Surface & Coatings Technology 302 (2016) 185–194

Contents lists available at ScienceDirect

Surface & Coatings Technology

journal homepage: www.elsevier.com/locate/surfcoat

Durable electroless Ni and Ni-P-B plating on aromatic polysulfonamide (PSA) fibers with different performances via chlorine-aided silver activation strategy

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ARTICLE INFO

Article history:
Received 31 March 2016
Revised 27 May 2016
Accepted in revised form 31 May 2016
Available online 01 June 2016

Keywords:
Aromatic polysulfonamide fiber
Chlorine
Silver activation
Electroless plating
Ni
Ni-P-B

ABSTRACT

Electroless Ni and Ni-P-B plating were conducted respectively on aromatic polysulfonamide (PSA) fibers following a new chlorine-aided silver activation system in the present work. Firstly, PSA fibers were treated in NaClO-HCl solution to impart chlorine to the surface area followed by immersion in $AgNO_3$ solution to convert the chlorine to AgCl particles. After subsequent reduction of AgCl to metallic Ag seeds in $NaBH_4$ solution, electroless Ni and Ni-P-B plating were performed respectively. These two kinds of adherent and continuous coatings activated and anchored by the silver seeds, which were both resistant against sonication, were deposited onto PSA fibers with different electrical, magnetic, electromagnetic shielding, and corrosion resistance properties. Both plated PSA fibers can act directly as electromagnetic interference shielding and static charge dissipation materials, or act as excellent base layers for other subsequent metallic coatings according to different requirements, and then show great potential applications in coaxial cables and wear protection for aerospace, aviation, microelectronics, military industry and telecommunications.

1. Introduction

Aramid fibers, usually known as Kevlar and Nomex, are recognized as important high-performance fibers and have attracted considerable commercial and academic interest for decades [1–7]. Aromatic polysulfonamide (PSA) fiber known as Tanlon is the first originally developed aramid fiber with sole intellectual property in China [8,9]. Its high modulus, lightweight, thermostability, and corrosion resistance have already made it an ideal material as a protective clothing, flue gas filter, insulation material, and reinforcement material in many industries. [10] Functional metal coatings on PSA fiber are of great importance considering the combined properties of the engineering fiber and the metal, thus further enhance the applicability of the fiber as a microwave absorption and reflection, electromagnetic interference shielding, and static charge dissipation material in aerospace, aviation, microelectronics, military industry and telecommunications.

Up to now, varieties of surface coating methods have been developed for polymeric and non-polymeric substrates and are still under progressing [11–26]. Notable examples of such methods include vapor deposition [11–13], electroless plating [14–24] and electroplating [26], among which electroless plating is the optimum selection for depositing metal on polymers regarding its simple equipment, easy operation, and high efficiency to create homogenous coatings over nonconductive substrates with complex shapes. Electroless nickel (Ni) and nickel alloy (Ni-P, Ni-B, Ni-Fe, and etc.) plating account for a large proportion of the electroless plating area with regard to their low costs, stable plating solutions, excellent adhesion to the substrates, and the obtained different yet competent coatings [27–33].

Conventional electroless plating employed requires coarsening/etching of smooth surfaces via chemical [34] or physical [35] means, followed by catalyzation process including sensitization and activation steps [17] before the plating procedure. However, coarsening process [36] mainly leads to a drastic loss of the mechanical properties of the substrate, while palladium (Pd) [15,25,37], as the most utilized catalyst to trigger the subsequent plating process, has a high price and undoubtedly has caused the increase of the cost of electroless plating. Nowadays tremendous research attention has been concentrated on modification of polymer surfaces via coating an adhesive polymer layer [38,39] or grafting functional molecule chain segments [14,40] as well as development of cheaper Pd-free catalyzers [41–43].

Aramid fibers, including PSA fibers, are difficult to coat and own inherently poor adhesion strength with the coated metal layer due to their dense, inert, and smooth surfaces. There are still research reports of traditional electroless plating on aramid fibers through etching treatment and expensive Pd catalyzation [44,45]. Recently, much effort has been expended to polymerize a binding layer such as polydopamine [46], polypyrrole [47,48], or chitosan derivative [49], which owns plenty

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http://dx.doi.org/10.1016/j.surfcoat.2016.05.087
0257-8972/

of reactive groups to chelate with the subsequent metal ions and improves the surface functionality and wettability without serious damage to the original mechanical performance of the aramid fiber. Nevertheless, the involved polymerization process is somehow very complicated and is not suitable for the actual industrial production. Several attempts [50] have also been made to catalyze the aramid surface via silver initiation instead of Pd. To the best of our knowledge, researches on electroless plating of aramid fibers still remain insufficient.

We have previously reported our investigations of electroless plating on Kevlar via different pretreatment methods, such as the traditional etching and $SnCl_2$–$PdCl_2$ catalyzation method [44,45] and then the swelling treatment and silver catalyzation method [51], neither of which is very suitable to pretreat aromatic PSA fibers owing to the significant strength loss after those treatments. Continuing our previous study of new catalyzation method and silverization of aromatic PSA fibers [52], the present study utilized a novel etchant-free, tin-free and Pd-free activation strategy for PSA fibers and then coated them via electroless Ni and Ni-P-B alloy plating, respectively. No complicated or expensive procedures were involved here. The exploitation of chlorine treatment and silver activation here was very simple and efficient to fix massive silver seeds into the fiber matrix and facilitate the ensuing electroless plating process with maintenance of the remarkable mechanical properties of the PSA fiber. Detailed effects of the chlorine-aided silver activation system on the fiber were studied via SEM and TEM observation in the following article. Morphologies, compositions and structures of both coatings were comprehensively investigated by SEM, XPS, XRD, and TEM measurements. Attention was finally refocused on the performances of both metallized fibers. All these results are thoroughly displayed and discussed in the article.

2. Experimental

2.1. Chemicals and materials

PSA multifilament strand (Tanlon® with structure formula listed in Fig. 1) was obtained from Shanghai Tanlon Fiber Co., Ltd., China. Each strand has 3000 monofilaments with an average diameter of 15 μm. The PSA fibers were cleaned ultrasonically in acetone and then in deionized water for 30 min, respectively, and dried in a dry oven at 100 °C for an hour before use.

Chemicals of analytical grade, including acetone (CH_3COCH_3), sodium hypochlorite aqueous solution (NaClO, Antiformin), hydrochloric acid (HCl), silver nitrate ($AgNO_3$), sodium borohydride ($NaBH_4$), nickel acetate ($Ni(CH_3COO)_2 \cdot 4H_2O$), sodium citrate ($Na_3C_6H_5O_7 \cdot 2H_2O$), sodium hypophosphite ($NaH_2PO_2 \cdot H_2O$), dimethylamine borane ($C_2H_{10}BN$, DMAB), ammonia ($NH_3 \cdot H_2O$), and sodium dodecyl sulfate ($C_{12}H_{25}SO_4Na$, SDS) were purchased and used as received from Sinopharm Chemical Reagent Co., Ltd., Shanghai. Deionized water was used to prepare all solutions.

2.2. Preparation of activated PSA

The schematic illustration of the chlorine-aided palladium-free activation system for electroless plating is demonstrated in Fig. 2. The system involved two parts: the chlorine treatment and the silver activation itself.

Chlorine treatment of cleaned PSA fibers was conducted via immersion in a NaClO-HCl solution (pH = 3.00) for 15 min at room temperature. A small quantity of chlorine, having a close affinity with PSA fibers and slightly soluble in water and then not washing away easily, was generated and imparted to the near fiber surface by adsorption. Fibers were then washed in deionized water until pH of the rinse water was near 6.50 (pH value of the clean deionized water used).

Silver activation process included the introduction of AgCl particles on the fiber surface area and the reduction to metallic Ag seeds. The undried chlorinated PSA (Cl-PSA) fibers were immersed in a 0.1 mol/L $AgNO_3$ aqueous solution for 15 min at 75 °C, and then were washed by deionized water until pH of the rinse water was near 6.50. The resulting fiber was denoted as AgCl-PSA fiber. AgCl was subsequently reduced to metallic Ag by dipping the AgCl-PSA fiber in a 0.25 wt% $NaBH_4$ aqueous solution for 15 min at room temperature. The fibers were then vigorously washed by deionized water until pH of the rinse water was near 6.50. The activated fiber is denoted as Ag-PSA fiber in the rest of the manuscript.

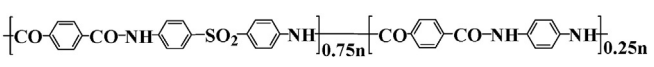

Fig. 1. Structural formula of aromatic PSA fiber (Tanlon®).

2.3. Electroless plating reaction

The bath compositions of both Ni plating and Ni-P-B plating after optimization are given in Table 1, containing nickel acetate as nickel salt, sodium citrate as complexing agent, sodium hypophosphite and DMAB as reducers, and SDS as wetter. The pH of the plating solution was adjusted by the addition of ammonia. Plating reaction was maintained at 60 °C for 30 min, and then the obtained metallized fibers were softly washed in deionized water and dried in dry oven at 80 °C for an hour.

2.4. Measurements

The fiber surface morphology was characterized by scanning electronic microscopy (SEM, JEOL JSM-7500F) equipped with Energy dispersive spectroscopy (EDS, X-act, Oxford). Samples were loosely mounted on Al sheets by means of double-sided conductive adhesive tapes, and a thin layer of platinum was sputtered before observation. Transmission electronic microscopy (TEM) was performed to investigate the fiber cross section at an accelerating voltage of 200 kV using a JEM-2010F high-resolution TEM (JEOL) equipped with EDS (INCA, Oxford). Selected area electron diffraction (SAED) and high angle annular dark field scanning TEM (HAADF-STEM) were also applied to go further in the study. The fiber was pre-embedded in epoxy resin and was cut into thin slices of approximately 70 nm thick by an ultramicrotome (EM UC7, Leica) with a diamond knife (DiATOME). Slices were collected on a copper grid and fixed on a double-tilting beryllium specimen holder for TEM observation.

X-ray photoelectron spectroscopy (XPS) measurements were carried out on a Thermo Scientific ESCALAB 250Xi XPS Microprobe (Thermo Fisher Scientific) with a monochromatic Al-Kα X-ray source (1486.7 eV). The sample fibers were compactly attached on Al sheets via double-sided conductive adhesive tapes. Survey spectra were recorded over the range of 0–1400 at 1 eV resolution, while high resolution scans had the resolution of 0.1 eV. Calibration for the binding energy was done based on the reference to C1s hydrocarbon peak at 284.6 eV to compensate for surface charging effects.

The crystal structure was examined by wide-angle X-ray diffraction (WXRD, D/Max 2200V/PC, Rigaku), which used Ni-filtered Cu-Kα radiation ($\lambda = 0.15406$ nm) generated at 40 kV and 40 mA. Diffraction patterns were recorded in reflection mode with the 2θ range of 3–90° and the scanning speed of 4°/min.

The fiber tensile test was performed using a XQ-1C tensile tester (Shanghai New Fiber Instrument Co., Ltd.) at room temperature on the basis of Chinese standard GB/T14344 (similar to ISO 5079). For each sample, 50 specimens were tested and the results were averaged.

The electrical resistance of the metallized PSA fiber was measured by a digital multimeter with Kelvin small resistance measurement at room temperature. The measurement was performed 30 times and the results were averaged for each sample. A physical property measurement system (PPMS) from Quantum Design (PPMS EverCool-II) was used to test the M–H curve of the metallized fiber with applied magnetic field