





Chemical Metallization of Insulating Polymeric Surfaces Through Simple Diazonium-Based Covalent Amination

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Abstract. Electroless plating or autocatalytic deposition on insulating polymeric substrates via surface amination is currently of potential interest since the grafted amine functionalities significantly decrease the total quantity of noble metal catalyst and offer good adhesion between the polymer substrate and the deposited films. Among various wet-chemical amination strategies available in the literature, diazonium-induced anchoring process appears to be very promising due to many advantages: one-step aqueous chemical process, provides covalent grafting of amine-terminated groups, carried out in open air and at room temperature. This work covers our recent studies on the grafting of aminophenyl and vinylpyridine groups through diazonium chemistry onto various polymers. We discuss the ability of these amine-terminated functionalities towards the chemisorption of acidic palladium chloride activators, which subsequently initiate autocatalytic deposition process. Our studied polymers functionalized with these palladium complexes perfectly suit the subsequent electroless nickel plating process. The covalently grafted amine groups provide excellent adhesion of the deposited nickel film on polymers. SEM, AFM, EDX and XPS techniques are used to characterize the electrolessly deposited metallic film.

Keywords: Diazonium chemistry · Covalent amination · Green chemistry
Palladium activation · Autocatalytic deposition

1 Introduction

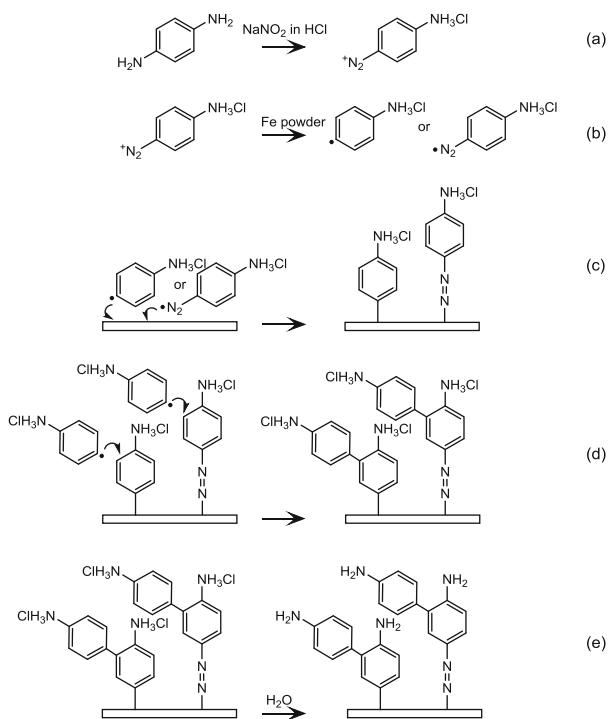
Electroless plating onto plastics is required not only for many daily life applications but also for advanced technologies, such as microelectronics, fabrication of micro/nano electromechanical systems [1]. However, chemical metallization of insulating polymers is challenging. Current industrialized processes of electroless plating onto plastics rely

on the chromic acid etching for oxidizing the surfaces, which increases the surface energy and wettability for the subsequent step of surface activation with noble metal catalysts. The use of chromic acid causes numerous health and environmental issues [2]. Thus, the development of simple, cost-effective as well as environment friendly strategies to metalize the surface of insulating substrates, such as avoiding chromic acid etching and/or minimizing the gravimetric use of relatively expensive noble metals, have attracted attention of several research works [1–5]. Electroless plating on insulating polymeric substrates via surface amination has appeared to be a promising alternative to the chromic-based strategy, as the amine groups allow a well-controlled amount of the noble metallic catalysts and good adhesion of the deposited film. Amination of polymeric substrates can be achieved through different plasma-assisted methods or through various multiple-step chemical methods [3–7]. Here, we report a one-step chemical process based on the diazonium chemistry to covalently functionalize the polymeric substrates of interest with either aminophenyl or vinylpyridine groups. These amine-terminated surfaces are activated by simply immersing the substrates in acidic palladium chloride solution. This results in stable electrostatic interaction between the protonated amine functionalities and the palladium chloride complexes. Such activated surfaces are suitable for the subsequent electroless nickel plating and provide excellent adhesion between the polymer substrates and the electrolessly deposited nickel films. Details concerning the mechanism of surface functionalization as well as the metallic behavior of the deposited thin film will be discussed based on the XPS, EDX, SEM and AFM results.

2 Amination of Plastics Through Diazonium-Based Chemical Process

Scheme 1 presents the mechanism for the grafting of aminophenyl groups onto any surfaces using diazonium induced anchoring process [8, 9]. First, the diazonium cations can be prepared in-situ from the paraphenylenediamine by adding one equivalent of NaNO_2 into acidic medium (a). It is important to keep the acidity of the working solution below a pH of 2 to stabilize the diazonium cations. Adding Fe powder reducing agent into the diazonium solutions will lead to the generation of the phenyl or azo-phenyl radical (b). These radicals immediately attach to any kind of substrate, either a conducting surface or an insulating one, which are put into the solution (c) and form the primer phenylene layer. The growth of the multi aminophenyl layers involves another radical(d). Finally, rinsing the modified surface with deionized water will help to deprotonate the aminophenyl groups, at least partially (e).

In this work KMPR photoresist has been selected to represent polymer substrates. While the XPS survey of the pristine KMPR surface shows only the typical C 1s and O 1s peaks of the epoxy polymer [1], a new N 1s peak appears on the diazonium treated surface (Fig. 1). This peak can be de-convoluted into two components (inset). An intense peak centered at 399.6 eV ascertains the presence of the amine groups of the



Scheme 1. The mechanism of aminophenyl grafting

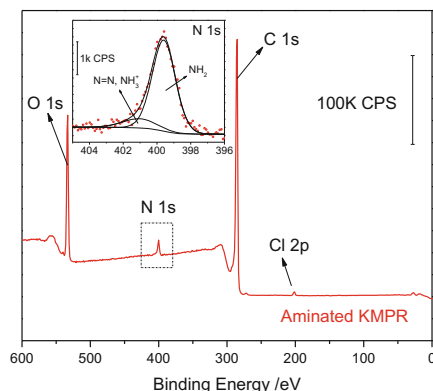


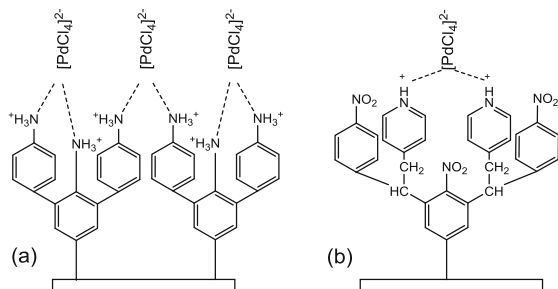
Fig. 1. XPS survey and N 1s core level spectra recorded on the diazonium treated KMPR surface

aminophenyl layer. The small peak at 401.0 eV may arise from the formation of -N=N- azo bridges as seen on the Scheme 1(e). A part of this broad peak may have resulted from the presence of the ammonium salt as the chloride anion traces are also observed on the modified surface (Fig. 1).

In the case where a certain amount of vinyl monomers (vinyl pyridine, acrylic acid...) is added to the diazonium solution; phenyl radicals not only do graft onto the substrate but also react with the double-bond of vinyl monomers soluble in the solution to generate secondary vinylic radicals [2, 10]. These latter, in turn, attach to the phenylene layer and consequently lead to the grafting of the vinylic functionalities onto the surface via the primary layer of phenylene. For details on the grafting of vinylpyridine onto Plexiglas® using nitrophenyl diazonium cations, the reader is referred to our recently published work [2].

3 Activation of Amine-Terminated Insulating Surfaces

Prior to the electroless nickel plating, activation of the polymeric surfaces using noble metal-based catalysts is usually required to initiate the autocatalytic plating process [1]. Our studied polymeric surfaces functionalized with aminophenyl or vinylpyridine are easily activated through simple immersion into acidic palladium chloride solution ($10 \mu\text{M PdCl}_2$ in 0.5 M HCl) for a duration of only a few minutes. In strongly acidic condition, palladium cations exist in the form of negatively charged PdCl_4^{2-} complexes, while the amine-terminated groups are protonated and become positively charged. Palladium activators are thus incorporated into the modified layer through stable electrostatic interaction as described in Scheme 2. As an example, X-ray photoelectron spectroscopy is allowed to confirm the presence of palladium activators after immersion of vinylpyridine-grafted Plexiglas® sample into PdCl_2/HCl solution, as seen in Fig. 2. The high resolution Pd 3d region (inset of Fig. 2) clearly shows the typical characteristics of palladium cation with two signals at 343.1 eV and 337.8 eV for 3d_{3/2} and 3d_{5/2} peaks respectively. The 3d_{5/2} peak positioned at 337.8 eV was reported to be partially related to the presence of the chloro-bridged Pd sites. In line to this argument, the peaks of chloride anion with the 2p_{3/2} and 2p_{1/2} peaks successively positioned at 197.4 and 199.1 eV are present in the XPS spectrum.



Scheme 2. Activation of aminophenyl (a) and pyridine (b) functionalities in PdCl_2/HCl solution

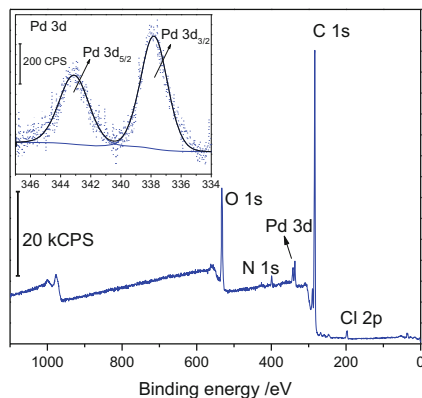


Fig. 2. XPS survey and high resolution Pd 3d spectra (inset) on the vinylpyridine-functionalized Plexiglas® after immersing in PdCl₂/HCl solution

4 Electroless Nickel Plating onto Activated Amine-Terminated Polymers

Electroless nickel plating takes place while immersing the substrate activated with Pd complexes into nickel solution containing a reducing agent [1]. In this case, we used a conventional nickel-plating bath containing 0.1 M nickel sulfate hexahydrate, 0.2 M citric acid monohydrate and 0.05 M dimethylamine borane (DMAB). Tetramethylammonium hydroxide (TMAH) was used to adjust the pH of the solution at 9. Electroless nickel plating can be achieved at an appropriate temperature (65°C). The whole deposition process can be briefly described as follows: Pd²⁺ cations are first reduced to Pd metal. This noble metal nuclei catalyzes the subsequent reduction of nickel cations to Ni metal atoms. Once metallic nickel is formed around the Pd nuclei, this metallic Ni catalyzes further reduction reaction of nickel cations from its solution. This autocatalytic reaction results in formation of a continuous film on the substrate. A metallic film entirely covers the Plexiglas® substrate functionalized with palladium vinylpyridine complexes after immersing 7 min in our plating solution (Fig. 3a, b). SEM and AFM results indicate the compactness and continuity of the deposited film (c, d).

The electrolessly nickel film deposited using DMAB reducing agent is usually an alloy containing a certain amount of boron. It is therefore essential to characterize the metallic behavior of the obtained film. Figure 4(a) presents the EDX spectrum recorded on top of Ni-B deposited Plexiglas® substrate. In addition to Ni and B, we also observe two smaller peaks of C and O on the spectrum which may have resulted from the Plexiglas® underlayer or from the unavoidable native oxide and the atmospheric contamination on the top surface [2]. A more accurate method to quantify the percentage of nickel in the film is thus required. Figure 4(b) shows the XPS survey spectrum of the Ni-B film after cleaning the surface with Ar ion. As anticipated, the bulk film contains only nickel metal and boron. The atomic % of Ni and B was evaluated to be equal to 71.8% and 28.2% through quantitative analysis of the XPS

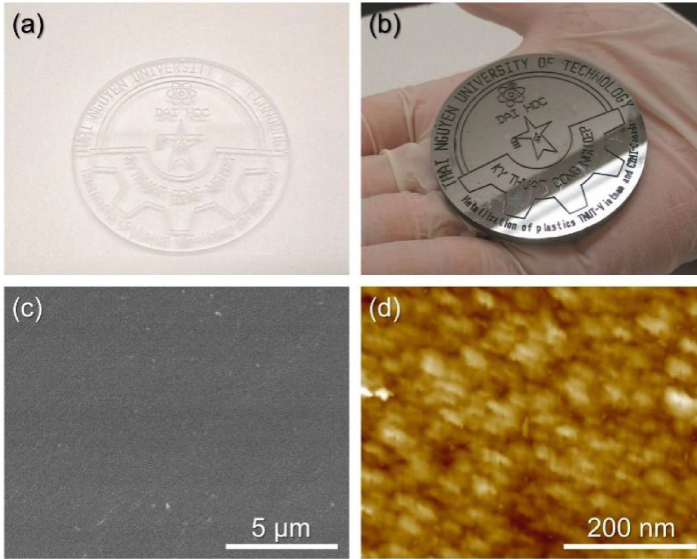


Fig. 3. Plexiglas® substrate before (a) and after (b) nickel plating. SEM (c) and AFM (d) images recorded on top of nickel film

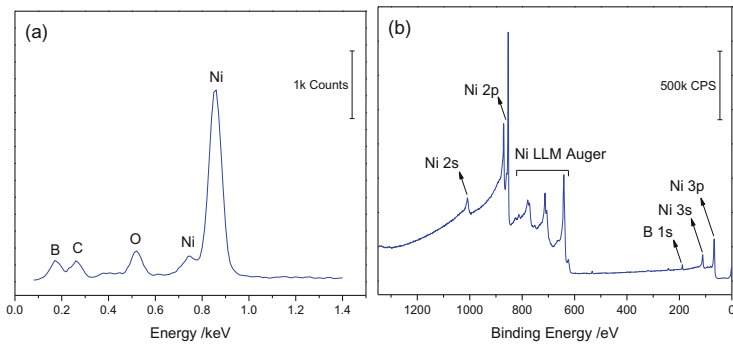


Fig. 4. EDX (a) and XPS survey (b) of Ni-B film deposited on Plexiglas® after cleaning the surface with Ar ions

data. One can calculate the boron weight percentage in the Ni-B alloy to be $\approx 6.7\%$, which is consistent with the literature [1, 11].

5 Conclusion

We summarized our main works in regards to one-step chemical process for covalent functionalization of plastic surfaces with aminophenyl and vinylpyridine groups by taking advantage of the versatile diazonium chemistry. The immersion of these amine-terminated surfaces into acidic palladium chloride solution leads to stable integration of palladium activators on the modified surfaces, and thus allows initializing the electroless nickel plating process. Thanks to the covalent grafted seed layer, the deposited nickel-boron alloy strongly adheres to the polymeric substrates. We believe that our efficient, completely aqueous and chromium-free plating route provides a comprehensive solution to combat the environmental concerns of the conventional processes of chemical metallization of polymers.

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