

Effects of Surface Modification by Oxygen Plasma on Peel Adhesion of Pressure-Sensitive Adhesive Tapes

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ABSTRACT: Surfaces of poly(isobutylene) (PIB) and poly(butylacrylate) (PBA) pressure-sensitive adhesive tapes were treated by oxygen plasma, and effects of surface modification on their adhesive behavior were investigated from the viewpoint of peel adhesion. The peel adhesion between PIB and PBA pressure-sensitive adhesive tapes and stainless steel has been improved by the oxygen plasma treatment. The surface-modification layer was formed on PIB and PBA pressure-sensitive adhesive surfaces by the oxygen plasma treatment. The oxygen plasma treatment led to the formation of functional groups such as various carbonyl groups. The treated layer was restricted to the topmost layer (50–300 nm) from the surface. The GPC curves of the oxygen plasma-treated PBA adhesive were less changed. Although a degradation product of 1–3% was formed in the process of the oxygen plasma treatment of the PIB adhesive. There are differences in the oxygen plasma treatment between the PIB and PBA adhesives. A close relationship was recognized between the amount of carbonyl groups and peel adhesion. Therefore, the carbonyl groups formed on the PIB and PBA adhesive surfaces may be a main factor to improve the peel adhesion between the PIB and PBA adhesive and stainless steel. The peel adhesion could be controlled by changing the carbonyl concentration on the PIB and PBA adhesive surfaces. We speculate that the carbonyl groups on the PIB and PBA adhesive surface might provide an interaction with a stainless steel surface. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 78: 1392–1401, 2000

Key words: poly(butyl acrylate); poly(isobutylene); oxygen plasma treatment; carbonyl group; surface modification; peel adhesion

INTRODUCTION

Adhesion using pressure-sensitive adhesive (PSA) tape easily joints two substrates, but the mechanism of the adhesion is complicated. The mechanism is related to surface science and rheology of the PSA tapes. The fundamental adhesion mechanism of the adhesion with PSA tape can be considered as due to three factors. For the

first factor, when the PSA adhesive touches the surface of the substrate, the contact area of the PSA adhesive and the substrate is increased. For the second factor, a bonding force between the PSA adhesive and the substrate surface is formed. For the final factor, when the adhesive joints are peeled off by external force, the PSA adhesive layers are deformed by the external force. The first two factors are related to the surface science of the PSA tape, and the last factor is related to the rheology of the PSA tape. Therefore, the adhesion behavior^{1–8} of PSA tapes may be interpreted in terms of a combination of surface

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science including wettability, interfacial bonding force, and rheology including viscoelastic properties, peel speed, and peel temperature. Many investigators have pointed out the importance of the viscoelastic properties of the PSA tape in manufacture of PSA tapes. Recently, in the field of the adhesive, many theories and experiment results focusing on the importance of the acid-base interaction have been reported.⁹⁻¹⁷ However, in the field of PSA tape, data on the case with the acid-base interaction is not found. However, some investigations have suggested that an interfacial bonding force induced from acid-base interaction contributed greatly to the peel adhesion of PSA tape with a stainless steel surface. It is thought that functional groups such as the carbonyl group on the PSA surface play an important role in adhesion with stainless steel. To confirm the effects of the functional groups in the PSA tape experimentally a tape sample, which changes only the surface without changing the bulk properties is needed.

There are many ways for the surface modification technique of polymers: flame treatment, ozonization, plasma treatment, UV treatment, laser treatment, graft copolymerization, etc. The plasma treatment¹⁸ is a surface modification method that is able to introduce functional groups into the surface layer without changing the bulk properties of polymers. The formation of functional groups on a polymer surface by plasma is interpreted from actions of the radicals in the plasma. When the radicals touch a polymer surface, hydrogen atoms in polymer chains are removed to form carbon radicals on the polymer surface. Some of the carbon radicals combine with other radicals in the plasma to form functional groups on the polymer surface. Other carbon radicals, when exposed to air after the plasma treatment, are oxidized to form oxygen functional groups such as carbonyl and carboxyl groups. The formation of these functional groups is restricted to few hundred nanometers in depth from the polymer surface. Therefore, oxygen plasma can make oxygen functional groups such as carbonyl groups on the PSA surfaces. How the functional groups contribute to adhesion with stainless steel will be investigated.

This study investigated what functional groups were formed on PSA surfaces by oxygen plasma, how deep the functional groups existed from the PSA surface, and how the oxygen functional groups contribute to the adhesion with stainless steel.

EXPERIMENTAL

Materials

Two adhesives,¹⁹ Poly(isobutylene) (PIB) and Poly(butylacrylate) (PBA) were used as raw materials of PSA tapes. PBA was polymerized in an ethyl acetate solution containing AIBN (0.2%) as an initiator at 60°C for 10 h. The molecular weight of the product was $M_w = 510,00$, $M_w/M_n = 7.2$. PIB was purchased from Exxon Chemical Co. (the trade name Bistanex MML-80). The molecular weight of PIB was $M_w = 690,000$ and $M_w/M_n = 1.67$. Poly(ethylene terephthalate) (PET) (trade name Lumira S-10, 38 μm thickness) and polypropylene (PP) films (trade name Torefan BO 40-T2745, 40 μm thickness) purchased from Toray Co., were used as backings for PSA tapes.

PSA tapes of PBA and PIB adhesives (PBA/PET and PIB/PP PSA tapes) were prepared by coating of PBA and PIB onto the PET and PP films, respectively. An ethyl acetate solution of PBA and a heptane solution of PIB were used as coating solution, and the coating procedure was done using a wire-bar apparatus. The PBA and PIB adhesives coated on the PET and PP films were maintained at 80°C for 3 min to evaporate the solvents from the adhesive layers. After evaporation of the solvents, to become 50% of the fraction of the gel the PBA adhesive layer was crosslinked by exposure to an electron beam (12 Mrad). The PBA and PIB adhesive layers of PBA/PET and PIB/PP PSA tapes were 30 μm thickness.

Oxygen Plasma Treatment of PSA Surfaces

A special reactor²⁰ was used for surface modification of the PSA surfaces by oxygen plasma. Details of the reactor are shown in Figure 1. The reactor consisted of a cylindrical Pyrex glass tube (45 mm in diameter, 1000 mm in length) and a columnar stainless steel chamber (300 mm in diameter, 300 mm in height). The Pyrex glass tube had a gas inlet for the injection of oxygen gas and a copper coil for the energy input of rf power (at a frequency of 13.56 MHz). The stainless steel chamber contained a Barocel pressure sensor (type 622, Edwards) and a vacuum system of a combination of a rotary pump (320 dm^3/min) and a diffusion pump (550 dm^3/s) (type YH-350A, Ulvac Co., Japan). The Pyrex glass tube was jointed to the columnar chamber using a Viton O ring flange.

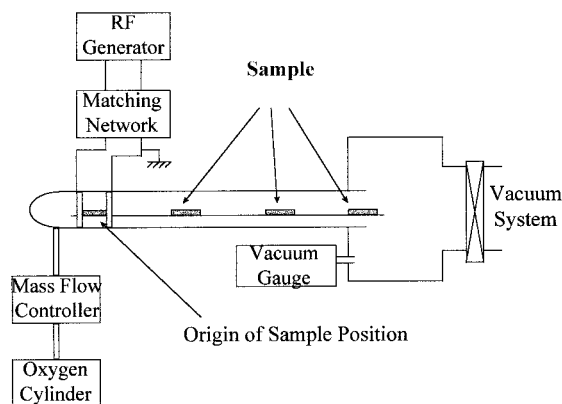


Figure 1 Schematic representation of plasma reactor.

Specimens (20 mm width and 50 mm length) of the PSA tapes were positioned at a constant distance of 0 to 800 mm from the center of the copper coil. Afterwards, the reaction chamber was evacuated to approximately 1.3×10^{-2} Pa, and then oxygen at a flow rate of 10 cm^3 (STP)/min was introduced into the Pyrex glass tube. The oxygen plasma was operated at rf powers of 50 to 100 W at a frequency of 13.56 MHz at a system pressure of 13.3 Pa. The specimens were exposed to the oxygen plasma for 30 to 120 s.

Peel Adhesion(180Peel Test) with Stainless Steel

The peel test was carried out according to the JIS (Japanese Industrial Standard) method Number C2107-1991. Specimens for the peel adhesion measurement were 20 mm width and 50 mm length. The specimens were touched with stainless steel substrates (SUS430BA), and pressed using a 2-kg roller that passed slowly over the specimen at a rate of 300 mm/min two times each in a lengthwise direction. The PBA and PIB PSA tapes/stainless steel joints were stored at room temperature for 48 h, and the peel adhesion in the 180° direction was measured at a peel rate of 300 mm/min at room temperature using an Instron type adhesion tester (Minebia Co., Japan; model TCM-1kNB). The peel adhesion was evaluated in a unit of N/20 mm.

X-Ray Photoelectron Spectroscopic (XPS) Analysis of the Oxygen Plasma-Treated PSA

PBA and PIB PSA surfaces were treated with the oxygen plasma, and analyzed on a Perkin-Elmer-Phi ESCA 5400 spectrometer with a nonmonochromatic MgK X-ray source at an anode voltage

of 15 kV, at an anode current of 20 mA. The take-off angle of photoelectrons against the PSA surface was 45°.

Even if the C1s spectrum is divided by deconvolution, the carboxyl group and ester group cannot be distinguished by the usual XPS technique. A gas chemical modification technique combined with XPS is usually applied to cope with these problems.²¹⁻²³ The concept of gas chemical modification is to label a functional group of interest selectively with an element that is not present in the original material, and has a large cross-section for XPS analysis. Reagents containing fluorine are often used for this purpose. To analyze for the carboxyl groups, the gas chemical modification technique combined with XPS²¹⁻²³ was used. Trifluoroethanol was used to detect the carboxyl group. The PSA tapes treated with oxygen plasma and treated with trifluoroethanol were analyzed for XPS analysis on a SSI Co. model SSX-100 spectrometer with a monochromatic Al K X-ray source at an anode voltage of 10 kV, at an anode current of 20 mA. The take-off angle of photoelectrons was 35°. The concentrations of the carboxyl groups were estimated from fluorine concentration.

FTIR Attenuated Total Reflection (ATR) Analysis of the Oxygen Plasma-Treated PSA

FTIR-ATR spectra of the PBA and PIB PSA surfaces treated with the oxygen plasma were obtained on a Perkin-Elmer Spectrum 2000 FT-IR using a Multiple Internal Reflectance Apparatus, for the surface analysis of the PSA. A germanium prism (45°) was used as an internal reflection element (IRE).

TEM Observation of the Oxygen Plasma-Treated PSA

Usually for the preparation of the TEM the specimens were imbedded in epoxy resin. However, the PSA might swell and the thickness of the PSA layer change when the PSA samples were imbedded in epoxy resin. A special preparation technique was applied to cope with this problem.

The oxygen plasma-treated PBA and PIB PSA tapes were laminated to other PSA tapes. After these specimens were bonded to the support stand, these PSA samples were trimmed and sections made using a cryosystem ultramicrotome (Leica Co., model Reichert-Nissei fcs and EM-Ultracut-S). The sample sections were dyed with

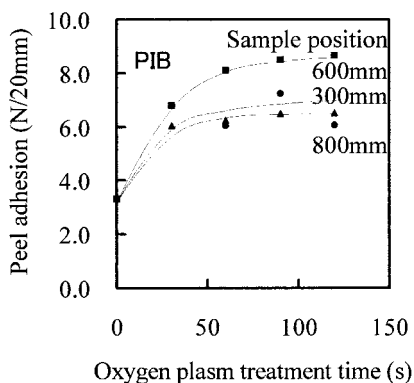


Figure 2 Peel adhesion of PIB PSA tapes treated with oxygen plasma at rf power 100 W as functions of plasma treatment time and sample position.

ruthenium oxide, and sliced using a cryosystem ultramicrotome. TEMs of the cross-sections of the sliced PSA layers were obtained on an Hitachi H-7100FA TEM.

GPC Analysis of the Oxygen Plasma-Treated PSA

GPC curves of the PBA and PIB PSA treated with the oxygen plasma were obtained on a TOSOH HLC-8120 GPC using a differential refractive index (RI) detector. The PSA samples were dissolved in tetrahydrofuran (THF), and adjusted to a 0.3% concentration. The PSA solutions were filtered with a membrane filter of 0.45 μm . The GPC curves of the filtered solutions, which excluded the gel, were measured.

RESULTS AND DISCUSSION

Peel Adhesion of the Oxygen Plasma-Treated PBA/PET and PIB/PP PSA Tapes

The PBA and PIB PSA surfaces were treated with the oxygen plasma at 50–100 W for 30–120 s, and then peel adhesions between the PBA PSA tape or PIB PSA tape and the stainless steel substrate were measured. Typical results of the peel adhesion are shown in Figures 2 and 3 as functions of the oxygen plasma treatment time and the sample position in the plasma reactor. The oxygen plasma treatment gave a large effect on the peel adhesion for the PBA and PIB PSA tapes. The peel adhesion for the PIB PSA tapes/stainless steel joint is shown in Figure 2. The peel adhesion of the PIB PSA tapes treated with oxygen plasma at an rf power of 100 W, 600 mm sample position

was increased from 3.3 N/20 mm to 8.7 N/20 mm by increasing the oxygen plasma treatment, leveled off after a treatment time of 90 s, and reached a maximum of 8.7 N/20 mm. The sample position also influenced the peel adhesion. The peel adhesion first increased, and then decreased with increasing the sample distance from the plasma. For example, when plasma treated, maximum peel adhesions were 6.1 N/20 mm at a sample position of 300 mm, 8.7 N/20 mm at 600 mm, and 6.5 N/20 mm at 800 mm. These effects of the oxygen plasma treatment on the peel adhesion suggest that oxygen plasma treatment is effective in improvement of the peel adhesion. This improvement may be due to the formation of oxygen functional groups.

The PBA PSA tapes also, when treated with oxygen plasma, showed large changes in the peel adhesion (Fig. 3). The peel adhesion of PBA PSA tapes treated with oxygen plasma at an rf power of 100 W, 800-mm sample position, as shown in Figure 3, was increased from 3.9 N/20 mm to 13.7 N/20 mm with increasing plasma treatment time reached a maximum, and then decreased. The sample position also influenced the peel adhesion. Maximum peel adhesions were 6.1 N/20 mm at 300 mm, 6.9 N/20 mm at 600 mm, and 13.7 N/20 mm at 800 mm.

From these results we conclude that the oxygen plasma treatment causes improvement of PIB and PBA PSA tapes peel adhesion. The improvements are related to plasma treatment time and also the sample position. We believe that the improvement results from the formation of oxygen functional groups on the PSA surfaces. The oxygen plasma-treated PSA surfaces were analyzed with FTIR-ATR and XPS.

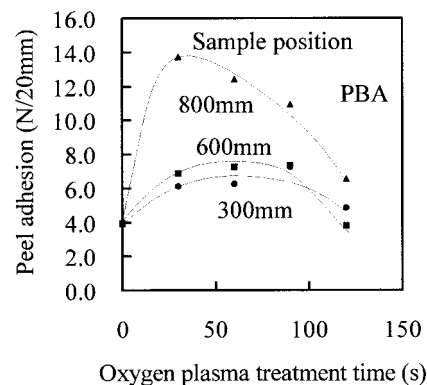


Figure 3 Peel adhesion of PBA PSA tapes treated with oxygen plasma at rf power 100 W as functions of plasma treatment time and sample position.

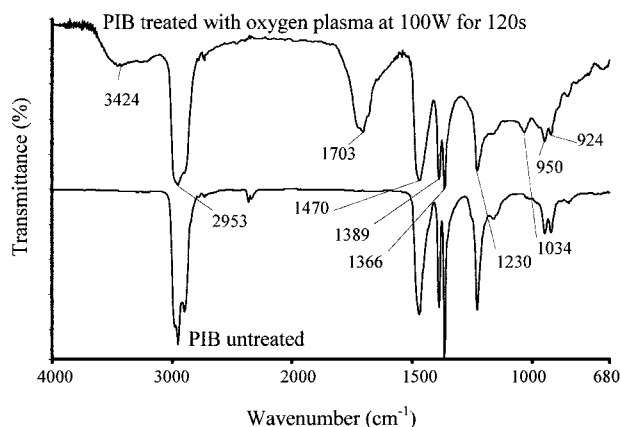


Figure 4 FTIR-ATR spectra of PIB PSA untreated and treated with oxygen plasma at rf power 100 W for 120 s.

Chemical Composition of the PIB, PBA PSA Surfaces Treated by Oxygen Plasma

To clarify functional groups formed by the oxygen plasma treatment, the treated PIB and PBA adhesives were analyzed by FTIR-ATR. Specimens for FTIR-ATR spectroscopy were PIB and PBA adhesives treated with the oxygen plasma at 100 W for 120 s. Typical IR spectra are shown in Figures 4 and 5. Theoretically, IR radiation penetration depth in adhesive layers depends on many factors, as shown by the equation²⁴ for the depth calculation.

$$d_p = \lambda/2 \pi n_c [(\sin \theta)^2 - (n_s/n_c)^2]^{1/2}$$

In the equation d_p is the penetration depth, λ is the wavelength, θ is the incidence angle, n_s is the refractive index of the sample, and n_c that of the IRE. The calculated penetration depth is about 0.4 μm in this FTIR-ATR method. Comparison between spectra for the oxygen plasma-treated PIB and untreated PIB (Fig. 4) shows a new absorption appearing at 3400 and 1700 cm^{-1} , which have been assigned²⁵ to a hydroxyl group and a carbonyl group. Comparison between spectra for the oxygen plasma-treated PIB and untreated PBA (Fig. 5) shows new absorption appearing at 3500, 3200, and 1700 cm^{-1} , also assigned²⁵ to a hydroxyl group and a carbonyl group. These new absorptions suggest that carbonyl groups and hydroxyl groups were formed on the PIB and the PBA adhesive surfaces.

To investigate the concentration of carbonyl groups, formed on the PIB and PBA adhesive

surface, the relative ratio ($A_{1703} \text{ cm}^{-1}/A_{1470} \text{ cm}^{-1}$) of the absorbance peak area at 1703 cm^{-1} and at 1470 cm^{-1} , which was due to carbonyl and CH_2 , CH_3 groups, calculated from the FTIR-ATR spectra (Fig. 4), respectively, was used to deduce the amount of carbonyl group introduced in the PIB adhesive. The ratio increased from 0.03 to 1.0 with increasing oxygen plasma treatment time, and then leveled off after a treatment time of 60 s. On the other hand, the relative ratio ($A_{1700} \text{ cm}^{-1}/A_{1730} \text{ cm}^{-1}$) of the absorbances at 1700 cm^{-1} and at 1730 cm^{-1} , which was due to carbonyl and ester groups and calculated from the FTIR-ATR spectra (Fig. 5) respectively, was used to determine the level of the carbonyl group introduced in the PBA adhesive. The ratio increased from 0.05 to 0.15 with increasing oxygen plasma treatment time, reached a maximum, and then decreased. Typical results of the increase of carbonyl groups are shown in Figures 6 and 7 as functions of the oxygen plasma treatment times and the sample position. The carbonyl groups were introduced into the PIB and PBA adhesives by the oxygen plasma treatment.

The concentration of carbonyl groups formed on the PIB and PBA adhesive surfaces was a function of the oxygen plasma treatment time. The variation of the carbonyl concentration with increasing oxygen plasma treatment is similar to that of the peel adhesion (Fig. 2 and 3). Influence of the carbonyl groups on the peel adhesion will be discussed in a later section.

The PBA and PIB adhesive surfaces treated with the oxygen plasma at 100 W for 120 s were analyzed by XPS. The O/C atomic ratio was esti-

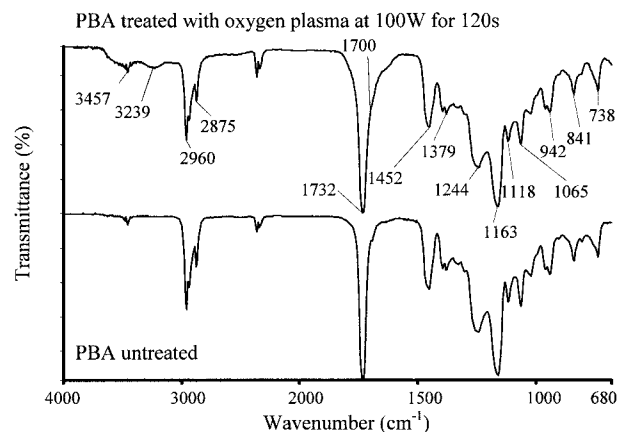


Figure 5 FTIR-ATR spectra of PBA PSA untreated and treated with oxygen plasma at rf power 100 W for 120 s.

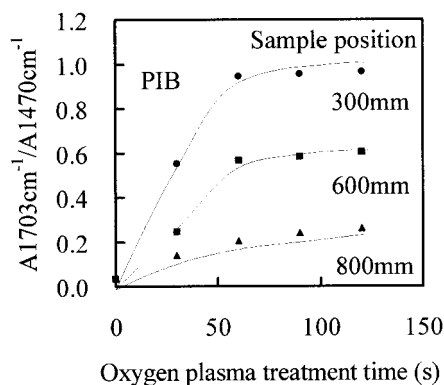


Figure 6 Concentration of carbonyl groups of PIB PSA treated with oxygen plasma at rf power 100 W as functions of plasma treatment time and sample position.

mated from the relative peak intensity of the O1s and C1s spectra (Table I). The O/C atom ratio for the PIB adhesive was increased from 0.01 (untreated) to 0.13–0.15 by the oxygen plasma treatment. The PBA adhesive also increased the O/C atom ratio from 0.26 to 0.29–0.44.

It is known that carboxyl groups in PSA are very effective in peel adhesion improvement,^{3,26} But, even if the C1s spectrum is divided by the deconvolution, the carboxyl group and ester group cannot be distinguished by the usual XPS technique.

Possible carbonyl groups formed by the oxygen plasma treatment are ketone, aldehyde, ester, and carboxyl groups. To clarify which carbonyl groups were formed by the oxygen plasma treatment, the treated PIB and PBA adhesives were

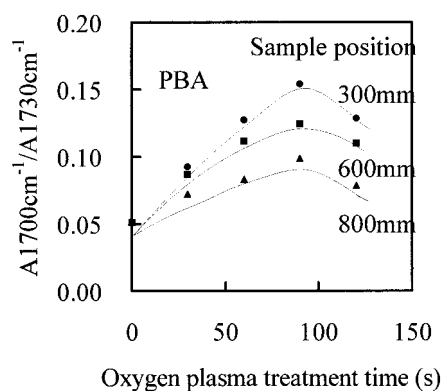


Figure 7 Concentration of carbonyl groups of PBA PSA treated with oxygen plasma at rf power 100 W, as functions of plasma treatment time and sample position.

Table I Chemical Composition of PIB and PBA Adhesives Treated with Oxygen-Plasma at 100 W for 120 s

Adhesives	Sample Position (mm)	O/C Atom Ratio	Concentration of Carboxyl Groups (Carbon Contents of Carboxyl Groups/All Carbons)
PIB	(untreated)	0.01	0.000
	0	–	–
	300	0.15	–
	600	0.14	–
PBA	800	0.13	0.002
	(untreated)	0.26	0.000
	0	0.34	–
	300	0.44	–
	600	0.37	–
	800	0.29	0.004

analyzed by a gas chemical modification technique combined with XPS^{21–23} and transcribed spectrum method of FTIR-ATR.

To detected the concentration of carboxyl groups, a gas chemical modification technique combined with XPS^{21–23} was used. The PBA and PIB adhesive surfaces treated with the oxygen plasma at 100 W for 120 s were analyzed by the gas chemical modification technique combined with XPS. The concentration of carboxyl groups was calculated as carbon contents of carboxyl groups in all carbons (the rightmost column of Table I). The concentration of carboxyl groups for the PIB was increased from 0.000 (untreated) to 0.002 by the oxygen plasma treatment. The PBA adhesive also increased the concentration of carboxyl groups from 0.000 to 0.004. However, the amount of carboxyl groups are less than the amounts of the increase of the oxygen functional groups.

The oxygen plasma-treated PSA tapes showed cohesive failure. Then, to judge the kind of carbonyl groups, the stainless steel surface residues, after the peel tests of oxygen plasma-treated PIB PSA tapes, were analyzed by Micro-FTIR-ATR, and the germanium IRE surface residues, after FTIR-ATR analysis of oxygen plasma-treated PBA PSA tapes, were analyzed by FTIR-ATR. This method is described as the FTIR-ATR transcribed spectrum method. A typical Micro-FTIR-ATR spectrum of stainless steel surface residue of oxygen plasma-treated PIB PSA tape is shown in Figure 8. Comparison between spectra for residue

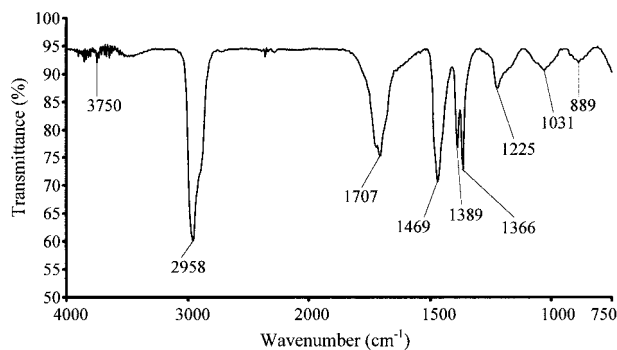


Figure 8 Micro-FTIR-ATR spectrum for stainless steel surface peeled off from stainless steel/PIB PSA tape treated with oxygen plasma at rf power 100 W for 120 s.

of PIB (Fig. 8) and oxygen plasma-treated PIB (Fig. 4) shows almost the same spectra. The 1710 cm^{-1} peaks were composed from several carbonyl peaks due to ketone, aldehyde, ester, and carboxyl groups. A typical FTIR-ATR transcribed spectrum of oxygen plasma-treated PBA PSA tape is shown in Figure 9. On the other hand, comparison between spectra for residue of PBA (Fig. 9) and oxygen plasma-treated PBA (Fig. 5) shows quite a difference. In this FTIR-ATR spectra (Fig. 9), several absorption appear at 3220 , 3060 , 2960 , 1730 , 1600 , 1430 , and 1170 cm^{-1} , which have been assigned²⁵ to hydrogen-bonded carboxyl groups, a carbonyl group, water adsorption, and a CH_2 band. These new absorptions suggest that a special carbonyl group like a peroxide structure was formed on the PBA adhesive surfaces by the oxygen plasma treatment.

Thickness of Treated PSA Layer and Bulk Properties of Adhesives

How deeply the PBA and PIB adhesives were affected by oxygen plasma was estimated from

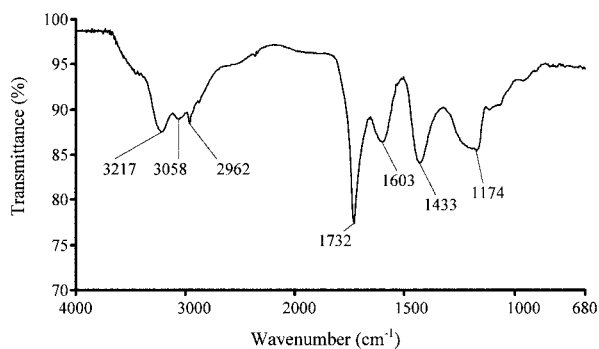


Figure 9 FTIR-ATR spectrum of germanium IRE surface after FTIR-ATR analysis of PBA PSA tape treated with oxygen plasma at rf power 100 W for 90 s.

TEMs. The PBA PSA tapes were treated with the oxygen plasma at 100 W for 30 s, the PIB PSA tapes were treated with the oxygen plasma at 75 W for 30 s, and then dyed with ruthenium oxide. The dyed PBA and PIB PSA tapes were sliced off using a cryosystem ultramicrotome, and the sliced PSA layer was observed with TEMa. Figure 10 shows the typical TEMs of the PBA and PIB PSA layers. The oxygen plasma-treated PBA adhesives showed a hyperchromic line on the TEMs. The line was estimated to be $120\text{--}270\text{ nm}$ wide from the magnitude of the photograph. The sample position influenced the thickness of dyed layer. The thicknesses of the dyed layers were 270 nm at 0 mm , 180 nm at 300 mm , 140 nm at 600 mm , and 120 nm at 800 mm . Similarly, the oxygen plasma-treated PIB adhesives also showed a black line that was estimated to be $50\text{--}280\text{ nm}$ wide. The sample position influenced the thickness of the dyed layer. The thicknesses of the dyed layers were 280 nm at 0 mm , 125 nm at 300 mm , 80 nm at 600 mm , and 50 nm at 800 mm . On the other hand, the untreated PBA and PIB adhesives never showed such a black line on the TEMs, even when the adhesives were dyed with ruthenium oxide. We believe that the dyed layer on the TEMs may be due to ruthenium atoms absorbed on the carbonyl groups, unsaturated groups, or long-lived free radicals in the adhesives. The thickness of the dyed layer was propor-

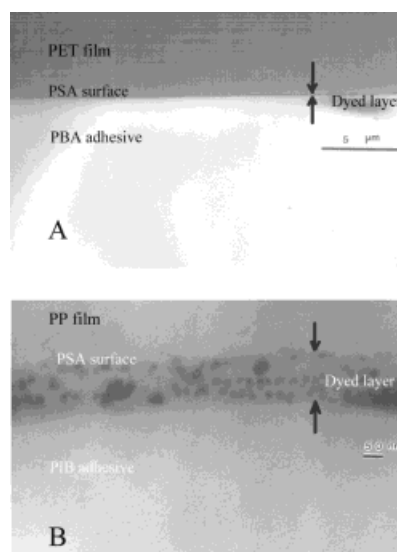


Figure 10 TEM photographs of PBA and PIB PSA tapes treated with oxygen plasma. (A) PBA PSA tape treated with oxygen plasma at rf power 100 W for 30 s. (B) PIB PSA tape treated with oxygen plasma at rf power 75 W for 30 s.

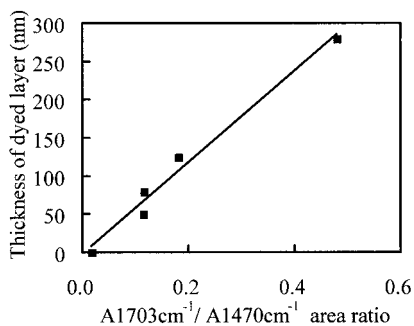


Figure 11 Relationship between the thickness of dyed layer and absorbance area ratio ($A_{1703\text{ cm}^{-1}}/A_{1470\text{ cm}^{-1}}$) of the carbonyl groups on PIB PSA surfaces treated with oxygen plasma at rf power 75 W for 30 s.

tional to the absorbance of increased carbonyl groups by FTIR-ATR spectrum (PIB data are shown in Fig. 11). This results suggested that the dyed thin layer on the PBA and PIB adhesive surfaces was a modified layer where the carbonyl groups were introduced by the oxygen plasma treatment.

From TEM observation, the layer affected by the oxygen plasma is extremely thin (50–300 nm) compared with the adhesive layer (30 μm). Even if viscoelastic properties of the treated layer were changed drastically, the whole of the adhesive layer shows little change in viscoelastic properties. We investigated how the whole adhesive layer was affected from the view point of the molecular distribution.

Figures 12 and 13 show GPC curves of the sol ingredient of PBA and PIB adhesives. There was less difference in the GPC curve between the oxygen plasma-treated PBA adhesive and the un-

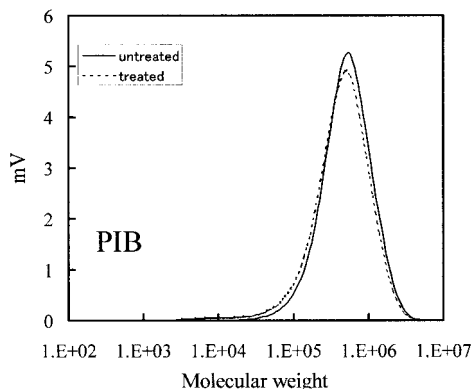


Figure 12 GPC curves of PIB PSA untreated and treated with oxygen plasma at rf power 100 W for 120 s.

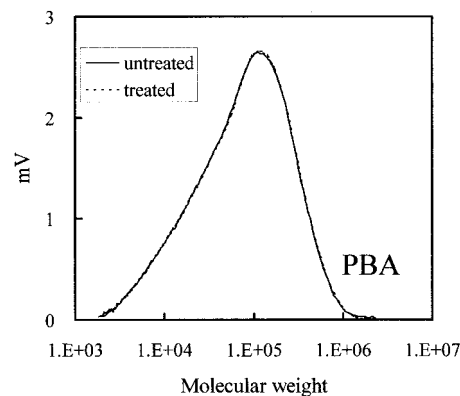


Figure 13 GPC curves of PBA PSA untreated and treated with oxygen plasma at rf power 100 W for 120 s.

treated. The weight-average molecular weight (M_w) and the ratio of the weight-average and number-average molecular weight (M_w/M_n) were $1.4\text{--}1.5 \times 10^5$ and $4.0\text{--}4.6$ for the oxygen plasma-treated PBA adhesives, and 1.4×10^5 and 4.3 for the untreated PBA adhesive. The oxygen plasma-treated PIB adhesive showed a new and small peak in addition to a main peak on the GPC curve. The main peak corresponded to a molecular weight of $5.4\text{--}6.3 \times 10^5$ and the new peak corresponded to a molecular weight of $4.3\text{--}8.1 \times 10^3$. The relative peak area of the two peaks was $99 : 1\text{--}97 : 3$. The untreated PIB adhesive showed a weight-average molecular weight of 6.9×10^5 . These GPC curves indicate that the oxygen plasma treatment gave less influence on molecular distribution of the adhesives, although a degradation product of 1–3% was formed in the process of the oxygen plasma treatment of the PIB adhesive. We believe that there is no change in viscoelastic properties for the whole adhesive layers.

What Contributes to Improvement of the Peel Adhesion?

The oxygen plasma treatment, as shown in Figure 2 and Figure 3, improved the peel adhesion. The peel adhesion, as described in the introductory section, is considered in terms of a combination of two factors—interfacial bonding force between the PSA and stainless steel surfaces, and viscoelastic properties of the whole PSA layer. We believe that the improvement of the peel adhesion by the oxygen plasma may be due to an interfacial bonding force rather than viscoelastic properties, because the treated layer was restricted to the

topmost layer (50–300 nm) from the surface, and the oxygen functional groups were formed in the treated layer.

To confirm the effect on peel adhesion of carbonyl groups formed on the PSA surface by the oxygen plasma, we performed correlation analysis of the peel adhesion and the concentration of carbonyl groups on the PSA surfaces. Typical results of peel adhesion for the oxygen plasma-treated PSA/stainless steel joints are shown in Figures 14 and 15 as function of the concentration of carbonyl groups on the PSA surfaces. The carbonyl concentration was estimated from FTIR-ATR spectra. The estimation of the peel adhesion for both joints, as shown in Figures 14 and 15, showed a linear relationship with the carbonyl concentration.

Figures 14 and 15 indicate that the carbonyl groups formed on the PSA surfaces may be a main factor in improving the peel adhesion between the PSA and stainless steel. The peel adhesion could be controlled by changing the carbonyl concentration on the PSA surfaces. We speculate that the carbonyl groups on the PSA surface might interact with a stainless steel surface.

CONCLUSION

The influence of the surface modification of PIB and PBA PSA tapes on their adhesion behavior has been investigated. Oxygen plasma treatment was used for the surface modification of the adhesives. Peel adhesions of PIB and PBA PSA tapes were evaluated as a measurement of their adhesion behaviors. Functional groups formed on the

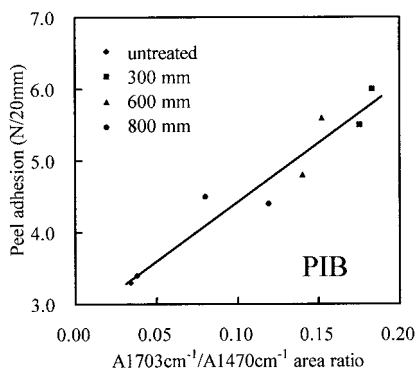


Figure 14 Relationship between the peel adhesion and absorbance area ratio ($A_{1703\text{cm}^{-1}}/A_{1470\text{cm}^{-1}}$) of the carbonyl groups on PIB PSA surfaces treated with oxygen plasma at rf power 50 W for 120 s.

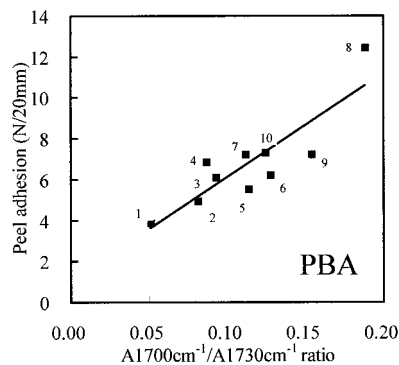


Figure 15 Relationship between the peel adhesion and absorbance ratio ($A_{1700\text{cm}^{-1}}/A_{1730\text{cm}^{-1}}$) of the carbonyl groups on PBA PSA surfaces treated with oxygen plasma at rf power 100 W for 30 to 90 s. (1) untreated, (2) 30 s at 0 mm position, (3) 30 s at 300 mm position, (4) 30 s at 600 mm position, (5) 60 s at 0 mm position, (6) 60 s at 300 mm position, (7) 60 s at 600 mm position, (8) 90 s at 0 mm position, (9) 90 s at 300 mm position, (10) 90 s at 600 mm position.

adhesive surfaces by oxygen plasma were analyzed, and thickness of treated PSA layer was measured. The contribution of introduced functional groups to the adhesion with stainless steel was discussed. The effects of surface modification by the oxygen plasma treatment are summarized as follows.

1. The peel adhesion between the PSA and stainless steel was improved by the oxygen plasma treatment. For the PIB PSA tapes, the peel adhesion improved with increasing the plasma treatment time, but leveled off after a treatment time of 90 s. For the PBA PSA tapes, the peel adhesion improved with increasing the plasma treatment time, reached a maximum, and then decreased. The sample position also influenced the peel adhesion.
2. A surface modification layer was formed on the PSA surfaces by the oxygen plasma treatment. The oxygen plasma treatment led to the formation of functional groups such as various carbonyl groups. The affected layer was restricted to the top-most layer (50–300 nm) from the surface.
3. The GPC curves of the oxygen plasma-treated PBA adhesive were less changed, although a degradation product of 1–3% was formed in the process of the oxygen plasma treatment of the PIB adhesive. There are differences in the oxygen plasma

treatment between the PIB and PBA adhesives.

4. A close relationship was recognized between the amount of carbonyl groups and peel adhesion. Therefore, the carbonyl groups formed on the PSA surfaces may be a main factor in improving the peel adhesion between the PSA and stainless steel. The peel adhesion could be controlled by changing the carbonyl concentration on the PSA surfaces. We speculate that the carbonyl groups on the PSA surface might have an interaction with the stainless steel surface.

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