



## Special Feature: Materials Analysis

Research Report

### Characterization of the Surface Region of a Cycloolefin Polymer Modified for Electroless Plating

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**■ABSTRACT■** The structure, chemical composition and mechanical properties were investigated for the surface layer of a cycloolefin polymer (COP) film modified with ozonized water and a Pd catalyst for electroless plating. Dynamic secondary ion mass spectrometry and transmission electron microscopy revealed that Pd nanoparticles were dispersed to a depth of 100 nm from the surface of the modified COP. X-ray absorption fine structure analysis clarified that the dispersed Pd catalyst was partially reduced to the metallic form in the modified COP. Depth analysis by infrared spectroscopy confirmed that the surface region to a depth of approximately 100 nm was oxidized by soaking in the ozonized water. The mechanical properties in the direction of depth were measured using a Surface and Interfacial Cutting Analysis System, which revealed that the ductility was decreased at the oxidized surface region compared to that of the bulk polymer. From these results, a mechanism for the formation of the Pd dispersion structure at the surface region of the modified COP was proposed.

**■KEYWORDS■** Cycloolefin Polymer, Electroless Plating, Surface Modified Layer, Transmission Electron Microscope, Dynamic Secondary Ion Mass Spectrometry, X-ray Absorption Fine Structure, X-ray Absorption Fine Structure, Fourier Transformed Infrared Spectroscopy, Dynamic Secondary Ion Mass Spectrometry, Surface and Interfacial Cutting Analysis System

#### 1. Introduction

Polymeric materials in which nanometer sized inorganic particles are dispersed have been expected to be useful for application to various technologies such as photonic devices and electroless metal plating.<sup>(1-2)</sup> It is well known that a nanocomposite layer consisting of a metallic catalyst and a polymeric material, is formed at near the surface of polymeric materials during the electroless plating process of metal on polymer.<sup>(2)</sup> Furthermore, the nanocomposite layer is expected to further affect the plating properties. Therefore, it is important to clarify the structure, chemical composition and mechanical properties of this nanocomposite layer in order to improve the plating properties.

Recently, Yanagimoto and Bessho reported that ozone pretreatment prior to formation of the nanocomposite layer contributes to significant improvement of the adhesion strength of metal plating on plastic without the need for surface roughening with hexavalent chromium acid, which is an environmentally

toxic substance.<sup>(3)</sup> The effect of ozone pretreatment was clarified for the plating properties of Ni on acrylonitrile-styrene copolymer.<sup>(3)</sup>

We report the structure, composition, and mechanical properties of a nanocomposite layer consisting of Pd catalyst formed near the surface of a cycloolefin polymer (COP) film, which has significant low-k characteristics, by modification with ozonized aqueous solution and Pd catalyst dispersion for electroless plating application. Furthermore, we describe the formation mechanism of nanocomposite layer.

#### 2. Experimental

##### 2.1 Materials and Surface Modification

A COP film was used as a polymeric support material for a metallic catalyst. The chemical structure of a typical COP is shown in **Fig. 1**. The polymer film was ozonated by immersion in 40 ppm ozonized water for 24 min, followed by immersion into a Pd catalyst dispersed solution. The polymer film supporting the

Pd catalyst was subsequently immersed into a reducing aqueous solution for activation of the Pd catalyst.

## 2.2 Characterization

The dispersion state of the Pd catalyst nanoparticles was evaluated by transmission electron microscopy (TEM; Jeol JEM-2000EX, 200 kV) and dynamic secondary ion mass spectroscopy (DSIMS; Ulvac-Phi 6650). A Au layer was prepared on the surface of the TEM samples for clear identification of the surface. DSIMS measurement was performed to obtain depth profiles of Pd using a  $\text{Cs}^+$  ion beam with an impact energy of 2 keV.

The structure of the Pd catalyst in the modified layer was estimated by X-ray absorption fine structure (XAFS) measurement. The Toyota Beam line (BL33XU) at SPring-8 was used as the X-ray source. The modified layer sample for XAFS measurement was concentrated as an insoluble residue from the modified polymer film by dissolving the unmodified part with cyclohexane.

The chemical structure of the surface region of the modified polymer was evaluated using Fourier transform infrared spectroscopy (FT-IR; Thermo Nicolet Avatar 360) with attenuated total reflection (ATR). For depth analysis with a sub-micron step size, a Daipia Wintes Nano Catcher<sup>®</sup> system including reflection FT-IR was used. A schematic illustration of the Nano Catcher<sup>®</sup> system is shown in Fig. 2.

The mechanical properties of the ozonated polymer film were analyzed using a Surface and Interfacial Cutting Analysis System (SAICAS; Daipia Wintes NN-3) with a diamond blade. A schematic illustration of the SAICAS is shown in Fig. 3.

## 3. Results and Discussion

### 3.1 Distribution of Pd in the Surface Region of Modified COP

The cross-sectional structure of the modified COP was observed using TEM to examine the surface region. Figure 4 shows a typical cross-sectional TEM image of a modified COP film that was immersed in a Pd catalyst dispersed solution. Nanoparticles were dispersed to a depth of ca. 70 nm from the surface.

DSIMS measurement was performed to identify the dispersion of elements under the polymer surface. Figure 5 shows a typical DSIMS profile of C and Pd

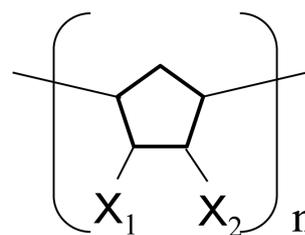


Fig. 1 Chemical structure of a typical COP.

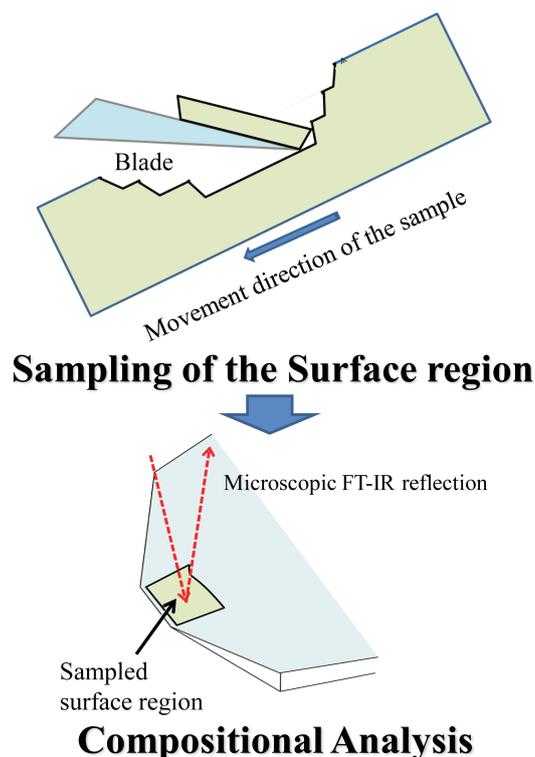


Fig. 2 Schematic illustration of the Nano Catcher<sup>®</sup> system.

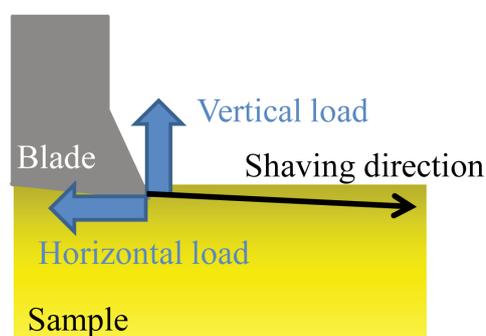
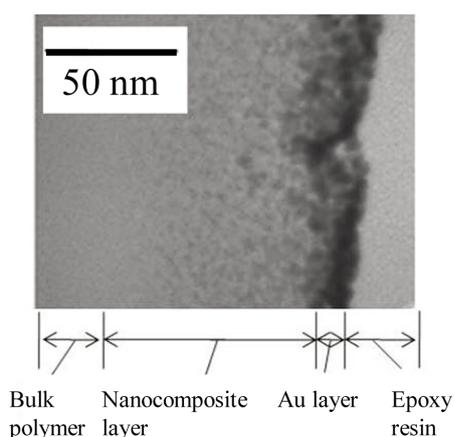


Fig. 3 Schematic illustration of the SAICAS.

ions for the COP film immersed in Pd catalyst dispersion. At first, the Pd intensity increased and then decreased to almost zero, which indicates that the nanoparticles observed by TEM are composed of Pd and these particles were concentrated near the surface of the modified polymer.

### 3.2 Structure of Pd in the Modified Polymer

The chemical structure of Pd in the surface region of the modified COP was evaluated by XAFS measurement. Typical Pd K-edge XAFS Fourier transforms for concentrated samples before and after



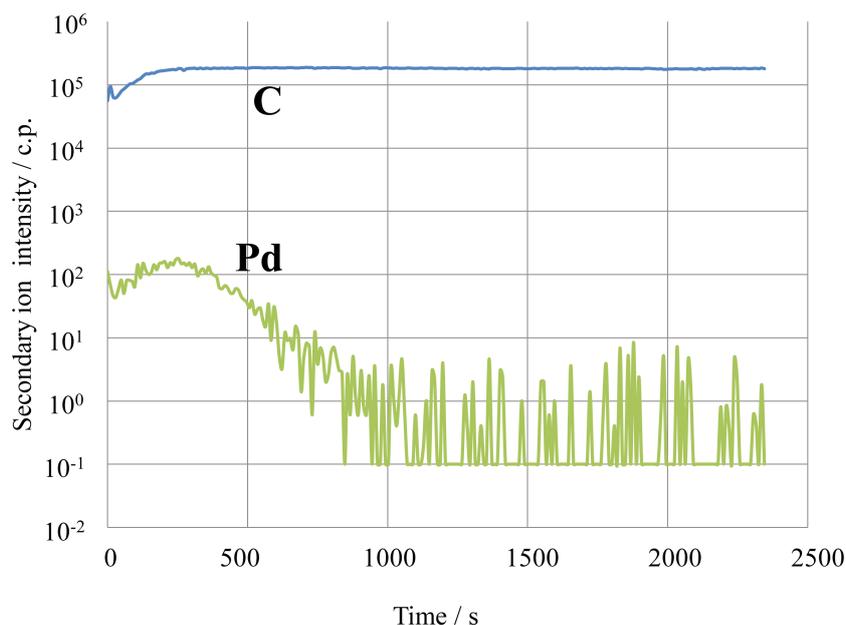
**Fig. 4** Typical cross-sectional TEM image of a COP film modified by immersion into a solution of dispersed Pd catalyst particles.

immersion into the reducing aqueous solution are shown in **Fig. 6**, in addition to that of Pd foil and  $\text{Pd}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$  as reference spectra. Three distinct peaks at 0.16 and 0.25 nm, which correspond to Pd-O and Pd-Pd bonds, respectively, were identified from comparison of the amplitude and phase functions with those of the standards [ $\text{Pd}$  foil and  $\text{Pd}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ ].<sup>(4-5)</sup> The reduction of the concentrated layer was associated with an increasing Pd-Pd bond peak and a decreasing of Pd-O bond peak, which indicates that the Pd catalyst in the surface region of the modified COP was reduced by the activation process. Furthermore, this result confirmed that the Pd catalyst and COP formed a nanocomposite.

### 3.3 Compositional and Mechanical Change of COP by Ozone Pretreatment

The results in previous 3.1 and 3.2 indicate that the nanocomposite structure is formed at the surface region of the modified COP. Changes in the structure and mechanical properties of COP by ozonation treatment were investigated to clarify the mechanism for the nanocomposite formation.

ATR-FT-IR spectra of the (a) unmodified and (b) ozonated COP films are shown in **Fig. 7**. The spectrum of ozonated COP has a peak at  $1710\text{ cm}^{-1}$  from the C=O bond, in addition to peaks originating from CH and  $\text{CH}_2$ , which were also observed for the unmodified COP. This result indicates that the surface of COP was



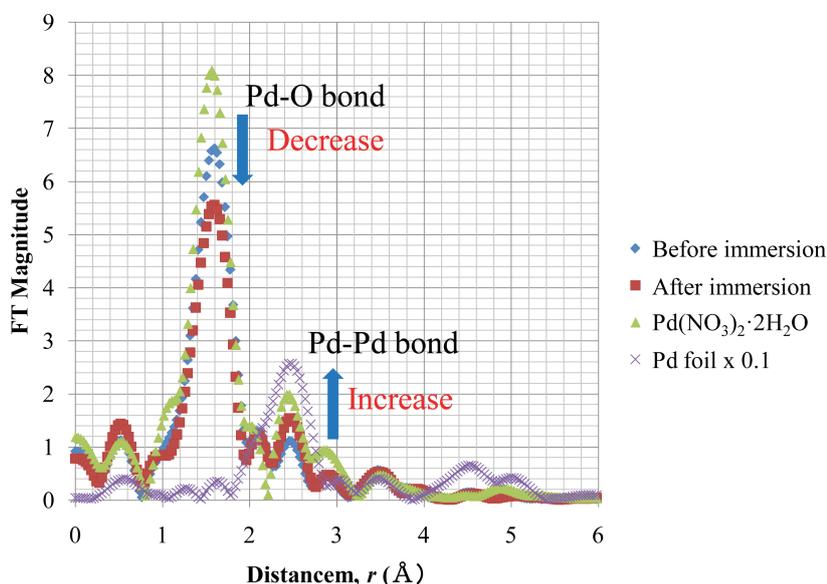
**Fig. 5** Typical DSIMS profile for C and Pd ions in a COP film modified by immersion into a solution of dispersed Pd catalyst particles.

oxidized by ozone treatment.

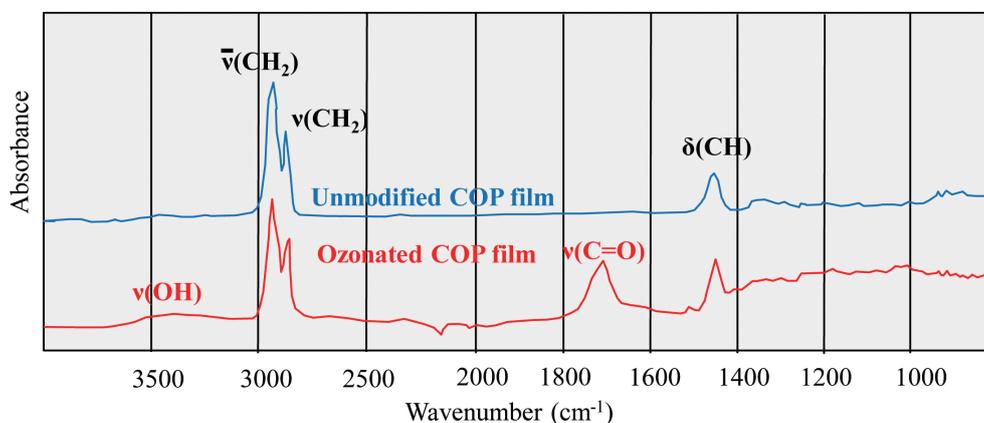
To clarify the depth of oxidation, IR depth analysis in sub-micron steps was conducted using the Nano Catcher<sup>®</sup> system. The sampling depth in one step was set to approximately 100 nm. The peak intensity of the C=O bond formed by oxidation was standardized with the peak at  $1440\text{ cm}^{-1}$  due to  $\delta(\text{C-H})$  of the COP. **Figure 8** shows the depth dependence of the peak intensity of C=O for the (a) unmodified and (b) ozonated COPs. At the first step (from the surface to a depth of 100 nm), the relative intensity of the C=O peak for the ozonated COP was significantly higher than that for unmodified COP. In contrast, the second step (from 100 to 200 nm depth) the C=O peak

intensity of the ozonated COP was only slightly larger than that of the unmodified COP, which indicates that the depth of oxidation by ozone treatment is approximately 100 nm. This depth is approximately the same as the Pd dispersion depth observed by TEM.

SAICAS measurement was performed to evaluate the mechanical properties of the COP surface. **Figure 9** shows the differential lateral drag of SAICAS data for unmodified and ozonated COP films. We have previously reported that a decrease or an increase of differentiated lateral drag corresponds to a decrease or an increase of material hardness, respectively.<sup>(6)</sup> In both cases of the unmodified and ozonated COP, the differentiated lateral drag increased from 0 to 250 nm



**Fig. 6** Typical Pd K-edge XAFS Fourier transform for concentrated sample before and after immersion into the reducing aqueous solution.



**Fig. 7** ATR-FT-IR spectra of (a) unmodified and (b) ozonated COP films.

of analysis depth. However, the blade is slightly tilted. Thus, it is assumed that the cutting edge was not attached in completely on the sample surface within this cutting process between 0 and 250 nm. Therefore, it is presumed that the surface of the sample exist above 250 nm of analysis depth. In the case of the ozonated COP film, a decrease in differentiated lateral drag was observed from an analysis depth of 250 to 350 nm. We assumed that the decrease of lateral drag assign the decrease of ductility. Thus, it suggests that the ductility of the region ca. 100 nm under the surface is decreased compared with that of the bulk polymer. This region can be assigned as the oxidation region observed by FT-IR and the nanoparticle dispersion region observed by TEM.

From these results, it is proposed that oxidation of the COP by treatment with aqueous ozone solution promotes Pd diffusion into the polymer to form the nanocomposite.

#### 4. Summary

(1) DSIMS and TEM measurements clarified that nanoparticles of Pd were dispersed to a depth of 100 nm from the surface of the modified COP.

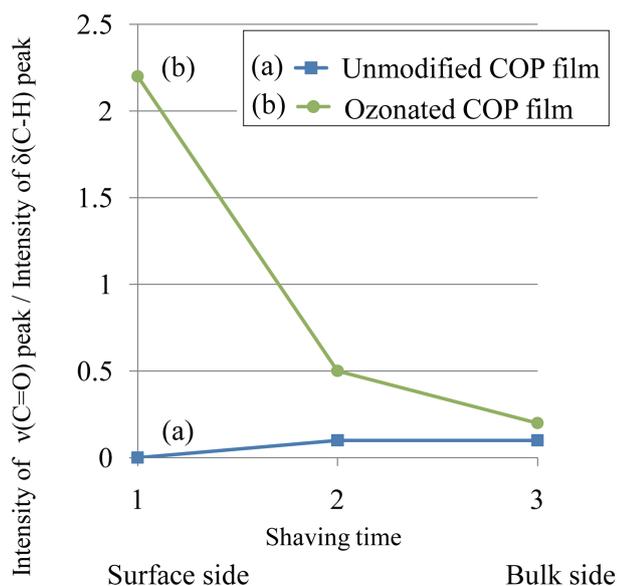
(2) XAFS analysis indicated that the dispersed Pd catalyst was partially reduced to the metallic form in

the modified COP.

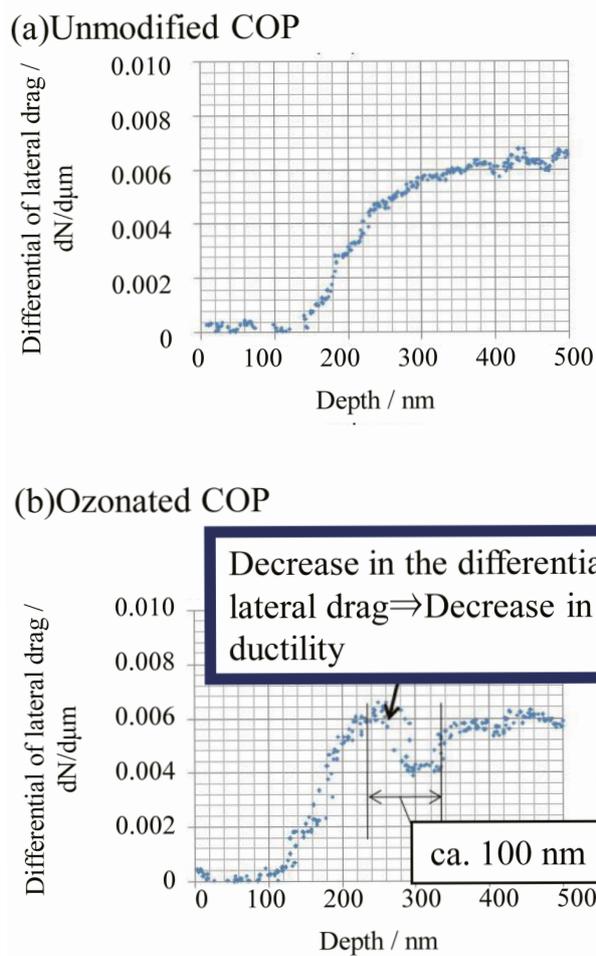
(3) Depth analysis using FT-IR revealed that the region approximately 100 nm from the surface was oxidized by immersion in the aqueous ozone solution.

(4) The mechanical properties in the depth direction measured using the SAICAS confirmed that the ductility was decreased at the oxidized surface region compared with that of the bulk polymer.

These results indicate that Pd metal nanoparticles are dispersed to a depth of 100 nm from the surface of the modified COP film. It is proposed that oxidation of the COP film surface by ozone solution promotes the dispersion of Pd into the surface region of COP film.



**Fig. 8** Depth dependence of the peak intensity of  $\nu(\text{C}=\text{O})$  for (a) unmodified and (b) ozonated COP.



**Fig. 9** Differential lateral drag from the SAICAS data for (a) unmodified and (b) ozonated COP films.

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Figs. 4-6 and 9

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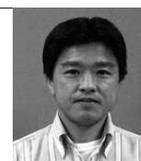
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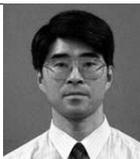
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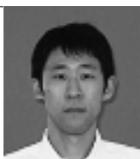


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