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Conductivity decay of cellulose–polypyrrole conductive paper composite prepared by in situ polymerization method

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ABSTRACT

Cellulose–polypyrrole (PPy) conductive paper composite was prepared using an in situ chemical polymerization process, and its conductivity stability was investigated. When the PPy-coated pulp fibers were dipped in an alkaline solution or the paper composite was exposed to an alkaline environment, the conductivity stability became poor. Contrarily, if the PPy-coated pulp fibers were dipped in an acidic solution or the paper composite was exposed to an acidic environment, the conductivity stability would be improved. The conductivity decay occurred when the paper composite was stored in air atmosphere at ambient temperature. The rate of conductivity decay also depended on temperature and atmosphere. The conductivity decay in air occurred quicker than that in nitrogen, especially at elevated temperature. The PPy-coated pulp fibers and the paper composite were characterized by TGA, XPS, SEM and SEM-EDX analyses to elucidate the mechanism of conductivity decay of the paper composite.

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1. Introduction

Electrically conductive paper composite would be very useful in various fields, including the manufacture of antistatic material, electromagnetic interference (EMI) shielding material, sensing elements, heating elements, and packing of electronic components and equipment, etc. (Jang & Ryu, 2006).

In recent years, conductive paper composite produced by in situ chemical polymerization of pyrrole and aniline in a pulp fiber system has aroused a great interest (Beneventi, Alila, Boufi, Chaussy, & Nortier, 2006; Chen & Qian, 2007; Ding, Qian, Shen, & An, 2010; Huang, Kang, & Ni, 2006; Johnston, Kelly, Moraes, Borrmann, & Flynn, 2006; Kim, Deshpande, Yun, & Li, 2006; Song, Qian, Wang, & Xie, 2006; Song, Qian, & Wang, 2006). The in situ polymerization process is a process that the monomer such as aniline and pyrrole is polymerized in the presence of pulp fibers and deposited onto the surface of the pulp fibers.

The conductivity stability is one of important properties of conductive paper composite. In our previous studies, we found that the conductivity stability of cellulose–polyaniline (PAn) conductive paper composite depended on the type of dopants used (Song, Qian, & Wang, 2006). *p*-Toluenesulfonic acid and sulfosalicylic acid in organic acids and sulfuric acid in inorganic acids were excellent dopants. In fact, the conductivity stability of the cellulose–PAn conductive paper composite doped with *p*-toluenesulfonic acid was very good. The surface resistivity remained almost unchanged after storing in air environment for 1 month. The increase in the surface resistivity was not beyond 15% even after storing in air environment for 5 months. However, the conductivity stability of cellulose–polypyrrole (PPy) conductive paper composite was much poorer as compared to that of cellulose–PAn conductive paper composite (Chen & Qian, 2007; Ding et al., 2010).

In general, the conductive PPy composites are less stable in air due to their reactivity with a variety of atmospheric chemicals, especially oxygen (Wu, Zhou, Too, & Wallace, 2005). Because of the low oxidation potential of PPy, the redox reaction of PPy is more sensitive to the oxygen than those polymers that are more difficult to oxidize (Ansari, 2006). Our recent studies showed that the conductivity stability of cellulose–PPy conductive paper composite in the atmospheric environment depended on the preparation conditions, especially pyrrole concentration, oxidant charge and reaction time (Chen & Qian, 2007; Ding et al., 2010). In addition, the use and recycling of this paper composite may involve various chemicals (including acids, alkalines and oxidants, etc.) as well as elevated temperatures. Therefore, for successful industrial application of the paper composite in future, its conductivity stability is one of the key properties that should be considered first.

In this work, the conductivity decay of cellulose–PPy conductive paper composite was investigated by observing the changes of surface resistivities with storage time under different treatment or storage conditions. The PPy-coated pulp fibers and the paper composite were characterized by TGA, XPS, SEM and SEM-EDX analyses to elucidate the mechanism of conductivity decay of the paper composite.

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2. Experimental

2.1. Materials

Pyrrole was chemical grade and was freshly distilled before use. All the other chemicals were of analytical grade and used without further purification.

The pulp used in this research was softwood bleached sulfite pulp (NBSP) and was obtained from Yanbian Shiyan Bailu Paper Co., Ltd. (Jilin Province, China).

2.2. Preparation of cellulose–PPy conductive paper composite

Ferric chloride solution and *p*-toluenesulfonic acid (PTSA) solution were added separately to the pulp suspension containing 2 g (oven-dry basis) of pulp. Then a given amount of pyrrole monomer was injected with a liquid injector. The mixture was stirred at ice bath temperature for 2 h. The resulting PPy-coated pulp fibers were repeatedly washed with tap water in a filter bag to remove any free PPy. Unless otherwise indicated, the preparation conditions of cellulose–PPy conductive fiber composite are as follows: pulp consistency 1%, pyrrole concentration 5 g L^{-1}, ferric chloride/pyrrole molar ratio 2:1, and PTSA/pyrrole molar ratio 2:1. For comparison, pure PPy powder was also prepared following the above procedure but without adding pulp fibers.

Next, the pulp fibers were made into a handsheet with a basis weight of 80 g m^{-2} on a ZCX-200 handsheet former. Finally, the handsheet was dried at 110 °C on a plate dryer for 3 min.

2.3. Measurement of surface resistivity

The resistance (R) of conductive paper was recorded with a YD2511A intelligent low resistance meter. The surface resistivity was calculated as follows,

$$R_s = \frac{R}{2.0 \times 0.8}$$

where R_s is the surface resistivity ($\Omega\,cm^{-2}$) and R is the resistance (Ω). The spacing of the electrodes was 2.0 cm and electrode width was 0.8 cm.

2.4. TGA, XPS, SEM and SEM-EDX analysis

TGA curves were obtained on a Perkin Elmer-Pyris6 thermo gravimetric analyzer under a dry nitrogen atmosphere operating at a heating rate of 15 °C min^{-1}.

XPS spectra were obtained using a Thermo Fisher Scientific's K-Alpha X-ray photoelectron spectrometer (XPS) system. An Al Kα X-ray source was used. The vacuum in the analyzing chamber was 1.0×10^{-8} Pa during analysis. The analyzer was operated at 50 eV pass energy for survey spectra. Elemental atomic concentrations were calculated from the XPS peak areas.

Scanning electron microscopy (SEM) observation was performed using an FEI Quanta-200 environmental scanning electronic microscope. The fiber samples were mounted on specimen stubs with double-sided adhesive tape, and coated with gold prior to SEM observation. SEM-EDX analyses were also carried out with the same instrument, but the paper samples were not coated with gold.

3. Results and discussion

3.1. Conductivity decay of the paper composite

3.1.1. Effect of chemical treatment

In this section, the PPy-coated pulp fibers were treated with NaOH solution, HCl solution, and H_2O_2 solution separately, the treated pulp fibers were then made into handsheets for conductivity decay tests. As shown in Fig. 1, by a treatment of PPy-coated pulp fibers with 3% NaOH solution for 30 min, a significant decrease in conductivity with storage time in air was observed. However, by a treatment of PPy-coated pulp fibers with 3% HCl solution for 30 min, the conductivity almost kept stable with storage time in air. This was because that the PPy on pulp fibers was changed to PPy (A^-) when dipped in an acidic solution and changed to PPy (OH^-) when dipped in an alkaline solution (Ansari, 2006). The surface resistivity slightly increased with storage time in air when the PPy-coated pulp fibers were treated with 3% H_2O_2 solution for 30 min, which is attributed to the oxidation of PPy by this oxidative compound. We also investigated the effect of time of treatment with 3% H_2O_2 solution on the conductivity of cellulose–PPy conductive paper composite. The result showed that the surface resistivity increased with increasing treatment time, but the extent of the increase declined when the treatment time was more than 30 min.

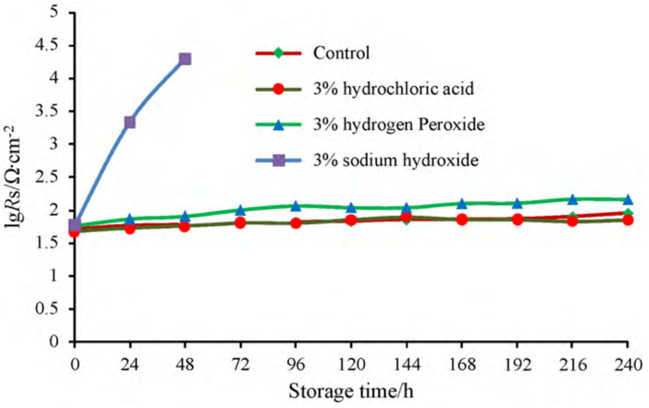

Fig. 1. Effect of chemical treatment on the conductivity decay.

3.1.2. Effect of temperature and atmosphere

As seen in Fig. 2, the paper composite stored in air at ambient temperature (25 °C) was electrically unstable. The conductivity stability decreased with increasing the storage temperature. The surface resistivity of the paper composite stored in air at 100 °C for 1 week increased by around four orders of magnitude. In addition, the conductivity stability of the paper composite stored in nitrogen was better than that stored in air, especially at elevated temperature. The above results showed that the conductivity stability of the paper composite was related to the oxidation of PPy. Temperature played an important role in determining product stability, increasing the temperature accelerated the oxidation of PPy.

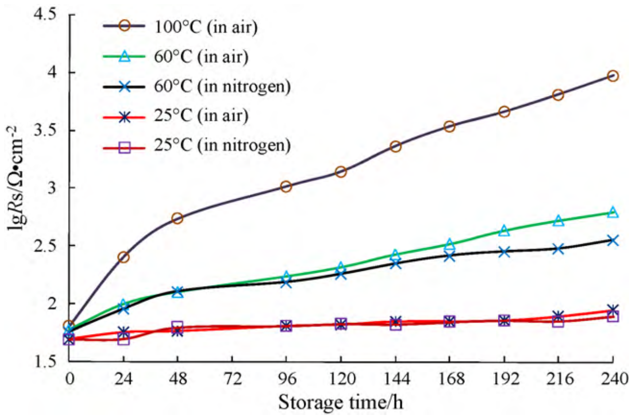

Fig. 2. Effect of temperature and atmosphere on the conductivity decay.

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