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Preparation of conductive wool fabrics and adsorption behaviour of Pd (II) ions on chitosan in the pre-treatment

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ABSTRACT

In this study, an effective deposition of Ni–P alloy on wool fabric is proposed by a chemical plating approach with $PdCl_2$ solution and a carrier agent chitosan (CTS). CTS possesses strong ability to absorb metal ions through several mechanisms, such as electrostatic attraction and chelation, depending on the pH of the solution. The lowest surface resistance of the wool fabric is achieved when Pd (II) ions are absorbed in acid condition (around pH = 2.5). Sorption isotherms are obtained and modeled using Langmuir and Freundlich model and kinetic curves nicely fitted to the pseudo-first-order equation. Also, isotherms have been introduced to obtain the thermodynamic parameters, such as Gibbs free energy, enthalpy and entropy. The resulting positive value of the enthalpy indicates that the adsorption is an endothermic process. Conductive wool fabrics are characterized by scanning electron microscopy (SEM), Fourier transform-infrared (FT-IR) spectroscopy. Evidenced by SEM, CTS–Pd is found on the surface of fabrics and effectively activated the chemical plating. FT-IR shows the adsorption of Pd (II) ions on CTS is mainly controlled by physical adsorption. Mechanical and physical tests were investigated and the encouraging results show no significant modification and open new perspectives for future application of wool fabrics.

1. Introduction

Recently, the emerging fields of interactive textiles and smart fabrics have attracted much attention for application of electrical conductive fibers. These materials exhibit a variety of outstanding properties, from the ability to dissipate static charges, to electric conductivity, shielding of electromagnetic radiations, dissipation of microwave energy, and effective heat generation [1]. The potential applications of conductive fibers span over a wide range of fields, from the traditional clothing sector, including sportswear and work clothing, to home (carpet, upholstery) and industrial textiles (building, automotive, filtration, etc.), as well as highly innovative electronics and biomedical end-uses. Typical examples are the production of conductive nanofibers incorporating nanostructure conducting materials [2], and the use of conducting polymers (polypyrrole (PPy)) supported onto textile surfaces as active interface for tissue engineering, which are able to regulate cell activity through electrical stimulation [3–5].

A great deal of work has been carried out on synthetic fibers, especially polyester [1,3], which takes the leading position in the world fiber market in terms of fiber production and consumption. Comparatively less attention has been paid to natural fibers, such as cotton [6,8], silk [7] and more recently, the in situ oxidative polymerization of pyrrole on wool was reported, aiming to produce electrical conductive textiles for apparel and technical end-uses. The electroless Ni–P plating stands out several benefits like water repellency, conductivity and anti-static. Compared to the surface electrical resistance of PPyr/wool (about 10–100 Ω/sq) [8], our new method described in this paper can significantly reduce the value to 0.5 Ω/sq.

It is well known that conventional fiber is not intrinsically conductive, therefore, chemical plating or electroless plating has to apply to catalytically activate the substrate surface before depositing metals onto them [2,3]. Because plating is initiated upon the catalyzed surface, and the plating reaction is sustained by the catalytic nature of the plated metal surface itself, properties of the plated materials are highly dependent on the pre-treatment method [7]. Further, catalyzation is a determinant step in metallization by the plating process, and this step allows us to establish strong chemical bonds between the substrate and metallic film. To be noted, it is usually carried out in $SnCl_2/PdCl_2$ mixed solutions [8,9]. Generally, adhesion property highly depends on the feature of the sensitized and activated substrate. For fibers in particular,

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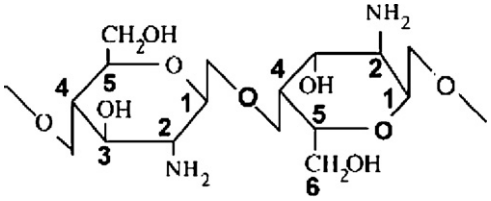

Fig. 1. Chemical structure of chitosan (CTS) [16].

Table 1
Composition and operating conditions plating of chemical Ni–P bath.[a,b]

Reagents	Concentration (g/L)
Nickel sulfate	20-30
Sodium hypophosphite	20-30
Sodium citrate	15-25

[a] Operating parameters: pH = 7.0; temperature = 60 °C; time = 30 min.
[b] The samples were rinsed with distilled water, ethyl alcohol and dried in an oven at 55 °C.

effective surface treatment process is required before Pd (II) ions chemisorption, due to their low surface activity.

In our research, chitosan, a natural available biopolymer with unique properties, such as biodegradability, nontoxicity, cationic nature, and antimicrobial activity [10–15], was utilized as a carrier for metal ions (see Fig. 1). Pd (II) ions are absorbed by the wool in the activation treatment and subsequently, the Ni–P layers are chemical plated on wool substrate. To be mentioned, effective surface treatment of CTS on wool fabric is required before Pd (II) ions adsorption. Conductive wool fabrics are prepared and adequately characterized by morphological, spectroscopic and thermal analyses in view of addressing the application of these novel wool-based conducting textiles.

2. Experimental

2.1. Materials and chemicals

100% wool fabrics (6 cm × 6 cm) obtained from Shanghai Datong Limeite Co., Ltd., are used as the substrate after scoured and crabbed. Chitosan (CTS), with a degree of deacetylation of 95%, is purchased from Dalian Xindie Chitin Co., Ltd. $PdCl_2$ (II) (AR) is obtained from Zhejiang Saintyear Co., Ltd. and $PdCl_2$ (II) is dissolved in 10% (v/w) HCl to prepare a 100 mg/L solution. The other reagents are analytical grade and used as received. All aqueous solutions in this work are prepared with deionized water.

2.2. Preparation of activation layer and chemical plating

The surface resistance Rs is measured by the four-probe method [16]. Rs is the resistance of a square sample. The units of Rs are commonly expressed as ohms-per-square or Ω/sq. The textile surface resistance is measured by square electric resistor (R235 DMR-1C, Nanjing Daming Instrument Company), and the results are averaged from the results of 20 runs.

2.2.1. Pre-treatment of CTS on wool fabric

We studied the effects of parameters in the CTS pretreatment process, such as the concentrations of CTS, citrate acid and sodium hypophosphite. They are measured by the orthogonal experiments under the condition of pretreatment formula shown in Table 2.

The specimens (0.5 g wool substrate) are dipped with the pretreatment solution with liquor ratio 40:1, and padded with the mangle pressure of 3 kg/cm^2. After twice dip-pad process, the solution pick-up reaches 85%, then dried in an oven at 90 °C for 5 min and cured at 145 °C for 30 min. The padding machine (PB01) is manufactured by Rapid Taiwan Company.

2.2.2. Activation process

During the batch experiments, the effects of the initial Pd (II) ions concentration (20, 40, 60, 80 and 120 mg/L), pH value (1, 2, 3, 4, 5, 6 and 7), reaction temperatures (20, 40, 60 and 80 °C) and reaction time (30, 50, 70 and 90 min) of the Pd (II) ions adsorption are also investigated. The Pd (II) ions concentrations are measured by a UV–vis spectrophotometer (Hitachi Model U-3310) at a wavelength corresponding to the maximum absorbance: 285 nm. Physical and electrical properties were determined in a conditioned laboratory (20 °C, 65% RH). Tensile properties were measured by a Materials testing machine from UK Hounsfield Company (H5KS), Abrasion tests were performed by an Atlas textile testing products (CROCKMETER CM-5) according to AATCC 116-2001.

2.2.3. Chemical plating

Chemical plating is carried out after activation, and then following rinsing and drying. The composition and operating condition of plating Ni–P deposition solution are listed in Table 1.

2.3. Adsorption isotherms

The experimental adsorption data was compared with Freundlich and Langmuir isotherm models. The Langmuir isotherm is based on the monolayer adsorption on the active sites of the absorbent. On the other hand, the Freundlich isotherm explains the adsorption on a heterogeneous (multiple layer) surface with uniform energy.

The amounts of Pd (II) ions on wool fabric are expressed as mg of Pd per g wool substrate shown as follows:

$$Q = V\frac{(C_o - C)}{m} \quad (1)$$

where C_o (mg/L) and C (mg/L) are the concentration of Pd (II) ion at the initial and reach the equilibrium stage; V (L) is the volume of solution (liquor ratio is 40:1); m (g) is the quantity of wool substrate.

The liner form of the Langmuir equation is given by:

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{q_0 b} \quad (2)$$

where q_e and q_0 are the amount of Pd (II) adsorbed per unit weight of the chitosan at equilibrium and the initial stage (mg/g); C_e is the equilibrium concentration in the solution (mg/L); q_m is the maximum adsorption at monolayer coverage (mg/g), and b (mL/mg) is the Langmuir adsorption equilibrium constant.

The experimental isotherm data were also plotted using the log-linearized form of the Freundlich equation (3):

$$\log q_e = \log k + \frac{1}{n}\log C_e \quad (3)$$

where q_e and C_e have the same definitions in Eq. (2); k is a Freundlich constant representing the adsorption capacity and n is a dimensionless constant.

2.4. Kinetics of adsorption

In order to investigate the controlling mechanisms of adsorption processes, such as mass transfer and chemical reaction, the pseudo-first-order, second-order and intraparticle diffusion equations were used to test the experimental data [16–19]. The pseudo-first-order kinetic model is given as follows:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \quad (4)$$