

Surface Modification of Thermotropic Poly(oxybenzoate-co-oxynaphthoate) Copolyester by Remote Oxygen Plasma for Copper Metalization

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ABSTRACT: Poly(oxybenzoate-co-oxynaphthoate) (POCO) film surfaces were modified with remote oxygen plasma, and the effects of the modification on the adhesion between the copper layer and POCO were investigated. The remote-oxygen-plasma treatment led to a noticeable decrease in the contact angle, which was mainly due to the C—O functional groups on the surface. The modification of the POCO surface by remote oxygen plasma was effective in improving the adhesion with copper metal. The peel strength for the copper

metal/POCO system was enhanced from 10 to 127.5 mN/5 mm by the surface modification. The failure mode of the copper metal/POCO system was an interface layer between the oxidized micro-POCO fibril surface and the copper metal layer. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 2400–2408, 2003

Key words: surfaces; cold plasma; adhesion; liquid-crystalline polymers (LCP)

INTRODUCTION

Poly(oxybenzoate-co-oxynaphthoate) (POCO) is a main-chain thermotropic liquid-crystal polymer, and it has received considerable academic and industrial attention because it offers an excellent combination of electrical, thermal, mechanical, and chemical resistance properties.^{1–4} In particular, POCO has a low dielectric constant of 3 in the range of 0.5–40 GHz and a low loss factor of approximately 0.004.⁵ Therefore, we believe that POCO may be an outstanding insulator of electrical currents with low and high frequencies (GHz) for the fabrication of high-density printed circuit board and semiconductor packing. For this purpose, the metalization process of POCO sheet surfaces is a basic technique for microelectronic technology.

In this study, we have focused on a composite of POCO and copper metal made through evaporation and electroplating. For a composite to be made, POCO sheet surfaces have to be modified because of their poor adhesion with copper metal. To avoid a loss of the excellent POCO properties, we did not consider wet processes such as grafting for the modification but instead used dry processes such as oxygen-plasma treatment.^{6,7} It is well known that an oxygen plasma can react with a wide range of polymers to produce a variety of oxygen functional groups such as C—O,

C=O, O—C=O, and CO₃ at the surfaces. Furthermore, oxygen atoms in oxygen plasma have the possibility of reacting with aromatic rings in POCO polymers to form phenolic OH groups. However, oxygen ions and electrons in oxygen plasma are troublesome species for the modification because their heavy collision with POCO surfaces leads to the bond scission of ester linkages in the POCO polymer chains. Figure 1 shows possible bond scission reactions on the POCO surface in oxygen plasma. As a result, many degradation products will be formed on the surface. These reactions will never contribute to an improvement of the adhesion because the degradation products act as a weak boundary layer deteriorating the adhesion. On the basis of this concept, we believe that the hydrophilic surface modification of POCO surfaces by oxygen plasma is a key to how oxygen radicals in oxygen plasma interact effectively with POCO surfaces without heavy attacks by oxygen ions and electrons. We chose remote oxygen plasma for the hydrophilic surface modification of POCO. A remote-plasma treatment is different from the conventional plasma treatment with respect to the relative distance of the sample position against the plasma zone. We call conventional plasma treatment the direct-plasma treatment to distinguish it from the remote-plasma treatment. Plasma is a mixture of electrons, ions, and radicals. These species disappear in the process of electron/positive-ion combination, positive-ion/negative-ion recombination, and radical-radical combination. The rate constants of these reactions are in the following

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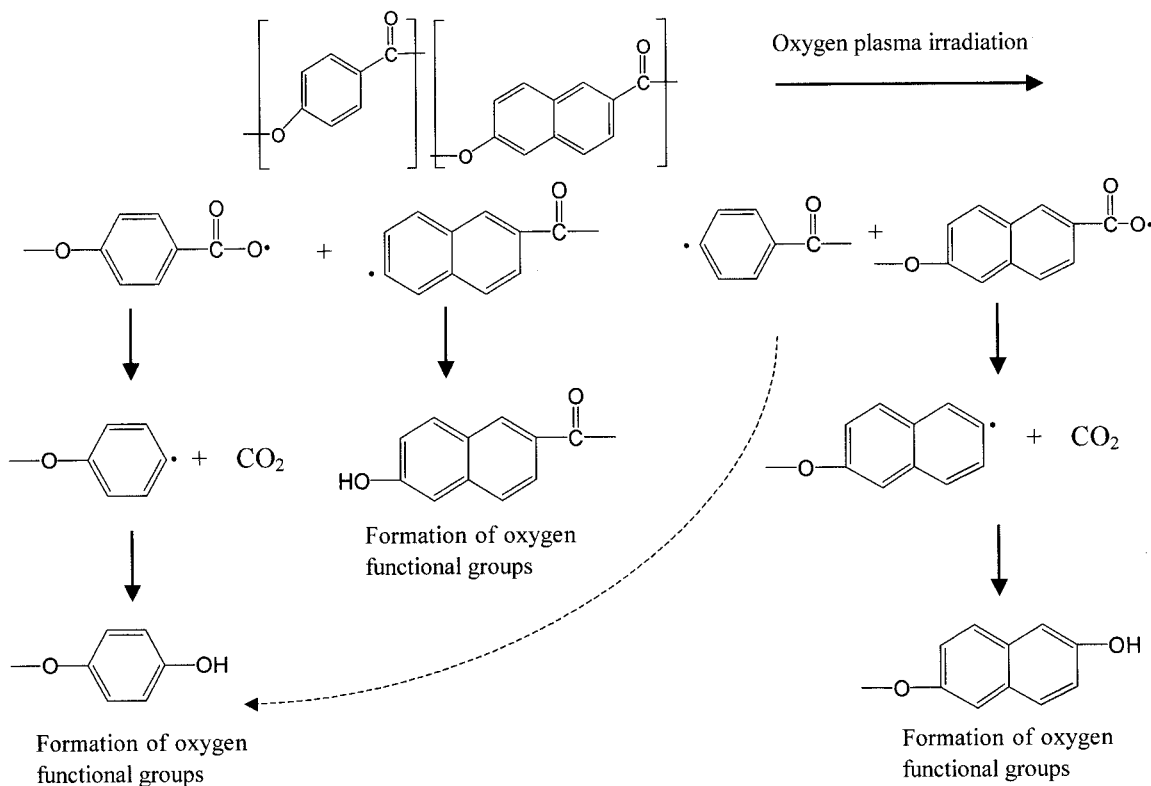


Figure 1 Possible reactions occurring on the POCO film surface in the oxygen plasma.

order: 10^{-7} , 10^{-7} , and 10^{-33} cm^3/s , respectively. Therefore, radicals in the plasma possess a longer lifetime than electrons and ions. As a result, at a position far away from the plasma zone (in the remote-plasma treatment), reactions with radicals occur predominantly, and reactions with electrons and ions scarcely occur. This is an essential difference in the plasma chemistry of the remote- and direct-plasma treatments.⁸⁻¹⁰ From this concept, we chose a remote oxygen plasma as a reagent for the surface modification of POCO, and we investigated how the surface modification of POCO by remote oxygen plasma contributed to the copper metalization of the POCO surface.

EXPERIMENTAL

Materials

A POCO sheet (Vecstar FA; 50 μm thick) was received from Kuraray Co., Ltd. (Japan). Figure 2 shows the chemical structure of POCO. The sheet was cut to 12 mm \times 90 mm and used for surface-modification experiments. Before the surface-modification experiments, the POCO films were washed with acetone in an ultrasonic washer and dried at room temperature *in vacuo*. Oxygen used for the plasma treatment was pure-grade (99.995%).

Remote-oxygen-plasma treatment of POCO films

A special reactor for the remote-oxygen-plasma treatment of the POCO film was used. The details of

the reactor were described previously.¹¹ The reactor consisted of a cylindrical Pyrex glass tube (45 mm in diameter and 1000 mm long) and a columnar stainless steel chamber (300 mm in diameter and 300 mm high). The Pyrex glass tube had two gas inlets for the injection of oxygen and argon gases and a copper coil of nine turns for the energy input of the radio-frequency (rf) power (13.56-MHz frequency). The stainless steel chamber contained a Borcel pressure sensor (model 622, Edwards, England) and a vacuum system consisting of a rotary pump (320 L/min) and a diffusion pump (550 L/s; model YH-350A, Ulvac Co., Japan). The Pyrex glass tube was joined to the chamber with a Viston O-ring flange (Hange, USA). The POCO films were positioned at a constant distance of 800 mm from the center of the copper coil and exposed to the oxygen plasma. First, the air in the reactor was evacuated to approximately 1.3×10^{-2} Pa, and then oxygen, the flow rate of which was adjusted to 10 cm^2 (STP)/min with a

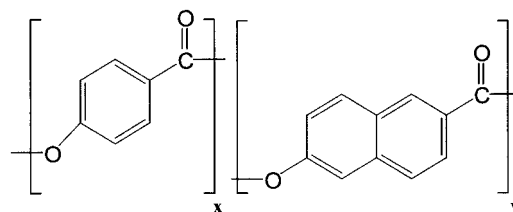


Figure 2 Chemical structure of POCO.

mass flow controller, was introduced into the Pyrex glass tube. The oxygen plasma operated at rf powers of 20–110 W at a 13.56-MHz frequency at a system pressure of 13.3 Pa for given times (10–200 s).

Contact angle of water on remote-oxygen-plasma-treated POCO film surfaces

With the sessile drop method, contact angles of water on the POCO surfaces treated with remote oxygen plasma were measured at 20°C with a contact-angle meter with a goniometer (model G-1, Erma Co., Ltd., Japan). An average contact angle was determined from 10 measurements with an experimental error of 3–4°.

X-ray photoelectron spectroscopy (XPS) of remote-oxygen-plasma-treated POCO films

XPS spectra for POCO surfaces treated with remote oxygen plasma were obtained on a Shimadzu ESCA K1 spectrometer (Japan) with a nonmonochromatic Mg K α photon source at an anode voltage of 12 kV, at an anode current of 20 mA, and at a pressure in the analytical chamber of 1.5×10^{-6} Pa. The XPS spectra were referenced with respect to the 285-eV C_{1s}. The spectra were not modified by the smoothing procedure. The C_{1s} and O_{1s} spectra were deconvoluted by the fitting of a Gaussian–Lorentzian mixture function (the mixture ratio was 80:20) to an experimental curve with a nonlinear, least-squares curve-fitting program (Escapac) supplied by Shimadzu. Sensitivity factors for the C_{1s} and O_{1s} core levels were $S(C_{1s}) = 1.00$ and $S(O_{1s}) = 2.85$. The O/C atomic ratios were calculated from the O_{1s} and C_{1s} intensities, and their experimental error was within 0.03.

Copper metalization of the POCO surfaces

A combination of two processes, evaporated plating and electroplating, was employed for copper metalization of the POCO surface. The total thickness of the copper metal layer deposited by the evaporating and electroplating was about 30 μm . A copper layer about 1000 Å thick was thermally evaporated onto the surface of the POCO film in a JEOL LEE-400 vacuum evaporator (Japan). The deposition was carried out at a pressure of 10^{-6} Torr or less and at a deposition rate of about 5 Å/s. The metalized POCO surface was electroplated with copper to a thickness of 30 μm . The electroplating procedure was carried out at a constant current of 10 A (current density = 300 A/m²) and at a constant voltage of 8 V at 24°C for 1 h in a sulfuric acid solution (190 g/L) containing copper sulfate (75 g/L), hydrogen chloride (50 ppm), and a glossy reagent (5 mL; PCM, Nippon Rironal Co., Ltd., Japan). Finally, the metalized POCO surface was washed with distilled water and dried at 80°C for 12 h *in vacuo*.

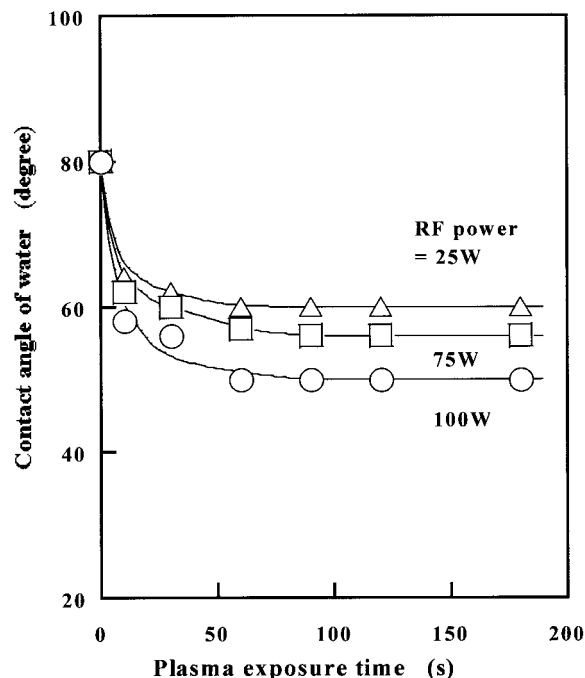


Figure 3 Contact angle of water on POCO surfaces treated with remote oxygen plasma as a function of the rf power and plasma-treatment time.

Scanning probe microscopy (SPM)

The surface morphology of the plasma-treated POCO film and peeled-off layers (the POCO film side and copper metal side layers) was scanned with a scanning probe microscope (SPM-9500, Shimadzu). SPM images were acquired in air with the contact or tapping mode.

Peel strength of the adhesive joint between the POCO film and copper metal

The T-type peel strength (5 mm wide) of the adhesive joint between the POCO film and copper metal was evaluated at a peel rate of 10 mm min⁻¹ with an Instron type tensile tester (AGS100-A, Shimadzu). The peel strength was determined from an average of 10 measurements.

RESULTS AND DISCUSSION

Modification of the POCO surface by remote oxygen plasma

Figures 3 and 4 show results for the contact angle of water on POCO surfaces modified by remote and direct oxygen plasmas as function of the plasma-treatment time and rf power. The contact angle of water of the remote-plasma treatment, as shown in Figure 3, showed a large decrease within a short treatment time and at a low rf power. The contact angle at 120 s was 60–50°, which depended on the magnitude of the rf power. In the case of direct-plasma treatment, as shown in Figure 4, the contact angle at 120 s was

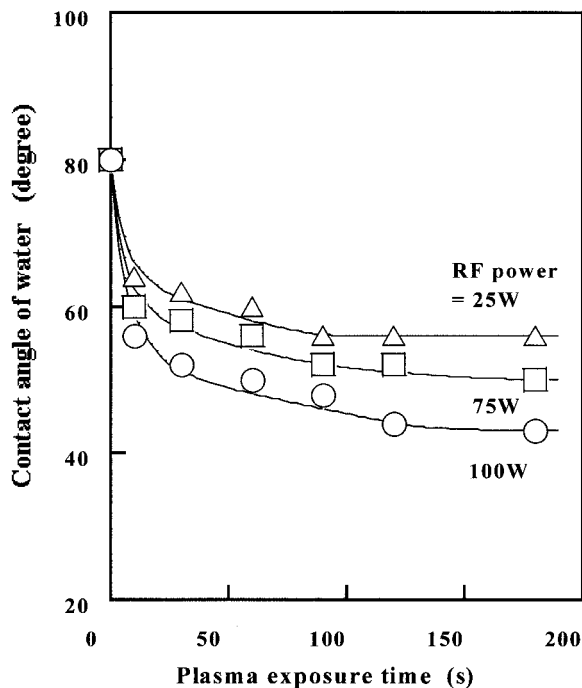


Figure 4 Contact angle of water on POCO surfaces treated with direct oxygen plasma as a function of the rf power and plasma-treatment time.

56–44°. Figures 5 and 6 show results for the weight loss on POCO surfaces treated by remote and direct oxygen plasmas as function of the plasma treatment and rf power. Direct-oxygen-plasma-treated POCO

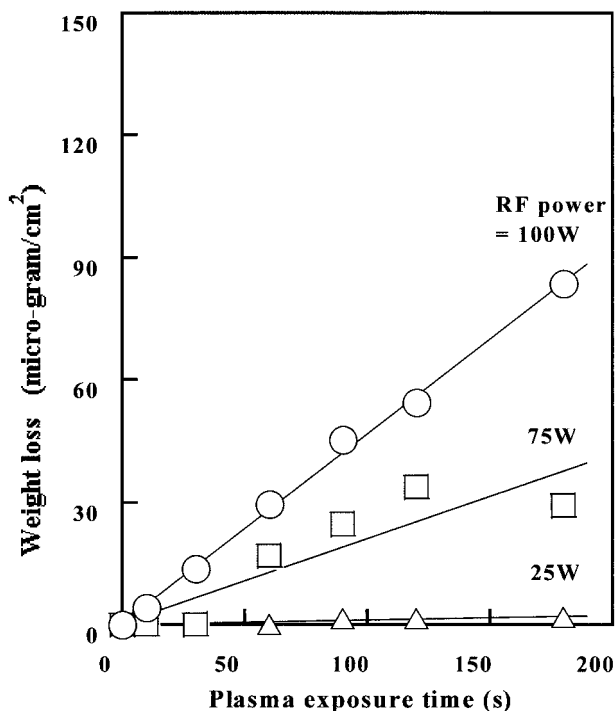


Figure 5 Weight loss on POCO surfaces treated with remote oxygen plasma as a function of the rf power and plasma-treatment time.

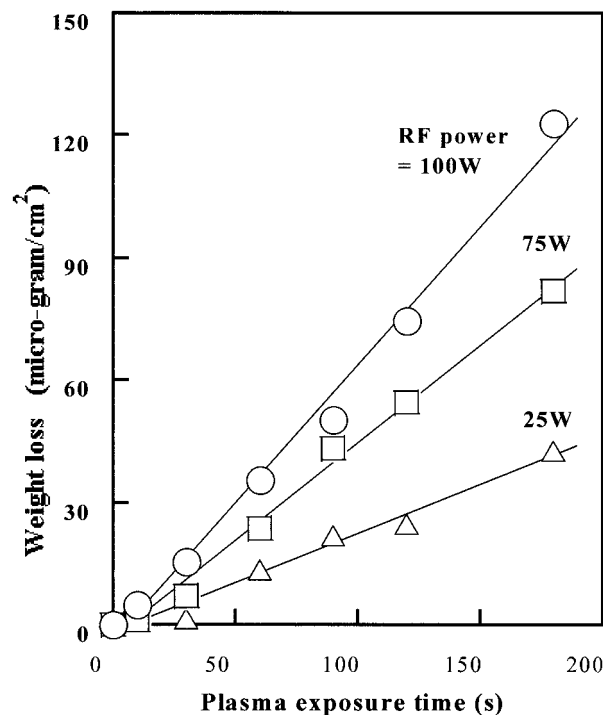


Figure 6 Weight loss on POCO surfaces treated with direct oxygen plasma as a function of the rf power and plasma-treatment time.

surfaces showed much more weight loss than remote oxygen plasma under all plasma-treatment conditions. The weight-loss rates of remote-oxygen-plasma-treated samples were 0.012, 0.208, and 0.464 $\mu\text{g}/\text{cm}^2 \text{ s}^{-1}$, and those of direct-oxygen-plasma-treated POCO surfaces were 0.241, 0.478, and 0.674 $\mu\text{g}/\text{cm}^2 \text{ s}^{-1}$, depending on the rf powers (25, 75, and 100 W). These results show that the hydrophilic properties of the remote- and direct-plasma-treated POCO surfaces did not really show a big difference, but the plasma degradation behavior did show a difference. This means heavy etching did not really modify the surface properties. We believe the difference in the weight-loss behavior between the remote and direct plasmas was in the direct-plasma zone, that is, reactions with electrons and ions, as well as radicals. Far away from the plasma zone (in the remote-plasma treatment), reactions with radicals occurred predominately, and the reactions with electrons and ions scarcely occurred. This is an essential difference in plasma chemistry between remote-plasma and direct-plasma treatments.

SPM showed that for an untreated POCO surface, which had a microfibril structure, 0.3–0.4-wide microfibrils met each other and fused into featureless amorphous regions [Fig. 7(a,b)].^{12,13} The POCO surface treated with remote and direct oxygen plasmas at 75 W for 60 s, as shown in Figure 7(c,d), showed many micropores 0.2–0.5 μm wide. In a comparison of the size and number of micropores, the remote-oxygen-plasma-treated one showed less than that treated by

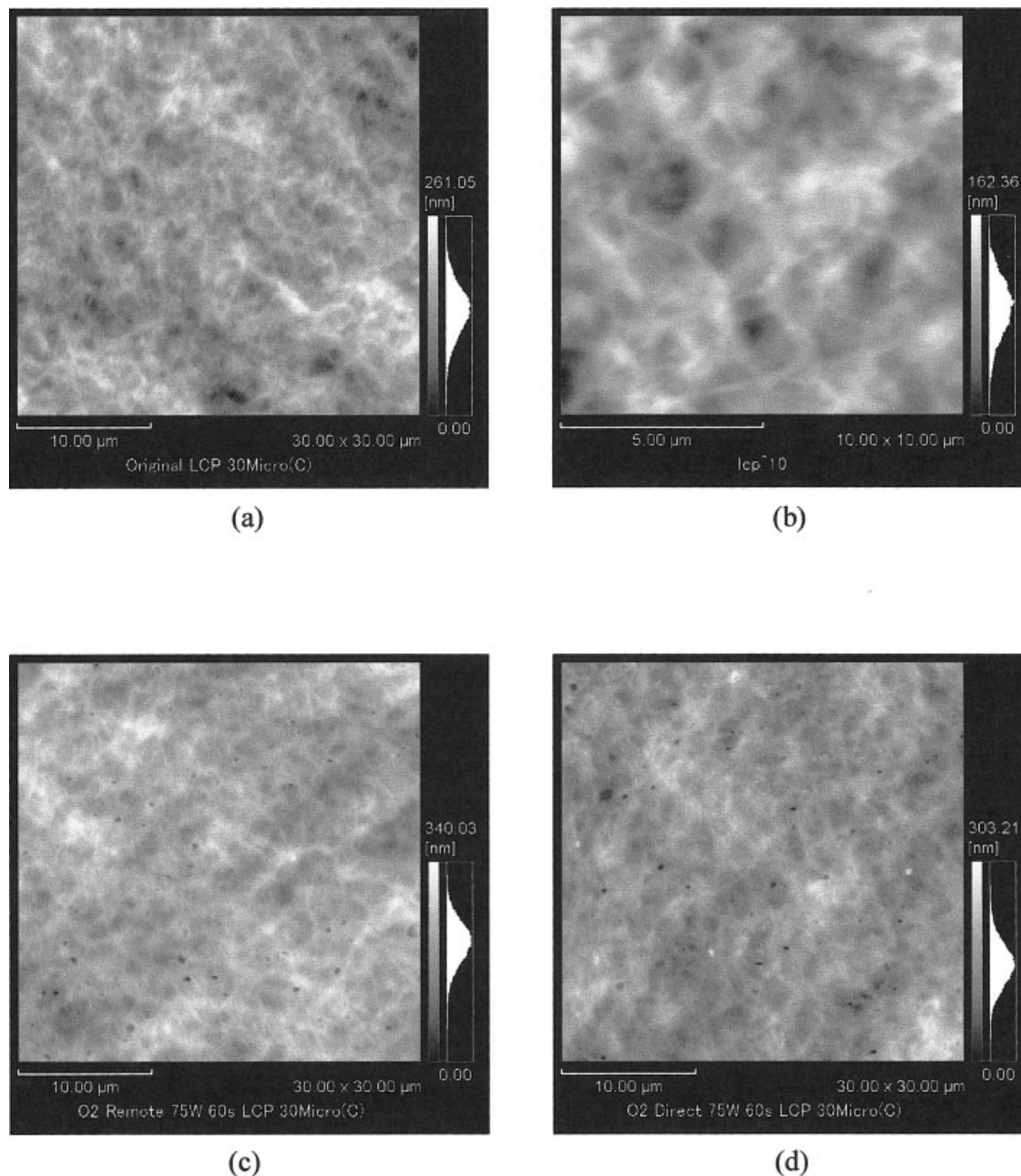


Figure 7 Large-scale contact-mode SPM images in air of POCO surfaces treated with remote and direct plasma: (a) original POCO (30 microscale), (b) original POCO (10 microscale), (c) POCO treated with remote oxygen plasma at 75 W for 60 s, and (d) POCO treated with direct oxygen plasma at 75 W for 60 s.

direct oxygen plasma. From the SPM images, we find that less of an etching reaction occurred in the remote-oxygen-plasma treatment, and heavy etching reactions occurred in the direct-oxygen-plasma treatment. These results coincide with the weight-loss results.

The POCO surface treated with the remote and direct oxygen plasmas at 75 W for 60 s were analyzed by XPS (C_{1s} and O_{1s} core-level spectra), and the atomic composition (O/C atom ratio) was estimated from the signal intensities. Table I shows the O/C atom ratio for the plasma-treated POCO surfaces. For the untreated POCO film, the O/C atom ratio was

0.24. The oxygen-remote- and direct-plasma-treated POCO films showed large changes in the O/C atom ratio. The O/C atom ratio increased from 0.24 to 0.34 for the oxygen-remote-plasma-treated sample to 0.24 to 0.33 for the direct-oxygen-plasma-treated one. Such high O/C atom ratios indicate that the oxygen-remote- and direct-plasma-treated POCO surfaces contained many oxygen groups. To investigate the chemical composition of the POCO surfaces treated by the remote- and direct-oxygen-plasma treatment, we analyzed C_{1s} and O_{1s} spectra. The C_{1s} spectrum for the untreated POCO surface was composed of four com-

TABLE I
Atomic Composition and Relative Concentration of C_{1s} and O_{1s} Components of POCO Surfaces Treated with Remote and Direct Oxygen Plasmas at 75 W for 60 s

Plasma	rf power (W)	Time (s)	Atomic composition O/C	Plasma-treatment condition					
				C_{1s} components (%)				O_{1s} component (%)	
				CH	C—O	C=O	$\pi \rightarrow \pi^*$	O=C	OC
Original		0	0.24	71.1	12.6	11.4	4.9	50.9	49.1
Remote O_2	75	60	0.34	65.7	19.7	10.0	4.6	44.9	55.1
Direct O_2	75	60	0.33	66.7	18.3	10.8	4.2	48.6	51.4

ponents due to CH groups at 285.0 eV, C—O groups at 287 eV, C=O groups at 289 eV, and a $\pi\text{-}\pi^*$ shake-up satellite near 291–292 eV. The italicized letter is the objective atom for the assignment. The O_{1s} spectrum, as shown in Figure 8, also consisted of two components, O=C groups at 532.2 and O—C groups at 533.9 eV. The relative concentrations of these C_{1s} and O_{1s} components are listed in Table I. For the POCO surfaces treated with remote and direct oxygen plasmas,

there was a decrease in the relative concentration of the CH component from 71.1 to 65.7% and from 71.1 to 66.7%, respectively. There were concomitant increases in C—O and OC functionalities and a decrease in the $\pi\text{-}\pi^*$ shake-up satellite. This result shows that remote and direct oxygen plasmas oxidized C—C bonds and aromatic rings to create C—O species. The extent of the oxidative functionalization and the loss of the shake-up structure are indicative of the oxidation of

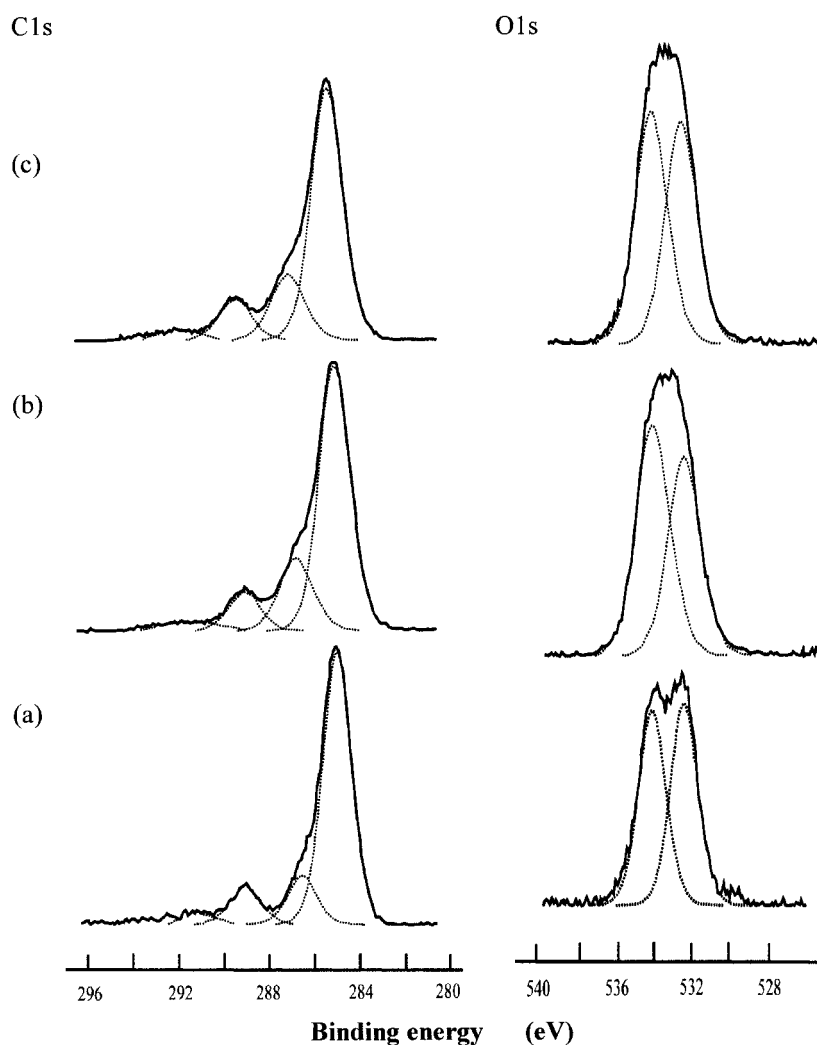


Figure 8 XPS (C_{1s} and O_{1s}) spectra of remote- and direct-oxygen-plasma-treated POCO surfaces: (a) original POCO, (b) POCO treated with remote oxygen plasma at 75 W for 60 s, and (c) POCO treated with direct oxygen plasma at 75 W for 60 s.

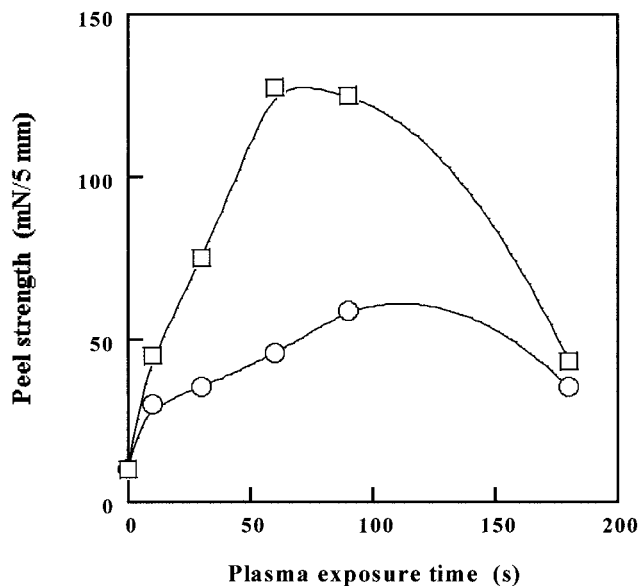


Figure 9 Peel strength for the copper metal/POCO system as a function of the plasma-treatment time at an rf power of 75 W: (□) remote-oxygen-plasma-treated POCO and (○) direct-oxygen-plasma-treated POCO.

the aromatic ring. It has been suggested that attenuation of the $\pi-\pi^*$ shake-up signal during oxygen-plasma treatment confirms substantial oxidative attack at the phenyl center.^{14,15} The POCO surface treated with remote oxygen plasma increased from 12.6 to 19.7% (C—O) and from 49.1 to 55.1% (OC) and decreased from 4.9 to 4.6% ($\pi-\pi^*$ shake-up satellite). The POCO surface treated with direct oxygen plasma increased from 12.6 to 18.3% (C—O) and from 49.1 to 51.4% (OC) and decreased from 4.9 to 4.2% ($\pi-\pi^*$ shake-up satellite). The remote oxygen plasma introduced noticeable C—O functional groups without

strong oxidative attack on the aromatic rings. In summary, the direct- and remote-oxygen-plasma treatments of POCO produced an important decrease in the contact angle due to the creation of C—O moieties on the surface. Furthermore, the remote oxygen plasma was more effective without a strong oxidative attack, which could occur in degradation during the plasma processing.

Copper metalization of the POCO surface by a combination of vacuum evaporation and electroplating

The effects of the surface modification by the direct and remote oxygen plasmas on the adhesion between copper metal and POCO were investigated with a T-type peel test. The POCO surfaces were treated with remote and direct oxygen plasmas at 25–100 W for 10–180 s, and then a copper metal layer (30 μm thick) was deposited by a combination of vacuum evaporation and electroplating. Figure 9 shows the peel strength for the copper metal/POCO system as a function of the plasma treatment at an rf power of 75 W. The untreated POCO showed 10 mN/5 mm and almost no adhesion with the copper metal layer. The surface-modified POCO by the remote and direct oxygen plasmas led to a large improvement in the adhesion with the copper metal. The peel strength, as shown in Figure 9, increased with increasing plasma-treatment time and reached a maximum of 127.5 mN/5 mm at the remote-oxygen-plasma-treatment time of 60 s. Afterward, the peel strength was decreased with increasing treatment time, and the decrease continued up to 180 s. This decrease in the peel strength might have been due to the microfibril structure of the surface layer removed by the plasma etch-

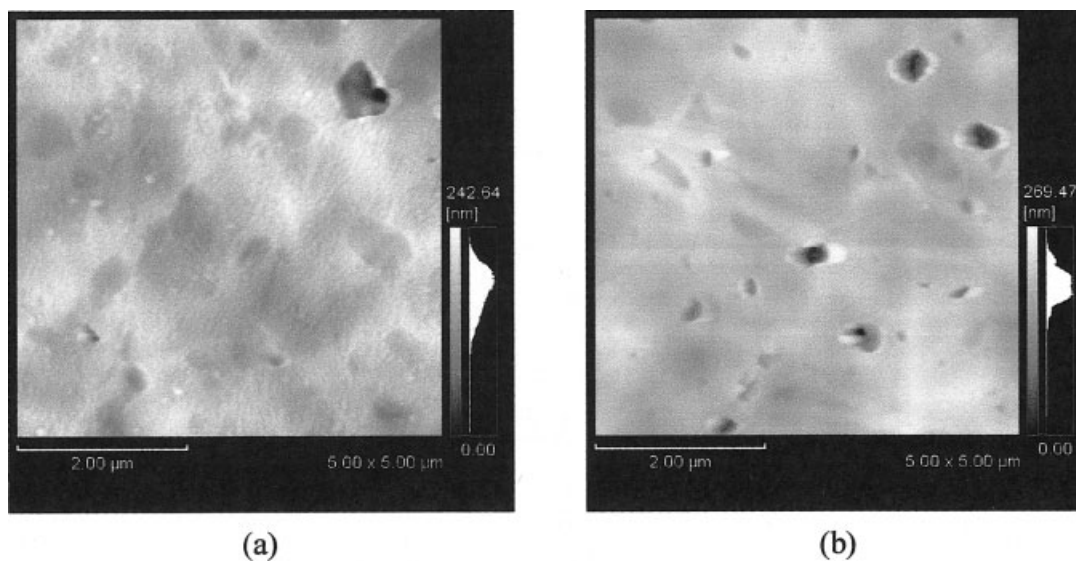


Figure 10 Large-scale contact-mode SPM images in air of POCO surfaces treated with remote and direct plasma: (a) treated with remote oxygen plasma at 75 W for 180 s and (b) treated with direct oxygen plasma at 75 W for 180 s.

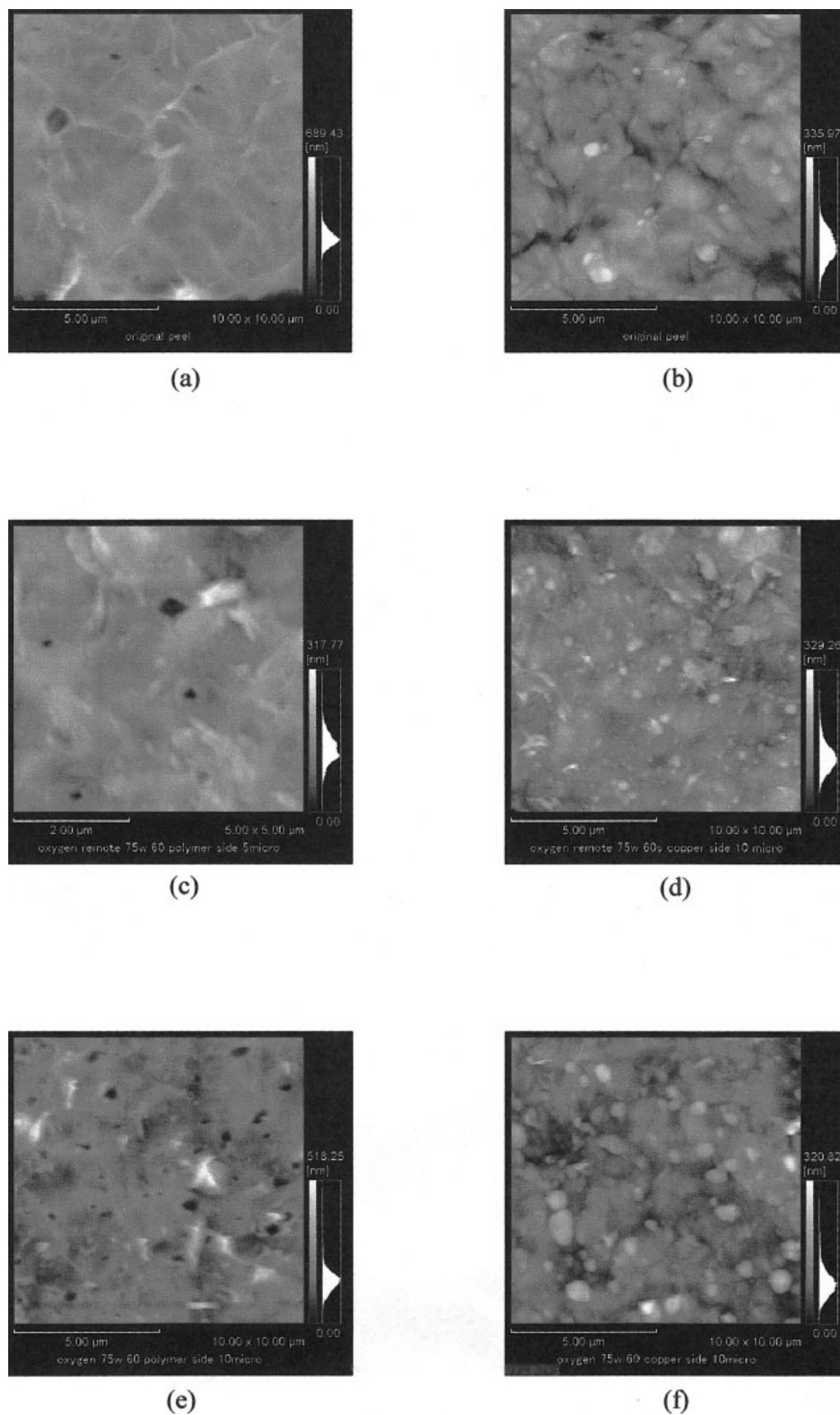


Figure 11 Large-scale tapping-mode SPM images of POCO and copper metal layers peeled off from POCO/copper metal adhesive joints: (a) original POCO polymer layer, (b) original copper metal layer, (c) POCO polymer layer (remote-oxygen-plasma-treated at 75 W for 60 s), (d) copper metal layer (remote-oxygen-plasma-treated at 75 W for 60 s), (e) POCO polymer layer (direct-oxygen-plasma-treated at 75 W for 60 s), and (f) copper metal layer (direct-oxygen-plasma-treated at 75 W for 60 s).

ing, which is shown in Figure 10. However, the direct oxygen plasma was not effective in improving adhesion, although the POCO surfaces were modified effectively. This might be the result of heavy etching destroying the microfibril structure. The comparison between the remote- and direct-oxygen-plasma treatments showed an important concept: heavy surface modification is not always effective in adhesion. In the remote-oxygen-plasma treatment, the POCO surfaces were kept from the energetic plasma and were modified mildly with less heavy etching. In the direct-plasma treatment, the POCO surfaces were always in the plasma zone and were exposed to energetic electrons, ions, and radicals. As a result, heavy etching and degradation occurred on the POCO surfaces. This is one of the main differences in the surface modifications of direct- and remote-oxygen-plasma treatments. To investigate one of the mechanisms of failure for the copper metal/POCO system, we observed, using SPM, two surfaces (POCO polymer and copper metal layers) from the system that failed. POCO films treated with remote oxygen plasmas at 75 W for 60 s were used for the adhesive joints. Figure 11 shows SPM images of the POCO polymer and copper metal layers peeled off from the copper metal/POCO system. The POCO polymer and copper metal layers peeled off from the copper metal/untreated POCO system [Fig. 11(a,b)] showed smooth surfaces without strong adhesion between the fibrous POCO layer and copper metal layer. However, the remote-oxygen-plasma-treated POCO/copper metal system showed quite a difference in comparison with the untreated POCO/copper metal system and the direct-oxygen-treated POCO/copper metal system. It showed strong adhesion between oxidized microfibrils of the POCO surface and copper metal layer. However, the direct-oxygen-treated POCO/copper metal system showed weak adhesion between microvoids, which occurred by direct-oxygen-plasma etching, and the copper metal layer. Therefore, the peeled-off copper metal layer showed round POCO polymer domains without strong adhesion to the microfibrils.

CONCLUSIONS

POCO surfaces were modified with remote oxygen plasma, and the effects of the modification on the adhesion between the copper layer and POCO were investigated. The remote-oxygen-plasma treatment produced a noticeable decrease in the contact angle, which was mainly due to the C—O functional groups on the POCO surface. The modification of the POCO surface by remote oxygen plasma was effective in improving the adhesion to copper metal. The peel strength for the copper metal/POCO system was improved from 10 to 127.5 mN/5 mm by the surface modification. The failure mode of the copper metal/POCO system was an interface layer between the oxidized microfibril surface and copper metal.

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