# Supercritical Fluid-Assisted Electroless Metal Plating onto Aramid Films: The Influence of Thermal Treatment

**Magali Belmas,[1] Isao Tabata,[2] Kenji Hisada,[1] Teruo Hori[1]**

[1]*Graduate School of Engineering, Fiber Amenity Engineering Department, University of Fukui, 3-9-1 Bunkyo, Fukui 910-8507 Japan*
[2]*Technical Department, University of Fukui, 3-9-1 Bunkyo, Fukui 910-8507, Japan*

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**ABSTRACT:** Although the production of electro-conductive aramid fibers is efficient, the method needs to be modified before it can be applied to aramid films. Whereas impregnation of an aramid film with a metal complex using supercritical $CO_2$ is achievable, the relatively low adhesion strength of the metal layer applied using electroless copper plating is problematic. To solve this problem, thermal treatment was conducted before, after, or both before and after electroless plating. The rationale for using thermal treatment to improve the adhesiveness of the plated layer was based on the findings that (1) an aramid film contains a significant amount of water (about 3.5 % w.o.f.), which might have a negative impact on adhesion; and (2) because an impregnated metal complex liberates metal catalyst by thermal decomposition during impregnation, a supplementary thermal action might liberate more catalyst and thereby improve adhesion. We found that thermal treatment improved adhesion of the metal layer to the aramid film. Moreover, we discovered that with respect to electroless copper plating, a short time-lag was crucial to obtaining a thin and homogeneous metal layer with strong adhesion. In addition, we demonstrate the affinity of an aramid film for $Pd(acac)_2$. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 119: 2283–2291, 2011

**Key words:** supercritical carbon dioxide; thermal treatment; electroless copper plating; organometallic complex; aramid film

## INTRODUCTION

In recent times, the metallization of polymers has been the subject of intensive studies.[1] Many polymers are used as substrates, including polyimides,[2] polyamides,[3] and polytetrafluoroethylene.[4] However, although aramid fibers are commonly used,[5] the use of aramid films for metallization has not been investigated thoroughly.

Supercritical carbon dioxide (sc-$CO_2$) is currently used as a pretreatment for plating.[6] It has low viscosity, high diffusivity, and is nonflammable and nonreactive under most conditions, and it has a low cost. It is also noteworthy that sc-$CO_2$ is environmentally advantageous in that it avoids water wastage, has no remnant at the end of the treatment process, and is totally recyclable.[7] These features make it a perfect replacement for organic solvents. Another reason to use sc-$CO_2$ in our process is its multiple effects on polymers—it plasticizes and most importantly, swells polymers, thereby ensuring that they accept solutes (mainly organometallic complexes) into their matrixes.[8] More specifically, in the case of aramid fibers, the organometallic complexes are palladium bis-hexafluoroacetylacetonate ($Pd(hfa)_2$)[9] and palladium bis-acetylacetonate ($Pd(acac)_2$).[10] The impregnation of an organometallic complex ensures the presence in the polymer of a catalyst, which reacts with the electroless copper plating solution to generate a metal layer on the surface of the film. In this study, the catalyst used is Pd.

Electroless copper plating was chosen as a replacement for plasma activation, laser irradiation, and ion beam irradiation,[11–13] which are inefficient processes for introducing surface modifications to the substrate, and which are needed to ensure strong adhesion between the polymer and plated layer. In addition, electroless copper plating is more environmentally friendly than these previously used methods for plating substrates, because the amount of waste water is decreased considerably. However, in the case of aramid films, the improvement conferred by electroless copper plating in terms of adhesion effectiveness is not sufficient to guarantee a strong bond between the polymer and the copper layer. Therefore, the original idea for this study was to add a thermal treatment to the process. As reported by Cayuelan et al.,[14] thermal treatment is commonly used in the textile industry to obtain the required dimensions, although thermal treatment also influences the crystallinity of a polymeric substrate.

*Correspondence to:* M. Belmas (belmasmagali@hotmail.com).


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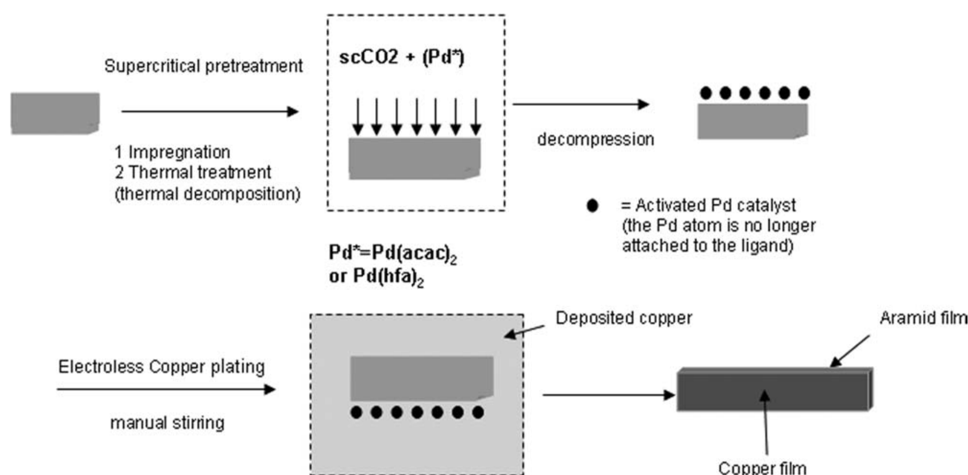


**Figure 1** Schematic diagram illustrating the processes of supercritical pretreatment (impregnation and thermal treatment, decompression, and electroless deposition of copper onto aramid films by magnetic stirring).

In this study, we focused on the influence of organometallic complex impregnation of an aramid film and determined the optimal conditions for thermal treatment. Thus, we establish the conditions for electroless copper plating onto aramid films.

## EXPERIMENTAL

### Materials

The aramid film (thickness of 16 μm) was provided by Teijin Advanced Films (Osaka, Japan). The $CO_2$ (purity: +99.99%) was purchased from Uno Sanso Co., Ltd (Fukui, Japan) and used as received. $Pd(acac)_2$ was purchased from Tokyo Chemical Industry (Tokyo, Japan), and $Pd(hfa)_2$ was purchased from Sigma-Aldrich (Tokyo, Japan); both were used without further purification. The electroless copper plating solutions were ATS-ADDCOPPER IW-A, ATS-ADDCOPPER IW-M, and ATS-ADDCOPPER IW-C (Okuno Chemical Industry Co. (Tokyo, Japan)).

### Method

The processes of supercritical pretreatment, impregnation of the Pd complex, and electroless deposition of copper onto the aramid fibers by magnetic stirring are shown schematically in Figure 1. The experimental conditions are listed in Table I.

#### Supercritical pretreatment

All experiments were performed in a batch-type supercritical extractor (SFE System 2000; ISCO). A simplified scheme of the experimental apparatus is shown in Figure 2.

The aramid film was cut into 1.5 cm × 5.0 cm pieces. Sample impregnation was conducted in a 10-$cm^3$ sample cartridge that was sealed with two plugs, one at the entrance for sc-$CO_2$ and the other at a high-pressure needle valve. The cartridge was setup as follows: at the bottom was placed a glass filter; above this, was placed the sample; followed by two glass filters with a specific amount of organometallic complex between the filters. The complex was introduced in large excess relative to the average solubility of the metal complex and the amount absorbed by the aramid film.

When the thermoregulated heater reached 150°C for both complexes, the cartridge was inserted, and treatment was conducted for 3 hours for $Pd(acac)_2$ or for 30 minutes for $Pd(hfa)_2$. The temperature and pressure of impregnation were kept constant for the duration of the treatment. When impregnation was finished, the cartridge was decompressed by releasing the $CO_2$ followed by extraction from the heater.

**TABLE I**
**Experimental Conditions**

| Metal complex impregnation using sc-$CO_2$ | Thermal treatment | Electroless copper plating | Thermal treatment |
|---|---|---|---|
| 150°C, 15 MPa, 1.5 cm × 5.0 cm<br>$Pd(C_5H_7O_2)_2$:<br>12 % w.o.f., 3 hours<br>$Pd(C_5HF_6O_2)_2$:<br>12% to 55% w.o.f., 30 minutes | 60°C to 200°C, 2 to 60 minutes | 42°C or 45°C, 40 seconds to 15 minutes | 60°C to 200°C, 2 to 60 minutes |

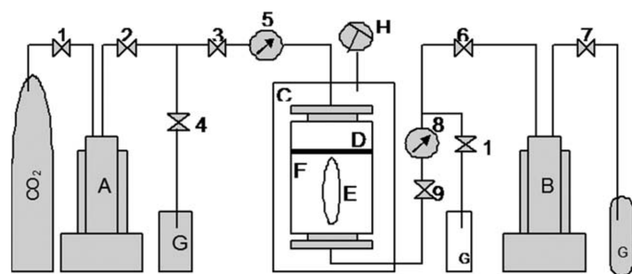


**Figure 2** Illustration of the reaction apparatus. (A) Syringe pump; (B) cleaning pump; (C) heater and high-pressure stainless-steel vessel; (D) organometallic complex; (E) sample; (F) sample cartridge; (G) washing solvent; (H) thermometer; (I) glass filter; (1, 2, 3, 4, 6, 7, 9, 10) valves; and (5, 8) pressures gauges.

### Thermal treatment

Thermal treatment was performed in a GC-12A Shimadzu gas chromatograph oven in air atmosphere. The sample was placed in a covered beaker and placed in the oven once the desired temperature was reached. When the treatment was finished, the sample was removed from the oven; subsequent steps were performed after the sample had cooled to room temperature.

This treatment was performed before, after, or both before and after electroless copper plating. The experiments were conducted over a temperature range of 60°C to 200°C and with duration of treatment that ranged from 2 minutes to 60 minutes.

### Electroless copper plating

The electroless plating method was used for the metal plating process. The electroless copper plating solution was created by adding 10 mL ATS-ADD-COPPER IW-A to 172 mL deionized water, followed by the addition of 16 mL ATS-ADDCOPPER IW-M and 2 mL ATS-ADDCOPPER C. The impregnated aramid film was dipped in the electroless copper plating solution at 42°C or 45 ± 2°C until a homogeneous metal layer was plated onto its surface or until the metal layer began to peel off. To achieve proper mixing and to avoid damaging the sample, the solution was stirred manually.

### Analyses

The adhesive strength of the plated metal layer after electroless copper plating was evaluated by the cellophane tape method.[15] The thickness of the plated metal layer was measured with a thickness measurement gauge at five different sites on the film, and the average thickness was calculated.

X-ray Photoelectron Spectroscopy (XPS) and Scanning Electron Microscopy (SEM) were conducted on samples with the most homogeneous and strongest metal layers. For XPS, the ULVAC Φ5500 spectrometer with Mg-$K_\alpha$ excitation was used with settings of 100 μmφ, 300 W, and 15 kV under a vacuum pressure of $1 \times 10^{-8}$ Pa. Before the XPS analysis, each sample was placed in a vacuum oven at 40°C for a minimum of 12 hours. SEM was conducted with the Hitachi S-2600H microscope at an accelerating voltage of 15 kV. Because the samples analyzed after impregnation were not conductive, they were coated with Pt/Pd alloy using the Coater E-1030 Ion Sputter. Regarding the samples that underwent electroless copper plating, their copper surfaces were sufficiently conductive to allow analysis without the need for coating.

## RESULTS AND DISCUSSION

### Impregnation of metal complexes

To identify the ideal complex for impregnation of an aramid film, two complexes were tested: $Pd(acac)_2$ and $Pd(hfa)_2$. Previous experiments showed that for $Pd(acac)_2$, a concentration of 12% weight of fabric (w.o.f.) was optimal. Therefore, this concentration was used initially for the impregnation of $Pd(hfa)_2$. However, the first results showed that the quantity of Pd catalyst impregnated into the aramid film was not sufficient to guarantee a homogeneous metal layer after electroless copper plating. Thus, it was necessary to increase the amount of $Pd(hfa)_2$ to 55% w.o.f., to obtain results similar to those obtained with $Pd(acac)_2$. Regarding the other experimental conditions, the pressure and temperature values were identical to those used previously, whereas the time of impregnation had to be set individually for each complex, i.e., 3 hours for $Pd(acac)_2$ and 30 minutes for $Pd(hfa)_2$.

The XPS analysis (Fig. 3) was conducted to determine whether the complexes were completely decomposed to Pd metal or only partially degraded, in which case a mixture of Pd metal and Pd complex would be impregnated into the films. A doublet peak corresponding to the Pd[16] was observed at 336 BE and 342 BE, corresponding to the $3d_{5/2}$ and $3d_{3/2}$ layers, respectively. The presence of a peak at 336 BE suggests that the aramid films are impregnated with the Pd metal. Moreover, comparison of the spectra for $Pd(acac)_2$ and $Pd(hfa)_2$ indicated that the amount of Pd impregnated into the aramid film was 7-fold higher for $Pd(acac)_2$ than for $Pd(hfa)_2$ (Fig. 4), even after the concentration was increased to 55% w.o.f. These results indicate that the aramid film has higher affinity for $Pd(acac)_2$, even though $Pd(hfa)_2$ is much more soluble in sc-$CO_2$ than $Pd(acac)_2$. It is interesting to note that this affinity pattern is the opposite of that observed for aramid fibers and ramie fabrics, both of which have higher affinities for $Pd(hfa)_2$.[9,17] $Pd(hfa)_2$ has a very high solubility in

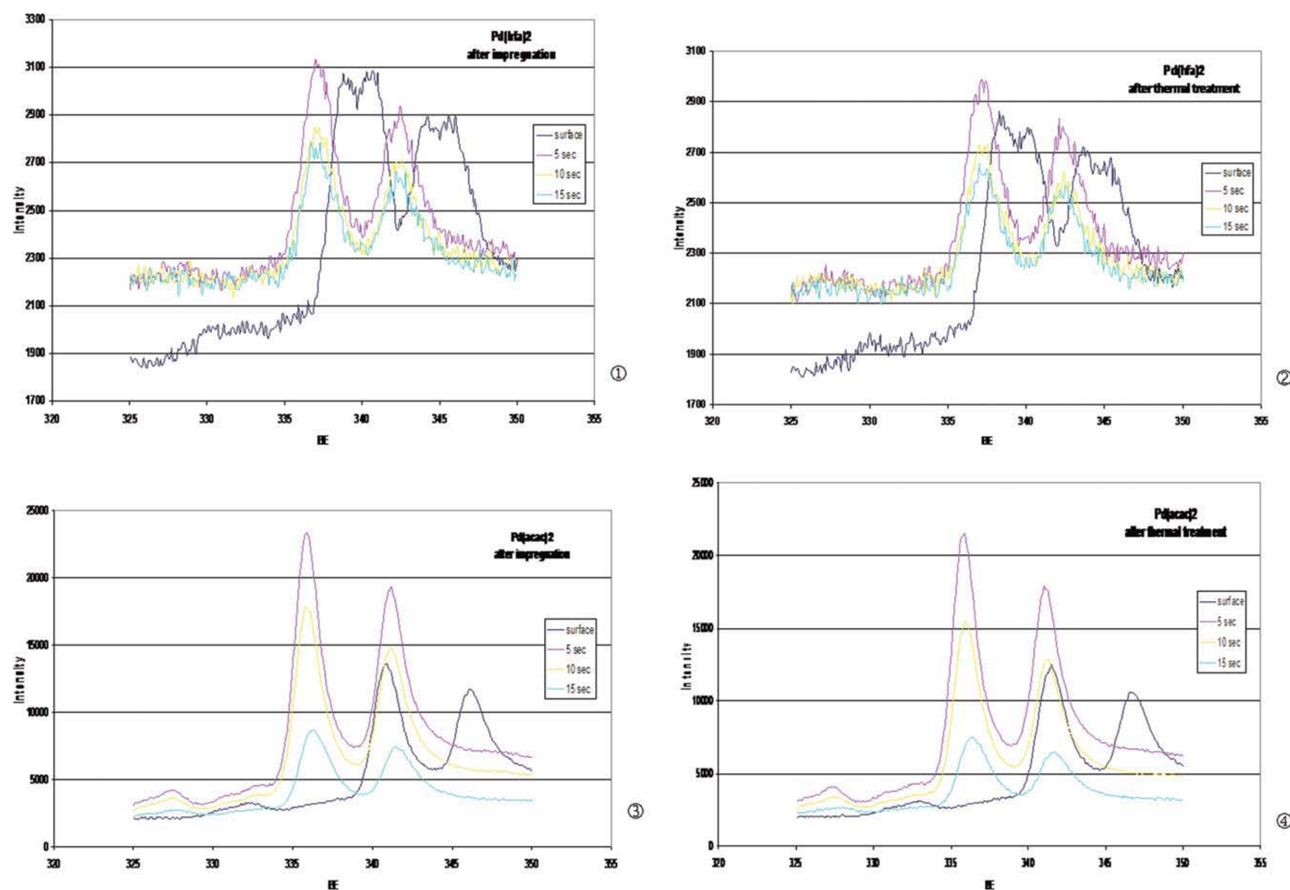


Figure 3 XPS spectra of depth profiles of aramid films impregnated with either $Pd(hfa)_2$ (1, after impregnation; 2, after thermal treatment) or $Pd(acac)_2$ (3, after impregnation; 4, after thermal treatment). The unit for the time of etching is second (sec). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

sc-$CO_2$, therefore it has a lower partition in the polymer phase which means a lower ability to absorb onto polymer phase from supercritical fluid phase.

The XPS analyses were also used to determine the depth profile of Pd impregnated using sc-$CO_2$. The impregnated films were etched three times for 5

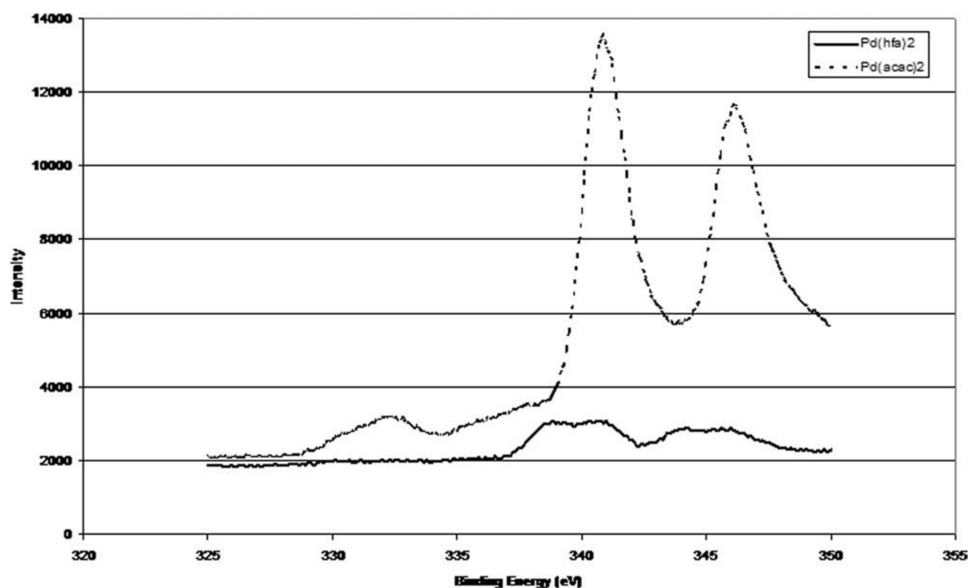


**Figure 4** XPS spectrum showing the relative amounts of Pd impregnated with $Pd(hfa)_2$ and $Pd(acac)_2$.

**TABLE II**
**Optimal Treatment Conditions for the Two Complexes**

| | $Pd(acac)_2$ | $Pd(hfa)_2$ |
|---|---|---|
| Percentage of metal complex for impregnation | 12% w.o.f. | 55% w.o.f. |
| Impregnation of metal complex with sc-$CO_2$ | 150°C, 15 MPa, 3 hours | 150°C, 15 MPa, 30 minutes |
| Thermal treatment | 180°C, 30 minutes | 200°C, 60 minutes |
| Electroless copper plating | 42°C, 40 seconds | 45°C, 40 seconds |
| Thermal treatment | 100°C, 30 minutes | 100°C, 30 minutes |

seconds. For both complexes, the Pd doublet corresponding to the film surface was shifted to a higher energy level; this phenomenon corresponded to charge-up of the surface of the film. The amount of Pd impregnated was lower at the surface, increased after the first etching, and decreased with subsequent etchings. This profile is characteristic of polymer films. From the depth profiles, we conclude that the impregnation of Pd is efficient even to a relatively great depth. This may explain the observed improvement in the adhesion of the metal layer. We hypothesize that the Pd is impregnated deep into the film, so that when the layer is plated, the layer and the film create a network that is anchored deep within the film, thereby ensuring stronger adhesion between the plated layer and the aramid film.

## Electroless copper plating

As a starting point for this study, the conventional method for electroless copper plating[9] was used. Indeed, the solution was heated to 42 ± 2°C and the impregnated films were dipped in it for 15 minutes. The films impregnated with $Pd(acac)_2$ were plated with a homogeneous, shiny, copper-colored layer, although the level of copper on the surface was too high (up to 35% w.o.f.) to allow strong adhesion between the plated layer and the film. The bonds between these components were not sufficiently powerful. Moreover, conventional electroless copper plating was not efficient for samples impregnated with $Pd(hfa)_2$, and it was not possible to obtain a homogeneous layer at the film surface even when the concentration of metal complex was increased to 55% w.o.f. As mentioned above, because of the high partition of $Pd(hfa)_2$ in sc-$CO_2$, the impregnation ratio of Pd metal into aramid film is low. It is, then, more difficult for the copper ions to have contact with Pd metal and therefore, the catalytic role of Pd metal is not involved in the reaction. As a result, the plating of films impregnated with $Pd(hfa)_2$ could not be homogeneous.

**TABLE III**
**Summary of Processes for Increasing Adhesion Strength**

| **Adhesion** **$Pd(acac)_2$** $Pd(hfa)_2$ | | **Temperature of thermal treatment before electroless plating (°C)** | | | | | |
|---|---|---|---|---|---|---|---|
| | | × | **60** | **100** | **150** | **180** | **200** |
| **Temperature of thermal treatment after electroless plating (°C)** | × | ××<br>×× | ××<br>×× | ×<br>×× | ××<br>×× | ○<br>×× | ××<br>×× |
| | **60** | ××<br>×× | ××<br>×× | | | | |
| | **100** | ××<br>×× | | ×<br>×× | ○<br>×× | ○○<br>×× | ○<br>○ |
| | **150** | ×<br>×× | | | ×<br>×× | | |
| | **180** | ×<br>×× | | | | ××<br>×× | |
| | **200** | ××<br>○○ | | | | | ○○<br>○○ |

○○, Very good; ○, good; ×, poor; ××, very poor.

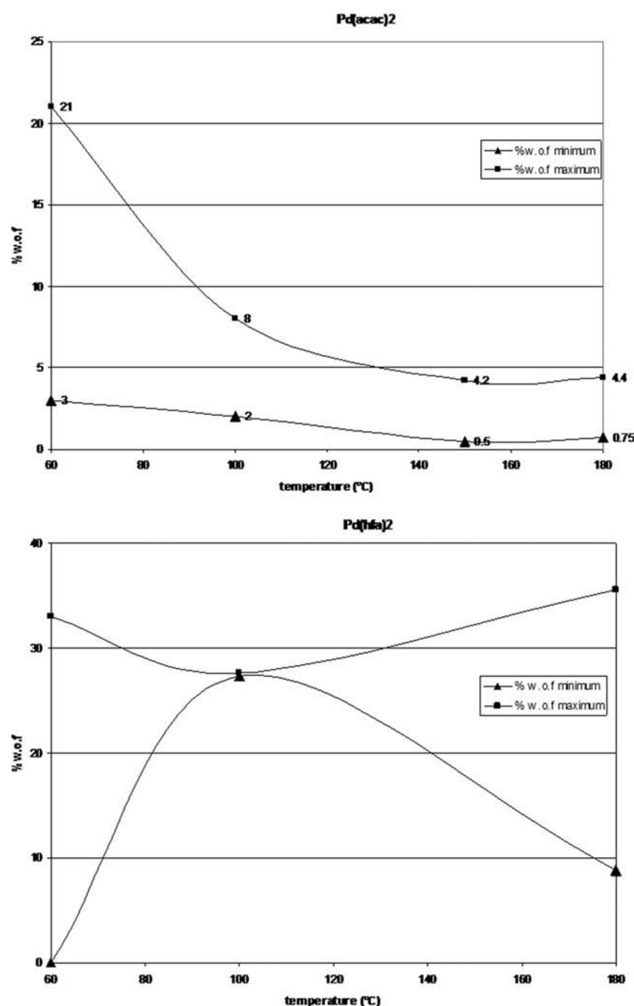


**Figure 5** Percentage of copper plated by electroless copper plating relative to the temperature used in the thermal treatment. 1, $Pd(acac)_2$; 2, $Pd(hfa)_2$. (Triangle marks: representation of the minimum amount of copper plated in w.o.f; square marks: representation of the maximum amount of copper plated in w.o.f).

The first adaptation to the traditional method of electroless copper plating involved the duration of treatment. It was observed that for films impregnated with $Pd(acac)_2$, the copper layer was spread homogeneously on the aramid film surface after a short time of dipping, i.e., 40 seconds. The thickness of this plated metal layer was about 0.25 μm on each side of the film. This thickness was doubled after 5 minutes of electroless plating and reached 2 μm after 15 minutes of treatment. Regarding $Pd(hfa)_2$, the copper layer was 3-fold thicker (0.75 μm) than that obtained for films impregnated with $Pd(acac)_2$ after 40 seconds of electroless copper plating, although the plated layer lacked homogeneity. After 15 minutes of treatment, the layer thicknesses for the samples treated with either complex were similar. Therefore, electroless copper plating starts faster with $Pd(hfa)_2$, but it is necessary to increase the temperature of the electroless plating solution to 45°C to decrease the time-lag to 15 seconds and to obtain homogeneous plating with $Pd(hfa)_2$. In contrast, the homogeneity of the metal layer thickness is better when the film is treated with $Pd(acac)_2$. By increasing the temperature of the plating solution, the movement of copper ions in the solution was speed up and therefore improves the probability of contact between Pd metal impregnated in aramid films and copper ions in the plating solution. Consequently, the plating started as soon as the films were dipped and led to a homogeneous copper layer.

As reported previously,[18] the main consideration in maximizing the adhesion of the plated layer is to use as short a time-lag as possible. In our case, under the treatment conditions listed in Table II, a time-lag of 15 seconds was assessed for both complexes. Thus, a thin metal layer was plated that had sufficient adhesion to pass the cellophane tape test (i.e., no metal was peeled off by the tape) (Table III).

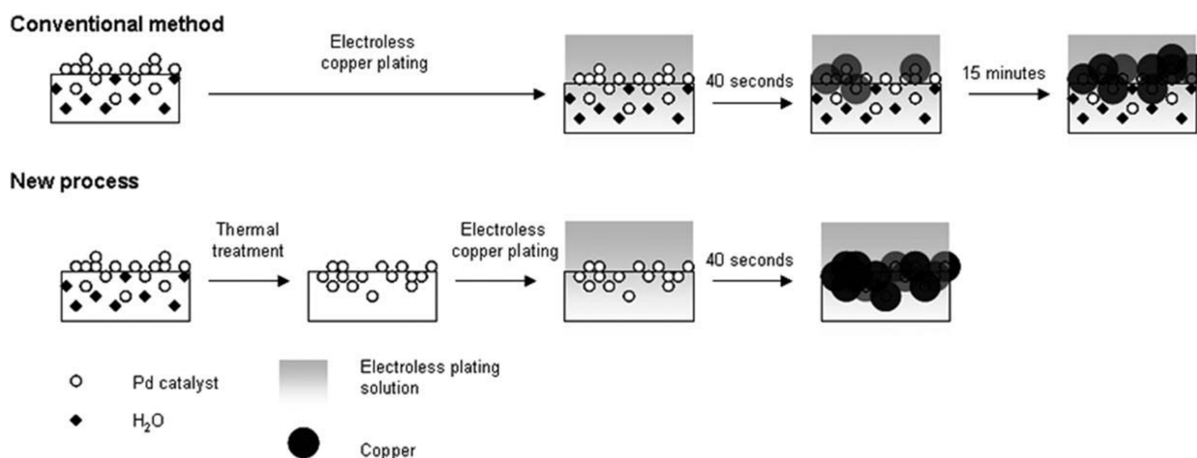


**Figure 6** Schematic representation of the differences between the conventional method and the novel process described in this study.

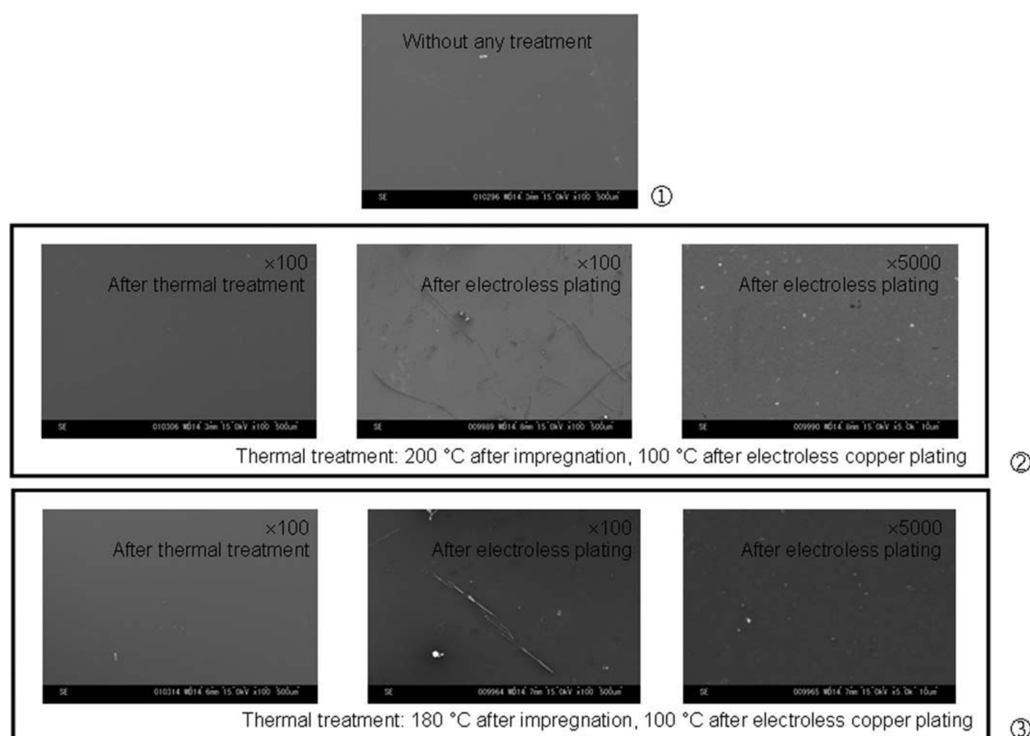


**Figure 7** SEM images of aramid films before any treatment φ), and aramid films impregnated with $Pd(acac)_2$ (κ) or $Pd(hfa)_2$ (λ) under various conditions.

Nevertheless, if the level of copper plated onto the film was >5% w.o.f., the adhesion of the layer was deteriorated (Fig. 5); as the layer thickened, adhesion became worse. Because the water normally contained in the aramid film was evaporated by the thermal treatment, it was easier for the electroless plating solution to reach the Pd catalysts impregnated deep in the film (Fig. 6). This led to faster plating and generated a thin and homogeneous metal layer.

Even though the visual check and measurement of the thickness of the metal layer plated onto the aramid film showed that the layer was homogeneous, SEM images were captured before and after electroless copper plating (Fig. 7). The surfaces of the aramid films without treatment and after thermal treatment were smooth. No impurity or defect was found in the aramid films, although it is possible that the coating was of sufficient thickness to conceal chemical or physical impurities. The images of the metal layer surfaces revealed some impurities and scratches. However, those marks were sporadic and therefore not typical of the whole surface. The SEM analysis confirms that the new experimental conditions generate a homogeneous metal layer on the surface of the aramid film and that this is true for both complexes. Regarding the sensitivity of SEM device, it was not possible to detect Pd particles impregnated into aramid films. Thus, those particles are nanosize, around 2 to 5 nm for one particle of Pd.

## Thermal treatment

The idea of adding a thermal treatment to the process of plating an aramid film was based on two premises. The first premise was that an aramid film contains water, and this water may have a negative

**TABLE IV**
**Percentages of Water Content Evaporated by Thermal Treatment of Non-treated Aramid Films**

| Time of thermal treatment | Temperature of thermal treatment | | | | |
|---|---|---|---|---|---|
| | 60°C | 100°C | 150°C | 180°C | 200°C |
| 30 minutes | 1.0% | 2.6% | 2.2% | 2.8% | 3.4% |
| 60 minutes | 1.3% | 2.6% | 2.8% | 2.8% | 3.3% |
| 180 minutes | 1.6% | 2.5% | 2.4% | 2.8% | 3.0% |

The % symbol refers to the percentage w.o.f.

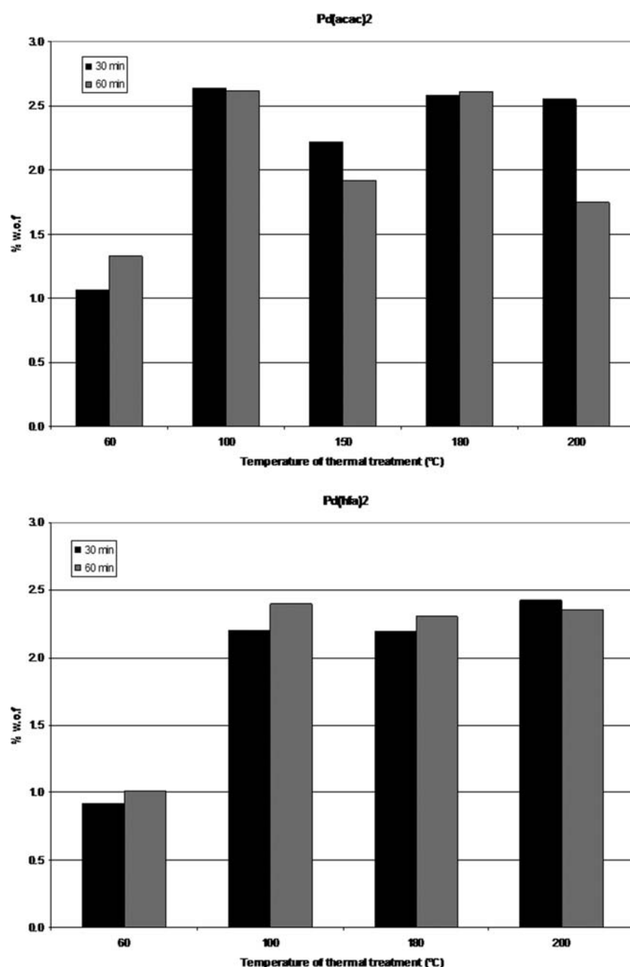


**Figure 8** Weight loss resulting from thermal treatment [1, $Pd(acac)_2$; 2, $Pd(hfa)_2$].

impact on the adhesion of a metal layer. Investigations of this specific aspect (Table IV) revealed that the films contained an average of 3.0% w.o.f. water. These results were obtained by heating nontreated aramid films in the same oven used for the thermal treatment as part of the process. Then, the amount of water evaporated by the last thermal treatment in the process was measured (Fig. 8), which showed that the majority of the water was evaporated by the thermal treatment, with the consequence that adhesion was improved significantly. The second premise was that because metal complexes become unstable on heating, an additional heat treatment might liberate more Pd metal, thereby accelerating the electroless copper plating so as to improve both the adhesion and homogeneity of the plated layer. XPS analysis (Fig. 3) was used to determine the chemical composition of the metal complex once it was impregnated into the films. Comparing the profiles before and after thermal treatment showed that there were no differences regarding chemical composition: and partition of the Pd metal and Pd complex was present to the same extent in both cases. Thus, thermal treatment does not change the composition of the impregnated material.

Regarding the experimental conditions, Table III shows that adhesion was improved more significantly when the thermal treatment was applied both before and after electroless copper plating. Moreover, increasing the temperature fastened the electroless copper plating (Fig. 9). However, the changes in temperature did not affect the samples treated with $Pd(acac)_2$ and $Pd(hfa)_2$ to the same extents. Indeed, a temperature of 150°C was required for the samples treated with $Pd(hfa)_2$ to produce a notable decrease in the time of electroless copper plating, whereas a temperature of only 100°C was necessary for the samples treated with $Pd(acac)_2$ to produce a decrease in the time of electroless copper plating. Based on those observations, we conclude that thermal treatment before electroless copper plating needs to be conducted at a higher temperature, i.e., 200°C for $Pd(hfa)_2$ and 180°C for $Pd(acac)_2$. The higher temperature might cause swelling of the aramid film to such an extent as to generate a space large enough for the Pd catalyst present on the surface to enter the polymer matrix (Fig. 6). The aramid polymer is mainly plasticized during the thermal treatment done before electroless copper plating. Indeed, the temperature is high enough (180°C for $Pd(acac)_2$ and 200°C for $Pd(hfa)_2$) to reorganize the

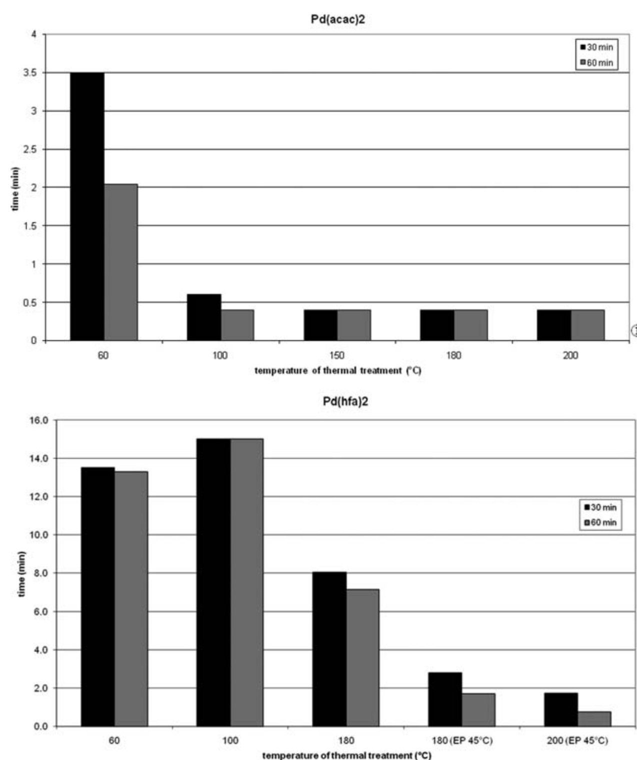


**Figure 9** Duration of electroless copper plating in relation to thermal treatment temperature [1, $Pd(acac)_2$; 2, $Pd(hfa)_2$].

molecular structure of the films. Between this phenomenon and the space that created the water evaporation, it is possible to conclude that the Pd metal is able to go deeper into the film. Thus, after electroless plating, the metal layer is largely anchored in the film and layer adhesion is stronger. In contrast, a higher temperature (above 180°C) damages the copper layer, even during a short treatment time (1 or 2 minutes). A more appropriate strategy is to treat at 100°C after electroless plating, because under these conditions, the maximum amount of water is evaporated. Therefore, the benefit of thermal treatment is maintained. As shown by the results in Table III, a thermal treatment after electroless plating is necessary to ensure the maximum improvement of the copper layer adhesiveness. Therefore, a single thermal treatment before the metal complex impregnation cannot be appropriate even if it is a significant gain of time and energy. Indeed, if this single treatment is done, the Pd catalyst is not included in the new molecular structure of the films and therefore the efficiency of the electroless copper plating decreases.

## CONCLUSION

This study describes the design of a new process for plating a copper layer with strong adhesion onto an aramid film. We demonstrate that for both complexes used, the films are successfully impregnated with Pd, although the amount of $Pd(hfa)_2$, impregnated is much less than the amount of $Pd(acac)_2$ impregnated. Therefore, unlike aramid fibers, aramid films have greater affinity for $Pd(acac)_2$. The depth profile revealed by XPS analysis indicates that the Pd metal is impregnated deep into the film, which supports the notion that this new process improves adhesive strength. Therefore, for electroless copper plating with $Pd(hfa)_2$, we recommend that the duration of treatment be reduced to 40 seconds and that the temperature of the electroless solution be increased to 45°C. These conditions ensure that the plated copper layer is thinner and more homogeneous. Finally, the addition of two thermal treatments, the first before and the second after electroless copper plating, improves adhesion of the plated copper layer to the aramid film. We believe that the water contained in the aramid film prevents bonding interactions between the copper layer, the Pd catalyst, and the aramid film. Indeed, the improvement of the adhesion strength is due to the combination of two phenomena: molecular restructuration of the polymer matrix and water evaporation. Both phenomena result from the thermal treatments. However, it is still difficult to quantify the relative influence of each phenomena on the improvement of the adhesive property of copper layer on aramid films.

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