

Surface Modification of Aromatic Polyamide Film by Aminoethanethiol Solution for Silicon Rubber Composites

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SYNOPSIS

The surface modification of poly(*p*-phenylene terephthalamide) (PPTA) film with 2-aminoethanethiol (AET) to adhere to silicon rubber was investigated. The combination of the AET treatment and the silane coupling treatment is an effective surface modification of the PPTA film for this adhesion. The x-ray photoelectron spectroscopy (XPS) analyses show that the AET treatment does not generate sulfur functionalities at the surface of the PPTA film but does generate oxygen functionalities. In the AET treatment process, a part of the amide groups near the surface of the PPTA film is hydrolyzed to form carboxylic acid groups and amino groups. The oxygen functionalities are condensed at the film surface, and nitrogen functionality is diluted at the film surface. The C(O)O moiety at the PPTA film surface may be a key factor for the adhesion with silicon rubber. The C(O)O moiety is mobile from the bulk of the PPTA film to the film surface. Hot water treatment of the original PPTA film makes the impossible adhesion with the silicon rubber possible. The hot water treatment, however, is not as powerful a surface modification as the AET treatment. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Poly(*p*-phenylene terephthalamide) (PPTA) is a super-performance polymer, and is usually provided as a form of fiber. This fiber possesses high tensile strength, modulus, and thermal resistance, and is a most suitable material for composites. In application of the PPTA fiber for the composites, poor adhesion with polymer matrices (such as epoxy resins) is a serious problem. Several modifications of the PPTA fiber have been attempted to improve the adhesion, including grafting, substitution reactions of hydrogen in amide groups, hydrolysis of amide groups, and the formation of oxygen functionalities by plasma treatment.¹⁻⁹ Some of these modifications have succeeded in improving the adhesion, but these modification processes necessitate expensive and special chemicals, bothersome and dangerous procedures, or time-consuming procedures.

The poor adhesion is attributed to a highly crystalline microstructure of the PPTA fiber and chem-

ically inactive components composing the PPTA polymer chains. We have proposed a surface modification process to improve the adhesion with silicon rubber,¹⁰ a combination of the oxygen plasma treatment and silane coupling treatment. In this study, another surface modification instead of the plasma treatment is sought. An answer is the modification reactions with 2-aminoethanethiol (AET) in water. The surface modification with AET has been reported in a form of Freilich's 1992 U.S. patent.¹¹ He applied this surface modification method to polyimide film, KaptonTM to improve the adhesion with copper metal. However, he did not provide details of the mechanism of this modification. Our interests are whether or not the surface modification with AET can extend to other nitrogen-containing polymers (especially aromatic polyamides) besides polyimides, and what chemical reactions occur at the surface of aromatic polyamide in the modification process. In this study, we investigate the adhesion between the AET-treated PPTA and silicon rubber to determine the AET treatment's applicability to the surface modification of aromatic polyamides, and further, we investigate spectroscopically the surface

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of the AET-treated aromatic polyamides to discuss what modification occurs at the polyamides' surface.

EXPERIMENTAL

Material

The aromatic polyamide film used in this study was poly(*p*-phenylene terephthalamide), or PPTA (Aramika™), kindly provided by Asahi Kasei Kogyo Co., was 500 mm wide and 25 μm thick. The PPTA films were washed with acetone in an ultrasonic washer prior to the surface modification experiments. 2-aminoethanethiol (AET) was purchased from Tokyo Kasei Kogyo Co. A silane coupling reagent, TSE322, was obtained as a form of a toluene solution (30 wt %) from Toshiba Silicon Co. Silicon rubber, KE981, was obtained from Shin-etsu Chemical Co.

Surface Modification

The PPTA films were modified by a combination of two consecutive processes: the AET treatment and the silane coupling treatment. First, in the AET treatment process, the surface of the PPTA films was treated with an aqueous solution of AET (5–10 wt %) at 100°C for 15–180 min. Then the PPTA films were rinsed with water and dried under a vacuum. Next, in the silane coupling process, the AET-treated PPTA films were dipped in a toluene solution of TES322 (30 wt %) for 10 min, removed from the solution, and then heated at 150°C for 1 h.

PPTA Film/Silicon Rubber Composite and Peel Strength of PPTA Film/Silicon Rubber Joint

The modified PPTA films were placed at the bottom surface of a mold (18 wide × 50 long × 5 mm deep), and the silicon rubber (KE981) was injected into the mold. The silicon rubber was cured under a pressure of 9.8×10^6 Pa at 150°C for 20 min.

The 180° peel strength of the adhesive joints between the PPTA film and the silicon rubber was evaluated at a peel rate of 50 mm/min with an Instron.

X-ray Photoelectron Spectra

The x-ray photoelectron spectroscopy (XPS) spectra of the surface of the PPTA films were obtained on a Shimadzu ESCA K1 using a nonmonochromatic MgKα photon source. The anode voltage was 10 kV,

the anode current 30 mA, and the background pressure in the analytical chamber 1.5×10^{-6} Pa. The size of the x-ray spot was 2 mmφ, and the take-off angle of photoelectrons was 90 degrees with respect to the sample surface. The spectra were referenced with respect to the 285.0 eV carbon 1s level observed for hydrocarbon, to eliminate the charge effect. The smoothing procedure of the spectra was not done. The C_{1s}, N_{1s}, and O_{1s} spectra were decomposed by fitting a Gaussian–Lorentzian mixture function (mixture ratio 80 : 20) to an experimental curve using a nonlinear, least-squares curve-fitting program, ESCAPAC, supplied by Shimadzu. The sensitivity factors (*S*) for the core levels were $S(\text{C}_{1s}) = 1.00$, $S(\text{N}_{1s}) = 1.77$, and $S(\text{O}_{1s}) = 2.85$.

Angular XPS spectra of the PPTA films were obtained at take-off angles of 45, 30, and 18 degrees on an ULVAC PHI ESCA system 5500 using a non-monochromatic MgKα photon source. The anode power was 300 W, the background pressure in the analytical chamber 7.5×10^{-7} Pa, and the size of the x-ray spot 7 mmφ.

RESULTS AND DISCUSSION

Adhesion Between PPTA Film/Silicon Rubber Adhesive Joint

The combination of the AET treatment and the silane coupling treatment was effective in the improvement of adhesion between the PPTA film and the silicon rubber. Needless to say, the untreated PPTA films showed no adhesion with either the silicon rubber or the PPTA films modified by the AET treatment and the silane coupling treatment. The reaction conditions of the AET treatment, rather than that of the silane coupling treatment, showed a large influence on the surface modification of the PPTA films. Figure 1 shows typical results of the 180° peel strength of the surface-modified PPTA film/silicon rubber adhesive joint as functions of the AET concentration and the treatment time in the AET treatment process. The magnitude of the peel strength, as shown in Figure 1, is related to both AET concentration and treatment time. We consider that modification of PPTA films with the AET solution is a heterogenous system and the reactions may be strongly diffusion-controlled. Therefore, homolitical modification requires some time for AET molecules to diffuse from the surface into the deep layers of PPTA film. The AET treatment for a period of less than 15 min was not done because of heterogeneity of the modification reaction at the

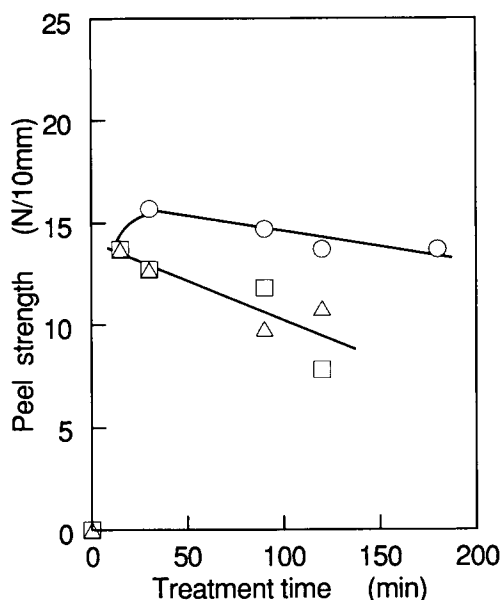


Figure 1 Peel strength of AET-treated PPTA film/silicon rubber adhesive joint as function of treatment time and AET concentration; ○, AET concentration of 5 wt %; □, 7.5 wt %; △, 10 wt %.

PPTA film surface. The treatment with the 5 wt % AET solution shows higher peel strength than those with the 7.5 and 10 wt % AET solutions. In the AET treatment process using the 5 wt % AET solution, the peel strength of the surface-modified PPTA film/silicon rubber adhesive joint increases from 13.7 N/10 mm for the PPTA films treated for 15 min to 15.7 N/10 mm for those treated for 30 min, and then decreases with increased treatment time. In the AET treatment with the 7.5 and 10 wt % AET solutions, the peel strength of the adhesive joints decreases with increased AET treatment time. Therefore, we conclude that treatment of the PPTA films using the 5 wt % solution for 30 min is an optimum condition for adhesion improvement. This conclusion shows that some factor of the 30-min AET modification improves adhesion. Possible factors to improve the adhesion are chemical modification of the

PPTA film by the AET solution, physical modification of the PPTA film, morphology, degree of crystallinity, etc. We believe that the chemical factor rather than the physical factor is important in this experiment. The SEM picture showed no change in surface morphology of PPTA film by the AET treatment. We will discuss the chemical factor in the AET treatment in a later section, from the viewpoint of XPS spectra.

In conclusion, the combination of the AET treatment and the silane coupling treatment is an effective surface modification of the PPTA film. The PPTA films modified by these combined treatments can adhere to the silicon rubber.

Chemical Composition of PPTA Film Surface Modified with AET

The chemical composition of the PPTA film surface treated with the AET solution was investigated with XPS. The XPS survey showed no sulfur atom at the surface of the PPTA films treated with the AET solution. The AET treatment led to increased oxygen concentration (O/C) at the treated PPTA film surface but no increase in the nitrogen concentration (N/C). Table I shows the O/C and N/C atomic ratios determined by the XPS for the PPTA films treated with the AET solution. Both O/C and N/C atomic ratios for the PPTA film are estimated to be 0.143 from the calculation of the repeating unit of the PPTA. The determined O/C and N/C atomic ratios for the original PPTA film, as shown in Table I, are 0.134 and 0.139, respectively, which are lower than the estimated ratios (0.143). This difference may be within an error of estimation by the XPS analysis. The treatment with the AET solution led to an increase in the O/C atomic ratio but did not lead to increased N/C atomic ratio: the O/C atomic ratio for the PPTA films treated with the 5 and 7.5 wt % AET solutions is 0.177 and 0.184, respectively; the N/C atomic ratio is 0.136 and 0.126, respectively. Moreover, the O_{1s} core level spectrum for the PPTA

Table I Elemental Composition of PPTA Film Surface Treated with AET

| Sample | AET Conc. (wt %) | Atomic Ratio | | FWHM Value (eV) | | |
|------------------|---------------------|--------------|-------|-----------------|----------|----------|
| | | N/C | O/C | C_{1s} | N_{1s} | O_{1s} |
| Original PPTA | 0 | 0.134 | 0.139 | 1.68 | 1.53 | 1.81 |
| AET-treated PPTA | 5.0 | 0.136 | 0.177 | 1.62 | 1.41 | 1.82 |
| AET-treated PPTA | 7.5 | 0.126 | 0.184 | 1.69 | 1.51 | 2.49 |

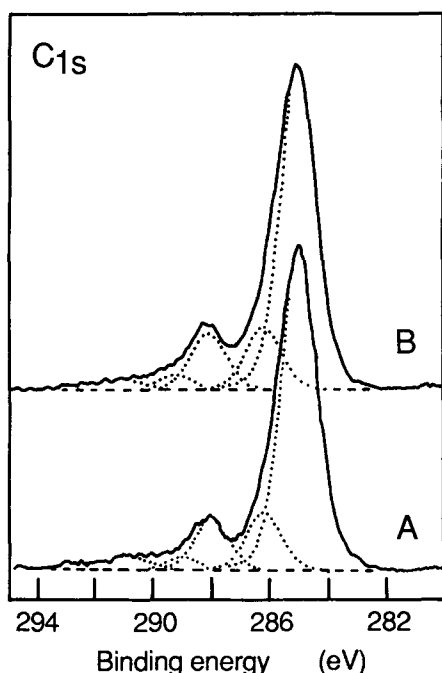


Figure 2(a) XPS (C_{1s}) spectra of (A) original PPTA film, and (B) AET-treated PPTA film.

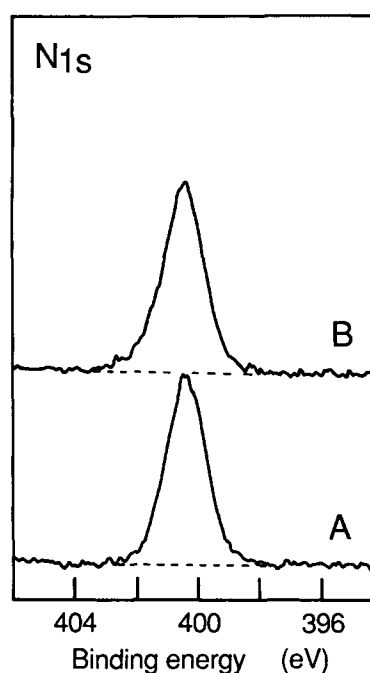


Figure 2(b) XPS (N_{1s}) spectra of (A) original PPTA film, and (B) AET-treated PPTA film.

film treated with 7.5 wt % AET solution distributed widely: the full width at half-maximum (FWHM) value, as shown in Table I, is 1.81 eV for the original PPTA film and 2.49 eV for the AET-treated PPTA film.

From these XPS results, we conclude that the AET treatment does not generate sulfur functionalities at the surface of the PPTA film but does generate new oxygen functionalities. The details of the oxygen functionalities generated at the PPTA film surface by the AET treatment will be discussed later from results of the narrow scanning XPS spectra.

The AET treatment led to a small change in the C_{1s} and N_{1s} core level spectra of the PPTA film but to a large change in the O_{1s} core level spectra. Figures 2(a), 2(b), and 2(c) compare representatively the C_{1s} , N_{1s} , and O_{1s} core level spectra of the AET-treated PPTA film with those of the original PPTA film, respectively. The PPTA films used for the XPS measurement were treated with an AET aqueous solution of 5.0 wt % for 30 min. The C_{1s} spectrum of the AET-treated PPTA film and that of the original PPTA film, as shown in Figure 2(a), are just alike, and show complex distribution with two peaks and a tail extending to high binding energy ranges of 293 eV. These C_{1s} spectra were decomposed by the curve-fitting procedure into five components: CH (at 285.0 eV), C—N (at 286.1–286.2 eV), C=O (at 288.0 eV), C(O)O (at 289.0–289.1 eV), and $\pi - \pi^*$

shake-up satellite (at 291.0–291.1 eV).¹² The question of whether the curve-fitting procedure of the C_{1s} core level spectra was reasonable, especially the decomposition into the C(O)O component, is ex-

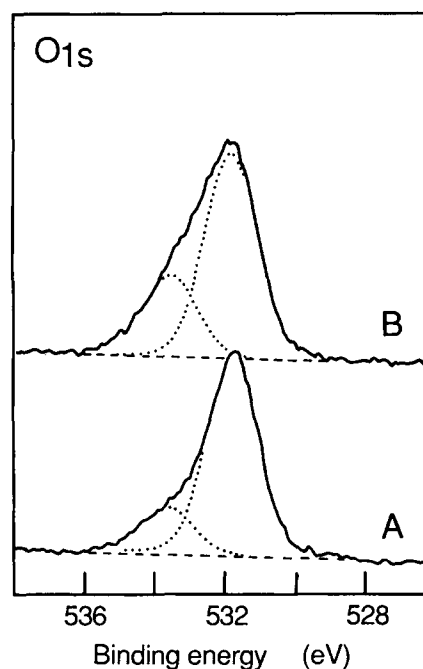


Figure 2(c) XPS (O_{1s}) spectra of (A) original PPTA film, and (B) AET-treated PPTA film.

Table II(a) XPS (C_{1s}) Spectra of PPTA Films Treated with AET

| Sample | AET Conc. (wt %) | C _{1s} Components (Binding Energy in eV and Relative Concentration in %) | | | | |
|------------------|---------------------|--|----------------|----------------|---------------|---------------|
| | | CH | C—N | C=O | C(O)O | $\pi - \pi^*$ |
| Original PPTA | 0 | 285.0 ^a (73%) ^b | 286.2 (13%) | 288.0 (11%) | 289.0 (3%) | 291.0 |
| AET-treated PPTA | 5.0 | 285.0 (72%) | 286.1 (12%) | 288.0 (13%) | 289.0 (3%) | 291.1 |
| AET-treated PPTA | 7.5 | 285.0 (70%) | 286.1 (14%) | 288.0 (13%) | 289.1 (3%) | 291.0 |

^a Binding energy in eV.

^b Relative concentration in mol %.

plainable. The O_{1s} core level spectra for these films, as shown in Figure 2(c), show a large FWHM of 1.81–2.49 eV, indicating surely that the AET-treated PPTA film and even the original PPTA film involve another oxygen functionality besides C=O moiety in amide groups. This is the justifiable ground of the curve-fitting procedure. The details of the O_{1s} core level spectra are shown in Figure 2(c). From the decomposition of the C_{1s} spectra, the relative concentration of the four C_{1s} components, CH, C—N, C=O, and C(O)O moieties, was estimated [Table II(a)]. In Table II(b), the $\pi - \pi^*$ shake-up satellite is excluded from the estimation of the relative concentration because it is not a chemical component of constructing the PPTA film. The relative concentrations of the CH, C—N, C=O, and C(O)O moieties estimated from the AET-treated PPTA films are 70–72, 12–14, 13, and 3 mol %, respectively, which correspond within an observational error to those of the corresponding components estimated from the original PPTA film (73 mol % for CH

moiety, 13 mol % for C—N moiety, 11 mol % for C=O moiety, and 3 mol % for C(O)O moiety). Therefore, there appears no difference in the C_{1s} spectra between the AET-treated PPTA film and the original PPTA film. The N_{1s} core level spectra of the AET-treated PPTA film and the original PPTA film, as shown in Figure 2(b), show a single and symmetrical peak at a binding energy of 400.2 eV with a small FWHM of 1.53 eV, which is assigned the nitrogen atom in NHC(O) or NH₂ moiety. The O_{1s} core level spectra of the AET-treated PPTA film and the original PPTA film, as shown in Figure 2(c), show asymmetrical distribution with a large FWHM value of 1.81 eV. This large FWHM value indicates that the O_{1s} core level spectra involve at least two oxygen functionalities with different binding energies. Therefore, we decomposed the O_{1s} core level spectra into two oxygen components, and the results of the decomposition are summarized in Table II(c). The two oxygen components appearing at binding energies of 531.7–531.8 and 533.4–533.9 eV are as-

Table II(b) XPS (N_{1s}) Spectra of PPTA Films Treated with AET

| Sample | AET Conc. (wt %) | N _{1s} Components NH—C(O) and NH ₂ |
|------------------|---------------------|---|
| Original PPTA | 0 | 400.4* (100%)** |
| AET-treated PPTA | 5.0 | 400.3 (100%) |
| AET-treated PPTA | 7.5 | 400.2 (100%) |

* Binding energy in eV.

** Relative concentration in mol %.

Table II(c) XPS (O_{1s}) Spectra of PPTA Films Treated with AET

| Sample | AET Conc. (wt %) | O _{1s} Components | |
|------------------|---------------------|----------------------------|----------------|
| | | O=C(NH) | O—C(O) |
| Original PPTA | 0 | 531.8* (81%)** | 533.6 (19%) |
| AET-treated PPTA | 5.0 | 531.8 (76%) | 533.9 (24%) |
| AET-treated PPTA | 7.5 | 531.7 (71%) | 533.4 (29%) |

* Binding energy in eV.

** Relative concentration in mol %.

signed the oxygen atom in C=O moiety (amide group) and the oxygen atom in C(O)O moiety (carboxylic acid or carboxylate group), respectively.¹³ For the original PPTA film, the relative concentration of the C=O and C(O)O moieties is 81 and 19 mol %, respectively [Table II(c)]. This indicates that the carboxylic acid units in the PPTA polymer chains are not completely polycondensed into amide groups but 19 mol % of the total carboxylic acid units are in the form of free carboxylic acid groups or ester groups. The AET-treated PPTA films also involve the C=O and C(O)O moieties, and the concentration of the C(O)O moiety in the AET-treated PPTA films is higher than that in the original PPTA film. The C(O)O concentration increases with increased AET concentration in the AET aqueous solution used for the surface modification [Table II(c)]: The C(O)O concentration is 19 mol % for the original PPTA film, and 24 and 29 mol % for the PPTA films treated with the AET solutions of 5.0 and 7.5 wt % AET, respectively. This indicates that the AET treatment leads to hydrolysis of amide groups in the PPTA film to form carboxylic acid groups and amino groups. This aspect can explain without contradiction the XPS spectra changes occurring in the surface modification process of the PPTA films using the AET aqueous solution: (1) There is no sulfur atom at the PPTA film surface treated with the AET solution. (2) The O/C atomic ratio of the AET-treated PPTA films is higher than that of the original PPTA film, but the N/C atomic ratio is unchangeable. (3) The O_{1s} core level spectra involve two components, C=O and C(O)O groups. (4) The C(O)O concentration in the AET-treated PPTA films increases with higher AET concentration in the AET solution used for the surface modification.

From these XPS inspections, we can conclude that the surface modification of the PPTA film with the AET solution is hydrolysis reactions. A part of amide groups near the surface of the PPTA film is hydrolyzed to form carboxylic acid groups and amino groups. However, how AET molecules contribute to the hydrolysis reaction of the PPTA film is not yet clear. From the combination of the adhesion results discussed in a previous section and the XPS analysis results discussed in this section, we can speculate and that the hydrolysis of the PPTA films forms new sites which are able to be coupled with the silane coupling reagent, TES322, and consequently, contribute to improvement of the adhesion between the PPTA film and the silicon rubber. In the AET treatment process, however, the heavy AET treatment will bring about bad rather than good effects for adhesion improvement because the hydrolysis of

the PPTA film is a bond scission of the PPTA polymer chains and is the formation of a weak boundary layer. Therefore, the heavy AET treatment, e.g., the treatment using highly concentrated AET solution and long treatment periods, should be avoided for the adhesion improvement. The heavy treatment may produce the weak boundary layers at the PPTA film surface, and consequently may disturb the adhesion between the PPTA film and the silicon rubber. This is an explanation of the effects of AET concentration and AET treatment time on the peel strength between PPTA film/silicon rubber adhesive joint in Figure 1: why is the AET treatment of 5 wt % more effective than those of 7.5 and 10 wt %, and why is short-time treatment of less than 30 min more effective than longer-time treatment? The AET treatment is hydrolysis of amide, which occurs at the PPTA film surface. As a result, functional groups of carboxyl and amino groups are formed at the PPTA film surface and this means the bond scission of the PPTA polymer chains. The bond scission generates a new weak boundary layer which may be a main disturb factor of the adhesion. Therefore, the AET treatment gives contrary effects for the adhesion: the formation of functional groups (positive effect) and the formation of a weak boundary layer (negative effect). Experimental results show that the C(O)O concentration for the AET-treated PPTA films with an AET solution of 7.5 wt %, as shown in Table II(c), is higher (29 mol %) than that (24 mol %) for the AET-treated PPTA films with an AET solution of 5.0 wt %. However, the peel strength of the PPTA films treated with a solution of 7.5 wt %, as shown in Figure 1, is not higher than the PPTA films treated with 5.0 wt % AET solution. These results are understandable from the concept of the AET treatment. Chatzi, Tidrick, and Koenig⁹ have pointed out a similar disturbance of the weak boundary layer. They hydrolyzed the surface of Kaver fibers using 10 wt % NaOH solution to form carboxylate groups on the surface.

Depth Profile of Carboxylic Acid Groups in the AET-treated PPTA Film

The concentration of carboxylic acid groups, as discussed in a previous section, is a parameter of the surface modification of the PPTA film with the AET solution. The depth profile of carboxylic acid groups in the AET-treated PPTA film was determined from the angular XPS spectra. Figures 3(a) and 3(b) show the O/C and N/C atomic ratios for the original PPTA film and the AET-treated PPTA film as functions of the sine of the take-off angle of pho-

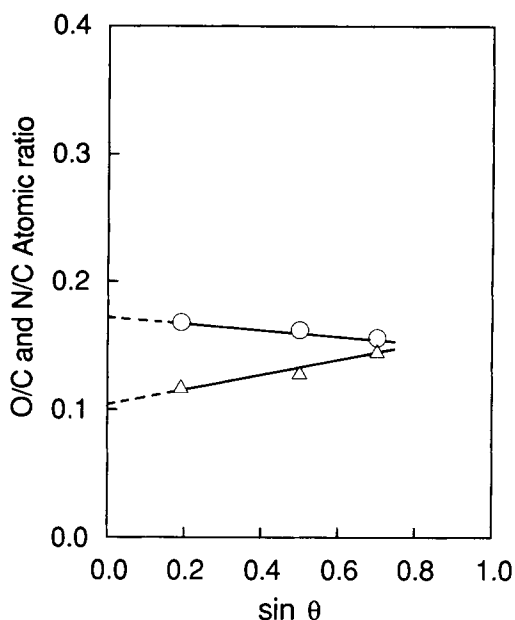


Figure 3(a) O/C atomic ratio (O) and N/C atomic ratio (Δ) of original PPTA film as a function of sine of take-off angle.

toelectrons. The take-off angles with respect to the PPTA film surface are 45, 30, and 18 degrees. Sine of the take-off angle means the sampling depth of photo-electrons, and the sampling depths at take-off angles of 45, 30, and 18 degrees correspond to about 35, 25, and 15 Å deep from the film surface, respectively, based on the assumption that the escape depth of electrons is 50 Å. The O/C atomic ratio for both AET-treated PPTA film and original PPTA film, as shown in Figures 3(a) and 3(b), increases linearly with decreasing the sampling depth of photoelectrons. On the other hand, the N/C atomic ratio decreases linearly with decreased sampling depth. These changes indicate two opposite tendencies: that the oxygen functionalities are concentrated near the PPTA film surface and that the nitrogen functionalities are diluted to the contrary. We assume that the gradient composition of the oxygen and nitrogen functionalities in these PPTA films extends to the film surface, and estimate the concentration of the oxygen and nitrogen functionalities at the surface of the PPTA film (the face of the film) from the extrapolation of the linear relationships between the O/C atomic ratio or the N/C atomic ratio and the sine of the take-off angle. The estimation is summarized in Table III. For both AET-treated PPTA film and original PPTA film, the O/C atomic ratio at the film surface, as shown in Table III, is 6–10% greater than that at 35 Å deep, and the N/C atomic ratio at the film surface

is 23–27% smaller than that at 35 Å deep. Therefore, regardless of the type of the AET-treated PPTA film and the original PPTA film, the oxygen functionalities are condensed at the film surface and the nitrogen functionality is diluted at the film surface. Moreover, the AET-treated PPTA film possesses a greater O/C atomic ratio than the original PPTA film.

The oxygen functionalities in both AET-treated and original PPTA film, as discussed in a previous section, include two components, amide groups and carboxylic acid group. The composition of the oxygen functionalities is determined from the decomposition of the O_{1s} core level spectra: the oxygen atom ($C=O$ moiety) in the amide groups appears at a binding energy of 531.7–531.8 eV, and the oxygen atom ($C(O)O$ moiety) in the carboxylic acid groups at 533.4–533.9 eV. Table IV shows the relative concentration of the oxygen functionalities determined by the decomposition of the O_{1s} spectra as a function of the sampling depth. The relative concentrations of the $C=O$ and $C(O)O$ moieties in the AET-treated PPTA film are 78 and 22 mol % at a sampling depth of 35 Å, respectively; and 76 and 24 at 15 Å deep, respectively. The relative concentrations of the $C=O$ and $C(O)O$ moieties in the original PPTA film are 82 and 18 mol % at a sampling depth of 35 Å, respectively; and 79 and 21 mol % at 15 Å deep, respectively. This indicates that the composition of the oxygen functionalities is change-

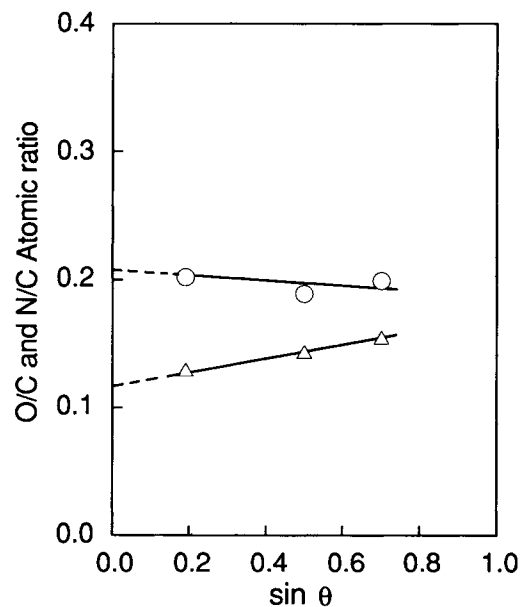


Figure 3(b) O/C atomic ratio (O) and N/C atomic ratio (Δ) of AET-treated PPTA film as a function of sine of take-off angle.

Table III Atomic Composition at the Surface of PPTA Film Treated with AET

| Sample | N/C Atomic Ratio | | O/C Atomic Ratio | |
|------------------|------------------|-------------------|------------------|-----------------|
| | At 35 Å Deep* | At Film Surface** | At 35 Å Deep | At Film Surface |
| Original PPTA | 0.146 | 0.106 | 0.156 | 0.173 |
| AET-treated PPTA | 0.155 | 0.120 | 0.199 | 0.210 |

* Sampling deep from the film surface.

** Estimated from the extrapolation.

less within the sampling depth of 35 Å from the film surface. We should notice that the thinner the sampling depth is, the more the oxygen functionalities (C=O and C(O)O moieties) are condensed.

In conclusion, the chemical composition of the AET-treated PPTA film and the original PPTA film is a function of the depth from the film surface. The oxygen functionalities in these PPTA films are condensed more at shallower depths from the film surface, and the nitrogen functionality is diluted more. The oxygen functionalities involve the C=O and C(O)O moieties. The relative composition of the C=O and C(O)O moieties is changeless within a depth of 35 Å from the film surface. The concentration of the C(O)O moiety at the film surface for the AET-treated PPTA film is 21% higher than that for the original PPTA film. This high concentration of the C(O)O moiety in the AET-treated PPTA film may contribute to the good adhesion with silicon rubber. If the C(O)O moiety in the original PPTA film can be concentrated at the film surface in some way, the PPTA film will adhere to the silicon rubber as tightly as the AET-treated PPTA film does.

Hydrophilic or hydrophobic moieties in the polymer chains (e.g., carbonyl and hydroxyl groups as hydrophilic moieties) which are generated in polyolefins by the oxygen plasma treatment, and fluorinated carbon groups as hydrophobic moieties, which are generated in polyolefins by the tetrafluoro-

romethane plasma treatment, move into the bulk of the polymer by changing the medium which contacts the surface of the polymer.¹⁴ It is a good example of the hydrophilic moieties moving that the advancing contact angle of water at the surface of polyethylene film modified hydrophilically by the oxygen plasma treatment or corona discharge treatment increases with increasing the aging time in air, and the polyethylene surface becomes hydrophobic a few weeks after finishing the surface modification. When the polyethylene film which lost its hydrophilicity is immersed in water for a few days, the hydrophilicity is recovered.¹⁵ This phenomenon can be explained by the concept that the hydrophilic moieties move from the film surface into the bulk of the film. The driving force for this moving of the hydrophilic moieties is due to interactions between the hydrophilic moieties and the medium (air or water).¹⁴

To move the C(O)O moiety in the original PPTA film to the film surface, the original PPTA film was immersed in hot water (100°C) for 15–90 min. The hot-water-treated PPTA film was adhered to the silicon rubber, and the adhesive joint was evaluated by the peel strength method. The results are summarized in Table V, together with those of the peel strength of the AET-treated PPTA film/silicon rubber adhesive joints. The hot water treatment, as shown in Table V, makes the impossible adhesion possible, and is an effective way to improve the

Table IV O_{1s} Components at the Surface of PPTA Films Treated with AET

| Sample | O _{1s} Components (%) | | | |
|------------------|--------------------------------|---------------|--------------|--------------|
| | C=O Group | | C(O)O Group | |
| | At 35 Å Deep | At 15 Å Deep* | At 35 Å Deep | At 15 Å Deep |
| Original PPTA | 82 | 79 | 18 | 21 |
| AET-treated PPTA | 78 | 76 | 22 | 24 |

* Sampling deep from the film surface.

Table V Peel Strength of PPTA Film Immersed in Hot Water/Silicon Rubber Joint

| Sample | Surface Modification | | Peel Strength* (N/10 mm) |
|-----------------------|-----------------------------|------------|-----------------------------|
| | Reagent | Time (min) | |
| Original PPTA film | Hot (100°C) water | 0 | 0 |
| | | 15 | 2.9 |
| | | 30 | 8.8 |
| | | 90 | 10.8 |
| AET-treated PPTA film | AET 5 wt % aqueous solution | 15 | 13.7 |
| | | 30 | 15.7 |
| | | 90 | 14.7 |
| | | 120 | 13.7 |
| | | 180 | 13.7 |

* 180° peel strength at a peel rate of 50 mm/min.

adhesion. The magnitude of the peel strength of the adhesive joint increases with increased treatment time in hot water. When the PPTA film is treated in hot water for 90 min the peel strength reaches 10.8 N/10 mm, which corresponds to about 70% of the peel strength for the AET-treated PPTA film/silicon rubber adhesive joint. The hot water treatment is not as powerful in the surface modification as the AET treatment but it is worth noticing that the hot water treatment makes the impossible adhesion possible. This success may be due to moving of the C(O)O moieties from the bulk of the PPTA film to the film surface, and suggests that the C(O)O moieties at the film surface play an important role in the adhesion between the PPTA film and the silicon rubber. From the viewpoint of the migration of the C(O)O moiety, the surface modification with the AET aqueous solution is not only the hydrolysis of amide groups at the PPTA film surface but also the moving of the C(O)O moiety from the bulk of the film to the film surface. The combination of both hydrolysis and moving may be a factor that allows the film surface to adhere to the silicon rubber. The C(O)O moiety may be a key factor in adhering to the silicon rubber. How the C(O)O moiety contributes to the adhesion is not clear at present but is a subject to be discussed in future.

CONCLUSION

The surface modification of the PPTA film with AET was investigated to improve the adhesion between the PPTA film and the silicon rubber. The effectiveness of the surface modification was evaluated from the peel strength of the PPTA film/silicon rubber adhesive joint. Changes in the chemical

composition of the PPTA film surface modified by the AET treatment were inspected by XPS. Results are summarized as follows:

- (1) The combination of the AET treatment and the silane coupling treatment is an effective surface modification of the PPTA film. The modified PPTA film can adhere to the silicon rubber.
- (2) The AET treatment does not generate sulfur functionalities at the surface of the PPTA film but does generate oxygen functionalities. In the AET treatment process, a part of amide groups near the surface of the PPTA film is hydrolyzed to form carboxylic acid groups and amino groups.
- (3) The AET-treated PPTA film and even the original PPTA film involve a C(O)O moiety as well as a C=O moiety in amide groups as oxygen functionalities. The oxygen functionalities are condensed at the film surface, and the nitrogen functionality is diluted at the film surface.
- (4) The C(O)O moiety at the PPTA film surface may be a key factor for the adhesion with silicon rubber. The concentration of the C(O)O moiety at the film surface for the AET-treated PPTA film is 21% higher than that for the original PPTA film.
- (5) The C(O)O moiety is mobile from the bulk of the PPTA film to the film surface. The hot water treatment of the original PPTA film makes the impossible adhesion with the silicon rubber possible. The surface modification by the hot water treatment, however, is not so powerful as that resulting from the AET treatment.

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