrix resin, and improve the mechanical properties of the composites. The mechanical properties of the composites with 2.5wt% amino carbon nanotubes decreased due to the agglomeration of carbon nanotubes. The results show that the erosion resistance of CNT / CF / bismaleimide three-phase composites is greatly improved after adding 1.5% mass fraction of aminated CNTs, and the wear quality of CNT / CF / bismaleimide three-phase composites is 42.86% lower than that of carbon fiber / bismaleimide composites without adding CNTs.

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