Surface Functionalization of a Poly(vinylidene fluoride): Effect on the Adhesive and Piezoelectric Properties

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ABSTRACT We studied the effect of the surface functionalization and crystalline phase change of poly(vinylidene fluoride) (PVDF) films on their adhesion and piezoelectric properties. The surface modification of PVDF was carried out with ion beam and/or plasma treatment. These surface modifications were found to alter the interfacial strength between PVDF and metal electrodes and the crystal structure of the piezoelectric PVDF film. A remarkable improvement was found in the interfacial adhesion of the films with thermally deposited metal electrodes, but some piezoelectricity of PVDF film was lost due to the changes in the crystal phase. The proper treatment condition for enhancing the adhesion and retaining piezoelectric structure was suggested.

KEYWORDS: piezoelectric properties • PVDF • surface modification • ion beam irradiation • plasma irradiation

INTRODUCTION

Poly(vinylidene fluoride) (PVDF) is a semicrystalline homopolymer (1). One of its crystal states is ferroelectric and is responsible for PVDF's piezoelectric properties (2). Because of this peculiar property, it is very useful in a wide range of applications such as nonvolatile memory devices, infrared sensors, and actuator applications (3, 4). In these applications as well as other general applications such as automotive materials, pipes and fittings, bearings, linings, and vessels, good interfacial adhesion between PVDF and metal electrodes or metal surfaces is highly demanded. However, fluoropolymers have very low surface energies and thus poor adhesion with metals (5−7). Various methods such as plasma treatment, corona discharge, and bombardment with charged particles have been used to improve the adhesion of PVDF with metals (8−13). Although these methods do provide some improvement in the adhesion of PVDF with metals, they always result in the degradation of piezoelectric properties (14, 15).

In this study, we have employed surface treatments consisting of Ar^+ ion beam irradiation and/or RF oxygen plasma treatment to improve the interfacial adhesion between PVDF films and thermally deposited copper metal layers. We have also investigated the deterioration of the piezoelectric properties of the PVDF films due to the resulting surface structural change. The optimum conditions for the treatment of the surfaces of PVDF films to enhance their adhesion with metal electrodes as well as retain the piezoelectric properties were sought.

EXPERIMENTAL SECTION

Materials. The materials employed in this study were commercial piezoelectric PVDF films and copper sheets with a thickness of 40 μm. The piezoelectric PVDF films were purchased from Kureha Inc. (Japan). The films were washed in an ultrasonication bath with methanol for 10 min and then dried in a vacuum oven at room temperature for 24 h to remove the residual solvent prior to surface modification.

Ion-Beam Irradiation and Plasma Treatment. The surface modification system consists of a low-energy ion beam irradiation apparatus with a reactive gas feeding system (IBO) and a conventional plasma treatment system. Since the reactive low-energy ion beam irradiation system is fully described elsewhere (16−19), we will give only a brief introduction here. It was composed of a conventional ion beam system (IB), a reactive gas feeding system, and a stand for the polymer samples. The flow rate of Ar gas was 2 sccm, and the oxygen gas was fed at a flow rate of 5 sccm. The working pressure in the reaction chamber was kept under 10^{-4} Torr. The Ar^+ ion beam was generated from a 5 cm cold hollow cathode ion source, and its potential energy was maintained at less than 1 keV. The currents of ions were controlled by the discharge voltage and the ion beam potential. The discharge voltage was 400 V, and the ion fluence was varied between 5×10^{15} and 1×10^{17} ions/cm^2. The ion flux was measured with a Faraday cup placed slightly above the sample. In the oxygen plasma treatment process (OP), a radio frequency (13.56 MHz) plasma was generated with an RF power source (RF5S-PF Power Products Inc.), and the plasma power was fixed at 100 W. The gas used in this system was O_2 with a fixed flow rate of 10 sccm. In another modification process (IBOP), the ion beam and plasma processes were applied sequentially; low-energy Ar^+ ion beam irradiation was carried out first in the absence of reactive oxygen gas to change the surface morphology and then O_2 plasma treatment was performed to functionalize the surface over the same amount of time as was used in the ion beam process. The radio frequency (13.56 MHz) plasma was again

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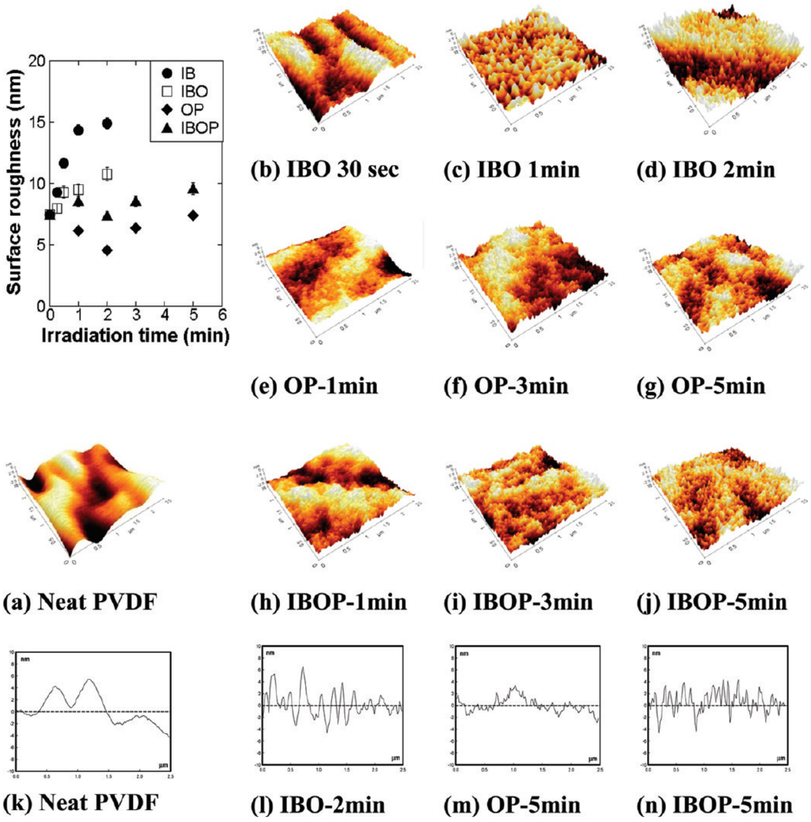


FIGURE 1. Plot of surface roughness change with irradiation time and AFM images of the modified PVDF surfaces: (a−j) 3D profiles; (k−n) 2D profiles.

generated with the RF power source, and the plasma power was fixed at 100 W. The O_2 gas flow rate was the same as that used in the OP process.

Modified Surface Characterization. Atomic force microscopy (AFM) images were obtained using a multimode scanning probe microscope (PDS II Inc.). Noncontact mode was used to obtain height imaging data with 125 μm long cantilevers. The lateral scan frequency was set as 1.0 Hz. The samples were moved in the $x-y$ plane, and a voltage was applied, which moved the piezoelectric driver over the z axis, in order to keep the probing force constant, resulting in a three-dimensional height image of the sample surface. SEM image analysis and XPS studies were employed for cleaved surface characterization. Scanning electron microscopy (SEM) observations of the samples were performed on a Hitachi S-2500C microscope. The fractured surfaces had been coated with gold in an SPI sputter coater. The morphology was determined using an accelerating voltage of 15 keV. In addition, the chemical components on the surfaces of PVDF and copper were analyzed by using X-ray photoelectron spectroscopy (XPS). A basic pressure of 2×10^{-10} Torr was maintained during the analysis. An energy resolution of 0.48 eV was kept. The XPS spectra were referenced to the main component of the C 1s peak of PEI at a binding energy of 284.6 eV. The irradiation treatment generally resulted in a small shift of all the peaks (up to ca. 0.6 eV) toward higher binding energies, implying an increased conductivity for the modified surfaces. Moreover, the referenced C1s binding energies of C−O, C=O, COO, and C−F were 286.5, 287.9, 289.0, and 289.6 eV and O1s binding energies of C=O and C−O were 531.9 and 533.1 eV, respectively. Overlapping peaks were resolved by using a peak synthesis method based on Gaussian and Lorentzian peaks.

Measurement of Adhesion Strength. A copper layer of ca. 200 nm in thickness was thermally evaporated onto each surface-modified PVDF film. This copper-deposited surface was then adhered to a copper sheet with an epoxy adhesive. The assembly was cured at 50 °C for 0.5 h and then subjected to the T-peel test with a universal testing machine (Instron 4204) at room temperature. The crosshead speed was 10 mm/min, and all the reported results are averages of 20 measurements.

Structure and Piezoelectric Properties. The crystal structures of the PVDF films modified with ion beam and/or plasma treatment were determined by using a wide-angle X-ray diffraction (WAXD) experiment of Rigaku Denki with Ni-filtered Cu Kα radiation at 40 kV and 100 mA. For the measurement of the piezoelectric properties, copper electrodes were thermally evaporated onto both surfaces of each surface-modified PVDF film by a vacuum thermal evaporation technique. The deposition was conducted under a pressure of 10^{-6} Torr up to approximately 200 nm. To measure changes in the polarization, the $P-E$ (where P is the polarization and E the applied voltage) hysteresis loop was obtained with a ferroelectric testing system (RT66A, Radiant Technology Precision) connected to a high-voltage interface. The piezoelectric constant in the thickness direction, d_{33}, was measured with a laser (633 nm He−Ne laser) reflection system (OFV-5000, Polytech) containing a high-voltage power supply and a high-voltage interface.

RESULTS AND DISCUSSION

Surface Characterization. Figure 1 shows the surface roughness change and AFM images of the PVDF surfaces resulting from the surface modification processes for various treatment times. The surface of neat PVDF is not completely smooth and flat: large hills and mounds and shallow valleys are present. The surface roughness decreases slightly at the commencement of plasma treatment, whereas the ion beam-only treatment (IB) results in a steady increase in the surface roughness. Surface modification by the ion beam

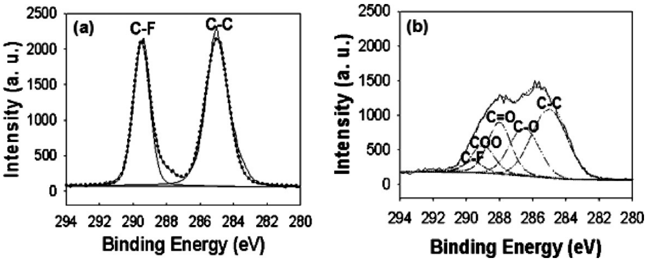


FIGURE 2. XPS spectra of (a) neat PVDF and (b) modified PVDF (IOBP 5 min).

and/or plasma is a process of interaction between the ion beam and/or the plasma and the surface of PVDF. There was a time limitation for Ar^+ ion beam irradiation due to the generated heat by the accelerated ion bombardment to the PVDF surface. In fact, after more than 3 min of ion beam irradiation, the 40 μm thick PVDF film partly melted and shrunk due to the high temperature of the heated surface.

During the ion beam and plasma treatments, the PVDF surfaces encounter many active species. Some C—C, C—H, or C—F bonds on the surface are broken during the processing (20), which results in rearrangement and etching on the surface and, thus, in changes in the surface morphology. Further, some of those active species encounter those broken bonds, resulting in the implantation of polar groups onto the surface and changes in the surface chemistry. During the plasma treatment, etching initially reduces but subsequently increases surface roughness. In contrast, surface modification during ion beam irradiation occurs as a result of collisions between Ar^+ ions and PVDF molecules on the surface. The kinetic energy of the ion bombardment enhances the roughening effect rather than the smoothing etching action. Reactive oxygen gas (or oxygen plasma in the IBOP process) is then incorporated into the surface. The etching pits, which appear at short irradiation times, evolved into grasslike structures, which became deeper and wider with increasing irradiation time as a result of the physical bombardment. By using AFM 2D profiles of modified PVDF surfaces (Figure 1k—n), we can obtain more information on surface morphology dependence depending on various surface-modifying methods. The oxygen plasma treatment makes small hillocks and depressions and forms grasslike structure with reduced size of globules, while the ion beam irradiation (IBO) makes the surface roughness steeper and forms a forestlike structure with larger globules. As a result, we could obtain very rough surfaces with mountainous regions as well as grasslike structures by the complex surface treatment (IBOP).

The two C1s peaks of neat PVDF in the XPS analysis shown in Figure 2a are symmetric with a narrow full width at half-maximum (fwhm). In contrast, the C1s peaks of the Ar^+ ion beam irradiated and O_2 plasma (IBOP) treated PVDF sample overlap, are reduced in intensity, and are asymmetric because of the oxygen-containing groups incorporated into the surface as well as defluorination (Figure 2b). This spectrum was decomposed into five peaks by using a Gaussian and Lorentzian peak fitting algorithm: a C—H or C—C peak at 285.0 eV, a C—O peak at 286.5 eV, a C═O peak at 287.9 eV, a COO peak at 289.0 eV, and a C—F peak at 289.6 eV. Table 1 shows the variation of the O/C atomic ratio of surface-modified PVDF with treatment time for different processes. For all three processes, the O/C atomic ratio increases with treatment time. However, after more than 5 min of plasma treatment and 2 min of ion beam treatment time, the O/C atomic ratio decreases. This result can be explained in terms of the carbonization of the PVDF surface and the re-etching effect: increasing the bombardment of the PVDF surface can result in not only cross-linking between polymer chains but also re-etching the functionalized surface (20). IBOP (5 min) results in the highest O/C ratio, while IB results in the lowest O/C ratio. In the IBOP process the effect of plasma treatment becomes more significant than the OP process due to the increased surface area and radical generation by previous ion beam irradiation. On the other hand, the oxygen plasma treatment is less efficient for the defluorination of PVDFs than ion beam irradiation with higher kinetic energy because the surface modification with incorporated oxygen groups on fluoropolymers such as PVDF and PTFE is not easy due to the resistance to oxygen attack of the fluorine atom (15). The change in the roughness during the plasma treatment process (OP) is also small due to its relatively low kinetic energy, while the effect of surface functionalization was good because of the electrically high potential which generates bonds with the polymer chains on the surface (17). The broken bonds on the PVDF surface and the active oxygen species generated by the collision between Ar^+ ion beam and oxygen gas or by the oxygen plasma encounter with each other, resulting in the implantation of polar groups onto the surface and changes in the surface chemistry. The formation of polar oxygen containing groups on the PVDF surface such as hydroxyl, carbonyl, and carboxyl groups contributes to the formation of a hydrophilic surface.

Table 1. O/C Atomic Ratio of Surface-Modified PVDF

treatment type	treatment time (min)	O/C atomic ratio
neat PVDF		0
IBO (Ar^+ ion beam + O_2 gas)	1	0.173
	2	0.199
OP (O_2 plasma)	1	0.489
	3	0.503
	5	0.543
IBOP (Ar^+ ion beam + O_2 plasma)	1	0.335
	3	0.533
	5	0.612

Changes in the functional-group concentrations on the PVDF film's surface lead to increases in the surface free energy. The effect of irradiation on the surface polarity is shown in Figure 3. It shows the change of the contact angle between water droplets and the virgin and modified PVDF surfaces with the irradiation time, respectively. After the surface treatment, the contact angle decreased with the irradiation time, owing to the effect of hydrophilicity. The PVDF film's surfaces treated with Ar^+ ion beam irradiation

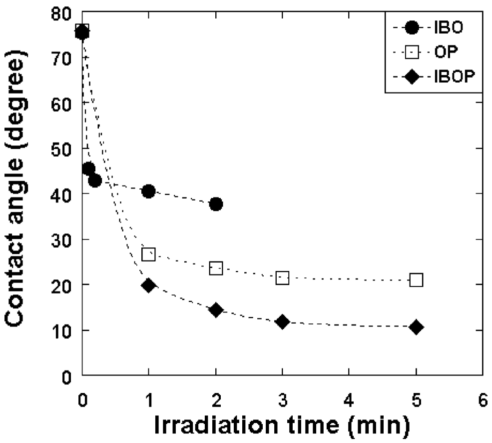


FIGURE 3. Plot of the variation of the contact angle of surface-modified PVDF with irradiation time.

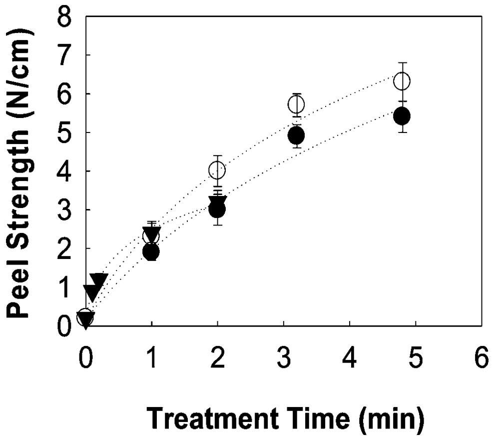


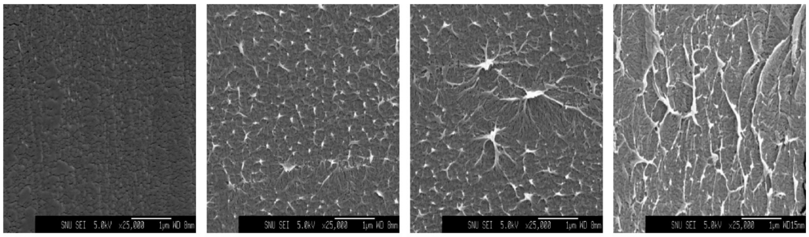
FIGURE 4. Variation of the peel strength of a surface-modified PVDF/copper interface with treatment time: (▼) IBO, ion beam irradiation with reactive oxygen gas; (●) OP, oxygen plasma treatment; (○) IBOP, ion beam irradiation plus oxygen plasma treatment.

under a reactive O_2 environment showed contact angles lower than those treated without O_2. The monotonic decrease in the contact angle can be ascribed to formation of hydrophilic functional groups. IBOP results in the largest contact angle drop-off, which coincides with the fact that IBOP provides the highest O/C ratio (Table 1).

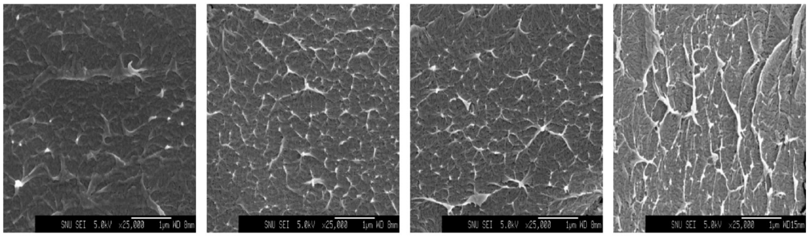
Interfacial Adhesion between Surface-Modified PVDF and Copper. Krupp et al. have reported that the presence of functional groups, such as ester or carboxyl groups, on a polymer surface can enhance its adhesion with the metals (21). Also, Goloub et al. have observed that carbon atoms in fluoropolymer chains are activated by defluorination and can then react with oxygen species (22). In our previous study, we found that changing the functional groups and morphology of poly(tetrafluoroethylene) dramatically increases its adhesion with copper film (17). Similarly, we expect that the adhesion between copper and PVDF films can be significantly enhanced by the generation of polar groups on the film surface with ion beam and/or plasma treatment. In the case of a PTFE/metal joint, the adhesion of several metals on roughened and fibrous PTFE surfaces was found to be enhanced by cross-linking and interlocking (17, 24, 25). However, PVDF does not exhibit the same behavior as PTFE. The strength of the adhesive joint between the PVDF films and the copper layer was found to vary with the treatment time (Figure 4).

A few facts are particularly worthy of note. The peel strength is severely affected by the changes in the functional groups and topology change on the surface. Untreated PVDF shows a very low interfacial strength under 0.1 N/cm, whereas the interfacial strength rapidly increases with the treatment time for all the surface modification processes. In particular, in the case of the OP process, although the surface roughness decreases slightly up to 2 min at the beginning of surface treatment, the peel strength increases significantly. This result indicates that the interaction between the functional groups on the PVDF surface and copper dominates the smoothing effects of etching. The SEM image in Figure 5 of fractured neat PVDF shows that it contains few developed fibrils, whereas all modified surfaces contain many developed fibrils of PVDF polymer chains due to strong adhesion at the interface (17, 23).

For the surface-modified PTFE/copper joint, the anchor-lock effect due to changes in the surface topography and the chemical interaction effect due to the functional groups



(a) Neat PVDF (b) IBO-2min (c) OP-5min (d) IBOP-5min



(e) IBOP-1min (f) IBOP-2min (g) IBOP-3min (h) IBOP-5min

FIGURE 5. SEM photographs of fractured PVDF surfaces.

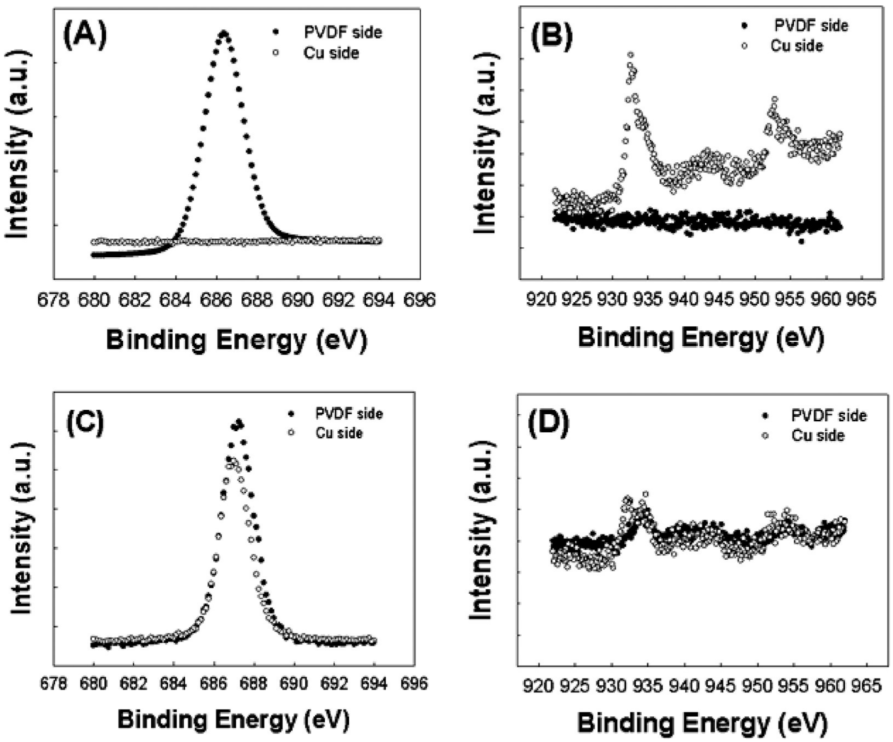


FIGURE 6. X-ray photoelectron spectra of the peeled-off surfaces: (A, B) neat PVDF/Cu joint; (C, D) modified PVDF/Cu joint. Solid and open symbols represent the PVDF side and the copper side, respectively.

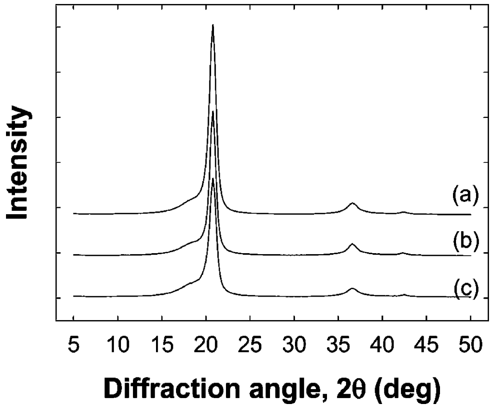


FIGURE 7. X-ray diffraction spectroscopy results for ion beam/plasma treated PVDF films: (a) neat PVDF; (b) IBOP (3 min); (c) IBOP (5 min).

formed on the PTFE surface were two main interactions that improve the peel strength between PTFE and copper (24, 25). The peel strength due to the anchor-lock effect dominated the peel strength due to surface functionalization (17). In the case of Ar^+ ion beam irradiation only, the change in the peel strength with the surface roughness for the PTFE/copper interface could be described using a logarithmic relation. Hence, we could separate the anchor-lock effect by using the roughness ratio between the system with a reactive gas added and the system with only Ar^+ ion beam irradiation. However, we could not observe such a relationship for a surface-modified PVDF/copper joint. In contrast to the PTFE case, the peel strength for the PVDF surface treated with only Ar^+ ion beam irradiation did not increase monotonously with the irradiation time. This means there were some weak points on the PVDF surface not filled with copper, possibly due to many shallow roughened valleys less than 3 nm (Figure 1) (17). Despite the faulty anchor-lock effect, the peel strength was significantly enhanced for all surface-modified samples, which implies that surface functionalization is a more decisive factor.

To investigate where the failure of the adhesive joint occurred, we observed the surfaces of failed parts by using SEM and XPS. As shown in Figure 5, the PVDF polymer layers that were peeled off from the neat PVDF/copper adhesive joint showed a flat surface, whereas those peeled off from the ion beam irradiated PVDF/copper adhesive joints show many fibrils formed by stretching the PVDF polymer. This indicates that the failure occurred at the PVDF/copper interface for the former case, while it occurred in the inner layer of the PVDF for the latter cases. The XPS analysis confirmed this (Figure 6). For the virgin PTFE/Cu adhesive joint, the copper side showed no F1s peak and a strong, sharp Cu2p3/2 spectrum. Meanwhile, the PVDF side showed no Cu2p3/2 spectrum. This indicates that the polymer surface and the copper surface were completely different in chemical composition and that the failure definitely occurred at the interface (adhesive failure). For the Ar^+ ion beam irradiated (IBOP) PVDF/Cu adhesive joint, the copper side and the PVDF side showed very similar spectra (especially a strong F1s peak on the Cu side) and almost no Cu2p3/2 spectrum was seen on either side. The two layers peeled off from the adhesive joint showed homogeneity in the chemical composition. This means that the failure occurred in the inner layer of the PVDF surface. Therefore, we can conclude that the ion beam treatment changed the failure mode from adhesive failure to cohesive failure; thus, the ion beam modified surface was significantly increased (17, 26).

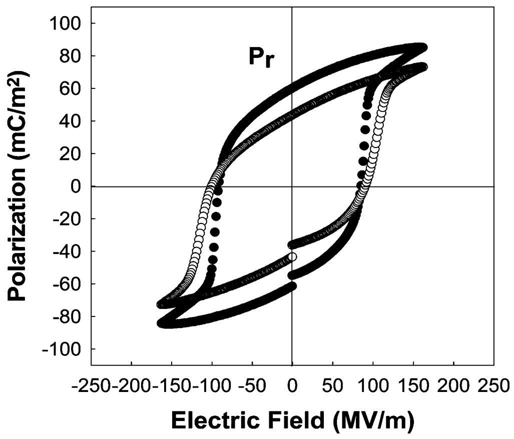


FIGURE 8. ***P*−*E* hysteresis loops for neat and surface-modified PVDF films: (●) neat PVDF film; (○) PVDF film modified with IBOP (5 min).**

Structure and Piezoelectric Properties of Surface-Modified PVDF. The wide-angle X-ray diffraction (WAXD) results in Figure 7 shows the change in crystal structure with IBOP treatment time. The crystallinity generally decreases with the oxygen plasma treatment time. In particular, the amount of polar β-phase crystal at a 2θ value of 20.6° (110) was decreased. This result is in agreement with that reported by Virk et al. (15): the reduction in peak intensity indicates that the crystalline structure of PVDF has evolved toward a more disordered amorphous structure as a result of the oxygen plasma treatment. Our samples were fully stretched and poled piezoelectric PVDF films; therefore, crystal form I (β phase) is well developed. After surface treatment, the β phase in the surface layer seems to be lost, since form I is relatively more unstable than form II (α phase) (2, 22). This can be corroborated by the fact that the sample surface treated by the IB process was degraded more severely. IB bombardment induced the generation of some spots with temperature higher than the surroundings; this makes chain scission easier and leads to the loss of the β phase. The kinetic energy of the collided ion beam brought up the occurrence of these two phenomena.

The ferroelectric polarization of PVDF can be characterized with a $P-E$ (polarization P (μC/cm^2) vs applied voltage E) hysteresis plot. A sinusoidal ac electric field (50 Hz) was applied across the polymer film with an amplitude of 250 mV/m. Figure 8 shows the changes in the PVDF remnant polarization (Pr) for IBOP-treated samples. Pr decreases after the surface modification, which interferes with the polarization of the stretched and poled PVDF film. This result agrees with the WAXD data. Park et al. have reported remnant P values increasing with the contact area between the polymer film and the electrode (23). The fact that the loss of polarization occurs in spite of the increase in the contact area by the surface treatment implies that loss of β phase crystallinity was more dominant than the increase by the contact area increase. Figure 9 shows the displacement change of piezoelectric PVDF modified by IBOP treatment. There are some displacement changes with the increase of treatment time, indicating some piezoelectric property degradation. However, the change does not seem to be severe. Meanwhile, δt values, the phase lags of response time to the applied voltage, are almost the same, regardless of the treatment time. This means the complex ion beam and plasma treatment not only can enhance the interfacial adhesion but also does not change the piezoelectric responding time with the same signal phase, although it brings some small degradation of piezoelectric properties. This is ascribable to the shallow depth of surface modification; the main body of PVDF was intact, as were the piezoelectric properties.

The piezoelectric constant, d_{33}, normal to the plane of the film, was measured to investigate the effects of surface modification on the piezoelectric properties of each drawn and poled PVDF film. The results in Figure 10 were obtained with a laser detecting system and the equation $d_{ij} = [\partial\epsilon_j/\partial E_i]\sigma_j$, where d_{ij} is the piezoelectric strain constant, ϵ_j is the strain, σ_j is the stress and E_i is the electric field. The

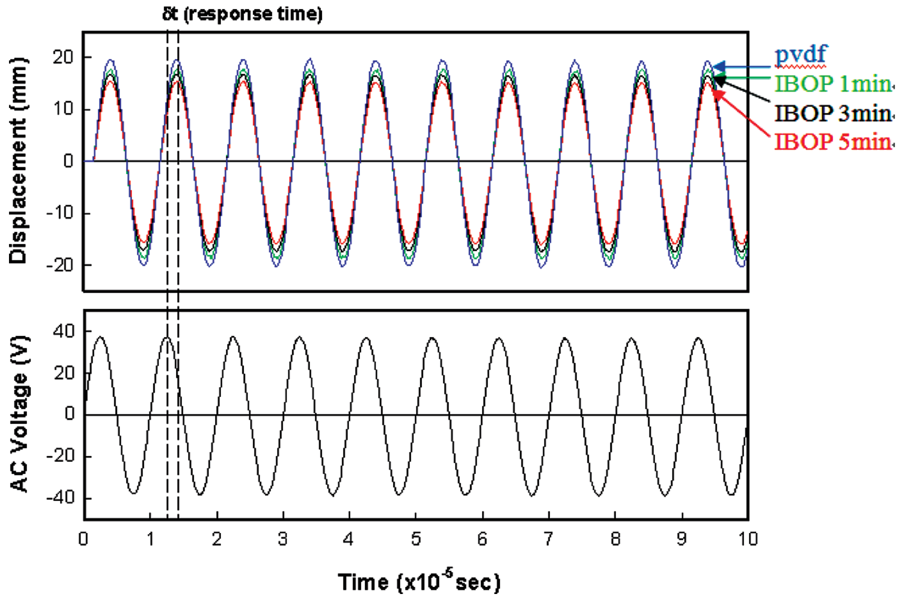


FIGURE 9. Displacement and applied ac voltage signal versus response time of PVDF modified by IBOP treatment.

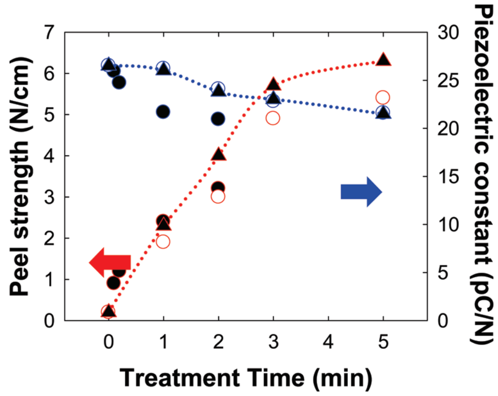


FIGURE 10. Adhesion strength and piezoelectric properties versus exposure time: (●) IBO, ion beam irradiation with reactive oxygen gas; (○) OP, oxygen plasma treatment; (▲) IBOP, ion beam irradiation plus oxygen plasma treatment.

piezoelectric constant in the 33 direction, which is the film thickness direction, was found to decrease with treatment time, but less significantly than for PVDF/aluminum joints (29). In fact, d_{33} of the surface-modified PVDF samples by ion beam only (IB) shows more rapid decrease than that of the other samples, because of the distorted and heated PVDF surface by the local heating that can result in the loss of the β phase and polarization. Therefore, in the surface modification of PVDF films, it is necessary to consider two opposing effects simultaneously: i.e., the improvement in the strength of adhesion between PVDF and metals and the (less significant) loss of piezoelectricity of poled PVDF. In the case of the IBOP process, which results in the most significant adhesion strength improvement and the least piezoelectricity loss, there is a treatment time in which the adhesive strength rapidly increases and the piezoelectricity loss is minimal. As shown in Figure 10, the optimum range of treatment time can be determined experimentally. For the IBOP case, when the ion beam pretreatment time was 30 s, it is between 2 and 3 min depending on the required adhesion strength. With the appropriate surface treatment processing conditions, not only can enhanced adhesion between the piezoelectric PVDF film and the copper layer be achieved but also high piezoelectricity can be retained.

CONCLUSIONS

The effects of modifying PVDF film surfaces with three different processes (IBO, OP, and IBOP) on their adhesion with metal films and their piezoelectric properties were experimentally investigated and compared. All processes effectively modify the surface both physically (morphology) and chemically (surface composition). After the treatment, the surface roughness increases due to etching by ion beam irradiation and/or plasma reaction and the incorporation of oxygen-containing polar groups into the surface. These changes (in morphology and composition) have positive effects on adhesion with metal films but negative effects on the polarization of PVDF due to the loss of the β phase. The combined ion beam/plasma process (IBOP) was found to be the most promising method, in that it results in a remarkable improvement in the adhesion between PVDF and the metal film and in less deterioration of piezoelectric properties. The presence of these opposing effects means that treatment time interval in the PVDF surface modification needs to be optimized, which should be decided depending on the demands.

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