Electroless Nickel Deposition of a Palladium-Activated Self-Assembled Monolayer on Polyester Fabric

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ABSTRACT: In this study, an alternative Pd activation process was developed for electroless Ni plating on polyester fabric modified with a self-assembled monolayer (SAM) of 3-aminopropyltrimethoxysilane (APTMS). The presence of a highly oriented amino-terminated SAM and the formation of Pd-activated APTMS were demonstrated by X-ray photoelectron spectroscopy analysis. After activation, electroless Ni plating was successfully initiated, and the Ni coating was deposited onto the surface of the polyester fibers. The resulting Ni coating was examined by scanning electron microscopy, energy-dispersive X-ray spectroscopy, and X-ray diffraction. The electromagnetic interference (EMI) shielding effectiveness (SE) and adhesive strength of the Ni-plated polyester fabric were evaluated. On the basis of the experimental results, the Ni coating produced with a Pd-activated SAM was uniform and dense. As the Ni weight on the treated fabric was 32 g/m^2, the EMI SE of the Ni-plated polyester fabric modified with APTMS obtained was more than 30 dB at frequencies that ranged from 2 to 18 GHz. Compared with the conventional two-step activation method, Ni coating on the Pd-activated polyester fabric modified with APTMS improved the coating adherence stability. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

INTRODUCTION

Electrically conductive textiles have attracted considerable attention because of their desirable properties, including electrical conductivity, flexibility, electrostatic discharge, electromagnetic interference (EMI) protection, and radio-frequency interference protection.[1,2] In general, textiles that are coated with metals, such as aluminum, copper, silver, and nickel, are important conductive materials. Currently, developed metal-coating techniques include sputtering, vacuum deposition, electroplating, and electroless plating.[3–5] Among them, electroless Ni plating has been used in many applications because of its deposit properties, including good electrical and magnetic properties, excellent corrosion and wear resistance, and deposit uniformity.[6]

The deposition of metallic layers onto polymer substrates, such as textile and plastics, by the electroless process requires the previous creation of catalytic sites on the polymer surface. For many years, palladium colloids have been used as effective catalyzers. Pd chemisorption can be carried out by two different procedures. In a two-step method, the substrate to be coated is immersed into tin(II) chloride first and then palladium(II) chloride solutions.[7] The one-step process uses a $PdCl_2$–$SnCl_2$ colloidal solution.[8,9] Then, it is necessary to remove the tin layer to make the Pd catalyst active for further metal deposition. From economic and environmental points of view and for simplicity in process operations and the fact that $SnCl_2$ is not an active catalyst for the electroless plating process,[10] it would be desirable to have an Sn-free, one-step activation process for electroless plating. However, it is difficult to directly chemisorb Pd effectively onto textile surfaces. In addition, the quality of the electroless coating of nonmetallic materials largely depends on the adhesion between the catalyst and the substrate. Thus, electroless deposition requires sufficient surface pretreatment to increase the adhesion of Pd^{2+} to the substrate surface. Previously, surfaces had to be chemically and physically roughened to enhance mechanical cohesion between the deposited metal and the substrate.[11,12] However, this type of pretreatment can change the surface state of the very sensitive selective layer. Also, the Pd nuclei formed in this way has poor adhesion to the substrate because of the absence of a chemical conjunction

between the Pd catalyst and the substrate. Desorption of the catalyst from the substrate may cause failure in the initiation of uniform metal deposition or may result in decomposition of the electroless plating solution.

Therefore, it is necessary to explore proper surface modification techniques for textiles for use before the electroless metallization process. An Sn-free pretreatment of the electroless coating of nonmetallic materials with surface hydroxyl groups has been developed[13,14] and has been given wide attention because of the chemical adhesion between the activator and the substrate. In this method, the substrate to be coated is first treated with an organic solution that contains a silane coupling agent with —NH$_2$ or —SH groups; a self-assembled monolayer (SAM) is formed on the surface of the substrate with —OH groups through covalent bonding and is then activated with an activation solution that contains Sn-free Pd(II) ions, which coordinately binds to the activated ions.[15] Recently, there has been growing use of 3-aminopropyltrimethoxysilane (APTMS) molecules to improve the absorption of metallic nanoparticles/ colloids to surfaces.[16,17] However, there have been few reports on the use of APTMS as an adhesion promoter on textiles to improve catalyst adsorption for electroless plating and the adhesion of electrolessly deposited metals.

In this study, an alternative activation method with an amine-terminated molecule of APTMS as the Pd(II)-based catalyst ligand in the initiation of electroless Ni plating on polyester fabric was developed. The APTMS was pretreated on polyester fabric, and the modified polyester surface was directly activated in a PdCl$_2$ solution for the subsequent electroless deposition of Ni. The composition and chemical structure of the Ni-plated polyester fabric modified with APTMS were investigated by X-ray photoelectron spectroscopy (XPS). The surface morphology, chemical composition, and crystal structure of the Ni-plated polyester fabrics were characterized by scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDX), and X-ray diffraction (XRD). The EMI shielding effectiveness (SE) and adhesive strength of the Ni coating were also evaluated.

EXPERIMENTAL

White, plain-weave, 100% polyester fabric (47 × 40 counts/cm^2, 84 g/m^2) was used as the substrate. All of the chemicals used were analytical grade.

The schematics of the electroless Ni-plating process on the APTMS-modified polyester fabric are shown in Figure 1. Before electroless deposition, the polyester samples were cleaned in 5% nonionic detergent at pH 7 and in deionized water. The samples were then immersed into a 1% APTMS–ethanol solution at room temperature for 24 h to form an SAM of APTMS on the surface of the fabric. After silanization, the samples were baked in an air oven at 70°C for 30 min to form an organosilane SAM. Subsequently, the substrate was cleaned in deionized water to remove excess silane molecules. The activation of the substrate covered with APTMS was performed by immersion into an aqueous PdCl$_2$ solution that contained 0.5 g/L of PdCl$_2$ and 20 mL of 37% HCl at room temperature for 10 min; the
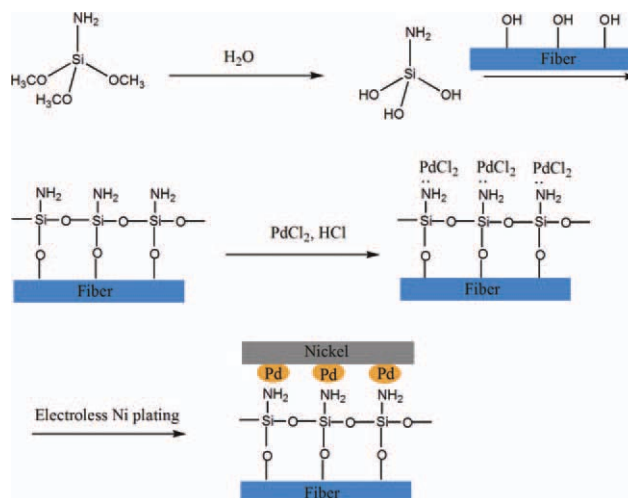

Figure 1. Schematic representation of electroless Ni plating with the Pd-activated APTMS-modified polyester fiber. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

substrate was then washed with deionized water to remove free Pd(II) ions. After that, the activated samples were coated via an autocatalytic reaction in an Ni-plating solution at 60°C for 5, 10, and 20 min, respectively. The composition of the plating bath was as follows: 15 g/L NiSO$_4$·6H$_2$O, 20 g/L C$_6$H$_5$Na$_3$O$_7$·2H$_2$O, 20 g/L H$_3$BO$_3$, and 20 g/L Na$_2$H$_2$PO$_2$·2H$_2$O. The pH value was adjusted with NaOH. Finally, the Ni-plated polyester fabric samples were immediately rinsed with deionized water after the metallizing reaction and then dried in an oven at 60°C.

For comparison, the electroless plating of Ni was also carried out on the polyester fabric via a conventional two-step Pd chemisorption process described in our previous work.[18] In this method, the polyester fabric was first sensitized by immersion in an aqueous solution that contained 10 g/L SnCl$_2$ and 40 mL/ L HCl for 10 min; this was followed by rinsing with doubly deionized water. The subsequent processes of activation in the PdCl$_2$ solution, electroless Ni plating, and posttreatment were similar to those described previously for the Sn-free process.

XPS was used for the surface analysis of the APTMS-modified polyester fabric before and after the activation process. XPS (PHI 5600, Physical Electronics) was performed with an Al Kα source (14 kV and 350 W). The binding energy scale was calibrated to 285.0 eV for the main C1s peak. The surface morphology of the coatings was determined by SEM (JSM-6335F). The elemental compositions of the Ni deposits were determined with an EDX analyzer that was attached to the SEM. The crystal structure of the Ni-plated fabrics was investigated with XRD (Bruker D8 Discover, Cu Kα radiation and graphite filter at 40 kV and 40 mA). The EMI SE of the Ni-plated polyester fabrics was measured with an Agilent-E8363A vector network analyzer. The frequency scanned was from 2 to 18 GHz. The attenuations under transmission and under reflection were measured. The former was equivalent to the SE. A crocking tester machine (Shimadzu AG-10TA) was used to measure the adhesion between the coating and the fabric substrate. After 10 complete
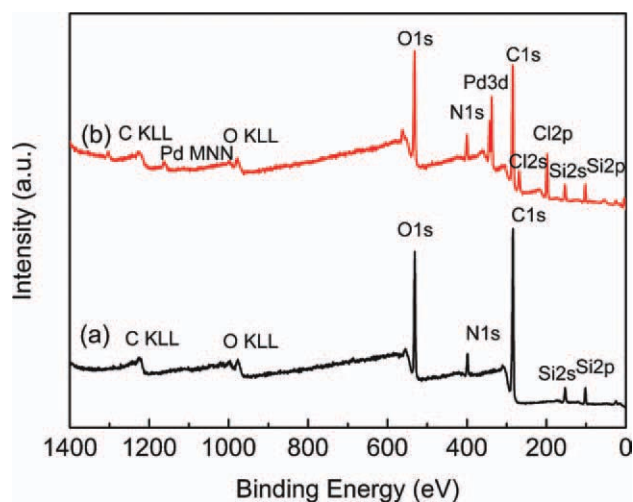
Figure 2. XPS wide spectra of the APTMS-treated polyester fabrics (a) before and (b) after Pd activation treatment. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

turns of crocking at a rate of one turn per second, images of the surface morphology and photos were taken by SEM and a digital camera. Colorfastness to crocking under dry conditions was also assessed in accordance with standard method AATCC 8-2004 (colorfastness to crocking). A white test cloth square was mounted on the crockmeter for comparison. The amount of color transferred from the specimen to the white test square was rated under examination by means of the Chromatic Transference Scale or the Gray Scale for Staining.

RESULTS AND DISCUSSION

XPS Analysis of the Activation Process

Pd activation is the key to the electroless Ni-plating process. An XPS analysis of the APTMS-modified polyester surface was carried out to quantify the orientation distribution of the $-NH_2$ groups on the polyester fiber. The binding mechanism of Pd ions with APTMS was also studied by XPS. The wide-scan XPS spectra of the polyester fabric before APTMS treatment and after APTMS activation are shown in Figure 2. The elements C, O, N, and Si were detected from the APTMS-modified polyester fabric before the activation process [Figure 2(a)]. N and Si were attributed to APTMS, whereas C and O were both from the APTMS and the polyester fabric. The APTMS easily reacted with the hydroxyl groups on the polyester fabric to form an SAM. It was confirmed that the APTMS was formed on the polyester substrate. After activation, Pd and Cl were observed on the APTMS-modified polyester fabric [Figure 2(b)]. The presence of Pd indicated that Pd activation was successful. A small amount of the element Cl was also found; this indicated that there was very little Cl inclusion in the coating.

The binding mechanism of Pd(II) to the amine-terminated SAM was further studied by XPS. Figure 3 shows the N1s XPS narrow spectra before and after the APTMS-modified polyester was dipped into the Pd(II) solution. The curve shape in Figure 3(a) indicates a peak of 398.1 eV for the N1s binding energy of $-NH_2$. This peak was assigned to free, outward-oriented amino

groups of APTMS.[19] The findings indicate the formation of an SAM on the polyester surface. As shown in Figure 3(b), an increase in the binding energy that represents N was observed; this resulted from the bonding of $-NH_2$ with Pd^{2+}.[20] After Pd adsorption, the N1s peak shifted from 398.1 eV [Figure 3(a)] to 399.1 eV [Figure 3(b)]. It was obvious that the N1s peak shifted to a higher binding energy position after the Pd treatment. The positive shift indicated the decrease in the electron cloud density around the N atoms; this suggested the formation of chemical bonds between the Pd ions and N atoms of APTMS. As is well known, the $-NH_2$ group is a strong electron donor and possesses a great ligand capability for transition-metal ions because of the lone pair of electrons of the nitrogen atom. On the other hand, Pd(II), as a soft metal ion whose outermost electron is configured as $4d^8 5s^0 5p^0$, has an empty lower energy orbital that can accept electrons.[21] Its coordination chemistry is satisfactory for the formation of stronger bonds with N than those with O and Cl. Relative theoretical considerations and XPS results strongly suggested that the formation of Pd—N coordination bonds was involved.

The Pd three-dimensional narrow XPS spectrum after activation is shown in Figure 4. Peaks at 337.0 eV for the 3d5/2 and 342.3 eV for the 3d3/2 binding energy of Pd, which indicated that the valence state of Pd was ionic according to the binding energy of Pd^0 at 335.1 eV,[22] were observed. The results reveal the presence of Pd^{2+} on the polyester surface, which originated from the bonding of $-NH_2$ of APTMS with Pd^{2+}. The presence of Pd^{2+} was in accordance with the binding energy shift of N1s, shown in Figure 3.

The mechanism of Ni plating on the APTMS-modified polyester fabric can be described as follows. The APTMS molecule had an amino group and an ethoxy group at each end. The ethoxy group formed a silanol group by hydrolysis reaction with a water molecule. Then, the silanol group of the APTMS formed an Si—O—Si bond with an —OH group on the polyester fiber surface by dehydration condensation. After all of the —OH
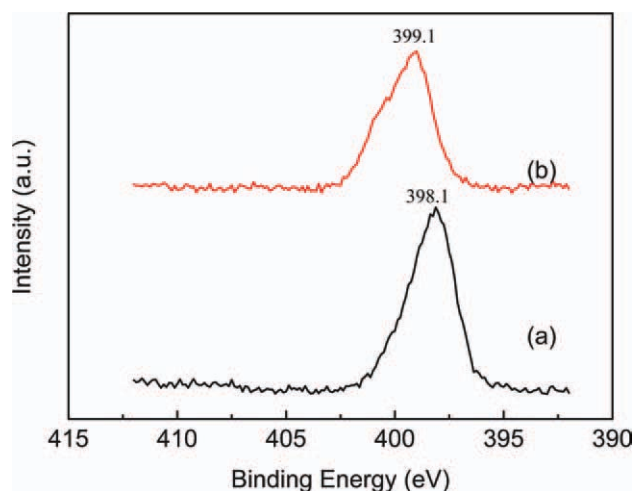

Figure 3. XPS N_{1s} spectra of the APTMS-modified polyester fabric (a) before and (b) after Pd activation. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
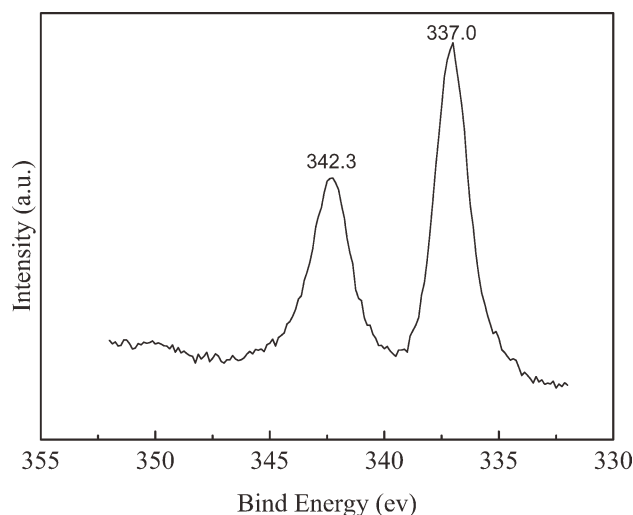
Figure 4. XPS Pd three-dimensional spectra of the APTMS-modified polyester fabric after Pd activation.

groups on the polyester fiber surface were bonded with the silanol groups of the APTMS, no further APTMS molecules were deposited, and the polyester fiber surface was covered by the APTMS monolayer. The amino groups at the ends of the APTMS molecules trapped Pd ions when they were dipped into a solution that contained Pd. The trapped Pd ions were reduced by a reducing agent in an Ni-plating solution and acted as a catalyst for electroless Ni plating.

SEM Analysis

SEM micrographs of the original, APTMS-treated, Pd activated fibers are presented in Figure 5. In comparison with the original polyester fiber shown in Figure 5(a), the surface of the polyester fiber was uniformly modified after APTMS treatment, as shown in Figure 5(b). However, the surface of the polyester fiber after Pd activation looked similar to the APTMS-modified fiber because the valence state of Pd was ionic on the fiber surface, as confirmed by XPS analysis [Figure 5(c)]. Figure 6(a–c) shows the SEM images of the Ni-plated polyester fibers for different deposition times. The microstructures showed that the polyester fibers were apparently completely covered with an Ni coating. It was also found that the Ni deposits were uniformly distributed and dense on the surface of the polyester fibers. The images also indicate that the Ni-plating layer had a nodular structure and that the particle size increased with increasing deposition time.

Deposit Composition, Weight, and Crystal Structure

Figure 7 shows the EDX spectra of the Ni-plated polyester fabric modified with APTMS. The elements Ni, P, C, and O were observed. The Ni and P peaks were attributed to the coating. It should be noted that APTMS was not detected after the electroless Ni plating; this indicated that the Ni coating was thick and dense. A small amount of C and O came from air. At the beginning of the Pd-catalyzed electroless plating process, Ni(II) was reduced rapidly to Ni(0), which in turn, catalyzed subsequent Ni–P codeposition. The process could be represented as

$$Ni^{2+} + 5H_2PO_2^- + 3OH^- \longleftarrow 3HPO_3^{2-}$$
$$+ 4H_2O + Ni + 2P + H_2 \quad (1)$$
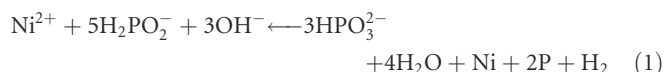
The P contents of the Ni deposits for different deposition times are illustrated in Figure 8. The results show that there was a moderate decrease in P content as the coating times were increased from 5 to 20 min; this might have been due to the smaller amounts of H^+ ions in the solution. See eq. (2):
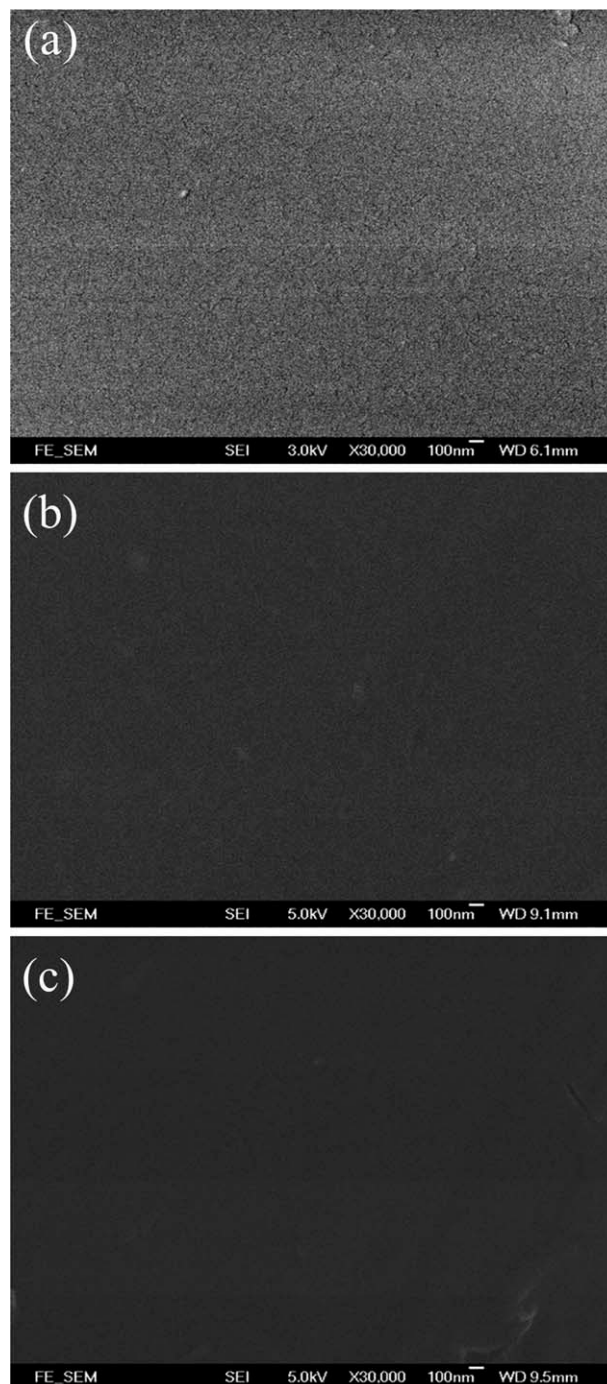

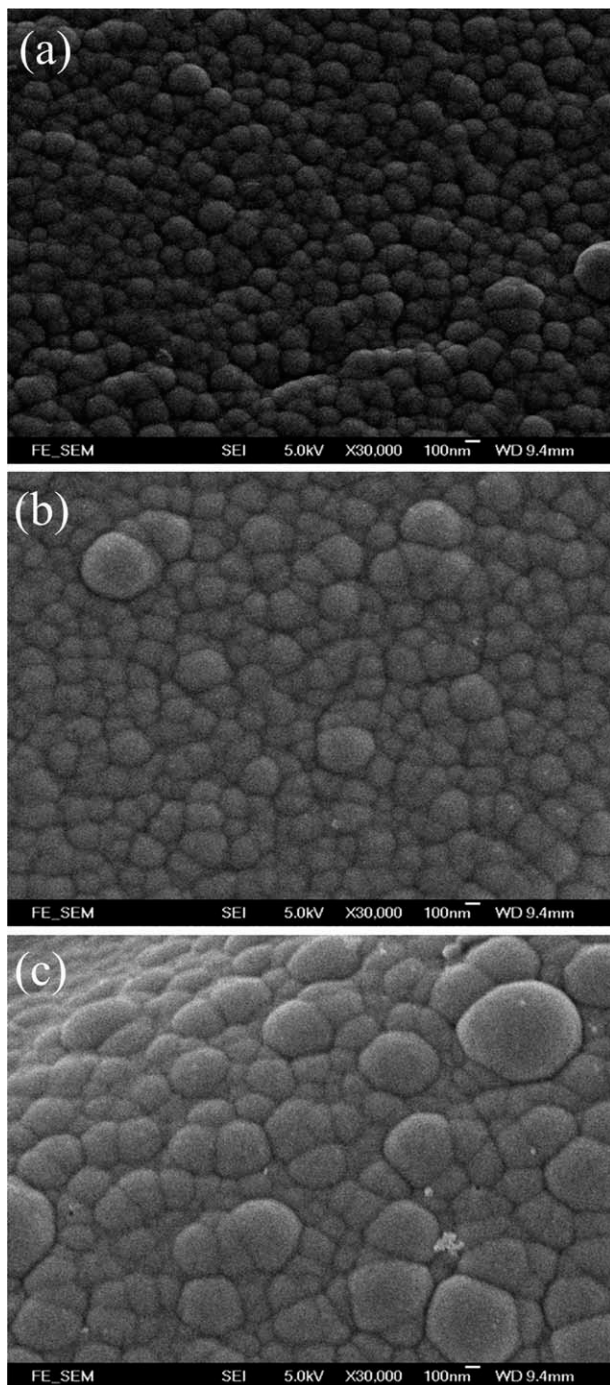**Figure 5.** SEM micrographs of the (a) original, (b) APTMS-treated, and (c) Pd-activated polyester fibers.

Figure 6. SEM micrographs of Ni plated polyester fibers for different deposition times (a) 5 min, (b) 10 min and (c) 20 min.

$$2H_{ad} \leftrightarrow H_2 \tag{2}$$

The thickness of the Ni coating on the polyester fabric could be expressed by deposit weight. The weight of the Ni deposits for different deposition times are shown in Figure 8. It is revealed that the coating thickness increased with increasing deposition time; this could be ascribed to the autocatalytic nature of the electroless plating. The deposition was initiated from the part of
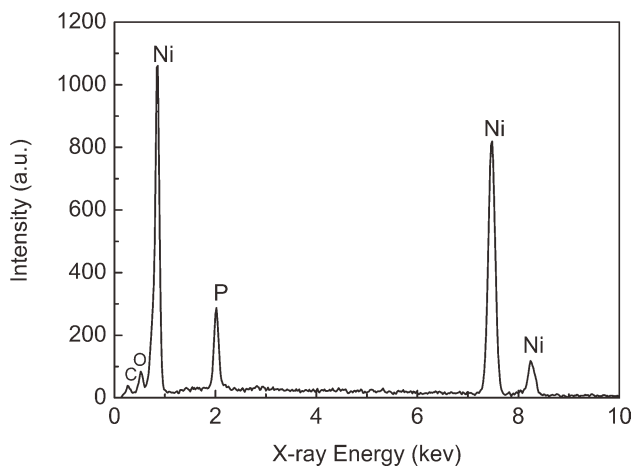

Figure 7. EDX analysis of the Ni-plated polyester fabric modified with APTMS.

the catalyst particles. Ni was deposited first on the composite at energetically favored and predeposited sites.[23] As the deposition proceeded, nucleation still occurred until deposit growth reached a transition thickness; this meant that the repetition of the catalysis process produced catalytic nuclei of different induction periods. The coatings were partial at lower thicknesses, and then, growth of the grains occurred, and some already merged with others at the transition thickness. The deposits covered the entire surface of the polyester fabric, and the coatings significantly increased their weight. The thickness of the deposits and the size of the Ni particles progressively increased; this led to a glossy and higher density coating, just as the SEM micrographs revealed [Figure 6(a–c)].

Figure 9 shows the XRD patterns of the Ni deposits for different deposition times. The XRD patterns exhibited only a single broad peak around a 2θ of 45°, which corresponded to an amorphous structure. This was in accordance with other research results in which electroless Ni deposits became amorphous when the P content was above 7 wt %.[24]

EMI SE

The EMI SE results of the Ni-plated APTMS-modified fabrics for different deposition times are shown in Figure 10. The EMI SE of
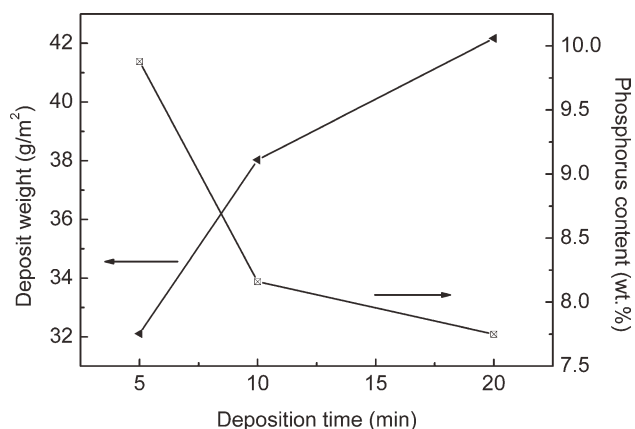

Figure 8. P content and weight of Ni deposits on the APTMS-modified polyester fabrics.
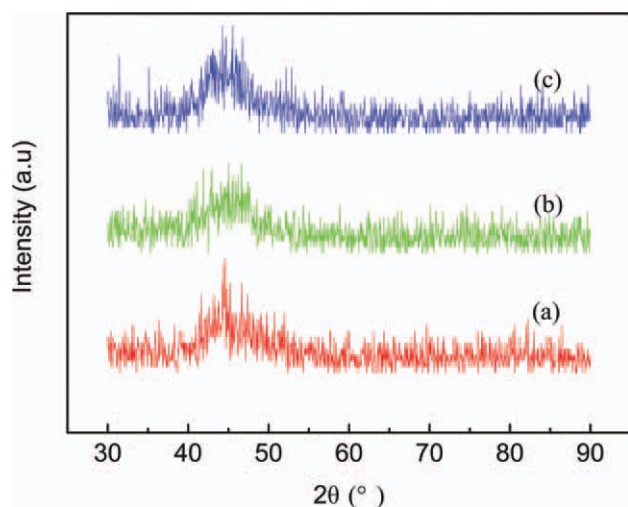
Figure 9. XRD pattern of the Ni-plated polyester fabrics at different deposition times of Ni: (a) 5, (b) 10, and (c) 20 min. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

all of the Ni-plated polyester fabrics was more than 30 dB at frequencies from 2 to 18 GHz. It was observed that the EMI SE of the Ni deposition was enhanced with increasing deposition time for electroless Ni plating. The increased EMI SE was attributed to the increased quantity of Ni deposits, lower P content, and larger grain size in the deposits because the contribution of electron scattering at the grain boundaries diminished. Compared with the Ni-plated polyester fabric without APTMS treatment reported in the previous study,[18] the EMI SE of Ni-plated polyester fabric modified with APTMS was improved because of the acceleration of Ni deposition, which resulted from the enhancement of catalyst adsorption in the electroless plating after APTMS treatment. The results reveal that the Ni-plated polyester fabrics with APTMS modification effectively met general EMI shielding requirements.
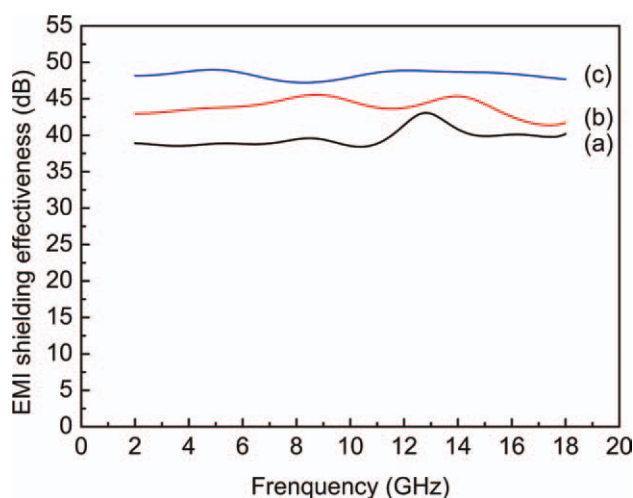

Figure 10. EMI SE of the Ni-plated APTMS-modified polyester fabrics at different deposition times: (a) 5, (b) 10, and (c) 20 min. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
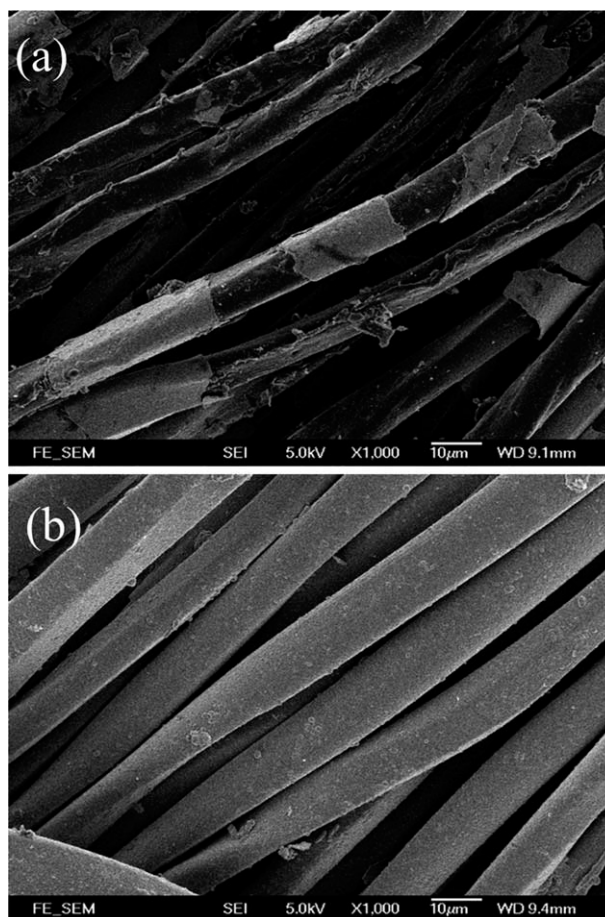

Figure 11. SEM micrographs of the Ni-plated polyester fibers after the crocking test (a) without and (b) with APTMS treatment.

Adhesive Strength

The adhesion of Ni to polyester fabric is one of the most important concerns in electroless Ni plating on polyester fabric. A crocking test was used to evaluate the adhesion of the films on the substrates, and it was repeated three times on each specimen. For comparison, Ni plating on polyester fabric with a conventional two-step activation process and without APTMS modification was also carried out. The morphologies of the Ni-plated polyester fabrics with and without APTMS modification after crocking are shown in Figure 11. A significant difference in the adhesive strength of the coatings was detected in the crocking measurement. Without APTMS treatment, the adhesion of the Ni coating to the substrate was comparatively poor. For samples without APTMS modification, the slack Ni coating was completely stripped off from the polyester surface during 10 turns of crocking [Figure 11(a)]. This was because there was only a weak van der Waals force, which interacted between the Ni layer and the polyester fabric and was not sufficient to provide an adequate adhesive interface. In contrast, as shown in Figure 11(b), no significant loss of the coating was observed in the Ni-plated fabric modified with APTMS. The adhesive strength of the Ni deposits on the APTMS-modified polyester surface improved remarkably because of the formation of
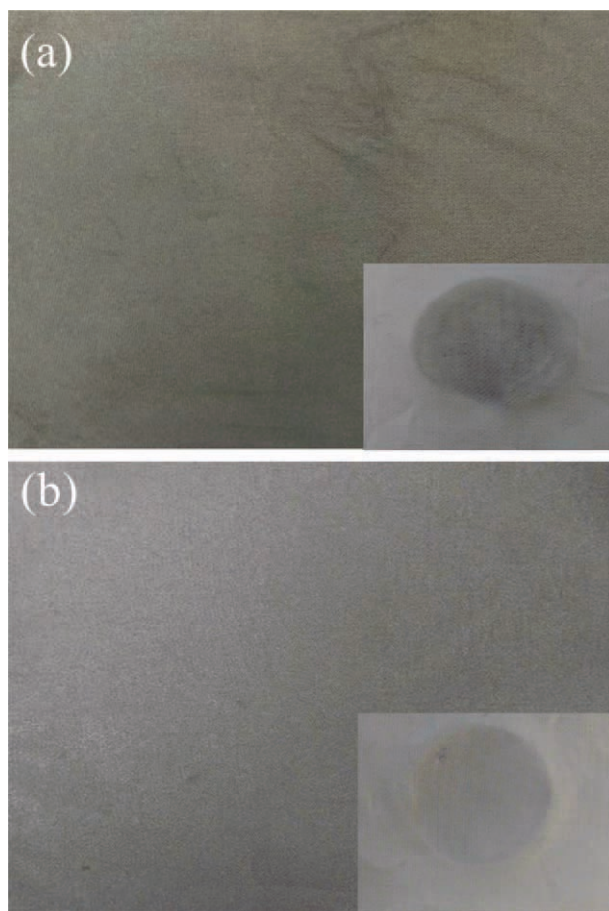
Figure 12. Effects of the Ni-plated polyester fabrics (big area) and a white test cloth (lower right area) after the crocking test according to AATCC 8-2004 (a) without and (b) with APTMS modification.

covalent bonds between the Ni coating and the polyester fiber. The binding force of a covalent bond is much stronger than a van der Waals force between the coating layer and the fiber. Thus, the effective contribution of APTMS modification is ascertained to improve the adhesion of Ni deposits onto a polyester fiber surface.

In addition, the colorfastness to crocking of the Ni-plated polyester fabrics without and with modification by APTMS was assessed in accordance with AATCC specifications, and the results are reported with the gray scale, as shown in Figure 12. The more gray the white test cloth square in lower right portion of Figure 12 was, the lower its grade in the gray scale was and the greater the number of nickel particles were lost from the fabric surface after crocking. Under dry crocking conditions, the colorfastness result of the Ni-plated polyester fabrics without APTMS treatment was rated as grades 3–4 [Figure 12(a)], whereas the Ni-plated fabric subjected to APTMS treatment was rated with grades 4–5 [Figure 12(b)]. The results show that fewer nickel particles were lost from the fabric surface during rubbing action after the fabric was subjected to APTMS treatment, as reflected in the color of white test cloth square shown in lower right area of the figure. This was due to covalent bonds

between the Ni coating and the polyester fiber after APTMS modification. The result implies that there was an improvement in color staining after APTMS treatment.

CONCLUSIONS

In this study, a Ni coating with good adherence stability was successfully fabricated onto an APTMS-modified polyester fabric by the electroless plating technique through the use of Pd as the activator. XPS studies showed that APTMS formed an SAM on the polyester fabric surfaces, and Pd colloids firmly anchored onto the APTMS-modified fabric surfaces via Pd—N bonds. SEM analyses indicated that the APTMS-modified fabric was completely covered by an Ni coating after electroless plating for 5 min, and the obtained Ni deposits had the advantages of uniformity and continuity. Additionally, the Ni film had an amorphous structure. The EMI SE of the Ni-plated polyester fabric was more than 30 dB at frequencies that ranged from 2 to 18 GHz. Furthermore, the sample that was prepared by the APTMS modification process showed effective adhesion between the Ni layer and the polyester fiber. The chemical bonding of the Ni layer with the fabric contributed to the interfacial adhesion. The results reveal that not only could APTMS be used as chemisorption sites for Pd ions in an Sn-free activation process for the electroless plating of Ni, but it also could serve as an adhesion promotion layer for Ni-plated polyester fabrics. This process could potentially be applied to textile finishing treatments.

REFERENCES

1. Schwarz, A.; Hakuzimana, J.; Kaczynska, A.; Banaszczyk, J.; Westbroek, P.; McAdams, E.; Moody, G.; Chronis, Y.; Priniotakis, G.; Mey, G. D.; Tseles, D.; Langenhove, L. V. *Surf Coat Technol* **2010,** *204*, 1412.

2. Liu, X. Q.; Chang, H. X.; Li, Y.; Huck, W. T. S.; Zheng, Z. J. *Am Chem Soc Appl Mater Interface* **2010,** *2*, 529.

3. Jiang, S. X.; Qin, W. F.; Guo, R. H.; Zhang, L. *Surf Coat Technol* **2010,** *204*, 3662.

4. Yuranova, T.; Rincon, A. G.; Bozzi, A.; Parra, S.; Pulgarin, C.; Albers, P.; Kiwi, J. *J Photochem Photobiol A* **2003,** *161*, 27.

5. Lu, Y. X.; Jiang, S. H.; Huang, Y. M. *Surf Coat Technol* **2010,** *204*, 2829.

6. Mallory, G. O.; Hadju, J. B. Electroless Plating; AESF: Orlando, FL, **1990.**

7. Guo, R. H.; Jiang, S. Q.; Yuen, C. W. M.; Ng, M. C. F. *J Appl Electrochem* **2009,** *39*, 907.

8. Holtzman, A.; Richter, S. *J Electrochem Soc* **2008,** *155*, D196.

9. Williams, M.; Pineda-Vargas, C. A.; Khataibe, E. V.; Bladergroen, B. J.; Nechaev, A. N.; Linkov, V. M. *Appl Surf Sci* **2008,** *254*, 3211.

10. Li, L.; Yan, G. P.; Wu, J. Y.; Yu, X. H.; Guo, Q. Z.; Kang, E. *Appl Surf Sci* **2008,** *254*, 7331.

11. Han, E. G.; Kim, E. A.; Oh, K. W. *Synth Met* **2001,** *123*, 469.

12. Yuen, C. W. M.; Jiang, S. Q.; Kan, C. W.; Tung, W. S. *J Appl Polym Sci* **2007,** *105*, 2046.

13. Sawada, S.; Masuda, Y.; Zhu, P. X.; Koumoto, K. *Langmuir* **2006,** *22*, 332.

14. Williamsa, M.; Nechaeva, A. N.; Lototskya, M. V.; Yartys, V. A.; Solberg, J. K.; Denys, R. V.; Pineda, C.; Lif, Q.; Linkov, V. M. *Mater Chem Phys* **2009,** *115*, 136.

15. Han, W. K.; Hwang, G. H.; Hong, S. J.; Kim, S. S.; Yoon, C. S.; Kwak, N. J.; Yeom, S. J.; Kim, J. H.; Kang, S. G. *Microelectron Eng* **2009,** *86*, 374.

16. Liu, D. L.; Yang, Z. G.; Zhang, C. *Mater Sci Eng B* **2010,** *166*, 67.

17. Liu, H. B.; Li, J.; Wang, L. J. *Appl Surf Sci* **2010,** *257*, 1325.

18. Guo, R. H.; Jiang, S. Q.; Yuen, C. W. M.; Ng, M. C. F. *J Mater Sci Mater Electron* **2009,** *20*, 735.

19. Asher, T.; Inberg, A.; Glickman, E.; Fishelson, N.; Shacham-Diamand, Y. *Electrochim Acta* **2009,** *54*, 6053.

20. Kowalczyk, D.; Slomkowski, S.; Chehimi, M. M.; Delamar, M. *Int J Adhes Adhes* **1996,** *16*, 227.

21. Dai, H. B.; Li, H. X.; Wang, F. H. *Appl Surf Sci* **2006,** *253*, 2474.

22. Vincent Crist, B. Handbook of Monochromatic XPS Spectra; Wiley: New York, **2000.**

23. Li, L. B.; An, M. Z. *J Alloys Compos* **2008,** *461*, 85.

24. Baskaran, I.; Sankara Narayanan, T. S. N.; Stephen, A. *Mater Chem Phys* **2006,** *99*, 117.