Study of Palladium Reduction and Its Effect on the Electroless Nickel Coating Adhesion on Carbon-fibre Reinforced Polyetherimide Composite

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Abstract. Polymer composite is frequently coated with metals by various metallization processes, one of which is electroless nickel (EN) plating process. EN plating has been accepted by industry as a reliable method to produce the high quality, bright reflective surfaces. Aesthetically, the well-established bright metal finishes also offer plastic components with important functional advantages, such as wear resistance and hygienic properties. To improve EN coating adhesion on the polymer composite, chemical etching is used as the pre-treatment method prior to EN coating. However, the immediate consequence of the chemical etching is the exposure of the composite carbon fibre, leading to poor surface finish. To overcome the challenges, chemical-etching-free pre-treatment methods are desirable. In this paper, the key factors controlling the adhesion of EN coating on carbon fibre reinforced polyetherimide (CF-PEI) were investigated. Surface chemistry at different treatment stages was studied by X-ray photoelectron spectroscopy (XPS) analysis. It is found that reducing palladium (Pd) ions into Pd atoms on the composite surface takes a critical role to develop a good adhesion of EN coating to CF-PEI composite surface. When hypophosphite is used as a reducing agent, elevated temperature increases the density of catalytic Pd metal sites. With a stronger reducing agent sodium borohydride ($NaBH_4$), more adsorbed Pd ions can be reduced at room temperature than the high temperature hypophosphite. Even though $NaBH_4$ is used, there is still more than 30% adsorbed Pd ions yet to be reduced.

Keywords: Plastic plating, metallization of polymer, surface activation, electroless nickel plating, coating adhesion

1 Introduction

Components made of polymer and polymer composite are frequently coated with metals by various metallization processes, one of which is EN plating process. EN plating has been accepted by industry as a reliable method to produce the high quality, bright reflective surfaces. Aesthetically, the well-established bright metal finishes also offer plastic components with important functional advantages, such as wear resistance and hygienic properties. As well-known, polymer surfaces lack catalytic properties and therefore require activating treatments that render them catalytic surface for initial nickel deposition [1]. In general, this activation is done by seeding the surface with a catalytically active metal such as Pd. In this process, surface sensitizing is carried out at the first in a solution containing reducing ions such as stannous ions (Sn^{2+}). The sensitizing Sn^{2+} ions adhered on the polymer substrate can reduce the Pd metal ions (Pd^{2+}) into Pd metal (Pd^0) from a catalyst solution containing palladium chloride ($PdCl_2$) according to the follow chemical reaction [2,3].

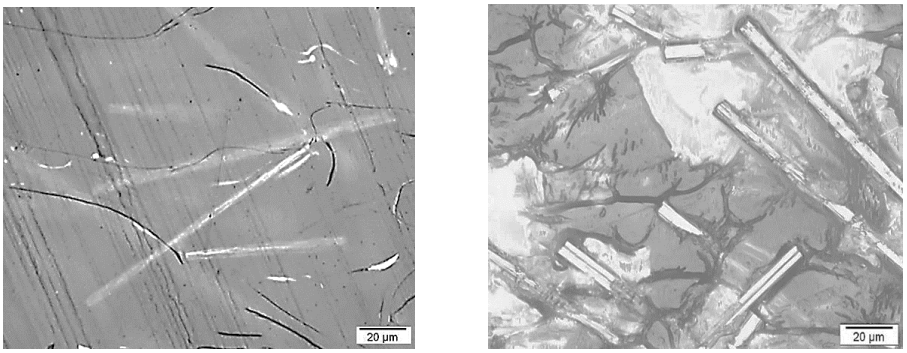
$Pd^{2+} + Sn^{2+} \rightarrow Sn^{4+} + Pd^0$

The alternate method of catalyzing and activating makes use of a mixed colloidal catalyst bath, so-called one-step activation. The colloid is reduced Pd metal nano particles stabilized by Sn^{2+} and Sn^{4+} ions [4].

The surface of an injection-molded plastic article normally is glossy and quite hydrophobic. Consequently, this surface is unreceptive to aqueous solutions used in electroless metal deposition. Since the sensitizing and activating solutions will not wet the surface, the metal ions are not adsorbed onto the surface and deposition of the metal cannot proceed. Many approaches rendering the polymer surface with hydrophilicity have been proposed, such as solvent conditioning [5,6], mechanical surface roughening [7], and chemical etching [8].

All the pretreatments of polymer substrate will produce coarse surface, leading to adhesion improvement

of EN coating by ether increasing surface area or forming microscale physical anchor layer being beneficial to the Pd catalyst adsorption. However, surface roughening techniques are not suitable for EN coating on the high precision components made of polymer composites. One example is the metallized carbon-fiber (CF) reinforced polyetherimide (PEI) composite, which has been widely used for electronics applications such as components for hard disk drives. The above-mentioned pretreatments prior to Pd activation and EN plating will strip off PEI polymer from the composite surface and then produce CF protrusion, as shown in Fig. 1. Besides the high precision requirements in electronics-related plating fields, plastic plating methods for circuit formation where resin-metal interface roughness must be minimized to avoid signal delay due to the skin effect have also been desired. For these reasons, many reports on new resin surface modification methods have been published [9-14].



(a) (b)

Fig. 1. Optical microscopic images of injection-molded PEI-30%CF composite substrates: (a) pristine, (b) CrO_3 etching in a solution containing CrO_3 (415 g/L) and H_2SO_4 (200 ml/L) at 70 °C for 3.5 min.

The surfaces after modifications without chemical/mechanical etching/roughening, however, may lead to less physical/mechanical contribution to the coating adhesion. Therefore, effective bonding of Pd catalyst and the electroless plating may become more influential to the overall coating adhesion. Understanding of the mechanisms behind the effect of modification on the surface chemistry and thereby the adsorption of Pd catalyst is essential to explore new processes for pretreatment of EN plating without chemical/mechanical etching. In this study, by using X-ray photoelectron spectroscopy (XPS) the effect of surface modifications on adhesion of EN coating on PEI-CF composite was investigated. The XPS surface chemistry analysis reveals that Pd reduction takes an important role in adhesion of EN coating on polymer substrate.

2 Experimental Procedures

Testing coupons were made of 30%CF reinforced PEI (PEI-30%CF, State-Kon) by injection molding process. The composite coupons were first cleaned with isopropyl alcohol (IPA) in an ultrasonic bath for 5 minutes and then nitrogen (N_2) spray dried. The cleaned coupons were immersed in an aqueous adhesion promoter containing 5% polyethyleneimine (Sigma-Aldrich, Mw750,000) at 80 °C for 60 min, followed by deionized (DI) water rinsing in an ultrasonic bath for 5 minutes to remove the excess polyethyleneimine from the PEI-CF composite surface, and immersion in an aqueous solution containing $PdCl_2$ (0.5 g/L) and HCl (10 ml/L) at room temperature for 5 minutes for Pd ions adsorption onto the chemically modified surface. After DI water rinsing for 5 minutes to remove the free Pd ions, the composite coupons were soaked in a water-based solution containing either NaH_2PO_2 or $NaBH_4$ at room or elevated temperatures for 5 minutes to reduce the adsorbed Pd ions to Pd atoms for surface catalyzation.

Table 1 Sample preparation with different treatments.

Treatment time (min) / Treatment conditions	#1	#2	#3	#4	#5
Polyethyleneimine (5g/L, H_2O), 80°C	0	60	60	60	60
NaH_2PO_2 (30g/L, H_2O), 25°C	0	0	5	0	0
NaH_2PO_2 (30g/L, H_2O), 98°C	0	0	0	5	0
$NaBH_4$ (19g/L, H_2O), 25°C	0	0	0	0	5

The Pd catalyzed coupons were then immersed in an EN plating solution (RONAMAX™ SMT*, R&H) at

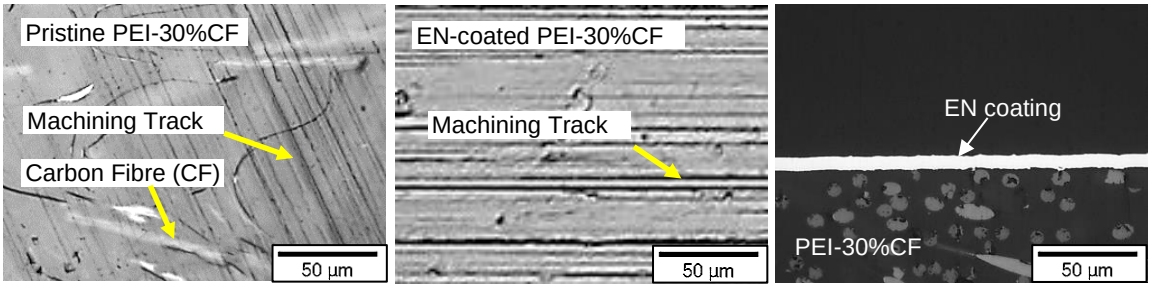
90 °C for 40 minutes, followed by DI water rinsing for 5 minutes and hot air dry by a hair drier prior to characterization. The sample preparation by following the above conditions is summarized in Table 1, denoted as #1, #2, #3, #4, and #5, respectively.

The characterization of the CF-PEI composite substrates with different surface treatments includes surface appearance and microstructure by optical microscopes, chemical analysis by XPS (Thermo Scientific), and adhesion by standard crosshatch tape test (ASTM D3359). XPS measurements were carried out with a monochromatized Al Kα X-ray source (1486.6 eV photons) at a power of 150 W (15 kV and 10 mA). The core-level spectra were obtained at the photoelectron take-off angle (α, with respect to the sample surface) of 90°. A pass-energy of 150 eV was used for the survey spectra and 40 eV for high-resolution scans. The pressure in the analysis chamber was maintained at 10^{-8} Torr or lower during each measurement. To compensate for surface charging effects, all binding energies (BEs) were referenced to the C 1s hydrocarbon peak at 284.6 eV. A computer program was employed to perform de-convolution with which one experimental peak could be fit precisely by more than one Gaussian curves, and the relative surface concentration of the specific chemical species in question was obtained from the product of the peak area and the corresponding atomic sensitivity factor. In peak synthesis, the line width (full width at half maximum or FWHM) of Gaussian peaks was maintained constant for all components in a particular spectrum. Surface elemental stoichiometry was determined from the peak area ratios and were accurate to within ±10%.

3 Results and Discussion

3.1 Morphological observation on the PEI-30%CF composite with and without EN coating

Fig. 2 shows the optical microscopic images of (a) the pristine PEI-30%CF composite molded by injection molding process, (b) the EN coated surface, and (c) cross-sectioned observation of the EN coated PEI-30%CF composite. It is noted that the straight dark lines on the surface of pristine PEI-30%CF (#1 in Table 1) as shown in Fig. 2(a) were replicated during injection molding from the conventional milling of ejector pin surface. The EN coating process didn't change the surface morphology significantly as shown in Fig. 2(b), which can be further verified by microscopic observation of the cross-sectioned EN coated PEI-30%CF composite samples, as shown in Fig. 2(c). The carbon-reinforced PEI composite surface is fully covered by about the 12 μm thick uniform EN coating without interface defect and carbon fiber protrusion.



(a) (b) (c)

Fig. 2 Optical microscopic images of the injection-molded PEI-30%CF composite: (a) as-molded pristine surface, (b) the EN coated surface, and (c) cross-sectioned observation of the EN coated PEI-30%CF composite.

3.2 Effect of surface treatment conditions on EN coating adhesion

Crosshatch tape tests were carried out by following ASTM D3359 after EN coating on Pd catalyzed PEI-CF composite coupons with different reduction conditions (refer to Table 1) and summarized in Table 2. It can be seen that surface treatment conditions, in particular, the type of reducing agent and the process parameters, have significant effect on metal/composite adhesion. When the Pd reduction is carried out in an aqueous solution containing 30g/L hypophosphite (NaH_2PO_2) at room temperature (25°C), the EN coating adhesion is ranked as 2B (#3 in Table 2), which is evaluated as "Failed" according to industry standards for hard disk drive. When the reduction process is conducted in the same solution at 98°C, a good adhesion ranked as 5B (#4 in Table 2) is obtained, which is the highest scale in the adhesion test (ASTM D3359). For benchmarking, a stronger reducing agent, $NaBH_4$, was used for reduction of the adsorbed Pd on the PEI-30%CF composite substrate at 25°C (#5 in Table 2), followed by EN coating. The same

adhesion testing result (ranked as 5B) as sample #4 was achieved. To understand the key factors controlling adhesion, XPS was employed to analyze the changes in surface chemistry of the composite substrate with various surface treatments.

Table 2 Summary on crosshatch tests of EN coated PEI-30%CF with different pretreatment processes.

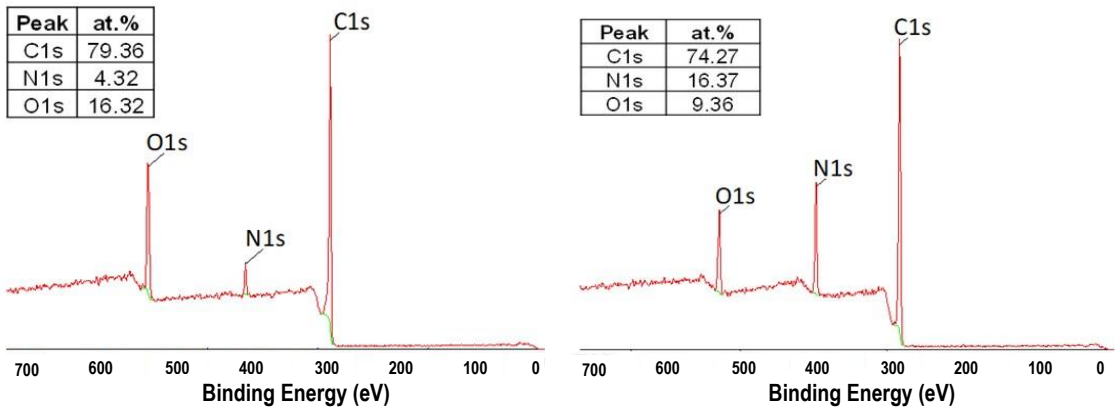
EN coating & Tape test / Treatment Sample	EN coating (min)	Tape test ranking	Evaluation
#3	40	2B	Failed
#4	40	5B	Pass
#5	40	5B	Pass

3.3 XPS analysis of PEI-30%CF surface with different treatment conditions

Effect of polyethyleneimine treatment on surface chemistry of PEI-30%CF

A basic requirement for substrate to be electrolessly plated is catalytic surface that provides active sites for reduction of metal ions. For EN plating, Pd metal is frequently used as its deposition catalyst. In an etching-free surface preparation of a polymer substrate for EN plating, the challenge is how to activate a polymer surface on which Pd metal catalytic particles are firmly fixed. One approach is modification of polymer surface with amine rich chemicals. In this study, a treatment in an aqueous solution containing branched polyethyleneimine is applied on the PEI-30%CF (#2 in Table 1).

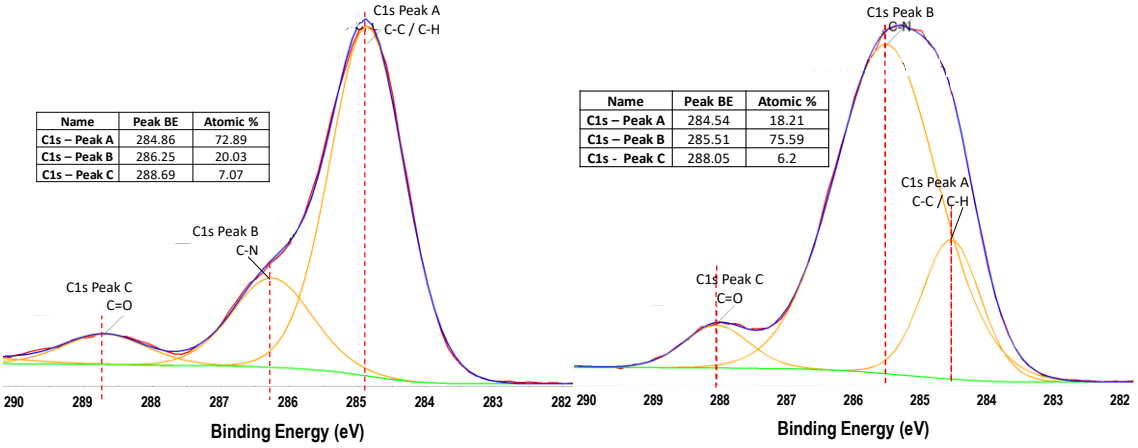
XPS wide scan of PEI-30%CF substrate treated with polyethyleneimine is shown in Fig. 3b, in comparison with that of pristine sample (Fig. 3a). After polyethyleneimine treatment, N content is significatly increased from 4.32 at.% of the pristine sample to 16.37 at.%. The high N on the modified surface is clearly originated from the primary, secondary and ternary amines in the polyethyleneimine molecules, which are attached onto the PEI-30%CF composite surface.



(a) (b)

Fig. 3 XPS wide scan and elemental contents on the surface of PEI-30%CF composite before (a) and after (b) polyethyleneimine treatment.

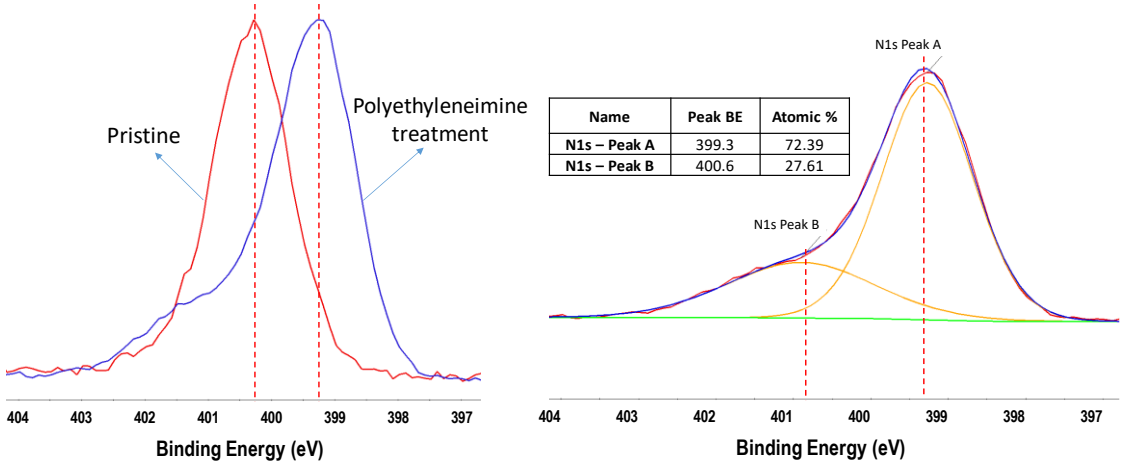
In Fig. 4, C1s core-level spectra of polyethyleneimine treated PEI-30%CF can be curve-fitted with 3 peak components with different BEs at about 284.5, 285.5, and 288.5 eV, attributed to the species of C-C/C-H, C-N, and C=O, respectively [15-17]. Compared with the pristine sample, C-N species are significantly increased from 20 to 75.6 at.% due to the contribution of the attached polyethyleneimine. Meanwhile, detected C-C/C-H species are decreased from 72.9 at.% of pristine surface down to only 18.2 at.% of the polyethyleneimine treated surface, which implies that the density of amine groups are the control species after the polyethyleneimine treatment.



(a) (b)

Fig. 4 Deconvoluted C1s core-level spectra of PEI-30%CF composite samples: (a) pristine, (b) treated with polyethyleneimine.

N1s core-level spectra before polyethyleneimine treatment (pristine) and after polyethyleneimine treatment (a) and deconvolution of the treated sample (b) are given in Fig. 5. As shown in Fig. 5a, polyethyleneimine treatment leads to N1s peak right shift. The N1s core-level spectra of the polyethyleneimine treated PEI sample can be curve-fitted two peak components at BEs of 400.6 eV and 399.2 eV as shown in Fig. 5b, which is attributable to the $–N-(C=O)_2$ and NH/NH_2 species, respectively [18]. Although the imide nitrogen is still detected from the XPS analysis, its percentage in the total N is only 27.6 at.%, much lower than the amine (72.4 at.%) that are basically contributed by the attached polyethyleneimine. This result is consistent with the above XPS analysis based on C1s, where the content of the imide carbon (N-C=O) species is 6.2 at.% out of the total carbon, as shown in Fig. 4b.



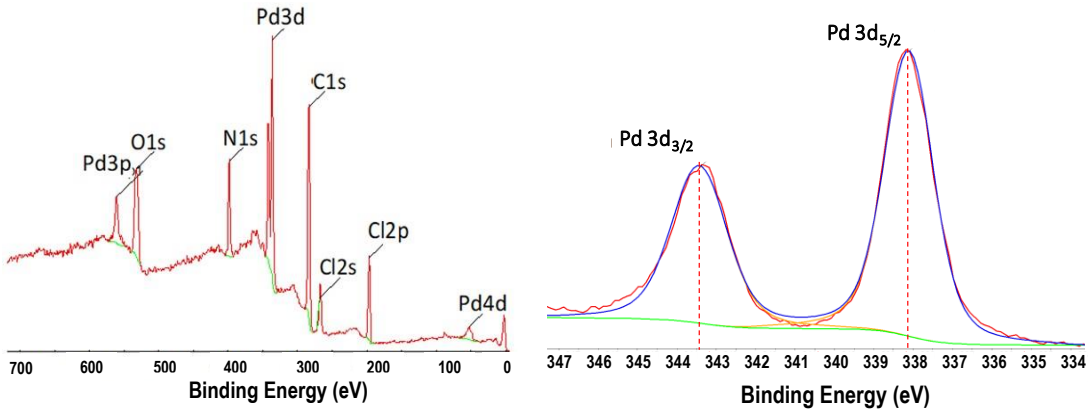
(a) (b)

Fig. 5 N1s core-level spectra of PEI-30%CF composite treated with polyethyleneimine: (a) peak shift, (b) deconvoluted peaks

Pd adsorption on the PEI-30%CF modified with polyethyleneimine

As mentioned above, in the chemical-etching-free activation process, no Sn^{2+} sensitization is needed, instead, the polyethyleneimine treated surface is directly immersed into the Pd^{2+} acidic solution, where the Pd^{2+} ions are chemically adsorbed onto the amine rich surface. To activate the surface, a reduction process is still needed to reduce the Pd^{2+} ions into the catalytic Pd^0 metal by reducing agents such as NaH_2PO_2 and $NaBH_4$.

Fig. 6(a) shows the XPS wide scan on PEI-30%CF composite surfaces after the polyethyleneimine treatment and immersion in $PdCl_2$ solution. It is shown that after Pd immersion treatment, Pd and Cl are detectable and the Cl/Pd atomic ratio is about 2, which is identical to that of theoretical value of $PdCl_2$ and implies that Pd exists on the polymer surface in ionic state (Pd^{2+}).



(a) (b)

Fig. 6 XPS wide scan on the polyethyleneimin treated PEI-30%CF composite surface after Pd immersion treatment (a); Pd 3d core-level spectra (b).

It is noted that DI water rinsing was applied for 5 minutes after Pd immersion treatment in order to remove any water-soluble species from the polymer surface, including Pd^{2+} and Cl^{-}. Therefore, the presence of a high concentration of Pd and Cl on the amine rich surface is probably due to the formation of Pd-N complex on PEI polymer surface. As the primary and secondary amine groups of the attached polyethyleneimin molecules provide strong electron donors [18] in the formation of the Pd-N complexes.

This speculation on the Cl-Pd-N complex is supported by the Cl $2p_{3/2}$ peak shift to the low binding energy (197.9 eV), which is usually in the range of 198.5-199 eV for metal chloride, and the lower BE shift is attributed to the formation of Pd-N coordination bond. XPS Pd 3d core-level spectra in Fig. 6(b) with the BEs of the spin-orbit-split doublet (Pd $3d_{5/2}$ and Pd $3d_{3/2}$) lying at about 338 and 343 eV, respectively, suggest the presence of predominantly the Pd^{2+} species [16].

Reduction of Pd ions with different reducing agents and working conditions

The Pd at the Pd^0 state has been considered as the catalyst for the electroless metal deposition process [19]. Therefore, reduction of Pd^{2+} adsorbed on the amine modified PEI surface to be Pd metal (Pd^0) is essential and important step in the pretreatment of polymer substrate for EN plating. A first trial of the reduction is carried out in a water solution containing 3 wt.% NaH_2PO_2 at 25 °C for 5 min.

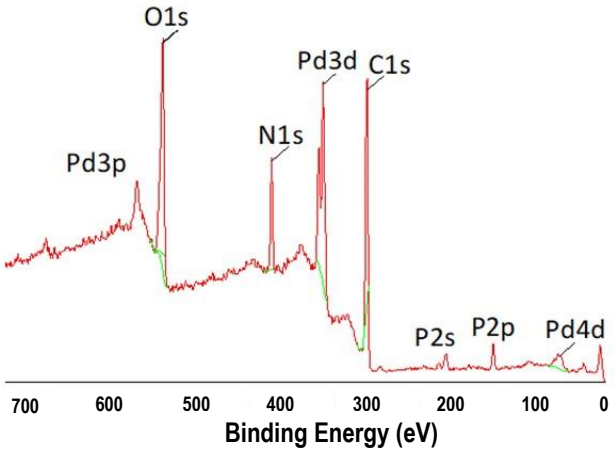


Fig. 7 XPS wide scan on the polyethyleneimin treated PEI-30%CF composite surface after reduction treatment in water solution containing 3 wt.% NaH_2PO_2 at 25°C for 5 min.

XPS wide scan spectra (Fig. 7) on the above sample reveal that the reduction removes the adsorbed Cl but P peak appears. It is found there is no Na element detectable and the P/Pd ratio is 1.1:1, implying that some insoluble P compounds are likely formed and adsorbed onto the polymer surface during the reduction process by using hypophosphite water solution at room temperature, by following below chemical reactions:

$Pd^{2+} + 2H_2PO_2^- + 2H_2O \rightarrow Pd^0 + 2H_2PO_3^- + 2H^+ + H_2$
$Pd^{2+} + 2H_2PO_3^- \rightarrow Pd(H_2PO_3)_2\downarrow$
In this alkaline based reduction solution, part of Pd^{2+} may not be reduced into Pd^0 and possibly exist in the forms of insoluble $Pd(H_2PO_3)_2$. Another possibility causing the existence of P is formation of a complex compound in combination with amine, leading to high P/Pd ratio. Theoretically, P/Pd ratio in between 0:1 (100% reduction of the adsorbed Pd^{2+}) and 2:1 (0% reduction of adsorbed Pd^{2+}). The measured 1.1:1 of P/Pd ratio implies that there are substantial Pd ions were not reduced into Pd metal.

This speculation can be further verified from the high resolution XPS Pd 3d core-level spectra after reduction in hypophosphite solution at 25 °C, as shown in Fig. 8(a). After Pd immersion and reduction, the spin-orbit-split doublet (Pd $3d_{5/2}$ and Pd $3d_{3/2}$) at BEs of 338 and 343 eV are still the main peaks, implying the presence of predominant Pd^{2+} species. Besides the Pd^{2+} doublet, a new doublet (Pd $3d_{5/2}$ and Pd $3d_{3/2}$) at lower BEs of 335 and 340 eV is observed, which is assigned to the Pd^0 species [16]. The fraction of Pd^0, however, is only about 30%, implying an insufficient reduction. In other words, 70% of Pd element is in ionic status, which may be responsible to the poor EN adhesion as indicated in Table 2.

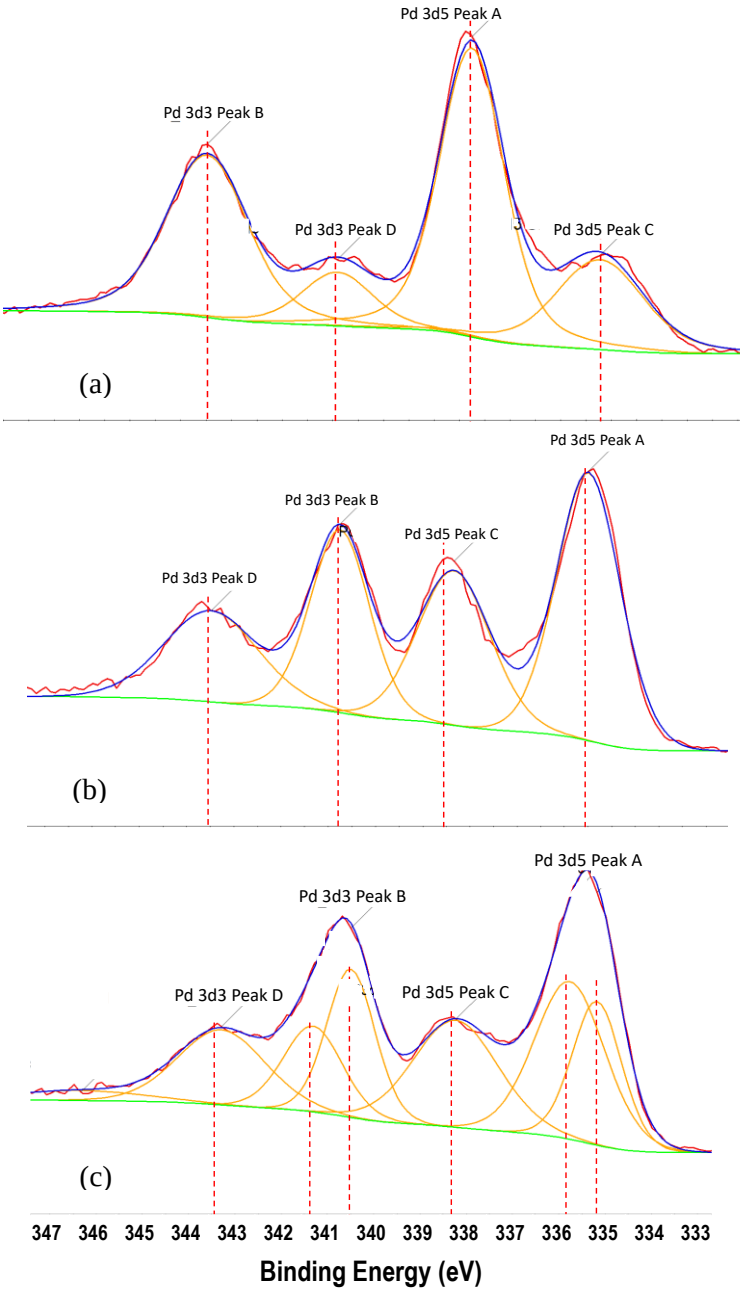


Fig. 8 Pd 3d core-level spectra of PEI-30%CF composite after Pd activation in $PdCl_2$ acidic solution and redution in NaH_2PO_2 water solution at 25 °C (a) and 98 °C (b), and $NaBH_4$ water solution at 25 °C (c).

In order to improve redution efficiency from Pd^{2+} to Pd^0 , the reduction treatment in hypophosphite solution is conducted at an elevated temperated, 98 °C. The high resolution XPS Pd 3d core-level spectra after reduction is shown in Fig. 8(b). Pd^0 is a predominant species after the treatment temperature is elevated, which increases the Pd^0 portion from 30% up to 58%. Therefore, the resulting high density of Pd^0 plays an important role in improving the EN coating adhesion.

The above results show that the reduction of Pd^{2+} to Pd^0 has remarkable effect on the adhesion of EN coating, which relies on the density of Pd^0 metal particles as catalytic sites on the polymer surface. To further prove this speculation, a strong reducing agent $NaBH_4$ is used to perform the reduction of adsorbed Pd^{2+}. The high resolution XPS Pd 3d core-level spectra after reduction in $NaBH_4$ water solution is shown in Fig. 8(c). This strong reducing agent reduces about 62% of adsorbed Pd^{2+} into Pd^0 metal, higher than that of hypophosphite at high temperature (98 °C). After peak decomposition, a minor doublet with the Pd $3d_{5/2}$ and Pd $3d_{3/2}$ peak components around 336 and 341 eV, respectively, indicates the existence of a third Pd species [20,21]. The exact nature of this state of Pd is yet to be determined but is probably associated with an NH_2-Pd complexes [18,22].

4 Conclusion

To understand the key factors controlling the adhesion of EN coating on to PEI-30%CF composite substrate, surface chemistry at different treatment conditions was studied by XPS analysis. It was found that amine species can be grafted through a treatment with polyethyleneimine at elevated temperature, which is essential for Pd activation prior to EN coating on a PEI composite without chemical etching. A further finding is that the reduction of adsorbed Pd ions on the amine-grafted composite takes a critical role in developing a good adhesion of EN coating to the polymer. When hypophosphite is used as a reducing agent, elevated temperature should be applied for increasing the density of catalytic Pd metal particles. When a strong reducing agent is used, e.g., $NaBH_4$, more adsorbed Pd ions can be reduced at room temperature than the high temperature hypophosphite. Even the strong reducing agent is used, there is still more than 30% adsorbed Pd ions yet to be reduced. The mechanism behind the finding is still not clear, which is worth to further investigate.

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