Preparation of Silver-Glass Fiber Composites by Plasma Treatment-Continuous Impregnation Method (Postprint)

Authors: Lu Ping, Chen Xiao, Yang Ming

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Abstract

A silver-glass fiber composite with good interfacial bonding was prepared by combining plasma treatment and a continuous impregnation method. SEM, AFM, and XRD results demonstrate that silver is uniformly coated on the glass fiber surface, exhibiting excellent comprehensive properties. Compared with traditional electroless plating methods, this preparation process is novel and simple. Following oxygen plasma treatment, the surface-active hydroxyl groups on the glass fibers demonstrate strong adsorption capability toward silver via multiple interactions. The coating thickness can be readily tuned by adjusting the dip-coating duration. Furthermore, the silver particles on the surface of the silver-glass fiber composites fabricated by this process exhibit higher activity compared with those prepared by conventional silver plating techniques. Owing to the excellent antibacterial and anti-infective properties of silver, such silver-glass fiber composites hold promising potential for broad-spectrum antibacterial applications.

Full Text

Preparation of Silver-Glass Fiber Composites by Plasma Treatment-Continuous Immersion Method

Lu Ping, Chen Xiao, Yang Ming
Research Center for Analysis and Measurement, Donghua University, Shanghai 201620, China

Abstract
A silver-glass fiber composite with excellent interfacial bonding was prepared by combining plasma treatment with a continuous immersion method. Characterizations by SEM, AFM, and XRD revealed that silver was uniformly coated on the glass fiber surface with favorable comprehensive properties. Compared

with conventional electroless plating methods, this preparation process is novel and simple. After oxygen plasma treatment, the active hydroxyl groups on the glass fiber surface exhibited strong adsorption capacity for silver through multiple interactions. The coating thickness could be readily adjusted by controlling the immersion time. Moreover, the silver particles on the surface of the composites prepared by this method showed higher activity than those produced by traditional silver plating processes. Given silver' s excellent antibacterial and anti-infective properties, this class of silver-glass fiber composites holds potential value for broad-spectrum antibacterial applications.

Keywords: glass fiber, silver coating, plasma, composites, atomic force microscope, scanning electron microscope

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Introduction

Glass fibers are fibrous materials formed by controlling molten glass through external force blowing or centrifugal spinning. They possess characteristics such as smooth surfaces, high strength, chemical stability, heat resistance, and sound insulation [1-5]. However, glass fibers have poor electrical conductivity. Coating their surfaces with metal [6-8] not only addresses the high cost of metallic conductive fillers but also expands their application fields through surface modification, such as in conductive fillers and electromagnetic shielding materials [9,10]. Silver-glass fiber composites, which are low-cost yet combine the excellent conductivity, chemical stability, and antibacterial properties of metallic silver with the high tensile strength and heat resistance of glass fibers, have found extensive applications [11-13].

Silver-glass fiber composites are typically prepared by electroless plating methods. While this technique offers advantages such as low cost, good product conductivity, and strong antistatic capability [14], it has several limitations. First, the main components of the silver plating solution—primary salts, complexing agents, and reducing agents—are unstable and have short lifespans. Second, the interfacial bonding between silver and glass fibers is weak, resulting in low silver deposition efficiency. Third, continuous production is difficult to achieve. Therefore, developing novel silver plating methods represents an urgent challenge in preparing silver-glass fiber composites [15]. This paper proposes a new method: plasma treatment-continuous immersion.

1. Experimental Methods

1.1 Preparation of Silver-Glass Fiber Composites To prepare the silver suspension, 5.86 g of polyvinylpyrrolidone (PVP, MW 40,000) was dissolved in 190 mL of glycerol at 50°C under slow stirring to obtain suspension A. Suspension A was heated to 90°C with gentle stirring until complete dissolution, then cooled to 50°C. Subsequently, 1.58 g of $AgNO_3$ was added to solution A

and stirred gently for 15 minutes. Then solution B, composed of 9.5 mL glycerol + 59 mg NaCl + 0.5 mL H_2O, was added. The mixture was stirred and heated to 210°C. After cooling to room temperature, the reaction solution was centrifuged at 5000 rpm for 5 minutes to separate the Ag nanowires. Deionized water was added to the separated Ag nanowires, which were ultrasonicated for 10 minutes to fully disperse them in aqueous solution, then centrifuged again at 5000 rpm for 5 minutes to obtain the secondary Ag nanowire precipitate. This precipitate was dispersed in 99% ethanol solution and ultrasonicated for 20 minutes to obtain a uniformly dispersed Ag ethanol solution with a concentration of approximately 10 mg/mL (silver stock solution).

Commercial glass fibers were ultrasonicated in acetone for 10 minutes, then dried in a 70°C oven for 90 minutes. The fibers were subsequently treated in a DT-01 oxygen plasma apparatus for 5 minutes. After plasma treatment, the fibers were continuously immersed in the silver stock solution, removed, and dried in a 70°C oven for 30 minutes to obtain the silver-glass fiber composites.

1.2 Characterization of Silver-Glass Fiber Composites Surface morphology was examined using a Veeco Nanoscope IV atomic force microscope. Fiber morphology and elemental analysis were performed using a Hitachi S-4800 high-resolution cold field emission scanning electron microscope equipped with a Bruker Quantax 400 X-ray energy spectrometer. Powder diffraction analysis was conducted using a Rigaku D/max-2550 PC X-ray diffractometer. Fourier transform infrared spectroscopy was performed using a Thermo Fisher Nicolet 6700 spectrometer.

2. Results and Discussion

[Figure 1: see original paper] shows FE-SEM images of pristine glass fibers after simple acetone hydrothermal treatment, at scales of 50 m, 10 m, and 5 m. The selected glass fibers exhibit uniform diameters of approximately 6-10 m. As shown in Figure 1C, the glass fiber surface is smooth and free of defects or wrinkles after acetone hydrothermal treatment. AFM surface morphology testing (Figure 2 [Figure 2: see original paper]) confirms the smooth surface, consistent with FE-SEM results.

Figure 3 [Figure 3: see original paper] (left) presents the EDS spectrum of pristine glass fibers, showing only constituent elements such as Ca, O, Mg, Al, and Si, with no noble metal elements like Ag (2.98 keV). The right side of Figure 3 shows FT-IR spectra of glass fibers before and after oxygen plasma treatment. The spectrum after plasma treatment reveals a distinct hydroxyl characteristic peak at 1648 cm^{-1}, indicating that abundant hydroxyl groups were generated on the glass fiber surface.

Figure 4 [Figure 4: see original paper] illustrates the preparation mechanism of the silver-glass fiber composites. After acetone hydrothermal washing, surface contaminants are removed, creating a pure, smooth surface structure. Subse-

quent oxygen plasma treatment grafts numerous hydroxyl groups onto the surface, forming a brush-like structure as shown in Figure 4. When these plasma-treated glass fibers are immersed in the nano-Ag ethanol solution, the surface hydroxyl groups adsorb silver, resulting in uniform silver coating on the glass fiber surface. The bonding between silver and the fiber matrix is primarily physical adsorption based on non-covalent intermolecular interactions. Although individual physical adsorption is relatively weak, the "multivalent binding" effect—where multiple non-covalent forces act synergistically—provides strong stability. Additionally, surface energy contributes to the composite' s properties.

The immersion time can be varied to adjust the coating amount and Ag shell thickness. This method modifies the glass fiber surface through plasma treatment, avoiding toxic solvents and reactants produced in traditional silver-glass fiber composite preparation, and operates under mild reaction conditions.

Characterization results from FE-SEM, AFM, EDS, XRD, and FT-IR for the silver-glass fiber composites are shown in Figure 5 [Figure 5: see original paper]. After immersion in the Ag ethanol solution, the plasma-treated glass fibers are uniformly coated with nano-Ag. Compared with conventional silver plating processes, the silver-glass fiber composites prepared by this method have rougher surfaces, thus possessing larger specific surface areas and higher surface energy, meaning the surface silver particles exhibit higher activity. Figures 5c and 5d reveal three silver morphologies on the glass fiber surface: rod-like, spherical, and triangular. These different silver morphologies, with varying aspect ratios, produce specific responses to different bacterial species [16]. Glass fiber color resembles natural tooth color, and its elastic modulus is close to that of dentin; as a non-metallic post, it has been used in clinical anterior tooth restoration [17]. Combined with silver' s excellent antibacterial and anti-infective properties, this class of silver-glass fiber composites demonstrates broad-spectrum antibacterial effects.

Figure 6 [Figure 6: see original paper] shows FE-SEM images of silver-glass fiber composites with different immersion times. At 15 minutes (Figure 6a), only partial glass fiber surfaces are covered with silver, with large exposed areas visible. At 30 minutes (Figure 6b), most of the glass fiber surface is coated with silver. At 45 minutes (Figure 6c), all regions of the glass fiber surface are coated with silver, and the silver coating has achieved substantial thickness. These results demonstrate that optimized silver-glass fiber composites can be obtained by simply adjusting the immersion time.

Figure 7 [Figure 7: see original paper] presents EDS mapping images of the silver-glass fiber composites. The images show strong silver signals while signals from glass main elements such as Al and Si are weak, because the glass fiber surface is completely coated with Ag. Figure 8 [Figure 8: see original paper] clearly shows that the surface roughness of Ag-coated glass fibers increases significantly, as the silver coating process is a self-assembly process that creates surface heterogeneity.

Figure 9 [Figure 9: see original paper] shows XRD patterns of pristine glass fibers and silver-glass fiber composites. The pristine glass fiber pattern shows no obvious crystalline peaks; the broad hump at 20-30° corresponds to amorphous silicate. In contrast, the silver-glass fiber composite pattern exhibits not only the amorphous glass fiber hump but also two sharp crystalline peaks corresponding to Ag (111) and (200) crystal planes. Figure 9b simultaneously displays characteristic peaks for both glass fibers and Ag, further confirming successful composite formation.

3. Conclusion

Silver-glass fiber composites can be prepared by plasma treatment-continuous immersion method, with good silver coating on glass fiber surfaces. After oxygen plasma treatment, the active hydroxyl groups on the glass fiber surface exhibit strong silver adsorption capacity through multiple interactions. By adjusting the immersion time in the Ag solution, the thickness of the Ag coating can be controlled to prepare composites with different silver loading amounts. This novel preparation method enables integrated coating of silver with different morphologies. Compared with conventional silver plating processes, the silver-glass fiber composites prepared by this method have rougher surfaces, larger specific surface areas, and higher activity of silver particles.

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Note: Figure translations are in progress. See original paper for figures.