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Preparation of electroless copper coated glass fiber and piezoresistive properties of copper coated glass fiber reinforced plastics

Jiandong Zuo[a,*], Shaojun Chen[a], Chaoyun Luo[b], Dazhu Chen[a]

[a] College of Materials Science and Engineering, Nanshan District Key Lab for Biopolymers and Safety Evaluation, Shenzhen University, Shenzhen 518060, China

[b] School of Applied Chemistry and Biological Technology, Shenzhen Polytechnic, Shenzhen 518055, China

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ABSTRACT

Metallized glass fibers have the excellent electric conductivity and low price compared with carbon fibers. Metallized glass fibers were fabricated by coating copper on the surface using different processing technologies and the effects of processing technology on the properties of copper coated glass fibers were discussed. By hand laying up molding, metallized glass fiber reinforced plastic (MGFRP) with good dispersion and interfacial cohesion was prepared successfully. The piezoresistive properties of MGFRP were compared with those of carbon fiber reinforced plastic (CFPR). The results show that copper coated on glass fibers with volume resistivity of 10^{-5} Ω·cm have the good electrical conductivity and cohesion between two phases through optimizing the pretreatment technology of glass fibers and the formula of chemical plating solution. MGFRP has the distinct and similar piezoresistive characteristics with CFRP and exhibits the better piezoresistive sensitivity to fracture.

1. Introduction

Carbon fiber attracts much attention as it improves not only the mechanical properties of materials but also the electric conductivity of composites. Volume resistivity of carbon fiber is between 1.2×10^{-3} Ω·cm and 3.0×10^{-3} Ω·cm, and thus carbon fiber reinforced plastics (CFRP) has been used as a kind of strain sensor in the concrete structure and feedback the change of stress in the inner of structure timely.

Glass fiber as a kind of low cost material has many properties similar with carbon fiber, such as good thermal stability, good chemical corrosion resistant and better mechanical strength. But glass fiber is electric insulation, it is usually compounded with carbon fiber [1], metal fiber [2,3] or carbon black to improve the electric conductivity when it is used in the smart materials.

Glass fibers coated with a metal layer are another good strategy to endow glass fiber with good electrical conductivity. Metalized glass fibers have low price and can be combined with resin more easily. The volume resistivity of metallized glass fiber can achieve 10^{-3}–10^{-4} Ω·cm, even 10^{-5} Ω·cm, which is ten times as low as that of carbon fiber. Reported in the former patent [4–6], glass fibers coated with nickel copper, gold, silver, etc. had many advantages, such as good conductivity, high strength, uniform plating layer and low cost compared with carbon fibers and it is expected to improve the piezoresistive sensitivity of fibers reinforced plastics. Yoshiki Okuhara [3] used glass fiber matching carbon black to improve the conductive sensitivity of materials and discussed piezoresistive property of composites. But so far, the research about piezoresistive properties of metallized glass fiber reinforced plastics is seldom concerned.

Copper coated glass fiber had been studied in previous literatures, but the plating layer on the surface of samples is not very uniform and compact [7–9]. We found that pretreatment on glass fibers was the key to gain the compact metal layer of glass fiber, which was usually ignored in the other literatures. In this work, copper coated glass fibers were successfully prepared by chemical plating. The effects of pretreatment technology before plating and chemical plating solution formula on the properties of copper coated glass fibers were studied carefully. Moreover, a novel composite, copper coated glass fibers reinforced epoxy, was fabricated and the electric resistance–stress characteristic, particularly piezoresistive sensitivity behaviors of composites, were compared with that of CFRP [8,9]. The cohesion between metallized glass fiber and matrix was also analyzed. All of these results provide a fundamental data for improving the accuracy of strain sensor and further broadening the applications of self-diagnostic materials.

* Corresponding author. Tel.: +86 755 26535133; fax: +86 755 26534457.
E-mail address: Jdzuo@szu.edu.cn (J. Zuo).

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2. Experimental

2.1. Materials

Alkali-free glass fiber (787) was obtained from China Jushi Group Co., Ltd. Carbon fiber (TC3612K) was gained from Taiwan Taili Co. Ltd.; palladium chloride, stannous chloride, sodium hydroxide, ammonium fluoride, copper sulfate, disodium ethylenediamine tetraacetate (EDTA Na), potassium ferrocyanide, formaldehyde, diethylene triamine, all came from Guangdong Chemical Reagent Company. Epoxy resin E51 and Curing agent T31 was provided by Guangzhou Hongsheng Chemistry Co. Ltd. Silver conductive adhesive came from Seazheng Shanghai Co., Ltd.

2.2. Sample preparation

2.2.1. Preparation of metallized glass fibers

The preparation procedure of metallized glass fiber can be divided into two steps: pre-treating glass fiber before chemical plating and chemical plating copper.

(1) Pre-treating glass fiber before chemical plating: the glass fibers with the length of 8–10 cm were cleaned by distilled water and then placed into an ammonium fluoride solution for coarsening. After that, glass fibers were activated in the activation solution (palladium chloride 0.3 g/L, stannous chloride 12 g/L, chlorhydric acid 10 mL/L) for 3 min and subsequently were immersed into NaOH solution for 1 min. Finally, the handled glass fibers were dried in air at room temperature. Two kinds of pretreatment methods (A) and (B) were used to prepare metallized glass fiber and the difference between the two methods was alkaline washing for two times before coarsening and after activation in the pretreatment method (B).
(2) Chemical plating: chemical plating solution composed of copper sulfate as main salt, formaldehyde as reducing agent and 10 wt% absolute ethyl alcohol as the basic solution. The chemical plating was conducted by immersing glass fibers into the chemical plating solution with pH value 12–13. After chemical plating, copper coated glass fibers were cleaned by distilled water and subsequently placed into the vacuum oven for drying one hour at 90 °C for heat treatment.

2.2.2. Preparation of copper plated glass fibers or carbon fibers reinforced epoxy resin

An epoxy resin and diethylene triamine were mixed at a weight ratio of 10:1 and the blend was degassed by vacuum equipment. Copper coated glass fibers and carbon fibers reinforced epoxy resin composites were respectively prepared by hand laying up molding in a silicon rubber mold, with fiber content 5%, 10% and 15% respectively [10,11]. The samples were cured at ambient temperature for 24 h and then two ends of the sample were coated with a layer of silver conductive adhesive. Finally, samples were placed into drying oven at 120 °C for 2 h for the further curing.

2.3. Characterizations

2.3.1. Analysis of copper coated glass fiber

The element components on the plating layer of copper coated glass fiber were determined using energy dispersive spectrometer (EDS), X-ray fluorescence spectrometer (XRF, S4-Explorer) and X-ray diffraction (XRD). The dots were random selected on the surface of the samples measured by EDS. Two ends of a certain amount of metallized glass fibers measured by XRF were pasted to the specimen stage and the element content was relative value to the original glass fibers.

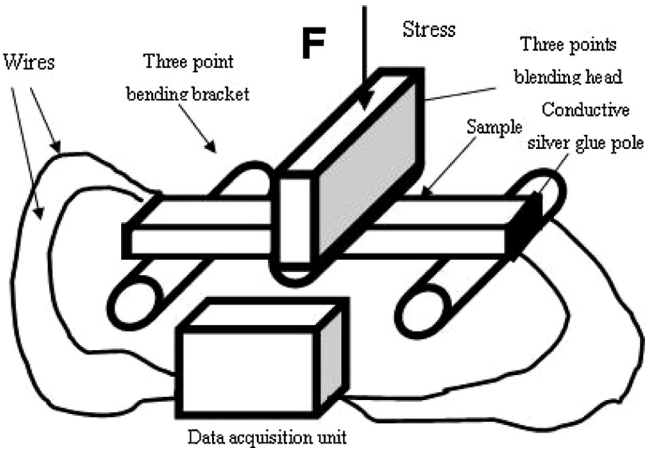

Fig. 1. Connection diagram of four-wire resistance measuring method.

Morphology of copper coated glass fiber was observed by scanning electron microscope (SEM, JSM-5910LV) from JEOL Co., Ltd in Japan. The samples were gold-coated for 60 s before observing.

The adhesion force between plating layer and glass fiber was evaluated by thermal shock test according to ISO 2819-1980, metallized glass fiber was heated to 250 °C in the electric tube furnace and then quickly took out and put into cool water. The heating and cooling processes were repeated for 8 times. The surface of plating layer was thoroughly examined to determine if any bubbles or peeling occurred.

2.3.2. Determination of volume resistivity of composites

Four-point probes method: a certain amount of fibers was evenly pasted to the paper and pressed by a platen press with the pressure of about 7 MPa. Then the thickness of samples was measured by vernier caliper and samples were put under four probes to obtain volume resistivity [7].

Direct current (DC) resistance method: the electric resistance of fibers were measured by DC resistance and volume resistivity was calculated by formula $\rho = RA/L$ (R is the electric resistance with a unit of ohm, L is length with a unit of cm, A is sectional area with a unit of cm^2, ρ is volume resistivity with a unit of Ω·cm). For each sample, volume resistivity was measured for several times and the average value was adopted.

2.3.3. Piezoresistive property of MGFRP and CFRP

Piezoresistive property of composites was measured by four-wire resistance measuring method. Fig. 1 is the concrete connection diagram of four-wire resistance measuring method. Agilent data acquisition unit (34970A) was provided by Agilent Technology, USA and was connected with conductive silver glue of the sample by wires. The data acquisition unit can collect the electrical resistance of samples in response to the pressure applied on the samples. The stress variation was measured by three-point bending load on an electronic tensile testing machine with loading rate of 1 mm/min [12].

3. Results and discussion

3.1. Effect of pretreatment technology on the properties of metallized glass fiber

Using the feature that each element relates with a specific X-ray photonic characteristic energy and cooperating with SEM, EDS can be used to analyze the element of the materials and the relative content of these elements such as the ingredients of surface plating layer of metallized samples. Two kinds of pretreatment methods,