# Improvement of Bond Strength of BPDA-PDA-Type Polyimide Film by Corona Discharge Treatment

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**ABSTRACT:** Aromatic polyimide film composed of biphenyl tetracarboxylic acid dianhydride (BPDA) and *p*-phenylene diamine (PDA) is a very stable polymer at high temperatures and very useful for the electronics industry. Bonding properties were improved by corona discharge treatment of this film. The chemical modification method was applied for generated functional groups, that is, carboxylic, hydroxyl, and amino groups in the gas phase, and the quantity of these functional groups was determined by X-ray photoelectron spectroscopy. The functional groups increased with corona energy, leveling off at a specific corona energy. The bond strength of the copper foil/adhesive/polyimide film was determined. The relationship between bond strength and functional group content was analyzed by multivariate analysis. Bond strength could be sufficiently correlated with functional group quantity. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 100: 3403–3408, 2006

**Key words:** polyimides; corona adhesion; XPS

## INTRODUCTION

Aromatic polyimides were developed in the 1960s for space flight applications. The first aromatic polyimide was commercialized in 1965. Aromatic polyimide is known as a highly heat-resistant polymer. It is used as a film and as a flexible print circuit board and is an indispensable material in equipment that uses liquid crystals. Demand has increased with expansion of the electronic industry year by year. There are several methods of preparing a circuit board, that is, sticking polyimide film to copper foil with adhesives, deposition of metal by sputtering[1–4] or electroless deposition from solution[5,6] on polyimide film, and coating or deposition of polyimide precursor[7–9] [poly(amic acid)] on copper foil, followed by heat treatment. In this study, we used the method that employs adhesives.

The chemical structure of aromatic polyimides shows them to be polar materials. We calculated the charge density distribution with software (WinMopac; Fujitsu Co. Ltd., Tokyo, Japan) based on a molecular orbital method. The charge density distribution of the polymers used in this study, biphenyl tetracarboxylic acid dianhydride and *p*-phenylene diamine, is shown in Figure 1. The oxygen and carbon atoms in the imide group had electron densities of $-0.225$ and $+0.291$ e.c.u., respectively, indicating strong polar properties. However, the imide group was always present in the

aromatic ring plane and could not easily make strong intermolecular interactions with other molecules such as hydrogen bonding. The poor bonding properties of polyimide films are sometimes caused by this chemical structure, though various adhesives and surface modification have been tried. The problem always occurs, not between copper foil and adhesive, but between adhesive and polyimide film or between the film and metal. In most cases, bond strength exceeding 800N/m is required, though in a lot of cases, this value is not reached. To improve bonding properties, the surface of polyimide film was modified and the adhesive was improved. Many attempts[1–11] to use plasma discharge treatment on polyimide film have been reported. However, no detailed report on corona discharge treatment has been published. Katnani et al.[2] and Inagaki et al.[12] claimed to have detected carboxyl and amide groups using X-ray photoelectron spectroscopy (XPS) and infrared spectra of plasma-treated polyimide. However, infrared spectra are not reliable for plasma-treated surfaces because under the usual conditions, plasma treatment changes the surface only to a depth of 200 nm. It is actually impossible to observe the surface change by this method. A peak observed around 290 eV in XPS spectra increased after plasma or corona discharge treatment. However, this peak was not necessarily a result of the carboxyl groups but may have been caused by the ester or other carbonyl groups. A more reliable method for investigating the functional groups after corona or plasma discharge treatment is needed. In the present study, several functional groups generated by corona discharge treatment were determined by XPS with chem-

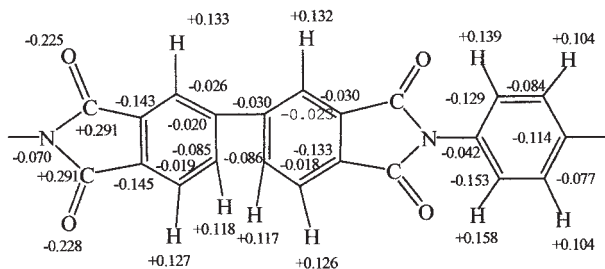*Correspondence to:* T. Ogawa (tsogawa@neptune.kanazawa-it.ac.jp).

**Figure 1**  Electron densities of UPLIEX S (numbers indicate electrochemical unit).



**Figure 3**  Infrared spectrum of adhesive sheet.

ical modification using fluorine-containing compounds. With this chemical modification method, we could accurately determine the functional groups.

Determining how functional groups contribute to bond strength is very important. In this study, the corona discharge–treated polyimide film was bonded with copper foil using an adhesive sheet, and bond strength was determined. The relationship between functional group content and bond strength was investigated by applying multivariate analysis.

## EXPERIMENTAL

### Materials

The polyimide film used was composed of biphenyl tetracarboxylic acid dianhydride (BPDA) and *p*-phenylene diamine (PDA). The film, 12.5 μm thick, was supplied by Ube Industries, Ltd. (Tokyo, Japan); its commercial name is UPILEX-12.5SN. The copper foil was prepared by electrolysis, and the microphotograph of the surface is shown in Figure 2. The foil, which was made at the Hukuda Metal Powder Co. Ltd. (Kyoto, Japan), was grade RCF-T8. The accurate chemical structure of the sheet-type adhesive used in this study is not known. The infrared spectrum of the
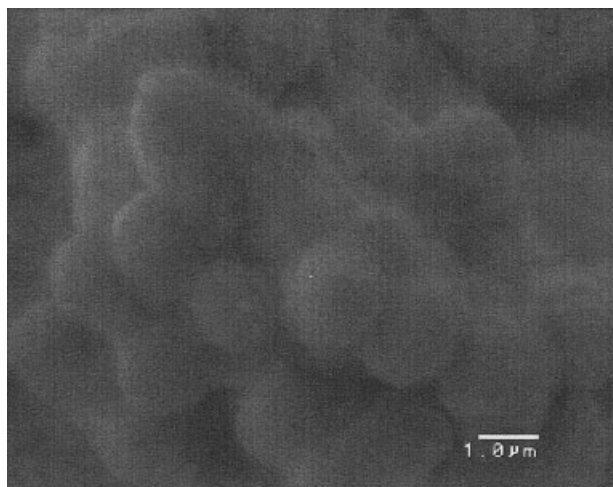


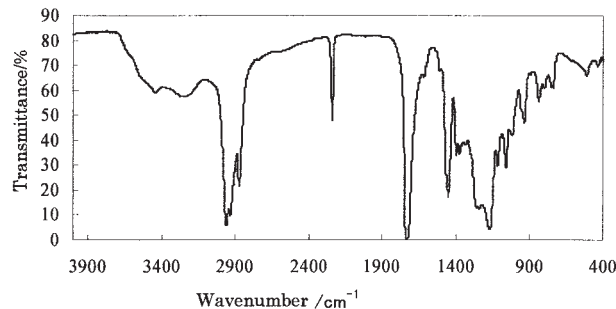**Figure 2**  Scanning electron microphotograph of copper foil.

adhesive is shown in Figure 3, and the element percentages determined by XPS are shown in Table I. The infrared spectrum shows that aliphatic esters (2964, 1728, and 1173 cm$^{-1}$) and acrylonitrile (2241 cm$^{-1}$) were present and that the ester was considered to be methacrylic acid ester, determined by comparing it with many standard spectra. Judging from these results, this adhesive was estimated to be a copolymer composed of butyl acrylate and acrylonitrile with a monomer ratio of around 3:7.

### Corona discharge treatment

Corona discharge treatment was performed in air using a commercially available apparatus, Model HPS-10 (Nihon Static Co. Ltd., Tokyo, Japan). The experiment was carried out in air with a wave number of 20 kHz and a maximum voltage of 15 kV. The discharge energy was calculated according to eq. (1):
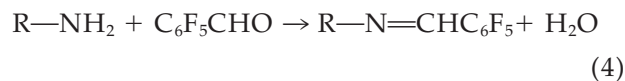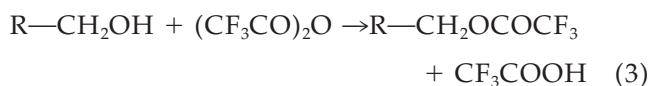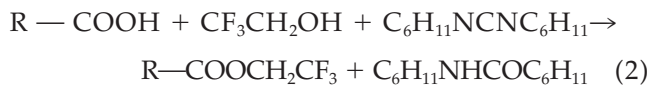
$$E = \frac{P}{L \cdot V} \tag{1}$$

where $E$ is the corona energy (J/m$^2$), $P$ is the discharge power (W), $L$ is the length of the electrode, and $V$ is the scanning speed of the sample (m/s). The distance between the sample and the upper electrode was 2.0 mm. The roll-type electrode (lower side) was covered with silicon rubber.

### Chemical modification

Fluorine-containing derivatives were prepared according to the following equations for carboxyl, hydroxyl, and amine groups, respectively[13]:

**TABLE I**
**Atomic Content (%) of Adhesive Sheet**

| $C_{1s}$ | $N_{1s}$ | $O_{1s}$ |
|---|---|---|
| 72.8 | 2.6 | 24.6 |

$$R — COOH + CF_3CH_2OH + C_6H_{11}NCNC_6H_{11} \rightarrow$$
$$R—COOCH_2CF_3 + C_6H_{11}NHCOC_6H_{11} \quad (2)$$

$$R—CH_2OH + (CF_3CO)_2O \rightarrow R—CH_2OCOCF_3$$
$$+ CF_3COOH \quad (3)$$

$$R—NH_2 + C_6F_5CHO \rightarrow R—N{=}CHC_6F_5 + H_2O \quad (4)$$

The reactions were carried out separately in the gas phase. The atomic ratio (%) of carboxylic acid carbon to all the carbon atoms detected is expressed by eq. (5):

$$R_{COOH} = \frac{[F_{1s}]}{(3[C_{1s}] - 2[F_{1s}])r} \times 100 \quad (5)$$

The atomic ratio (%) of hydroxyl carbon to all the carbon atoms detected is expressed by eq. (6).

$$R_{OH} = \frac{[F_{1s}]}{(3[C_{1s}] - 2[F_{1s}])r} \times 100 \quad (6)$$

The atomic ratio (%) of primary amine nitrogen to all the nitrogen atoms detected is expressed by eq. (7):

$$R_{NH_2} = \frac{[F]}{5[N_{1s}]r} \times 100 \quad (7)$$

where brackets indicate the atomic content of all the atoms observed. The yield of the reaction, $r$, was determined in advance using model polymers or the compound for eqs. (5)–(7). Poly(acrylic acid) for the carboxyl group, poly(vinyl alcohol) for the hydroxyl group, and 4,4′-diamino diphenyl ether for the primary amine were used as the model materials, and the values obtained by our laboratory for $r$ were 0.38, 0.67, and 0.87, respectively.

### XPS analysis

Surface characterization was carried out by XPS with Model ESCA3400 (Shimadzu Co. Ltd., Kyoto, Japan). The pressure of the analyzing chamber was kept below $10^{-5}$ Pa. Excitation was performed by X-ray of the Mg K$\alpha$ line ($hv$ = 1253.6 eV), with the emission voltage and current of the source set to 8 kV and 30 mA, respectively. The value of 285.0 eV of hydrocarbon $C_{1s}$ was used as the standard for the energy scale.

### Measurement of bond strength

The laminated sheet composed of the surface-modified polyimide film, the adhesive sheet, and the copper foil was prepared to a size of $10 \times 30$ mm by using a test press with a pressure of 100 N/cm$^2$ at 200°C for 30 min. The peel test from the T-peel method (ASTM D-1876) was carried out with a tensile tester at a peel speed of 5 mm/min using a sample 20 mm in width. The maximum value used in the stress-versus-displacement curve was that of the bond strength.

### Contact angle

The contact angle with water was measured using a Model CA-A contact meter (Kyowa Interface Science Co. Ltd., Tokyo, Japan) for corona-treated polyimide film. The measurement was carried out within 2 h of the corona treatment. The average of 10 measured values was adopted as the contact angle measurement.

## RESULTS AND DISCUSSION

### Generation of functional groups

It is well known that many functional groups are generated by corona discharge treatment with and without chain scission. The addition of some functional groups to the phenyl ring is possible. However, destruction of the phenyl ring of the polymer is rare, though the introduction of a carbonyl group by the destruction of a phenyl group is believed to have occurred in some cases.[14] Further, oxygen- or nitrogen-containing functional groups are likely to be generated because the corona discharge treatment is carried out in air. For polyethylene, it has been shown[15] that peroxide-, hydroxyl-, carbonyl-, carboxyl-, epoxy-, and a small amount of nitrogen-containing groups are generated by corona discharge treatment. The functional groups strongly related to adhesion are carboxyl and hydroxyl groups.[16,17] For aromatic polyimide, the primary amine group is also important, though this has not been proven. That is why we considered carboxyl, hydroxyl, and primary amine groups in this study. The XPS peak most sensitive to functional groups was that of $C_{1s}$, as shown in Figure 4. However, it actually was impossible to distinguish between ester, ketone, and aldehyde or between alcohol and ether by the $C_{1s}$ peak. However, the existence of the functional groups was clearly proven by the chemical modification, as shown in Figure 5. Thus, the quantity of the above three functional groups was determined as a function of corona discharge energy by XPS after chemical modification of these functional groups. The results are shown in Figure 6. The surface content of the primary amine and carboxyl groups increased steeply with corona energy and leveled off at a corona energy of around $2 \times 10^4$ J/m$^2$. In addition, the behavior of the primary amine group seemed to be slightly different from that of the carboxyl group in the region greater than $2 \times 10^4$ J/m$^2$. On the other hand, the hydroxyl group content was almost constant at all energy levels. The surface content of the hydroxyl group was probably within the error. These
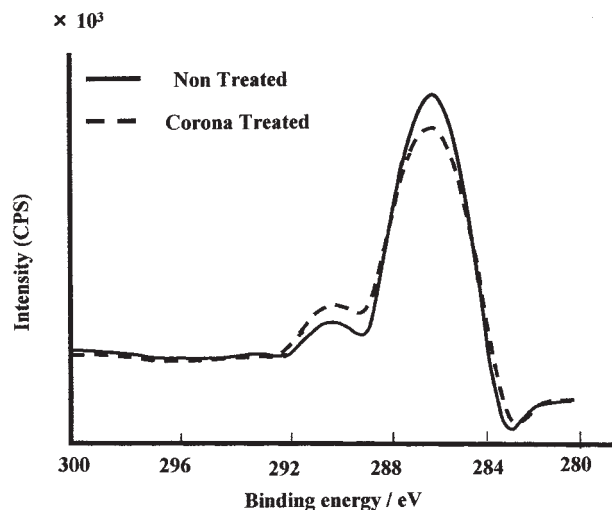
**Figure 4**  $C_{1s}$ peak in XPS spectrum of UPILEX S.

results showed that the amount of carboxyl and primary amine groups remained nearly constant regardless of corona energy in the higher region. Further, the results suggest that water molecules were added to polyimide molecules after excitation by corona discharge. In other words, apparently the polyimide polymer was hydrolyzed by corona discharge. Judging from the functional group content, hydrolysis probably advanced, as shown in Figure 7. The left-hand side of the chemical structure bonded to the usual polyimide chain. The surface functional groups determined by XPS were for a depth of 5 nm. So the chemical structure shown on the left-hand side of
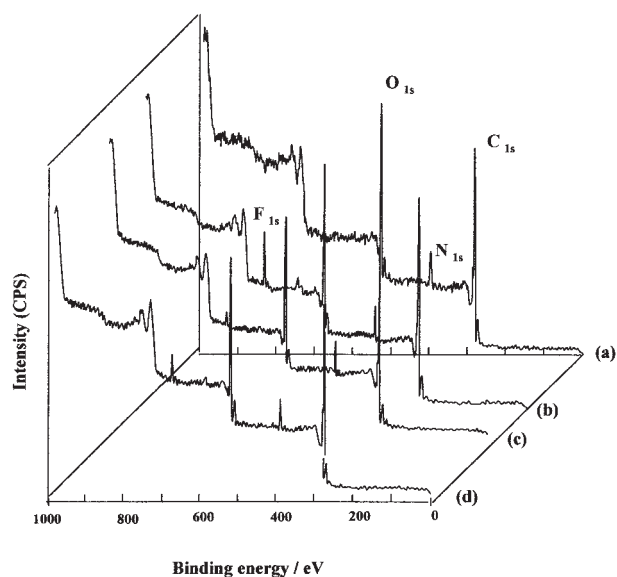


**Figure 5**  XPS spectra before and after chemical modification: (a) corona discharge–treated spectrum ($2 \times 10^4$ J/m$^2$); (b) for carboxyl group after chemical modification [eq. (2)]; (c) for hydroxyl group after chemical modification [eq. (3)]; (d) for primary amine after chemical modification [eq. (4)].
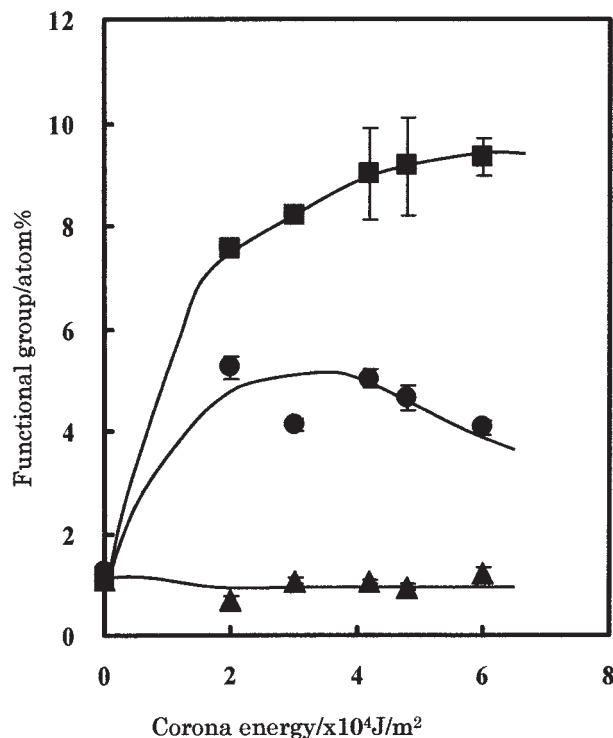


**Figure 6**  Functional group content as a function of corona energy.

Figure 7 was only determined by XPS. The primary amine group content, shown in Figure 6, was apparently larger than that of the carboxyl group. This was because the values are expressed as the ratio of carbon or nitrogen observed to all the carbon or nitrogen atoms in the polymer. The molecular weight of the part with five repeating units shown in Figure 7 was about 4000. This part would easily disappear from the film surface by the sputtering effect after the scission of the polymer chain, because the surface content of these functional groups did not increase even if we increased the corona energy.

## Contact angle

The contact angle with water for this film decreased steeply with corona energy, leveling off at around $2 \times 10^4$J/m$^2$, as shown in Figure 8. This tendency cor-
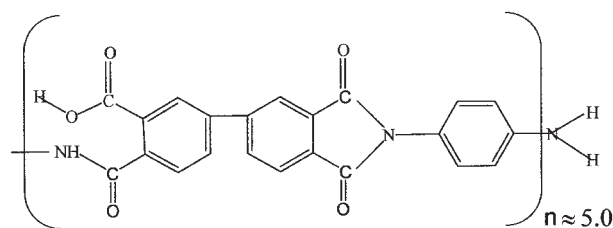


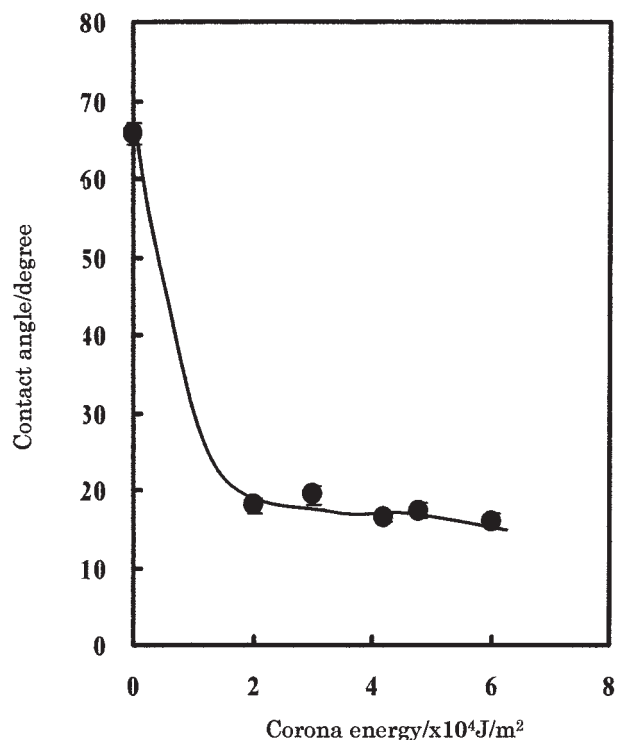**Figure 7**  Estimated chemical structure of UPILEX S after corona discharge treatment.

**Figure 8**  Contact angel of water as a function of corona energy.



**Figure 9**  Bond function as a function of corona energy in copper foil/adhesive strength/polyimide film system.

responds to the behavior of the functional groups. Surprisingly, the contact angle reached 20°, showing high surface tension and strong hydrophilic properties. Such a low contact angle suggests that very polar functional groups were present on the surface because the contact angle of water in plasma-treated polyethylene[18] is around 40° under the best conditions.

### Bond strength

The bond strength of the laminated film composed of polyimide film, adhesive, and copper foil was determined by the peel test, and the results are shown in Figure 9. Bond strength increased with corona energy, except in the high-energy region, where it decreased slightly with corona energy. This phenomenon could be caused by the degradation of the polymer in this region.

This behavior also corresponds to that of functional groups. When untreated polyimide film was used, bond strength was around 250 N/m. However, with corona discharge treatment, bond strength reached around 1200 N/m, showing the excellent effects of the treatment. In the peel test, the place of failure is very important. It could be seen with the naked eye that the adhesive always remained on the Cu side. Further, the XPS spectra of the peeled surface are shown in Figure 10. The XPS spectrum of the polyimide side after peeling was similar to that of the film as received. The spectrum of the copper-foil side was similar to that of the adhesive sheet. It is clear from this that peeling
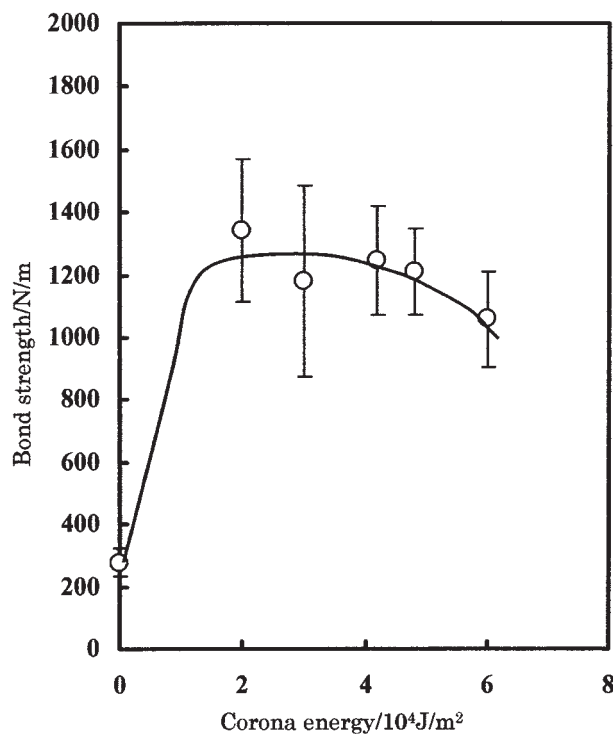
mainly occurred between the polyimide film and the adhesive.

### Multivariate analysis

Bond strength between the polyimide film and the adhesive was expected to be largely influenced by the
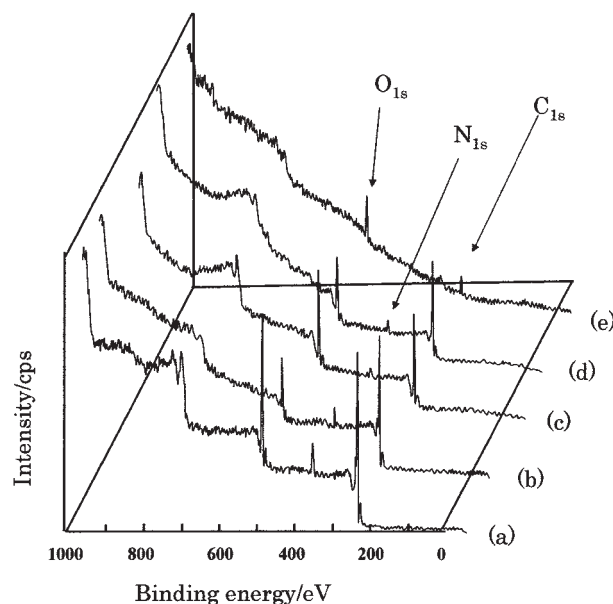


**Figure 10**  XPS spectra of as received, peeled, and corona discharge surfaces: (a) polyimide film as received; (b) polyimide film after peeling; (c) adhesive sheet; (d) copper foil after peeling; (e) copper foil.
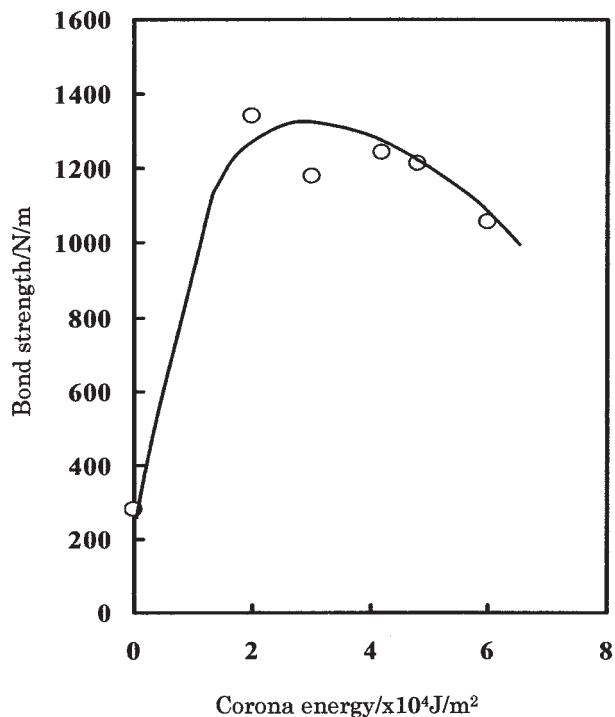
**Figure 11** Comparison of experimental points with estimated curve obtained by multivariate analysis.

quantity of functional groups generated. Therefore, multivariate analysis was carried out with the bond strength as the criterion variable and the quantity of functional groups as the explanatory variable. The quantity of hydroxyl groups was neglected because this did not change over the whole corona energy range tested. The equation obtained [eq. (8)] was:

$$F = 277.0 \cdot X_1 + 19.7 \cdot X_2 - 15.7 \qquad (8)$$

where $F$ is the bond strength, $X_1$ is the quantity of carboxyl groups, and $X_2$ is the quantity of primary amine groups. The predicted curve with experimental points is shown in Figure 11. The coefficient of determination was 0.98, and multicollinearity was not observed. Using this relationship, we were able to predict bond strength with high accuracy from the quantity of functional groups on the surface. However, the extent of the contribution of the functional groups to bond strength was not clear from eq.(8). When it was normalized, we obtained eq. (9):

$$F' = 0.845 \cdot X_1' + 0.159 \cdot X_2' \qquad (9)$$

This equation showed that the contribution of the carboxyl groups of 0.845 was larger than the contribution of 0.159 of the primary amine groups.

## CONCLUSIONS

Surface modification was carried out by corona discharge treatment for aromatic polyimide film composed of tetracarboxylic acid dianhydride and *p*-phenylene diamine. The functional groups on the surface, such as carboxyl and primary amine groups, were determined by XPS with chemical modification. Further, the polyimide film was laminated with copper foil using adhesive. The relationship between bond strength and functional group content was analyzed by multivariate analysis. Bond strength was quantitatively correlated with functional group content.

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