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Supercritical carbon dioxide-assisted electroless nickel plating on polypropylene—The effect of copolymer blend morphology on metal–polymer adhesion

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ABSTRACT

Supercritical carbon dioxide ($scCO_2$)-assisted electroless Ni–P plating with co-polymer-based hydrophilic modification was investigated for polypropylene (PP) substrates. The technique consists of three steps: the first step is a hydrophilic modification of PP, the second is $scCO_2$-assisted impregnation of the substrate with $Pd(hfa)_2$, and the third is the electroless plating reaction. Due to the hydrophobic nature of PP, the aqueous plating solution cannot diffuse into a plain PP substrate to form Ni–P metal. In this study, a block copolymer PP-b-polyethylene oxide (PEO) (PP-b-PEO) was blended with PP by injection molding to modify the hydrophilicity of the PP-plate surface. The blend morphology of PP-b-PEO and PP strongly affected the adhesiveness of the metal layer to the substrate. Five grades of PP with different viscosities were used to investigate the effects of the viscosity ratio of PP to PP-b-PEO on the blend morphology and the adhesiveness of the metal to the polymer. By bringing the viscosity ratio close to a value of approximately twelve, the degrees of elongation and orientation of the PP-b-PEO domains near the surface were maximized, resulting in the thickest metal–PP composite layer and the highest adhesiveness. By controlling the blend morphology, a uniform Ni–P layer was successfully formed with an average adhesive strength of 8.8 ± 1.8 N/cm to the PP blend substrate.

1. Introduction

The metallization of plastic surfaces is of great interest for various applications [1], such as printed circuits, diffusion barrier coatings, decorative coatings and wear protective coatings. For example, aluminum coated foils are used for food packaging, copper plated housings shield computers from electromagnetic radiation and precious metals are layered on jewels for finishing [2]. Several techniques such as physical–chemical vapor deposition, metal-powder coating and electroless plating have been proposed to metalize polymer substrates [3]. Among these methods, electroless plating has been the most widely used technique, especially in the automotive, aerospace and microelectronics industries [4]. The electroless plating process has several advantages, such as the possibility of a partial coating, flexibility in the plating volume and thickness, automatic monitoring of chemical replenishment and controllability of surface brightness [1]. The conventional electroless plating technique consists of a multistep processes: cleaning or degreasing, chemical etching, seeding of a catalyst for the electroless plating reaction and the electroless plating reaction, as shown in the left-hand side picture of Fig. 1.

In the chemical etching process of conventional electroplating technique, strong oxidative acids such as sulfuric acid or chromic acid roughen the surface of the plastic parts [1]. The surface treatment is needed before metal deposition to ensure stronger metal–polymer adhesion [5]. Because these strong acids are harmful to humans, as well as environments, surface treatment using such strong acids creates one of the major issues in conventional electroless plating processes. In addition to harmful acids, wastewater treatment is another issue to consider because chemical etching and catalyst deposition produce a huge amount of wastewater. From an environmental protection viewpoint, these chemical-etching stages should be eliminated. An electroless metal plating technique that does not require chemical etching is desired as an environmentally benign production process.

Hori et al. [6,7] and our group [8] have been independently developing a so-called supercritical carbon dioxide ($scCO_2$)-assisted electroless plating scheme for polymeric materials, in which no acid is needed for roughening the substrate surface and infusing the catalyst into the polymer substrate. Hori's $scCO_2$-assisted electroless plating method was developed mainly for polymeric fibers. For example, Pd(II) hexafluoroacetylacetonate $Pd(hfa)_2$ was infused into Kevlar® fibers with $scCO_2$ and

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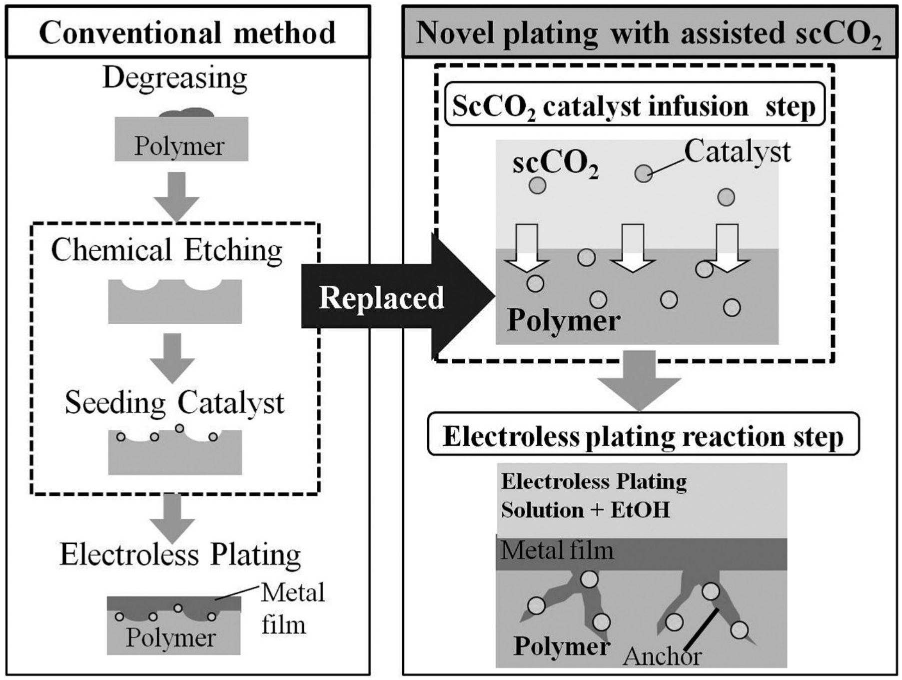

Fig. 1. Schematics of conventional and developed $scCO_2$-assisted electroless plating processes.

simultaneously activated by over-heating to use the complex as a catalyst for the plating reaction [6]. The Kevlar was then immersed in an electroless copper (Cu) plating solution to coat the Kevlar with a Cu metal layer. Hori and co-workers extended their plating technique to other polymeric fibers and studied the effect of thermal treatments on the adhesion strength of the metal to the poly-(p-phenylene terephthalamide) (PPTA), i.e., aramid fibers [7]. In contrast, we developed an electroless plating technique method for extrusion or injection molded-plastic parts, especially those based on Polyamide 6 (PA6) [8]. The method consisted of two steps, as illustrated in the right hand side picture of Fig. 1: the first step was the $scCO_2$-assisted impregnation of the substrate with a catalyst precursor, Pd(hfa)$_2$, and the second step was an electroless nickel–phosphorus (Ni–P) plating reaction. In the first step, the $scCO_2$ was used as a solvent for the catalyst precursor and a plasticizer to soften the surface of the polymeric substrates. The catalyst precursor was dissolved in $scCO_2$, and the substrate was exposed to the $scCO_2$, impregnating the substrate with the catalyst precursor. Then, the precursor was thermally reduced [9]. One of the differences between our method and the approach used by Hori's group [6,7] was the addition of alcohol in the plating solution to further soften the polymeric substrates during the electroless plating reaction. With the addition of alcohol, our method could achieve strong adhesion of the metal film to the polymer.

Sone's group [10] developed a new electroplating technology for metallic parts in which an electroplating solution was emulsified with a non-ionic surfactant and $scCO_2$. Their investigation studied the effects of dense CO_2 on the formation of a Ni film and found that the low viscosity of dense CO_2 and its miscibility with hydrogen made the surface of the plated Ni-film smooth and uniform [11]. Later, their research group applied a $scCO_2$-emulsification technique to the electroless plating of a polymer [12–14]. Their group has also reported that performing a palladium (Pd)-bis(acetylacetonate)-catalyzed reaction in $scCO_2$ influenced the electroless plating mechanism on the PI substrate. Finally this laboratory further extended their plating method to a polymer/metal-hybridized substrate and prepared a functionally graded Pd/γ-alumina composite membrane [15].

We previously observed that a Ni–P metal–polymer composite layer was formed between the metal layer and the polymer matrix during the electroless plating reaction and concluded that the thicker composite layer provided stronger adhesion between the metal layer and the polymeric substrate. Moreover, we speculated that the higher mass transfer rate of the plating solution into the polymeric substrate could increase the metal–polymer composite layer thickness and the adhesive strength of the metal layer to the polymer. Because the major ingredient in the plating solution is water, the mass transfer rate of the plating solution into the polymer substrate was strongly affected by the hydrophilicity or moisture content of the polymer. Unfortunately, most polymers are highly hydrophobic; thus, our method has been limited to polymers with a moderately high water absorption rate, such as poly(methyl methacrylate) (PMMA) or PA6 [8].

Polypropylene (PP), acrylonitrile–butadiene–styrene (ABS) and other polyolefin resins have increasingly been used for automotive applications; thus, there is great interest in applying this newly developed and environmentally benign electroless plating technique to these polymers. The contact angle between PA6 and water is only 69.2° [16]. On the other hand, the contact angle between PP and water is ranging between 87.5° and 116.2° [17–19]. Due to the higher degree of hydrophobicity, the PP substrate was barely metalized by our novel electroless Ni–P metal plating method. The electroless plating reaction occurs only on the surface of the PP substrate because the initial electroless-plated metal layer prevents the plating solution from penetrating further inside the polymeric substrate. This mechanism prevents the metal–polymer composite layer from forming inside the substrate. Thus, there was less of an anchor effect, and the adhesive strength of the metal layer to the polymeric substrate was reduced [8].

The surface of the PP substrate, as well as those of other highly hydrophobic polymers, must be modified by a hydrophilic surface treatment to perform our electroless plating method. So far, various techniques have been employed to modify the hydrophilicity of the polymer surface such as flame treatment [20], corona discharge [21], plasma treatment [22], mechanical abrasion and wet-chemical treatment [23]. Green et al. [24] have investigated