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Electroless silver plating on tetraethoxy silane-bridged fiber glass

Wan-Fu Lien[a], Po-Chen Huang[b], Shi-Chang Tseng[c], Chia-Hsiang Cheng[b], Shih-Ming Lai[b], Wen-Chang Liaw[b,*]

[a] Department of Cultural Heritage Conservation, National Yunlin University of Science and Technology, 123, Section 3, University Road, Touliu, Yunlin 640, Taiwan, ROC
[b] Department of Chemical and Materials Engineering, National Yunlin University of Science and Technology, 123, Section 3, University Road, Touliu, Yunlin 640, Taiwan, ROC
[c] Department of Mechanical Engineering, National Yunlin University of Science and Technology, 123, Section 3, University Road, Touliu, Yunlin 640, Taiwan, ROC

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ABSTRACT

Tetraethoxy silane was used to functionalize the surface of fiber glass (FG) for adsorption with the electroless plated silver shell. The performance of electroless silver plated FG with tetraethoxy silane modification was compared to that of unmodified FG in terms of mechanical and electrical properties. The silane bridge provided more stability for binding with different concentrations of electroless plating silver ions. The characterization was investigated by using field emission scanning electron microscope (FESEM), X-ray diffraction patterns (XRD), energy-dispersion X-ray (EDX), metal microscope (MM) and electric resistance. The Ag coating on TEOS modified FG was more durable than that of unmodified FG in the ball milling test, as confirmed by the data of electric resistance and residue weight. The optimized conditions for producing the Ag coating FG were also investigated. The Ag–Si–FG-3-*c* product in this study has the lowest electrical resistance of 1.56×10^3 Ω/cm^2 and good mechanical stability as exhibited in ball milling tests.

1. Introduction

Since the last century, fiber glass (FG), because of the convenience of processing and manufacturing, has been widely applied in the field of composite materials as reinforcing material. FG has the advantages of good mechanical properties, medium density, cheapness, and compatibility with many types of resins; and it is functional as a material in outdoor furniture, automobiles, boats, and high electric resistance print-circuit boards [1]. Nevertheless, the very high electric resistance of FG can be a disadvantage and should be modified for application in the composite fields that need low electric resistance, such as antistatic or electromagnetic interference (EMI).

Recently, most antistatic or EMI materials were made from homogenous mixing of polymeric matrix and conducting additives. The conducting additives include organic cationic surfactants and inorganic conducting fillers. However, the electric resistance of the materials that were prepared by addition of organic cationic surfactants in polymers would increase after a short time, due to the high solubility of the organic surfactants in water. The organic surfactants migrate easily and are lost. On the other hand, the addition of inorganic conducting filler would produce a material with permanent low resistance. The conducting fillers include metallic powder, conductive carbon black, carbon fiber, and carbon nanotubes, etc. [2–5]. Nevertheless, these conducting fillers are very expensive.

The composites that are made from this modified FG (with a high length to diameter ratio and coated with a layer of high conducting metal) and polymers, would have both high mechanical properties and electric conductivity. The polymers could be either thermoplastic or thermosetting. However, only a few studies have been done on the metal modification of FG to increase electric conductivity [6].

In the field of metallic coating, there are some processes that have been studied and used, such as electric plating, chemical electroless plating [7,8], physical vapor deposition (PVD) [9,10] and chemical vapor deposition (CVD) [11], etc. Among these processes, electric plating is a traditional process that has been used for a long time. However, in this process, the substrate must be a conductive material, which is anchored on the cathode of the electric plating bath. The electric plating bath contains the ions of plating metal obtained by dissolving the salt of this metal. The plating metal is anchored on the anode and oxidized as the plating process starts. The metallic ions in the plating bath migrate to the surface of the substrate (cathode) and is reduced and deposited on it.

Chemical electroless plating is another alternative process for metallic coating of non-conducting substrate such as plastics. In 1984, McKnight and Ibrahim [12] have successfully used sodium hypophosphite to reduce nickel ions to form a nickelous alloy. This method can be easily used for the metallization of conductors, semiconductors, and non-conductors. In this process, the substrate

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[*] Corresponding author. Tel.: +886 5 5342601 4618; fax: +886 5 5342071.
E-mail address: liawwc@hotmail.com (W.-C. Liaw).

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must be pre-treated before metallic reduction and plating. The pre-treated processes include decontamination, coarsening, sensitization, and activation. The sensitization process was conducted by tin chloride right after the cleaning and coarsening process to accelerate the reduction reaction of the plating metal ions. On the other hand, for improving the stability of the metal plating, the sensitized surface must be activated before reduction reaction by a noble metallic salt, such as palladium chloride ($PdCl_2$). After the pre-treated process, the metal ions in the plating solution are reduced with a reducing agent and deposited on the surface of the substrate as an elementary metal form. The obtained metal plating substance has the advantages of uniform plating and low cost. In the literature, metals such as Al [13], Cu [14,15], Ag [7,16,17], and Ni [18] have been studied for chemical electroless plating.

Metallic coating on non-conducting substrates can also be achieved by the PVD process, where the vaporized metal deposits on the substrate surface form into a uniform and tight layer. However, this PVD process needs a high vacuum and large energy supply system and suffers from high costs [9,10]. Another CVD process was also used to prepare metallic coating on a similar substrate and the product obtained has as good of quality as PVD. However, the CVD process also has the same disadvantage as PVD-high cost. It also needs reactive starting materials for the plated reaction [11]. It would be interesting to compare the cost and qualities of the end product of metal coating for all of the above methods. However, such comparison would not be practical until available technologies have been thoroughly studied [19,20].

In electroless plating, the pre-treated processes of sensitization and activation need to use noble metals and therefore this raises the cost. In recent years, the prices of noble metals such as Au and Pd have gone up sharply. If the process of activation could be omitted or substituted by another method, the cost of the electroless plating would be reduced. In other words, introducing organic functional groups on the substrate surface would decrease the cost of electroless metal plating. The organic functional groups could be mutually adsorbed with the plating metal ions. For this purpose, many candidate functional groups such as amino, carboxyl, thiol and silane have been used to substitute palladium chloride [14,21–23]. If the FG has not been modified, only the Ag is intrinsically adsorbed to the FG by a weak van der waals force [21].

Warshawsky and Upson [23] reported about the mechanism of electroless plating on functionalized polymer particles of various sizes. The functional groups (amino, carboxylic or thiol) on the surface of polymers served as catalytic sites for activation through binding the noble metal ions by coordination or ionic bonding, and this was followed by chemical reduction of the metal ions to a zero valent metal state.

Lu [21] investigated the electroless deposition of Cu on poly (ethylene terephthalate) (PET) fabric with the modification of 3-mercaptopropyltriethoxysilane. They have successfully produced a composite with good stability and high electric conductivity by mixing the Cu plated PET and polymer matrix.

For the metal plating on FG, which is used to prepare a reinforced and conducting composite from this hybrid fiber and polymer matrix, the chemical electroless plating without activation is the best choice in this study. PVD and CVD processes have the disadvantage of high cost.

In the literature, Moon et al. [16] have studied an electroless silver coating on glass particles. The silver and glass composite powders were prepared to impart electric conductivity of these particles. They have successfully obtained low density Ag-coated glass particles used for preparing conducting materials for electromagnetic interference (EMI) shielding. Sn sensitization has been used in the surface pretreatment. Their techniques for controlling the uniform thickness of silver coating can be employed to prepare the biosensor materials.

Huang et al. [6] have studied Ni–Co–P alloys electroless plating on FG. They have investigated the deposit composition with sensitization and activation, the plating rate, structure, and crystallization process. They have obtained conductive FG that has great properties and their product will be used as a kind of filler for absorbing electromagnetic waves.

In this study, the FG was plated with silver. As noted in the previous discussion, the directly plated metal without activation or a functional group would more easily peel off from the FG. Therefore, in order to increase the stability of the electroless silver plating on FG without using sensitization and activation, the inorganic instead of organic functional group was used in this study. Tetraethyloxy silane (TEOS) was used to carry out such surface modification on FG. This silane has four alkoxysilyl groups which would change to a hydroxyl group after hydrolysis, and then condensates with the Si–OH group on the surface of FG to form $(FG)–Si–O–Si(OH)_3$ bonding. After this modification of FG, the silver ions are absorbed to form $(FG)–Si–O–Si(OH)_2–O\cdots Ag$, and the silver ions were reduced to elementary silver. The alkoxysilyl group has been used as a covalent bridge between FG and the silver metal for increasing the stability of the hybrid fiber. The optimized conditions for preparing the silver plated FG were studied. The morphology and mechanical properties of Ag plated FG were also investigated.

2. Experimental

2.1. Materials

The fiber glass (FG, diameter 6–9 μm) was obtained from Taiwan Chao-Tung Company, Taiwan. The tetraethoxy silane, the silane coupling agent, was obtained from Shin-Etsu Silicone Taiwan Co., Ltd., Taipei, Taiwan, and was used without purification. The formaldehyde (HCHO) was obtained from Union Chemical Works Ltd., Taiwan. The hydrofluoric acid (HF), nitric acid (HNO_3), and hydrochloric acid (HCl) were purchased from Fluka, Milwaukee, USA. The silver nitrate ($AgNO_3$) and ammonium hydroxide (NH_4OH) were obtained from Aldrich, Super Chroma Enterprise Ltd., USA. All chemical reagents were of analytical grade and were distilled at 40 °C/12 mmHg. Deionized water was used in experiments.

2.2. Functionalization of fiber glass

The FG was sequentially cleaned by ultrasonic in acetone for 15 min and in ethanol for 15 min, and was dried at 80 °C for 1 h. The cleaned fiber glass was suspended in 0.1 mol/L hydrofluoric acid solution and vibrated by ultrasound for 10 min at room temperature. Then the FG was rinsed with deionized water.

The FG treated with HF was functionalized with tetraethoxy silane solutions of 1, 5, 10, 20 and 30 g/L in methanol/water at room temperature for 30 min and the pH was controlled at 2 by using HCl. The functionalization conditions are shown in Table 1. After being isolated from the silane solution, the FG was heated at 140 °C for 1 h to form a silica treated layer.

2.3. Electroless silver plating of FG

The functionalized FG was plated with silver by an electroless plating process. The composition of electroless silver plating solution and processing conditions are listed in Table 2. The electroless plating of FG was performed in a 500 mL silver bath and ultrasonic-assisted environment. After the plating was finished, the silver coated FG was carefully rinsed with deionized water and dried in an oven at 110 °C for 2 h.