

Surface Modification of Poly(tetrafluoroethylene) Film by Chemical Etching, Plasma, and Ion Beam Treatments

SUNG R. KIM

SamYang Central R&D Center, 63-2 Whaam-dong, Yuseong-gu, Taejeon, Korea

ABSTRACT: Chemical etching, plasma, and ion beam treatments were used to modify the surface of Polytetrafluoroethylene (PTFE). Each surface treatment method developed different surface characteristics. In addition to morphological observation, contact angle, atomic chemical composition, and adhesion strength were measured after treatment with various methods. The different adhesion strengths were explained based on the morphology and atomic chemical composition of the treated PTFE surfaces. The chemical etching showed substantial defluorination, and the adhesion strength was fairly high. The argon plasma treatment introduced very large amounts of oxygen into the surface, and the surface was very smooth with a crater-like structure. Ion beam treatment induced a form of spires whose dimensions were of several micrometers, depending on the ion dose, whereas the oxygen plasma-treated samples showed short spires with spherical particles on the top. The spire-like surface morphology and increased surface area during bonding by ion beam treatment appear to be the reason for a higher adhesion strength than that of the oxygen plasma-treated PTFE. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 77: 1913–1920, 2000

Key words: surface modification; PTFE; surface structure; adhesion strength

INTRODUCTION

Polytetrafluoroethylene (PTFE) has many desirable properties, such as chemical resistance, electrical stability, low coefficient of friction, and low dielectric constant. The properties of PTFE have led to many successful applications, such as lining for reactors and electrical cables, substrate for printed circuit boards, antisticking coating for kitchen utensils, and adhesive tapes. However, its poor adhesion properties and poor wettability have presented considerable problems in many application fields.^{1–4}

There have been many studies on improving the surface properties of PTFE using various surface modification methods. Along with wet chemical treatment, plasma and ion beam treatments are considered as the efficient surface modification techniques. Among these methods, the chem-

ical etching using a sodium naphthalene solution has been used in industry for many years.⁵ The changes in surface chemistry caused by chemical etching treatments were studied using X-ray photoelectron spectroscopy (XPS). The surface treatment of PTFE with sodium naphthalenide for 30 s reduced the F/C ratio in the surface from 2 to 0.17, and introduced substantial quantities of oxygen (O/C ratio = 0.2).⁶ Dwight et al.⁷ treated the fluorinated ethylene–propylene copolymer (FEP) with sodium in liquid ammonia. Complete defluorination took place, and large quantities of oxygen were introduced into the surface, including carbonyl and carboxylic acid groups.

Many plasma methods were employed to modify fluoropolymer surfaces, and have continued to the present.^{8–12} It was found that the wettability and the critical surface tensions were changed considerably with plasma exposure, and that periods of several tens of a second were long enough to cause changes.¹³

The improvement of adhesion and changes of wettability by ion beam treatment were studied. Koh et al.¹⁴ reported the effectiveness of ion beam treatment on the improvement of PTFE adhesions. Chang et al.^{2,3} showed that ion beam texturing of PTFE could enhance the adhesion between PTFE/Cu.

There has been no previous study in which the differences of chemical etching, plasma treatment, and ion beam irradiation to the PTFE properties were studied. In this study, we examined the effects of the chemical etching, plasma, and ion beam treatment on the morphology, contact angle, atomic chemical composition, and adhesion strength. In particular, the differences of adhesion strength between plasma-treated PTFE and ion beam-treated PTFE were studied. The morphology, contact angle, atomic chemical composition, and adhesion of the surface-treated PTFE were compared using a scanning electron microscope (SEM), contact angle meter, XPS, and tensile tester, respectively.

EXPERIMENTAL

Sample Preparation

A sheet of skived PTFE (Norton Performance Plastics Co.) was cut into sizes of $60 \times 60 \times 0.15$ mm³. The samples were cleaned by isopropyl alcohol and dried in an oven at 60°C for 1 h to remove any contaminant. Then, the sample surfaces were treated by different treatment methods.

Chemical Treatment

PTFE was chemically treated using a sodium/naphthalene based solution (Fluoroetch®, Acton Co.). PTFE was immersed and waved in the 50°C Fluoroetch for 60 s. It was rinsed by isopropyl alcohol for 20 s and by acidic water for 60 s. The detailed chemical and processing information of Fluoroetch can be found elsewhere.⁵

Plasma Treatment

Plasmas used were excited by a capacitively coupled 13.56 MHz radiofrequency (Korean Vacuum Co.) generator capable of delivering a continuously varying power output from 0.05 to 150 watts. The diameter of electrodes was 120 mm. The reactor contained mass flow controllers for

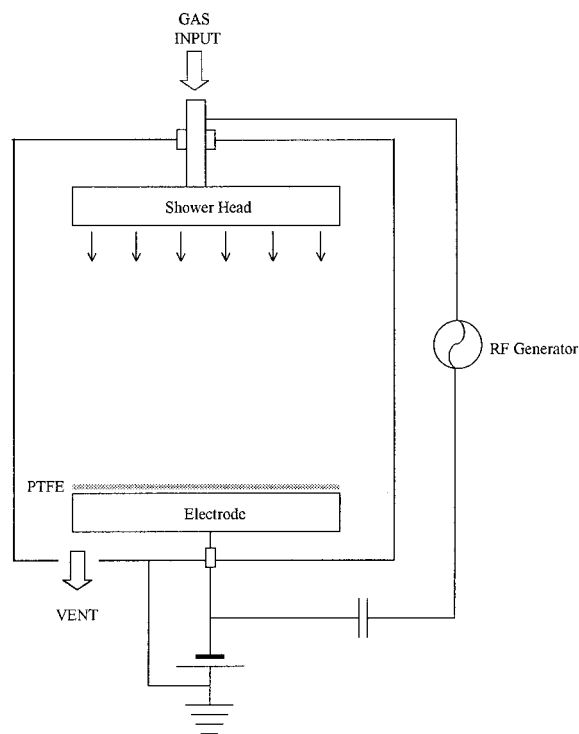


Figure 1 Experimental setup of plasma apparatus.

argon and oxygen gas inlet, a Baratron® pressure gauge, a rotary pump, and a diffusion pump. The top surface of a PTFE sample was treated with a 30-watt argon and oxygen plasma with various treating times. The lower end of the electrode (Fig. 1) was biased with -100 volts to produce the effect of plasma etching. The base pressure of the plasma chamber was down to 1 mTorr, and the treating gas was fed to the chamber until the pressure reached the working pressure of 20 mTorr. A schematic presentation of the plasma treatment apparatus used is given in Figure 1.

Ion Beam Treatment

The ion beam system used was similar to that used in previous studies, and detailed information can be found elsewhere.¹⁴ An RF grid-type ion gun was used with an ion dose of argon and oxygen ions of 5×10^{15} to 1×10^{17} ions/cm². The ion dose was measured by a Faraday cup. The ion beam energy was 1000 eV, and ion current was 25 mA. Argon and oxygen gases were fed into the ion gun to produce ionized beams, and the purity of each gas was 99.99%. The base pressure of vacuum chamber before irradiation was 3×10^{-5} Torr, and it became 2.5×10^{-4} Torr after irradiation.

ation. The samples were placed normal to the ion beam, and the distance between the ion gun source and the sample was 22 cm.

Characterization

The control and surface-modified films were characterized using SEM. A JEOL-type JSM-35CF apparatus was used. The films were sputtered with gold (with a Balzers Union Sputter apparatus), and analyzed at an angle of 60° at different magnification.

Changes of the chemical bond environment of the treated samples were examined using the ESCALAB 200R XPS system (V.G Scientific, U.K.). Al K-alpha line (300 W) was used as a source of excitation. A take-off angle was 90° with respect to the sample surface. Whenever fluorine-containing surfaces were analyzed, a clean PTFE sample was also analyzed to determine a correct empirical sensitivity factor for the fluorine 1s peak.

The wettability of PTFE was measured before and after treatment using a contact angle meter (Tantec Co., Model: CAM FILM). The test liquid was triple distilled water. The contact angle measurements were performed on all modified and control surfaces at room temperature. The values of contact angles were taken as average values of five drops at different places on untreated and modified surfaces.

The adhesion strength of the treated PTFE was measured by means of a T-peel test with a PTFE/epoxy adhesive/PTFE configuration. The width of test film was 5 mm. Devon® 2-Ton Epoxy was mixed with hardener in the ratio of 1 : 1 by weight to use as an adhesive for measuring peel strength. The adhesion strength was measured after 3 h curing at 60°C. The epoxy adhesive bonded sample was tested in a United® tensile tester with a crosshead speed of 50 mm/min.

RESULTS AND DISCUSSION

Scanning Electron Microscopy Studies

The morphology of an untreated virgin PTFE surface by SEM is shown in Figure 2. The surface showed a porous structure with different pore sizes up to 1 μm .

The chemical etching using Fluoroetch is known to be a very effective method for PTFE.

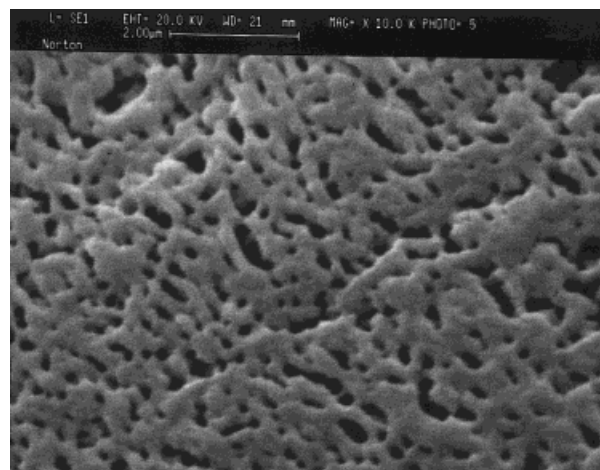


Figure 2 SEM photograph of untreated PTFE.

The surface morphology of the chemically etched PTFE for 1 min is shown in Figure 3(a). Deep mud cracks were formed on a virgin PTFE surface using a Fluoroetch. Crack density (number of cracks/unit area) and crack depth were increased with increasing the etching time, and all the cracks had random directions. There were no globules or spires on the treated surface, which were characteristics of plasma or ion beam-treated PTFE surfaces. The PTFE was discolored to dark brown by the chemical treatment.

The interactions of plasma gases with a polymer surface include physical bombardment by energetic ions, UV irradiation, and chemical reactions at the surface, which results in cleaning (etching), crosslinking, and formation of new chemical groups.¹⁵

We evaluated the influence of plasma treatment time, and used gas on the morphology of the plasma-treated PTFE. The argon and oxygen gases were used to see effects of feed gas on the surface properties of plasma-treated PTFE. Figure 3(b) and (c) shows the photographs of PTFE surface after 30 min of argon and oxygen plasma treatments, respectively. The surface morphology was altered by the plasma treatments. The oxygen plasma-treated PTFE gave different morphology compared to that of the argon plasma-treated PTFE. The spire-like structure with spherical particles on the peak was observed after treating samples with oxygen plasma, whereas a relatively smooth layer with a crater-like morphology was observed with the argon plasma treatment. The reasons for the different morphologies with different gases have not been clearly understood.

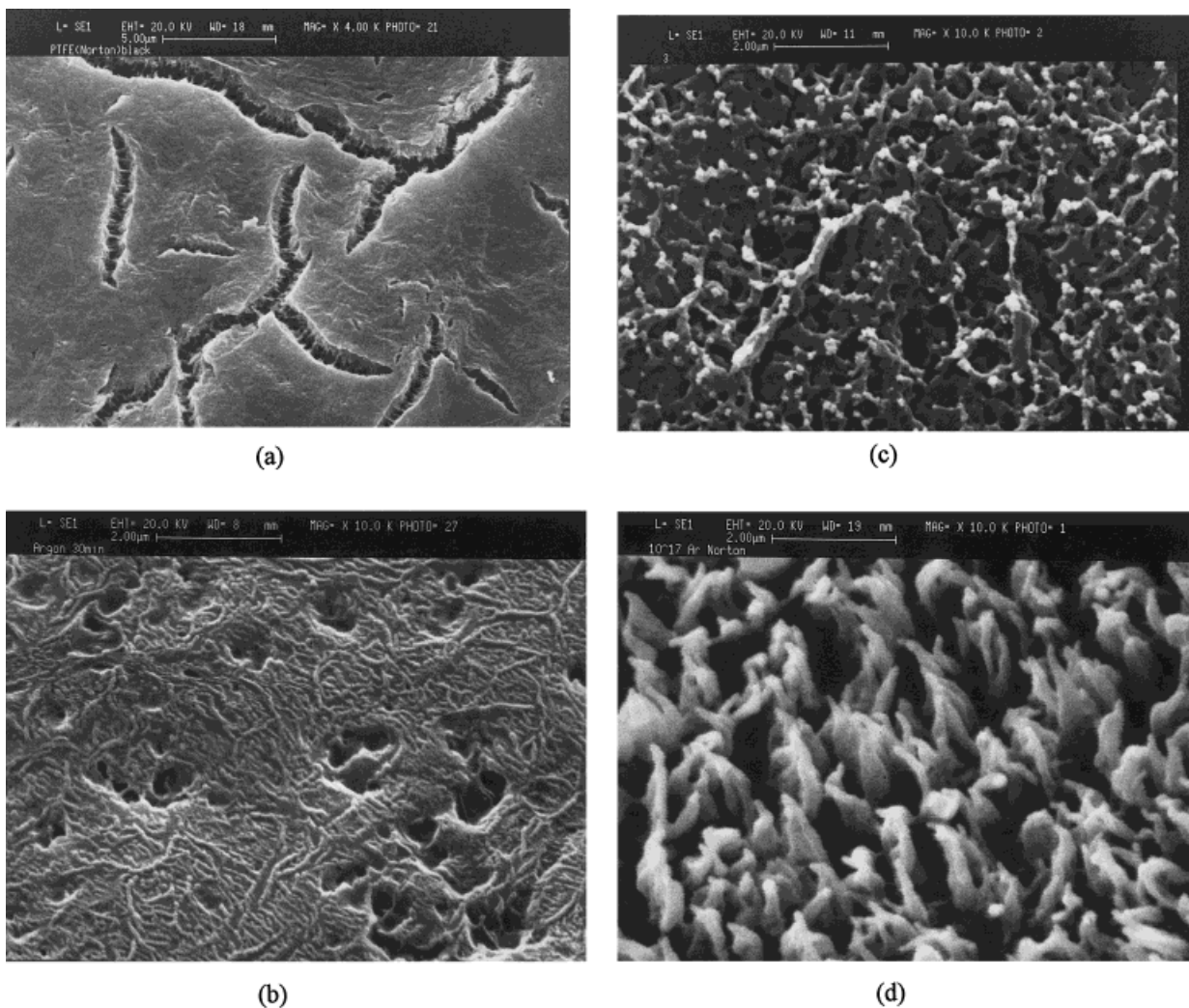


Figure 3 SEM photographs of (a) chemically treated, (b) argon plasma-treated, (c) an oxygen plasma-treated, and (d) an argon ion beam-treated PTFE.

The different reaction mechanism could lead to different morphologies. It seems that surface structure was substantially changed by the argon plasma treatment. A longer irradiation time than 180 s with an argon plasma of 100 watts caused heavy degradation of the PTFE surface.⁸ Relatively long treatment time with -100 V bias in this study might have induced the heavily damaged morphology by argon plasma treatment, as shown in Figure 3(b). Figure 3(c) shows that several spherical particles are hung over the top of the peak on the oxygen plasma-treated PTFE. It is believed that the spherical particles are produced by plasma polymerization at oxygen plasma environments. The plasma polymerization of heavily etched PTFE particles and work-

ing gases might be facilitated at a relatively high processing pressure of plasma treatment.

The SEM photograph of the argon beam-treated PTFE at a 1×10^{17} ion dose is shown in Figure 3(d). The apparent morphology changes were observed after the ion beam treatment. The ion beam treated sample shows a widely spaced spire-like surface at 1×10^{17} ions/cm². The argon and oxygen ion beam treatment gave very similar surface morphologies. The ion beam-treated PTFE showed different morphologies compared to the oxygen plasma-treated samples in Figure 3(c). It does not show any spherical particles on the top of spires. Taller spires are observed with the ion beam treatment than that of the oxygen plasma treatment. The spires became sharper and taller

Table I XPS Results of PTFE

Sample	F/C Ratio	O/C Ratio
Untreated PTFE	1.975	—
Chemical etching (Fluoroetch®), 1 min	0.021	0.348
Ar 30 min plasma	1.435	0.488
Ar 30 min plasma and tape peeled	1.766	0.083
O ₂ 30 min plasma	1.863	0.044
O ₂ 30 min plasma and tape peeled	2.097	0.019
Ar ion beam 5 × 10 ¹⁵	1.921	0.021
Ar ion beam 1 × 10 ¹⁶	1.851	0.023
Ar ion beam 1 × 10 ¹⁷	1.879	0.003
O ₂ ion beam 5 × 10 ¹⁵	1.841	0.040
O ₂ ion beam 1 × 10 ¹⁶	1.667	0.057
O ₂ ion beam 1 × 10 ¹⁷	1.825	0.031

upon increasing the ion dose, reaching several micrometers at longer ion beam treatment times. The morphology changes are comparable to those shown in the previous studies.^{4,5,14}

X-ray Photoelectron Spectroscopy Studies

The chemical changes in atomic composition of the material can be effectively investigated using an XPS.

The atomic composition ratio changed markedly by chemical etching. The F/C ratio decreased to 0.021, and the O/C increased up to 0.348, in a 60-s chemical treatment as shown in Table I. Apparent defluorination and oxidation occurred by the chemical treatment. There was no significant difference in the atomic chemical composition between 60-s and 5-min treatments. It appears that most of the chemical change occurred in a very short time. The 60-s treatment was sufficient to cause substantial modification of the surface, and a longer treatment time caused only a small additional modification.

The argon plasma-treated PTFE sample has a larger O/C ratio (0.488) than that of the oxygen plasma-treated PTFE, as can be shown in Table I. The former is 10 times higher than the latter. This observation is in marked contrast to the very low oxygen content observed by Youxian et al.¹⁰ It appears that oxygen functional groups are formed on the PTFE surface by argon plasma treatment. The lower values of the contact angle support the

higher O/C ratio at the argon plasma treatment. Polymerization might have occurred during plasma treatment or during aging in air, which lead to a high O/C ratio. Peroxy groups were formed on the treated surface of PTFE by a combination of argon plasma irradiation and air exposure.¹² When PTFE was irradiated with argon plasma, radicals were easily formed on the PTFE surface. The radicals were rapidly modified into corresponding peroxy radicals by contacting with air. The newly formed peroxy radicals were stable at room temperature for a long time.¹³ At the same time, the F/C ratio decreased to 1.435 by the argon plasma treatment. The value is very low compared to the theoretical ratio of 2 of the untreated PTFE and the ratio of ion beam-treated samples in this study.

Oxygen plasma promoted etching via preferential attack of the carbon-carbon bonds.¹⁶ Continuous etching may keep the freshly revealed PTFE surface all the time and the O/C ratio become very low, and it may not change with time.

To see the atomic composition change in the thickness direction of the treated PTFE samples, a 3M double-sided acrylic adhesive tape was bonded onto the plasma-treated PTFE surface and was subsequently peeled from the surface. The F/C ratio of the new surface increased from 1.435 to 1.766 for the argon plasma-treated sample. A similar increase from 1.863 to 2.097 was observed for the oxygen plasma-treated sample (Table I). The O/C ratio decreased on the surface after adhesive tape was peeled from the argon and oxygen plasma-treated samples. The weakly bound oxygen-containing materials formed during plasma treatments were detached from the surface by the adhesive tape.

The small amount of the oxygen groups was formed by ion beam treatments. The F/C ratio was minimum, whereas the O/C ratio was maximum by argon ion beam treatment at a 1 × 10¹⁶ ion dose. The same trend with the ion beam dose was observed by oxygen ion beam treatment. The oxygen content decreased to near zero at a 1 × 10¹⁷ argon ion dose.

Wettability and Aging Tests

Measurement of the contact angle with the surface permits a rapid and qualitative evaluation of polymer surface energy. The water contact angle of the untreated PTFE was found to be ca. 105°, and this high contact angle of PTFE is very spe-

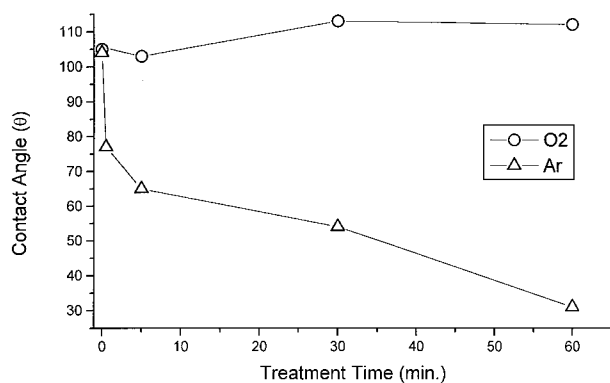


Figure 4 The contact angle with various plasma treatment time.

cial among polymeric materials. It implies that PTFE has a very low surface energy.

Chemical etching lowered the contact angle of PTFE to 50° , and defluorination might be the reason for the very low contact angle. The contact angle was greatly lowered by the argon plasma treatment, as shown in Figure 4. It decreased to 30° by 60 min of the argon plasma treatment. This low value of the contact angle of treated PTFE is very unusual among the treatment methods used in this study. A rapid decrease of the contact angle by the argon plasma treatment could be related to the dramatic change in surface chemistry. The very high O/C ratio and the low F/C ratio of the argon plasma-treated sample might lead to the low contact angle. The contact angle was slightly increased by oxygen plasma treatment. The result is consistent with previous result.¹¹ Fluoropolymers were resistant to oxygen attack, and both surface degradation and oxygen incorporation were found to be small for oxygen plasma-treated PTFE.¹⁷

The contact angle of PTFE was increased by argon and oxygen irradiation. The contact angle of the ion beam-treated PTFE samples were larger than 140° at a 1×10^{17} ion dose, and the water droplet had a tendency to roll on the PTFE surface. The composite surface,¹⁸ characterized by spire-like peaks and open spaces between peaks, is the reason for the enhanced nonwetting characteristics of PTFE. Little difference in contact angle between oxygen and argon ion beam treatments was observed. It could be thought that the morphology is dominant, and the chemical effect by different gas is negligible.

To investigate the effects of aging or posttreatment, the treated surfaces of PTFE were exposed

to air for various times. The changes in the contact angle of the chemically etched, plasma-treated, and ion beam-treated surfaces as a function of air exposure time are shown in Figure 5. The contact angle of the chemically etched surface increased to 65° from 50° after an hour of air exposure, but it remained constant afterwards. This is one of the evidences that the chemical functional group formed during chemical etching may disappear in an hour, but the effect of defluorination is effective for a long time. The defluorinated PTFE has similar contact angles to that of polyethylene.

The contact angles of argon plasma and oxygen plasma-treated PTFE decreased in 1 and 5 h of aging, respectively. The decreased contact angles were unchanged by a long time exposure.

The ion beam-treated samples did not show any changes of contact angle with aging. The spire structure made the water drop to roll on the PTFE even after a long aging time. This implies that the ion beam-treated samples maintained the spire-like structure, and there is no significant chemical change on the surface.

Adhesion Tests

Adhesion is a complex phenomenon related to both physical and chemical effects.¹⁹ The peel strength of Fluoroetch was about 100 g/mm. The high peel strength of Fluoroetch-treated PTFE may well be due to a combination of defluorination and introduction of an oxygen group together with a favorable surface topography. Defluorination took place more effectively by chemical etching than the other surface treatments.

Figure 6 shows the peel strength of plasma-treated PTFE with various treatment times. It

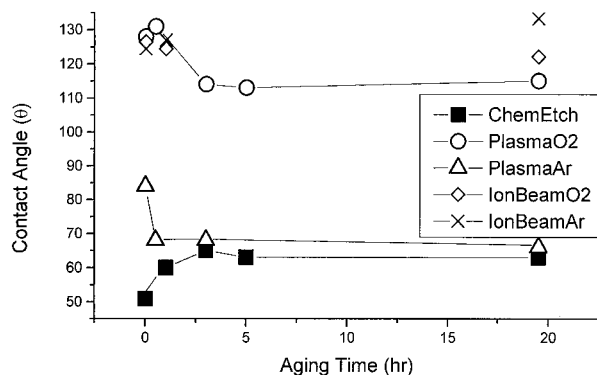


Figure 5 The contact angle changes with various air exposure time.

shows that the adhesion strength increases with treatment time. The peel strength was near zero without any surface treatment. It increased to about 8 g/mm after 60 min of oxygen plasma treatment, and to 28 g/mm after 60 min of argon plasma treatment. The increase of adhesion strength of PTFE by plasma treatments can be related to the formation of the chemical functional groups on the sample surfaces. If we ignore the different morphology effects onto adhesion strength, the higher adhesion strength of argon plasma-treated PTFE than that of the oxygen plasma-treated PTFE can be explained by the higher ratio of O/C (0.488) with the argon plasma treatment. The adhesive tape peeling after bonding to the plasma-treated PTFE had the particles on the top of the spire detached. This implies that a weak bond exists between the spherical particles on the spire and the base spire. This could be one of the reasons why the oxygen plasma-treated sample has a lower peel strength than the ion beam-treated sample.

The increase of peel strength with ion dose is shown in Figure 7. Argon and oxygen ion beam treatments showed roughly the same values of peel strength at each ion dose. The peel strength at the ion dose of 1×10^{17} is about 80 g/mm. It is 10 times larger than that of the 60-min oxygen plasma-treated one. The surface morphology and atomic chemical composition differences between ion beam treatment and oxygen plasma treatment appear to produce the different peel strengths. The high peel strength of the ion beam-treated PTFE with epoxy adhesives could be related to its large contact area of spire-like surface

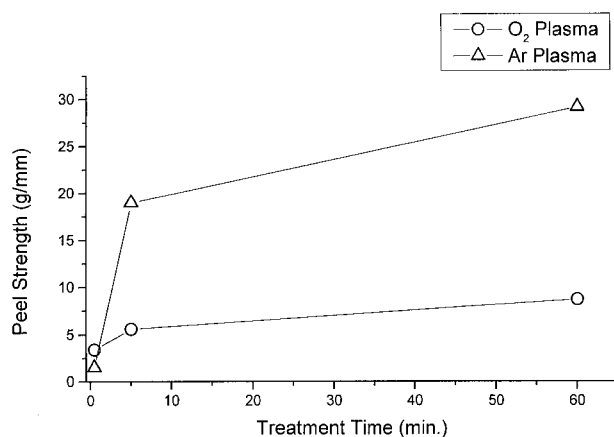


Figure 6 The peel strength with various plasma treatment time.

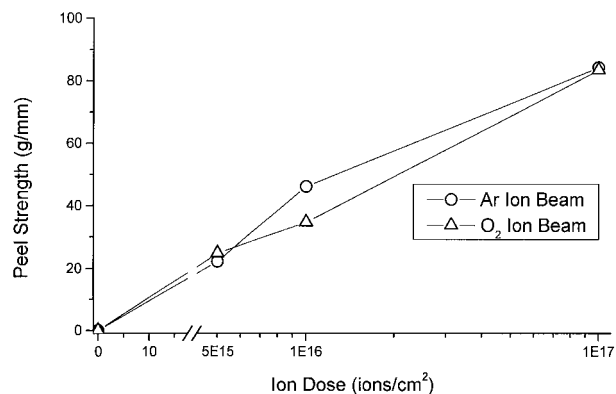


Figure 7 The peel strength with various ion beam dose.

structure of PTFE. The XPS study shows that only a very small amount of oxygen is incorporated on the surface during the ion beam treatment, and the contribution to the adhesion strength by the chemical change appears to be very small. This fact was confirmed by the contact angle measurement with aging. The contact angle did not change with aging in air for the ion beam-treated samples, as shown in Figure 5. The peel strengths were not related to the differences in F/C and O/C ratios of the ion beam-treated samples.

Therefore, it may be concluded that the major factor for adhesion enhancement of the ion beam-treated PTFE is morphology. From the mechanical point of view, formation of the regularly textured spire-like surfaces of PTFE allows an increased surface area for bonding and strong peel strength.

The author thanks Ms. Ju-Yeon Lee for the peel tests, and Ms. Sun-Hee Lee for SEM photographs.

REFERENCES

1. Mathieson, I.; Brewis, D. M.; Sutherland, I. *J Adhesion* 1994, 46, 49.
2. Chang, C. A.; Baglin, J. E. E.; Schrott, A. G.; Lin, K. C. *Appl Phys Lett* 1987, 51, 103.
3. Chang, C. A.; Chan, C. J.; Jones, F. *Appl Phys Lett* 1991, 59, 1069.
4. Brewis, D. M.; Mathieson, I. In *Modern Fluoropol-*

- mers; Scheirs, J., Ed.; John Wiley & Sons: Chichester, 1997.
5. Rusnock, J. A. 11th Annual Microwave Integrated Circuit Workshop "MIC-92," San Diego, CA, April 26-29, 1992.
 6. Brecht, V. H.; Mayer, F.; Binder, M.; *Angew Makromol Chem* 1973, 33, 89.
 7. Dwight, D. W.; Riggs, W. M. *J Colloid Interface Sci* 1974, 47, 650.
 8. Rong, C. J.; Wakida, T. *J Appl Polym Sci* 1997, 63, 1933.
 9. Inagaki, N.; Tasaka, S.; Goto, Y. *J Appl Polym Sci* 1997, 66, 77.
 10. Youxian, D.; Griesser, H. J.; Mau, A. W.; Schmidt, R.; Liesegang, J. *Polymer* 1991, 32, 1126.
 11. Morra, M.; Occhiello, E.; Garbassi, F. *Langmuir* 1989, 5, 872.
 12. Kuzuya, M.; Ito, H.; Kondo, S. I.; Noda, N.; Noguchi, A. *Macromolecules* 1991, 24, 6612.
 13. Hirotsu, T.; Ohnishi, S. *J Adhesion* 1980, 11, 57.
 14. Koh, S. K.; Park, S. C.; Kim, S. R.; Choi, W. K.; Jung, H. J.; Pae, K. D. *J Appl Polym Sci* 1997, 64, 1913.
 15. Shi, M. K.; Selmani, A.; Martinu, L.; Sacher, E.; Wertheimer, M. R.; Yelon, A. *J Adhesion Sci Technol* 1994, 8, 1129.
 16. Smolinsky, G.; Vasile, M. J. *J Eur Polym* 1979, 15, 87.
 17. Golub, M. A.; Wydeven, T.; Cormia, R. D. *Langmuir* 1991, 7, 1026.
 18. Garbassi, F.; Morra, M.; Occhiello, E. *Polymer Surfaces*, John Wiley & Sons: Chichester, 1994.
 19. Mittal, K. L. *J Vac Sci Technol* 1976, 13, 19.