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Improvement of Plating Characteristics Between Nickel and PEEK by Plasma Treatment and Chemical Etching

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Surface of PEEK(poly-ether-ether-ketone) was modified by chemical etching, plasma treatment and mechanical grinding to improve the plating adhesion. The plating characteristics of these samples were studied by the contact angle, plating thickness, gloss and adhesion. Chemical etching and plasma treatment increased wettability, adhesion and gloss. The contact angle of as-received PEEK was 61°. The contact angles of chemical etched, plasma treated or both were improved to the range of 15~33°. In the case of electroless plating, the thickest layer without blister was 1.6 μm. The adhesion strengths by chemical etching, plasma treatment or both chemical etching and plasma treatment were 75 kgf/cm^2, 102 kgf/cm^2, 113 kgf/cm^2, respectively, comparing to the 24 kgf/cm^2 of as-received. In the case of mechanically ground PEEKs, the adhesion strengths were higher than those unground, with the sacrifice of surface gloss. The gloss of untreated PEEK were greater than mechanically ground PEEKs. Plating thickness increased linearly with the plating times.

***Keywords** : PEEK, electroless plating, nichel plating, plasma treatment, adhesion*

1. Introduction

The rapid development of communication industry demanded light weight of wireless communication parts. The heavy weight and expensive machining process of metallic parts lead to the usage of the plastic materials. However, the plastics should have thermal stability, weather resistance and fabricability since the parts are used outdoors.[1),2)]

PEEK is characterized by a high melting point(>573K) and high oxidative and thermal stability, good fatigue, abrasion resistance and fire resistance. These properties widened the application field to chemical processing, electronics, automotive, aerospace and medical industries in spite of the high price.[3),4)] The risk of electromagnetic interference(EMI) of PEEK has limited for the wireless communication parts. This problem could be solved by metal plating. However, good adhesion to metallic layer was not easy to achieve since PEEK have a dense molecule-chain and high chemical resistance.

In this study, Ni metallic layer was plated by electroless plating and sputtering. The chemical etching, plasma treatment and mechanical grinding were employed to improve adhesion strengths between PEEK and plating layer. Also the plating characteristics of these samples were studied by the contact angle, plating thickness, gloss and adhesion.

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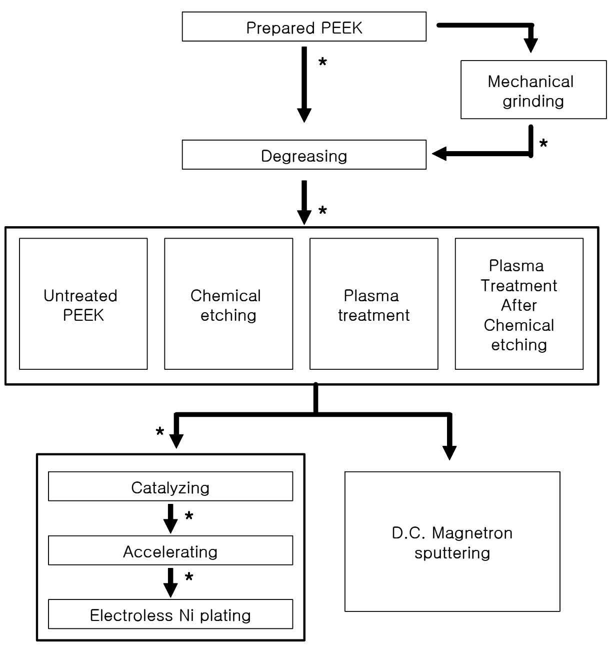
2. Experimental procedures

2.1 Materials and surface pretreatment

PEEK were provided by Victrex Public Limited Company in the form of thin film(100.3 μm) whose proper-



* water rinse

Fig. 1. Process diagram of Ni plating

Table 1. Properties of PEEK*

Property	Test Method	Units	Result
Thickness	TM-VX-83	㎛	100.3
Tensile Strength at break	ISO 527-3	MPa	113
Tensile Elongation at break	ISO 527-3	%	220

Table 2. Conditions of degreasing, catalyzing and accelerating

process	solution	temperature	time
degreasing	MEK	25℃	5min
catalyzing	H_2O 700㎖/ℓ HCl 150㎖/ℓ NP-8* 150㎖/ℓ	25℃	3min
accelerating	H_2SO_4 100㎖/ℓ	50℃	2min

* trade name

Table 3. Conditions of DBD plasma treatment[8)]

gas	parameters
0.3 slm Helium + 30sccm Oxygen	500eV, 1.10Am 0.8cm/s , 5~30pass

ties were presented in Table 1. These samples were cut into rectangular shape with the size of 25 mm × 25 mm in size. In fig. 1, the experimental procedure was presented schematically. The specimen was pretreated to increase the adhesion after degreasing.

Conditions of degreasing, catalyzing and accelerating are shown in Table 2. Both sides of PEEK samples were ground by emery paper up to #2000, followed by methyl ethyl ketone(MEK) degreasing at 25 ℃ for 5 min. Chemical etching was performed with 1%~6% solutions of potassium permanganate($KMnO_4$) in orthophosphoric acid. 1g~6g $KMnO_4$ was dissolved in 100 ㎖ H_3PO_4 in conical flask and stirred. Deionized water(30 ㎖) was added and the solution was vigorously stirred for uniform etching at 25 ℃for 30min.[3),5)]

PEEK's surface was modified by low pressure plasma treatment in the atmosphere of mixed gas (He 3slm + O_2 30 sccm). They were operated by 500 eV, 1.10 A, 8 mm/s, from 5 to 30 pass. A conditions of DBD(dielectric barrier discharge) plasma treatment is shown in table 3.[6),7),8)]

2.2 Plating

In this study, two plating method was employed, i.e. electroless plating and sputtering.

For electroless Ni plating, the surface was catalyzed for nucleation site to increase the reduction reaction. Palladium in catalyzing solution gave metal nucleus on PEEK surface during electroless plating. In this work, the NP-8 solution by KPM Tech was employed as catalyzing solution that contains Pd^{2+} and Sn^{4+}. Accelerating was performed with 10% H_2SO_4 at 50 ℃ for 2 min. Compositions of electroless Ni plating is shown in table 4. Electroless Ni bath employs sodium hypophosphite monohydrate as a reducing agent. Also citric acid was used as complexing agent. The bath were left undisturbed for 24hour at room temperature before use.[9)] The pH 5.5 of the solution was obtained by adding dilute NaOH solution. Plating time was 10~40 min.

Table 4. Compositions of electroless Ni plating

Bath compositions		
Nickel sulfate	$NiSO_4$-$6H_2O$	29 g/ℓ
Reducing agent	NaH_2PO_2-H_20	25 g/ℓ
Complexing agent	$C_6H_8O_7$	15 g/ℓ
Accelerator	CH_3COONa	5 g/ℓ
Stabilizer	$PbNO_3$	2 ppm
conditions		
Temperature		55±0.5℃
pH		5.50±0.05
Time		10~40min

To compare the adhesion of electroless plating, the PEEK was nickel plated by D.C. Magnetron Sputter(V&P International). Same pretreatments as the electroless plating were done for sputtering, except catalyzing and accelerating process.[8),10)] High purity Ni (99.99%, OS International Corp.) was used as a target, whose thickness and diameter were 1/8inch, 3inch, respectively.

2.3 Surface analysis and characterization

Contact angle measurement was performed in 1000 class clean room after surface treatment (SEO 300A, SEO. Co., Ltd). Testing liquid was the deionized water. Measurement temperature and humidity in clean room were 18.0 ± 0.1 ℃, 40%, respectively. Roughness measurements were performed by α-step(ET3000, Kosaka laboratory Ltd.,) Measured length and force were 10 mm and 100 μN, respectively. Surface morphology was analyzed by using scanning electron microscopy(Quanta 200F, FEI). The samples were coated with platinum in a sputter coater. Thickness of Ni plating layer was measured by X-ray fluorescence analysis (XRF-2000, Micropioneer). The gloss of Ni plating layer was measured by PG-1M Gloss Meter (Nippon Denshoku) according to the specifications of ASTM D 523. The source of gloss meter was tungsten lamp and reflected intensity was compared to that of source. The areas were 10.0×10.6 mm, 10.0×20.0 mm, 10×40.1 mm in the reflected angle of 20, 60, 85 degree, respectively. The average of 5 different sites was adopted. Adhesion strength between PEEK and Ni plating layer was measured Microload frame 105 ML(R and B Co.). The specially designed grips(contact area 1cm^2) were bonded to the plated surface with araldite after 12 hours curing.

3. Results and discussion

3.1 Contact angles

As increasing etching time and the number of pass of plasma treatment, contact angle of PEEK surface were decreased. The contact angle of etched PEEK(22.2°) was lower than untreated PEEK(61.3°), since the etchant changed morphology on PEEK surface and has endowed high surface energy. The contact angle of plasma treated PEEK decreased to 17.5° from 24.2°. The contact angle of plasma treated PEEK after etching in 5% etchant was the lowest in all conditions. The contact angles of untreated PEEK, chemical etching, plasma treatment and plasma treatment after etching were 61.3°, 22.2°, 17.5° and 16.0°, respectively. It means that chemical etching and plasma treatment have increased wettability. Also wettability of plasma treatment is greater than chemical etching. Etching prior to the plasma treatment did not show noticeable effect on the wettability. It can be concluded that plasma treatment is sufficient to wet the PEEK surface for nickel plating.

3.2 Roughness

Chemical etching and plasma treatment increased the roughness of PEEK. The values were 83 nm, 102 nm, respectively, comparing to the 53 nm of untreated PEEK. Roughness of mechanically grounded PEEK(231 nm) was higher than untreated PEEK in the magnitude of 4 times. The etching and plasma after grinding increased roughness on PEEK surface. In the case of etching and plasma treatment after grinding, much higher roughness(511 nm) was botained. The combination of three processes showed the

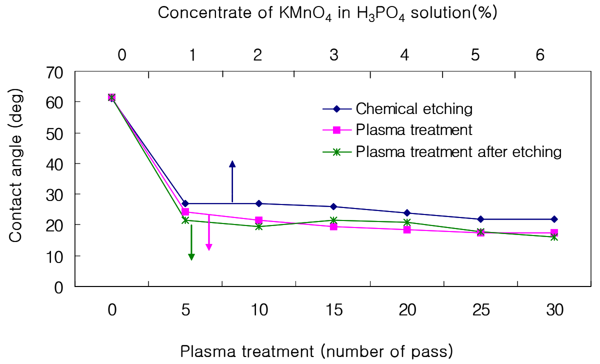


Fig. 2. Contact angle on PEEK surface

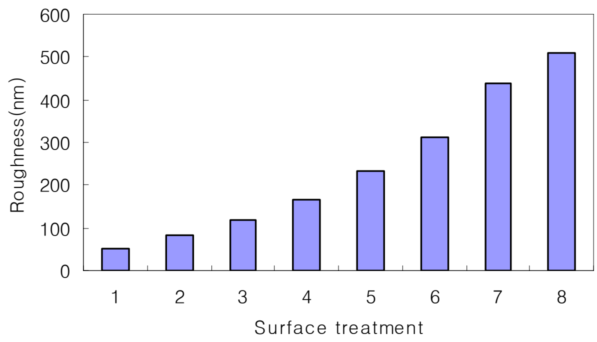


Fig. 3. Roughness of PEEK pretreatment

1. Untreated PEEK, 2. Chemical etching, 3. Plasma treatment, 4. Plasma treatment after chemical etching, 5. Mechanical grinding, 6. Chemical etching after mechanical grinding, 7. Plasma treatment after mechanical grinding, 8. Chemical etching and plasma treatment after mechanical grinding.

highest roughness among the studied conditions.

3.3 Surface morphology

SEM micrographs of the untreated PEEK samples revealed a smooth and uniform surface without major irregularities (fig. 4a). After chemical etching of the PEEK samples, wavy surface of various sizes were observed on the surface (fig. 4b). This wavy surface was lamellar of revealed PEEK by etching.[5] Plasma treated PEEK revealed particle(fig. 4c). This particle could be an anchoring point to improve the adhesion of nickel layer. However, the composition of particle did not show any noticeable difference from background by EDS. Fig. 4(d),which shows the surface after chemical etching with the aid of plasmatreatment, shows almost same morphology as fig. 4(c) except the wavy form. Fig. 4(e) revealed mechanically grounded PEEK surface, which was rather flat, with some cracks. PEEK surface is uniform and has a little scratch. In the case of etched PEEK after grinding, scratch of surface was deeper(fig. 4f). Also surface has a heavy deformation and etchant has eroded scratch area. Plasma treatment, on the other hand, has no defect except for particle(fig. 4g). Etched and plasma treated PEEK surface after grinding is shown to erosion from chemical etching and particle from plasma(fig. 4h).

3.4 Thickness of Ni plating layer

Plating thickness was shown in fig. 5a. Average of plating rate was 36 nm/min. Plating thickness of untreated PEEK was 0.3 ㎛. In the case of chemical etching, plasma treatment and plasma treatment after etching, plating thickness were same to 0.4 ㎛. Because chemical etching and plasma treatment have changed morphology of PEEK surface and have increased surface area, plated PEEK surface

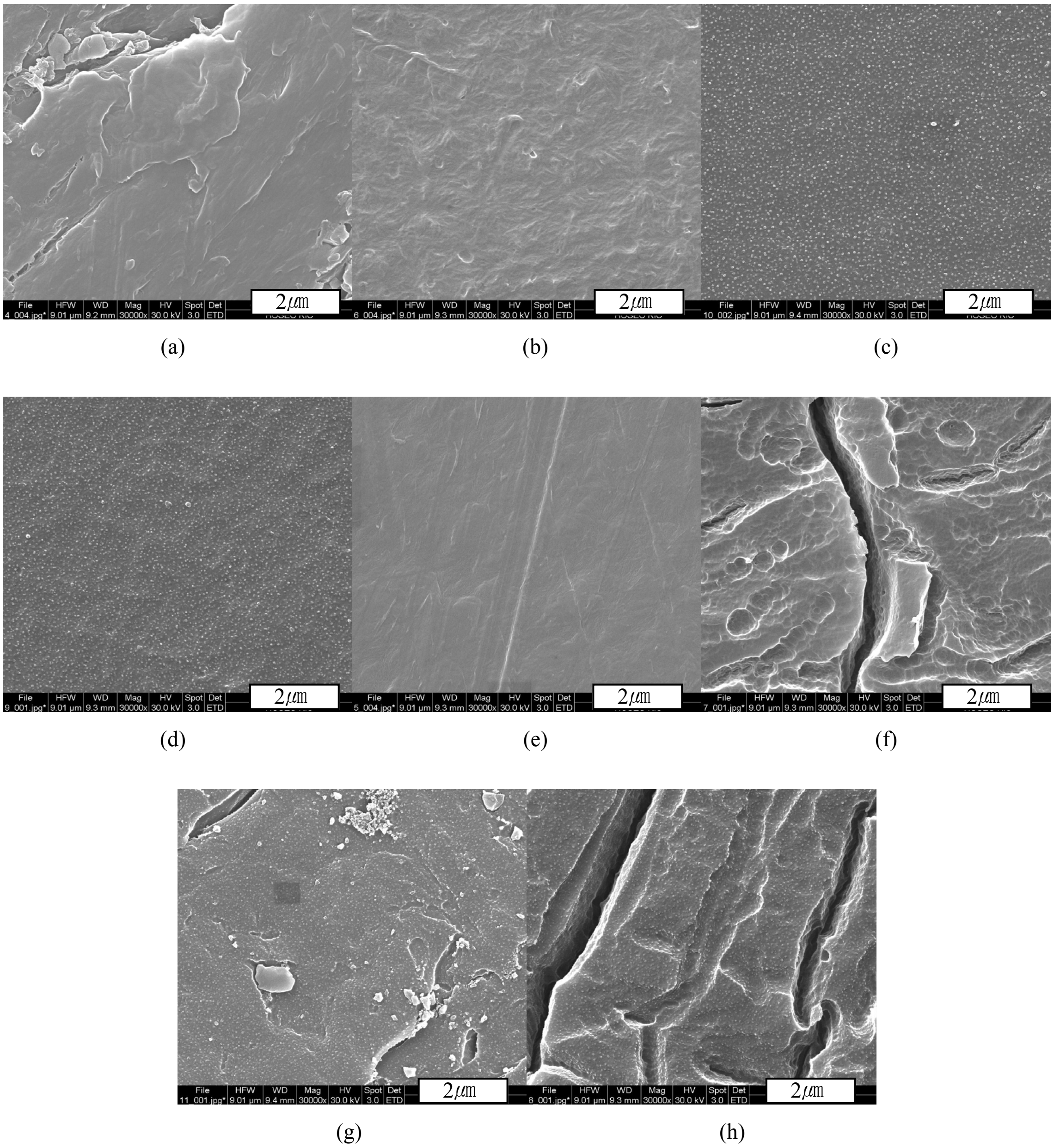
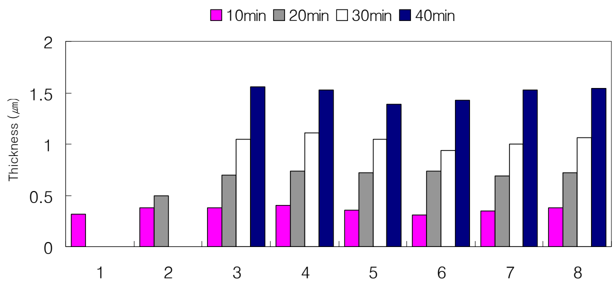


Fig. 4. PEEK surface treated by SEM(30000×)

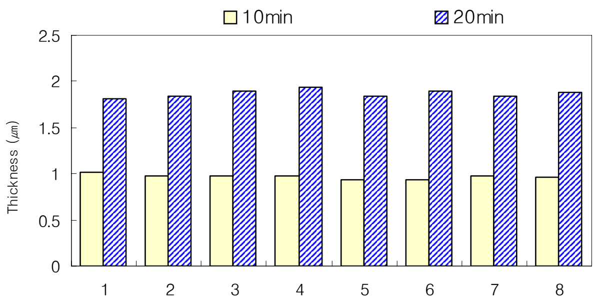
a. Untreated PEEK, b. Chemical etching, c. Plasma treatment, d. Plasma treatment after chemical etching, e. Mechanical grinding, f. Chemical etching after mechanical grinding, g. Plasma treatment after mechanical grinding, h. Chemical etching and plasma treatment after mechanical grinding.

was uniformed and plating rate was fast.

However, plating layer of untreated PEEK and etched PEEK was delaminated after 10 min, 20 min, respectively, since the PEEK surface has residual stress. As increasing plating time, plating thickness were increased. In the case of plating above 1.6 ㎛, plating layer was delaminated by residual stress. Plating thickness of Ni sputtering was shown in fig. 5b. Pretreatment process was same to electroless plating. Catalyst and accelerating were excluded in sputtering. Ni sputtering was performed at 90 watt for 10 min, 20 min. Average of sputter plating rate(100 nm/min) was faster than electroless plating(36 nm/min) in the magnitude of 3 times. When the plating times were 10 min and 20 min, the plating thickness were 0.9 ㎛, 1.8 ㎛. respectively. The plating thicknesses were similar in all conditions regardless of pretreatment process.



(a) Thickness of Ni layer by electroless plating



(b) Thickness of Ni layer by D. C. Magnetron Sputtering

Fig. 5. Thickness of Ni layer by plating.

1. Untreated PEEK, 2. Chemical etching, 3. Plasma treatment, 4. Plasma treatment after chemical etching, 5. Mechanical grinding, 6. Chemical etching after mechanical grinding, 7. Plasma treatment after mechanical grinding, 8. Chemical etching and plasma treatment after mechanical grinding.

3.5 Gloss

The gloss of electroless plating and sputtering was shown fig. 6. The gloss of etched PEEK(438) and plasma treated PEEK(473) was higher than untreated PEEK(349). The gloss(430) of plasma treated PEEK after etching was 10% lower than plasma treated PEEK because of the diffused reflection of deformed surface. The gloss of mechanically ground PEEKs were lower than untreated PEEKs due to the serious surface deformation. The gloss of etched PEEK and plasma treated PEEK after grinding was 244, 307, respectively. The gloss of plasma treated PEEK(271) by Ni sputtering was lower than in electoless Ni plating(473due to the high sputtering temperature. In the case of plasma treated PEEK after grinding and etching, , the gloss was the lowest among the studied conditions regardless of the plasma treatment.

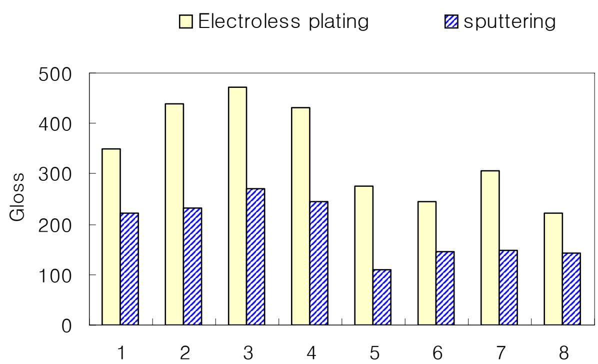


Fig. 6. Gloss of Ni plating.

1. Untreated PEEK, 2. Chemical etching, 3. Plasma treatment, 4. Plasma treatment after chemical etching, 5. Mechanical grinding, 6. Chemical etching after mechanical grinding, 7. Plasma treatment after mechanical grinding, 8. Chemical etching and plasma treatment after mechanical grinding.

3.6 Adhesion strength

Adhesion strength of electroless Ni plating was shown in fig. 7. In the case of plated PEEK for 10 min, adhesion of mechanical ground PEEK(41 kgf/cm^2) was higher than untreated PEEK(24 kgf/cm^2) in the 2 times. Chemical etched PEEK(75 kgf/cm^2) and plasma treated PEEK(102 kgf/cm^2)was greater than untreated PEEK. As results, by changing molecule chains, chemical etching deformed PEEK surface. Also, according to giving a physical energy and making an effecter using oxygen, plasma treatment reformed PEEK surface. Adhesion of plasma treated PEEK after etching was similar to plasma treated PEEK. Adhesions of etched PEEK and plasma treated PEEK after mechanical grinding was 115 kgf/cm^2, 118 kgf/cm^2, respectively, and adhesion of etching and plasma treated PEEK after grinding was 125 kgf/cm^2. As increasing plating time, adhesion strength was decreased by residual stress on PEEK surface. In the case of electroless plating, the thickest layer without blister was 1.6 ㎛.

Adhesion of Ni sputtering was shown in fig. 8. Adhesion of Ni sputtered PEEK for 10 min was higher than electroless plated PEEK for 30 min, in the magnitude of

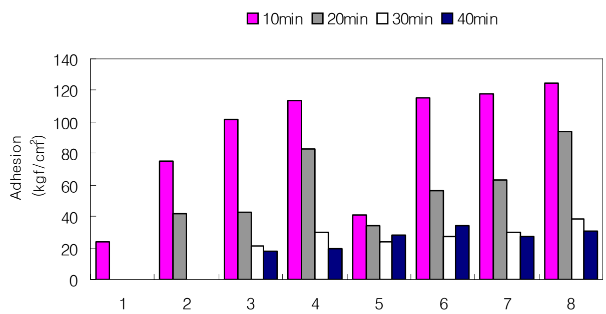


Fig. 7. Adhesion test of electroless Ni plating

1. Untreated PEEK, 2. Chemical etching, 3. Plasma treatment, 4. Plasma treatment after chemical etching, 5. Mechanical grinding, 6. Chemical etching after mechanical grinding, 7. Plasma treatment after mechanical grinding, 8. Chemical etching and plasma treatment after mechanical grinding.

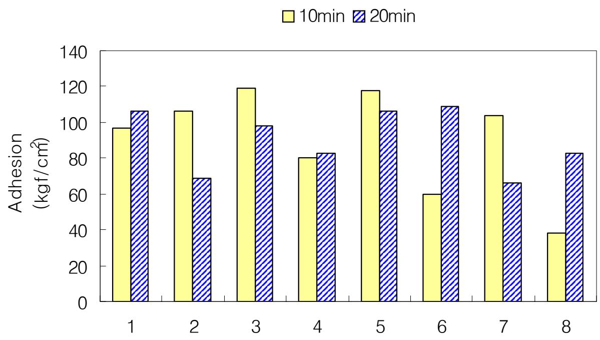
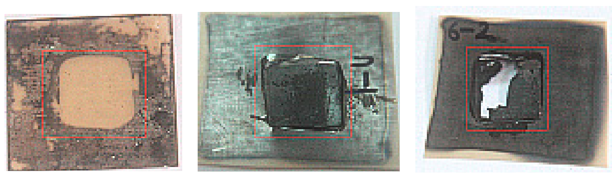


Fig. 8. Adhesion test of Ni sputtering.

1. Untreated PEEK, 2. Chemical etching, 3. Plasma treatment, 4. Plasma treatment after chemical etching, 5. Mechanical grinding, 6. Chemical etching after mechanical grinding, 7. Plasma treatment after mechanical grinding, 8. Chemical etching and plasma treatment after mechanical grinding.



(a) (b) (c)

Fig 9. Image of adhesion tested PEEK after plating (a) electroless plating (b) sputtering (c) sputtering

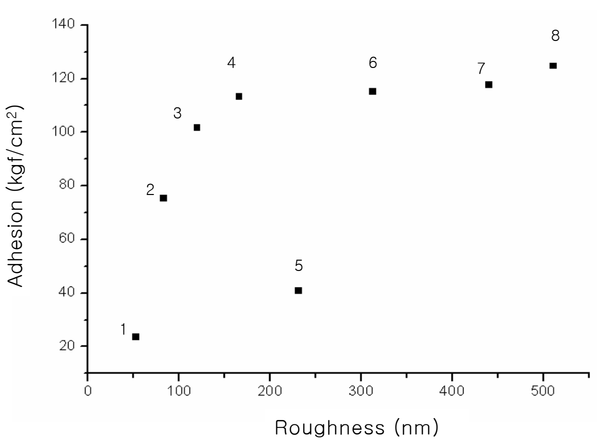


Fig. 10. Roughness of PEEK surface vs. Adhesion of electroless Ni plating.

1. Untreated PEEK, 2. Chemical etching, 3. Plasma treatment, 4. Plasma treatment after chemical etching, 5. Mechanical grinding, 6. Chemical etching after mechanical grinding, 7. Plasma treatment after mechanical grinding, 8. Chemical etching and plasma treatment after mechanical grinding.

4 times. Electroless Ni plating layer has completely peeled from PEEK surface(fig. 9a). The plating layer of sputtered PEEK, on the other hand, has not peeled and caused defect of PEEK surface(fig. 9b,c), because of high temperature generated from sputtering process. Adhesion was presented with roughness in fig. 10. As increasing roughness, adhesion strength was decreased, except for mechanical ground PEEK. Therefore, adhesion and roughness were not always related. Also, complete adhesion from mechanical grinding only could not achieved. Plasma treatment and etching have synergistic effect with mechanical grinding on adhesion.

4. Conclusion

Chemical etching and plasma treatment increased wettability, adhesion strength and gloss. The contact angle of etching, plasma treatment or both plasma treatment and etching decreased. Plating thickness in all the studied pretreatment conditions was similar and increased linearly with the plating times. The gloss of untreated PEEK was greater than mechanically ground PEEK. The mechanically ground PEEKs showed higher adhesion strengths with the sacrifice of surface gloss.

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