Adhesion Properties of Acrylic Copolymers Modified with Si-Containing Copolymer

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We made clear the cause of the increase in peel strength of pressure sensitive (PS) adhesives as a function of contact time, and investigated how to modify PS adhesives to maintain a low and constant peel strength for a long time. It was found that polar groups in the adhesive orient to the interface between the adhesive and the (stainless steel) metal substrate (SUS 304) so as to minimize interfacial free energy during adhesion, and the orientation increased affinity between the adhesive and the metal material and increased the peel strength as a result. The use of modifier which contained both P(MMA-co-SiMA) and PDMS showed an excellent modification effect, although modification with only PDMS or P(MMA-co-SiMA) was not sufficient. It was suggested that PDMS which migrated to the surface was extended uniformly over the surface by PDMS segments of P(MMA-co-SiMA) and that the enriched layer of PDMS on the adhesive surface worked as a barrier to prevent the orientation of polar groups in bulk. Therefore, low and constant peel strength could be achieved.

KEY WORDS surface modifier; adhesive; SUS 304; polydimethylsiloxane (PDMS); ESCA; peel strength; surface; interface; adhesion.

1. INTRODUCTION

Some polymer materials are evaluated according to the properties of their surfaces and various modifications of polymer surfaces and interfaces have been investigated. The simplest and most practical ways to achieve modification are coating and blending of modifiers onto or into polymer materials. Accordingly, much attention has been given to the study of polymers having surface or interfacial activities.[1-5] In addition, studies[6,7] on molecular design of modifiers, analysis[8-10] of surface-active behavior, or characteristics[11,12] of surface structure have been conducted from both basic and applied research points of view.
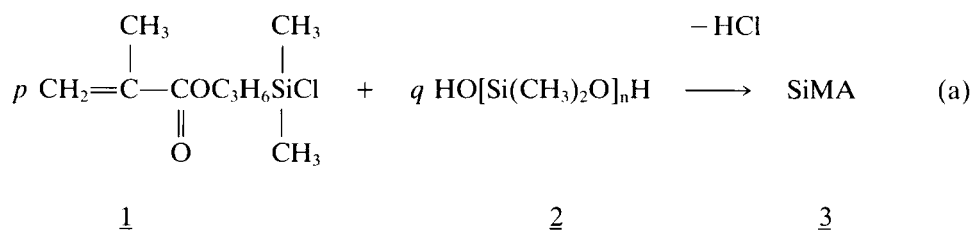

We have already reported on a new method[13,14] for synthesizing block copolymers using polymeric peroxide. We also have reported that fluorine-containing block copolymers[15,16] and siloxane-containing block copolymers,[17,18] obtained by this method, are very useful as surface modifiers and that hydrophobic and hydrophilic block copolymers could be applied as interfacial modifiers for polymer materials.[19]

Adhesives are typical polymer materials whose surface properties closely relate to their function. It is well-known that peel strength of PS adhesives increases with contact time. In this study, we have attempted to explain the increase in peel strength of such adhesives, affixed to a metal substrate, by using ESCA analysis. Furthermore, we have investigated how to modify these adhesives so as to keep a low and constant peel strength for a long time. Though polydimethylsiloxane (PDMS) is a well-known surface modifier, it did not show sufficient effect for this modification. We have investigated the modification of adhesives by blending with P[MMA-co-(PDMS-methacrylate)] but it alone was also not sufficient. However, we have discovered that the use of P[MMA-co-(PDMS-methacrylate)] together with PDMS showed an excellent modification effect. We report these results in this paper.

2. EXPERIMENTAL

2.1. Synthesis of Surface Modifiers

As mentioned in the Introduction, mixtures of P[MMA-co-(PDMS-methacrylate)] and PDMS were excellent surface modifiers for PS adhesives. We synthesized these modifiers as follows. PDMS-methacrylate (SiMA) was prepared by the reaction of γ-methacryloxypropyl dimethyl chlorosilane (1) and silanol (2) as shown in Eq. (a). In this reaction, it was possible to prepare SiMA containing various amounts of PDMS by changing the ratio of p/q.

$$p\ CH_2{=}C(CH_3)COOC_3H_6Si(CH_3)_2Cl\ +\ q\ HO[Si(CH_3)_2O]_nH\ \xrightarrow{-HCl}\ SiMA \qquad (a)$$

$$\underline{1} \qquad\qquad \underline{2} \qquad\qquad \underline{3}$$

Polydimethylsiloxane-methacrylate (SiMA) A certain amount of 2, the same weight of tetrahydrofuran (THF) as 2, and 1.2 times the amount of triethyl amine (TEA) as 1 were charged into a reactor equipped with a thermometer, a stirrer, a nitrogen inlet and a reflux condenser, heated at 50°C and the same mole quantity of 1 as 2 was added dropwise into the reactor over a period of 30 minutes. After keeping the reaction mixture at 50°C for 5 hours, the TEA hydrochloride salt was removed by washing with water and a small residue of water was further removed with Glauber's salt. 3 was obtained upon removal of the THF under reduced pressure.

P(MMA-co-SiMA)   9 g of 3 and 21 g of methyl methacrylate (MMA) was copoly-merized with 1 g of t-butyl peroxy 2-ethylhexanote in 69 g of toluene at 75°C for 12 hours under nitrogen atmosphere. The conversion of MMA was over 96% as determined by gas chromatography. PDMS, with molecular weight (M_n) between 1000 and 5000, was used to prepare SiMA. Copolymerization reactivity of SiMA, the M_n of which was over 2000, with MMA was poor. Therefore, mixtures of mono- and dimethacrylate of PDMS were also used, because of dimethacrylate of silanol has good copolymerization reactivity with MMA. Mixtures of mono- and dimeth-acrylate of PDMS were prepared with a mole ratio *(p/q)* of over 1.0.

P[MMA-co-(methoxypolyethyleneglycol methacrylate)]   Methoxypolyethyleneglycol methacrylate (MPEGMA) with M_n of 1000 instead of SiMA was used to prepare P(MMA-co-MPEGMA) in methyl ethyl ketone using the same copolymerization conditions.

2.2. Characterization of Copolymers

SiMA incorporated into the copolymers was determined as follows. After removing toluene in the copolymerization products under reduced pressure, the powdered copolymers were extracted by refluxing in hexane for 40 hours, using a Soxhlet apparatus, to remove unreacted PDMS and SiMA. The amount of SiMA incorpo-rated into the copolymers was calculated from the extracted amount of PDMS and SiMA. M_n of the copolymers were determined in THF with a gel permeation chro-matograph, using standard polystyrene.

2.3. Preparation of Adhesive Films

An acrylic polymer, with an acid value of 23, T_g of $-42°C$, and M_n of 110,000 (Trade mark: Corponeel 8851, The Nippon Synthetic Chemical Ind. Co., Ltd.) was used as the adhesive. Modifiers shown in Table 1 were added to the adhesive with hexamethylene diisocyanate trimer (3.5 wt% of the adhesive). The modified adhe-sive was cast onto corona-discharge-treated polyethylene film from 30 wt% toluene solution. The cast films of 30 μm dry thickness were cured at 60°C for 20 hours.

TABLE I
Preparation of modifiers and their characteristics

| | SiMA | | monomer (wt) | | | PDMS (%) | |
Run	M_n of PDMS	*p/q*	MMA/SiMA/MPEGMA			(incorporated/feed)	M_n
1			70	—	30		9800
2	2000	1.4	70	30	—	77	11500
3	2000	1.0	70	30	—	60	10400
4	2000	0.7	70	30	—	43	8400
5	2000	0.5	70	30	—	25	6600
6	1000	monomethacrylate[a]	70	30	—	67	13900
7	3200	1.4	70	30	—	68	9400
8	5000	1.4	70	30	—	72	11900

[a]Polydimethylsiloxane-monomethacrylate (Chisso Corp., trademark FM711).

2.4. Analysis and Measurement

The adhesive film, which was composed of the acrylic polymer layer and polyethylene film, with a width of 25 mm and a length of 120 mm, was adhered to a SUS 304 stainless steel panel by pressuring the opposite side of the acrylic polymer layer, using a roller with a load of 2 kg. After storing the SUS 304 stainless steel panel with the adhesive film attached for certain times at 60°C, the steel panel was mounted in an Autograph. The 180° peel strength was measured by peeling the adhesive film from the steel panel in a 180° configuration at a 300 mm/min crosshead speed at 25°C, keeping the adhesive film in a stretched state.

A Shimazu X-ray photoelectron spectrometer, ESCA 850, was used for surface analysis, with a Mg Kα X-ray source. The X-ray gun was operated at 8 kV and 30 mA and the analyzer chamber pressure was $1 \times 10^{-6} \sim 10^{-7}$ Pa. A take-off angle of 90° was used for the samples.

3. RESULTS AND DISCUSSION

3.1. Copolymerization of Polydimethylsiloxane-methacrylate and MMA

Table 1 gives a summary of the modifiers prepared in this work and their characteristics. Polydimethylsiloxane-methacrylate (SiMA) prepared with a p/q ratio of 1 is mainly monomethacrylate and its copolymerization efficiency with MMA is about 60%. The remaining 40% of SiMA in the polymerization product works as free PDMS. SiMA prepared with a p/q greater than 1 (Run 2 in Table 1) consists of mono- and dimethacrylate which has good copolymerization reactivity. Copolymerization efficiency with MMA is about 77% in this case and the remaining 23% SiMA works as free PDMS. With these procedures, we could control the ratio of incorporated PDMS in copolymers/free PDMS in the modifiers.

3.2. Change of Peel Strength

The dependence of peel strength on contact time of the adhesives is shown in Figure 1. The peel strength increased remarkably with time, especially in the adhesive blended with P(MMA/MPEGMA). ESCA spectra of the SUS 304 surface before and after contact with the adhesive for 15 hours at 60°C are shown in Figures 2 and 3. On the initial SUS 304, no metal peaks, due to $Fe_{2p3/2}$ at 707 eV and $Cr_{2p3/2}$ at 575 eV, were detected as shown in Figure 2, nor was $Ni_{2p3/2}$ at 855 eV detected. However, O_{1s} of the metal oxide, and O_{1s} and C_{1s}, originating from some organic contamination, were detected in spite of careful washing and drying. It was found that the spectra of O_{1s} and C_{1s} on the SUS 304 surface from which the adhesive film had been removed was different from the original, as shown in Figure 3. The O_{1s} spectrum could be divided into three components, due to M—O($\underline{1}$), C=O($\underline{2}$) and C—O($\underline{3}$), and the C_{1s} spectrum could also be divided into three components, due to C—C($\underline{4}$), C—O($\underline{5}$) and C—O($\underline{6}$). M—O($\underline{1}$) and C—C($\underline{4}$) peaks were relatively high on the initial SUS 304 surface. Contrarily, the C=O($\underline{2}$) and C—O($\underline{3}$) peaks increased, compared with M—O($\underline{1}$), and the C—C($\underline{4}$) peak decreased, relatively,
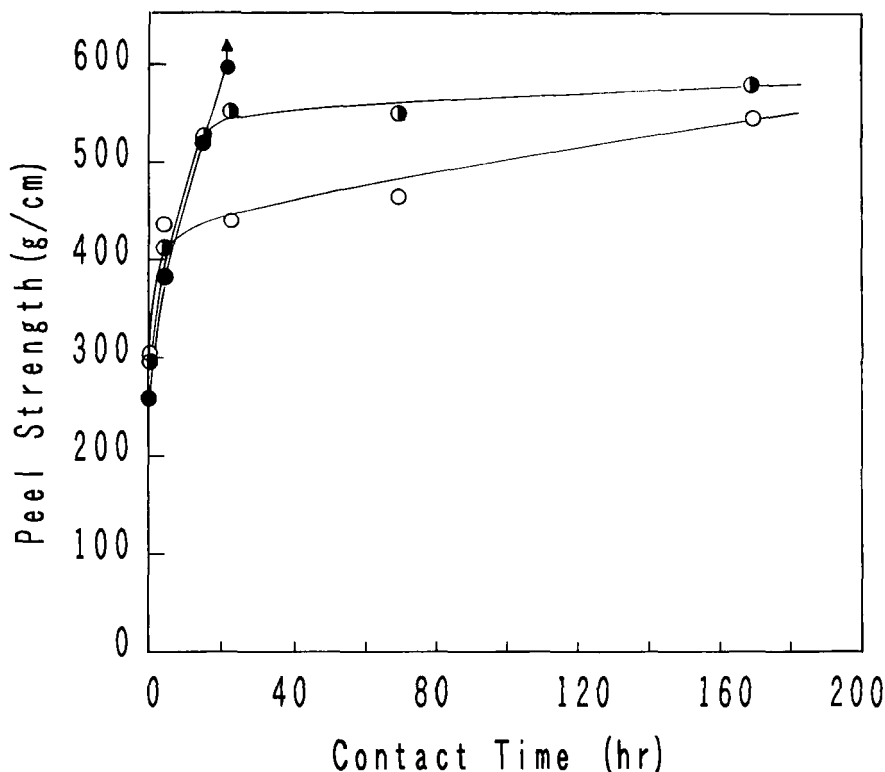
FIGURE 1   Time dependence of peel strength of adhesives on SUS 304 panel. O: control; ◑: blended with 3 phr of P(MMA-co-MPEGMA); ●: blended with 10 phr of P(MMA-co-MPEGMA).

on the SUS 304 surface after removal of the adhesive. These changes were associated with an increase in peel strength as shown in Figure 1.

These results suggest that polar carboxyl and oxyethylene groups orient to the interface between the adhesive and SUS 304 so as to minimize interfacial free energy during adhesion and the orientation increases the affinity between the adhesive and the metal material. Orientations of polar components to the interface may cause cohesive failure when the adhesive film was removed from SUS 304.

3.3.   Control of Adhesion Properties with PDMS-containing Modifier

Figure 4 shows the ESCA spectra of adhesives blended with P(MMA-co-SiMA) [II], P(MMA-co-SiMA) and SiMA monomer [I]. PDMS contents, shown as Si_{2p}/C_{1s} in Figure 4, of the adhesive surface modified with I is higher than that of the surface of the adhesive modified with II. Table II shows peel strength of adhesives modified with only SiMA, with I, and with II, respectively. Modification with only SiMA or with only P(MMA-co-SiMA) does not produce low and constant peel strength. On the other hand, a mixture of both shows low peel strength.

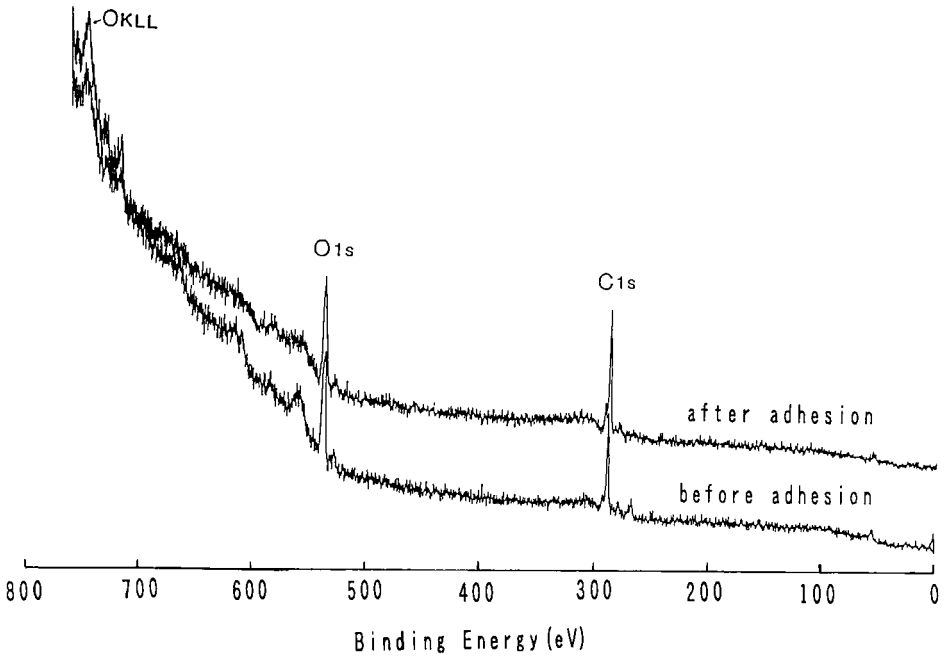In order to make clear why the mixture showed excellent low peel strength,

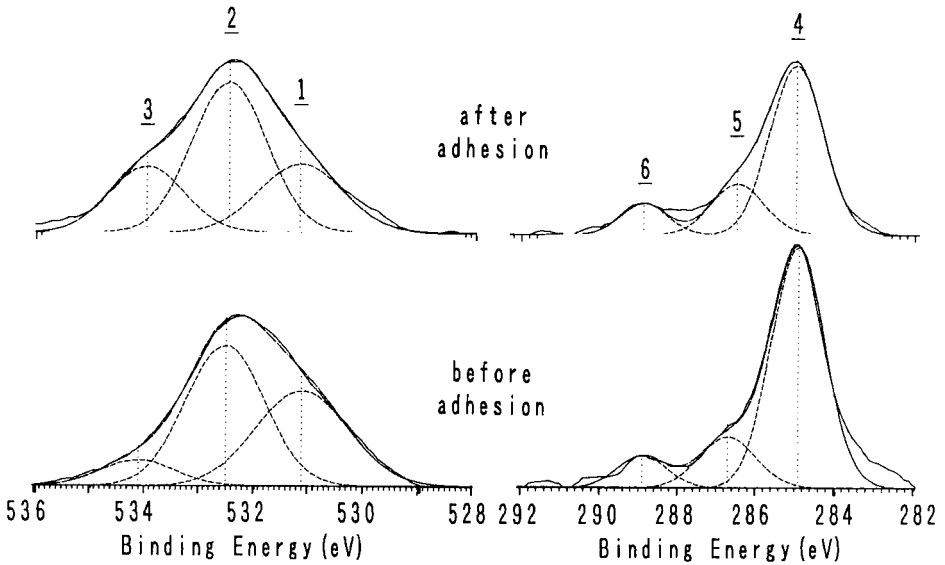FIGURE 2   ESCA spectra of SUS 304 surface before and after adhesion.

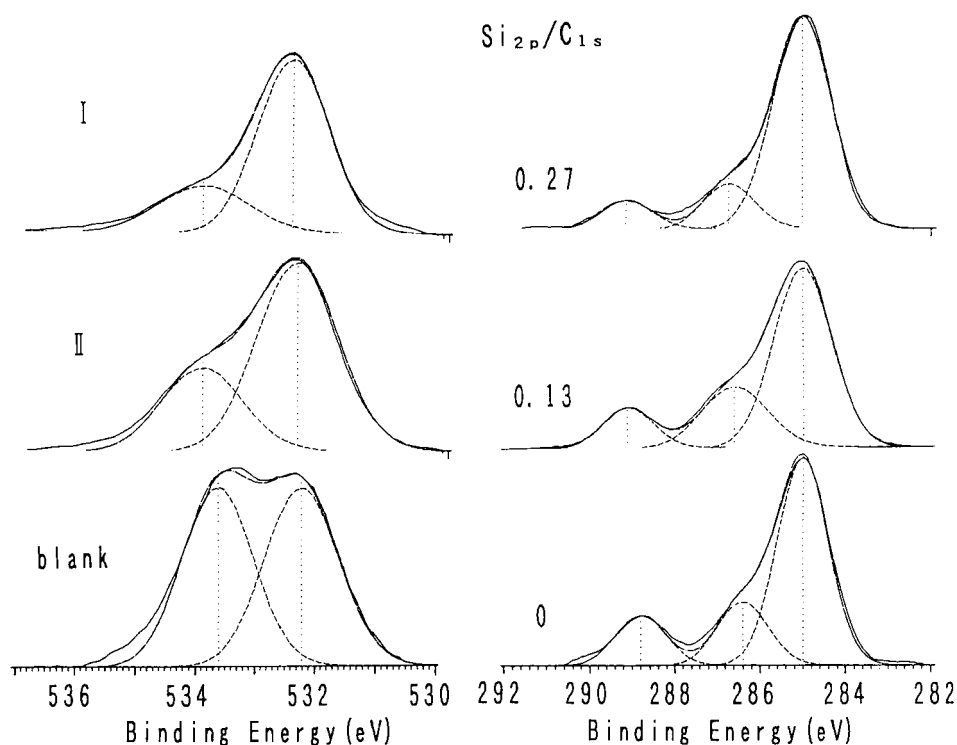FIGURE 3   ESCA spectra of SUS 304 surface before and after adhesion.

Si_{2p}/C_{1s}

FIGURE 4   ESCA spectra of adhesive blended with PDMS-containing surface modifier. I: P(MMA-co-SiMA) and SiMA 0.88/0.12 phr; II: P(MMA-co-SiMA) 0.88 phr MMA/SiMA wt ratio in P(MMA-co-SiMA) = 70/18.

TABLE II
Peel strength of adhesives blended with modifier on SUS 304

Modifier	Addition (wt%)	Peel strength (g/cm)	
		Initial	After 24 hrs[a]
control	0	306	433
SiMA	0.9	241	412
P(MMA-co-SiMA)	0.88	146	320
P(MMA-co-SiMA) and SiMA	0.88 + 0.12	24	108

[a]Contact time at 60°C.

compared with modification by PDMS or P(MMA-co-SiMA) alone, additional effects of the four modifiers which had a different content of SiMA monomer were investigated. The ESCA spectra of adhesives blended with 3 wt% of the above modifiers are shown in Figure 5 and the peel strengths on SUS 304 in these cases are shown in Figure 6. The ratio Si_{2p}/C_{1s}, which shows the degree of formation of the PDMS layer on the adhesives, increased with an increase in SiMA monomer content. When the ratio of SiMA monomer to total SiMA in the modifier exceeded
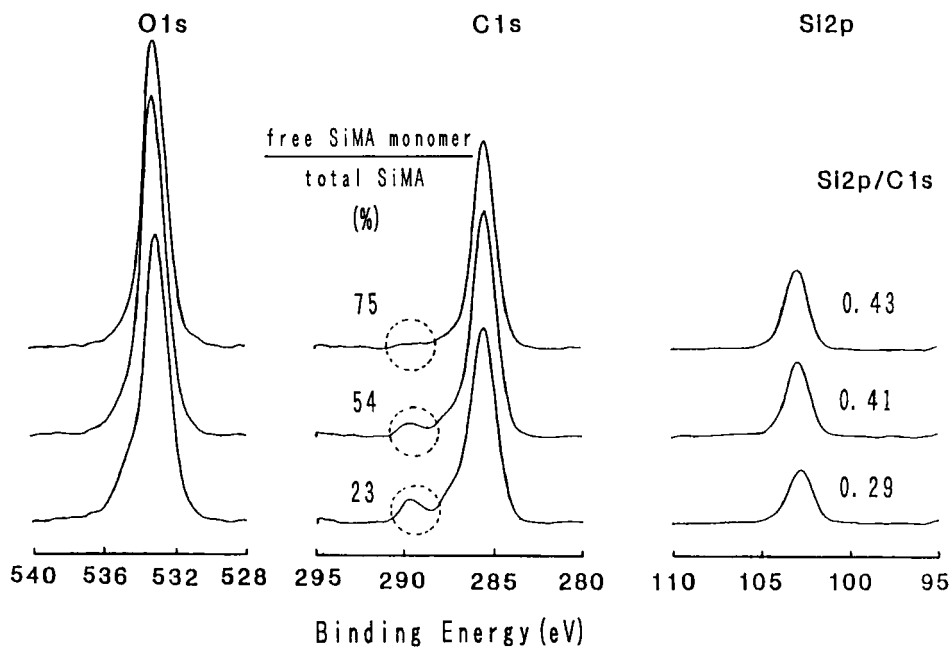
FIGURE 5   ESCA spectra of adhesive blended with 3 phr of modifiers having different content of free SiMA monomer. Modifier: P(MMA-co-SiMA) and SiMA $[70/30 - \alpha/\alpha]$; free SiMA monomer/ total SiMA $= \alpha/30$.
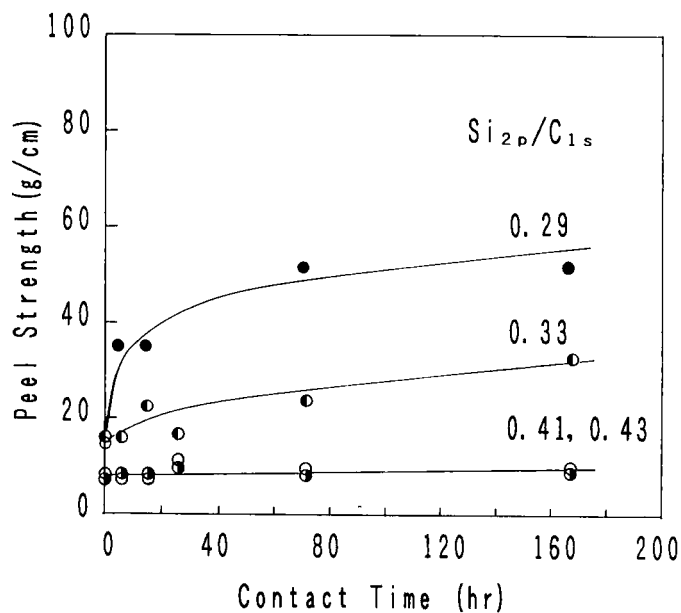
FIGURE 6   Time dependence of peel strength of adhesive blended with 3 phr of surface modifier. Modifier: P(MMA-co-SiMA) and SiMA $[70/30 - \alpha/\alpha]$; ●: free SiMA monomer/total SiMA $(\alpha/30) =$ 23%; ◖: 40; ◑: 54; ○: 75.

50%, the C=O peak at 289 eV in Figure 5 almost disappeared and the Si_{2p}/C_{1s} ratio was higher than 0.4. It was also found that low and constant peel strength was achieved with increase in the Si_{2p}/C_{1s} ratio. From the results shown in Table II and Figures 4, 5 and 6, it is suggested that low peel strength is not detected because PDMS, which migrates to the surface of adhesives, makes micelle-like "islands" on the surface in a "sea" of acrylic polymer adhesive in the case of modification with only PDMS. In the case of modification with only P(MMA-co-SiMA), the PDMS content on the surface is not high enough to result in low peel strength, although P(MMA-co-SiMA) has surface activity. On the other hand, in the case in which the mixture of PDMS and P(MMA-co-SiMA) is used as a surface modifier, it is suggested that PDMS which migrated to the surface was extended uniformly over the surface by PDMS segments of P(MMA-co-SiMA) to make a uniform PDMS layer on the surface. Consequently, low peel strength is found.

It was also found that both initial peel strength and changes over time depended on the amount of blended modifier as shown in Figure 7. The lower the amount that was added, the more the initial peel strength increased, causing more remarkable changes over time. Furthermore, the Si_{2p}/C_{1s} ratio and the peel strength were related to the molecular weight of SiMA as summarized in Table III. Unchanged and low peel strength was achieved in the case in which the M_n of SiMA was between 2000 and 3000. On the other hand, modifiers in which the M_n of SiMA was 1000 or 5000 did not achieve the same performance. It is suggested that a modifier con-
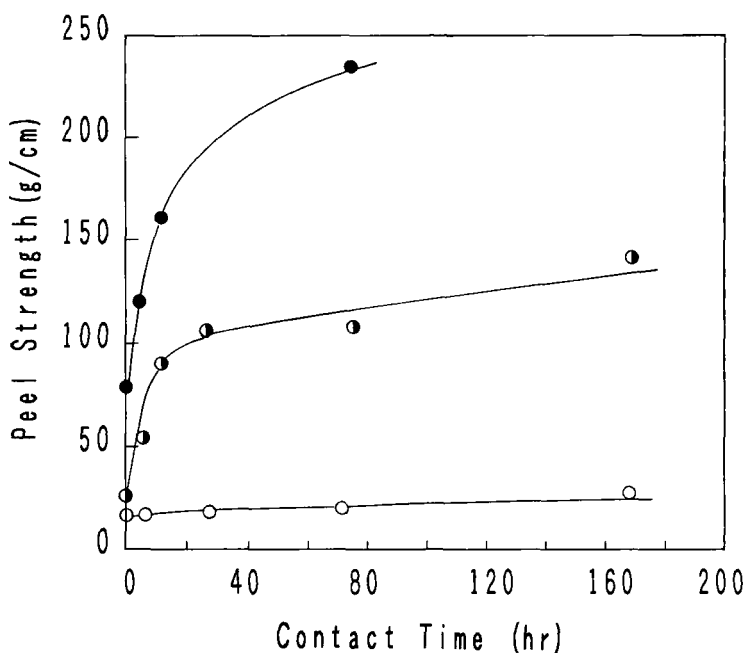

FIGURE 7 Time dependence of peel strength of adhesive blended with Modifier I. Modifier I: P(MMA-co-SiMA) and SiMA [70/18/12]; ●: 0.5 phr; ◑: 1; ○: 3.

TABLE III
Dependence of molecular weight of SiMA contained in modifiers (3 phr)
on surface composition and peel strength of adhesives on SUS 304

Composition of modifier				Peel strength		
M_n of SiMA	P(MMA-co-SiMA)		SiMA	Si_{2p}/C_{1s}	0 hr	24 hr[a]	168 hr[a]
1000	70	20.1	9.9	0.19	13	182	426
2000	70	23.1	6.9	0.29	15	37	50
3200	70	20.4	9.6	0.33	10	19	30
5000	70	21.6	8.4	0.23	29	48	150

[a]Contact time at 60°C before peel strength measurement.

taining SiMA whose M_n is 1000 has a little compatibility with the adhesives and is lacking in surface activity. In the case of the modifier whose M_n of SiMA is 5000, micelle formation by the aggregation of PDMS segments takes place during the polymerization process. It is suggested that the extension of PDMS segments on the surface of the adhesive is relatively decreased because of the aggregation of PDMS segments.

Figure 8 shows the relationship between peel strength and siloxane content on the surface of the adhesives. As described above, it was found that the Si_{2p}/C_{1s} ratio depended on the amount of blended modifier, the amount of SiMA monomer in the modifier and the molecular weight of SiMA. In addition, the peel strength on
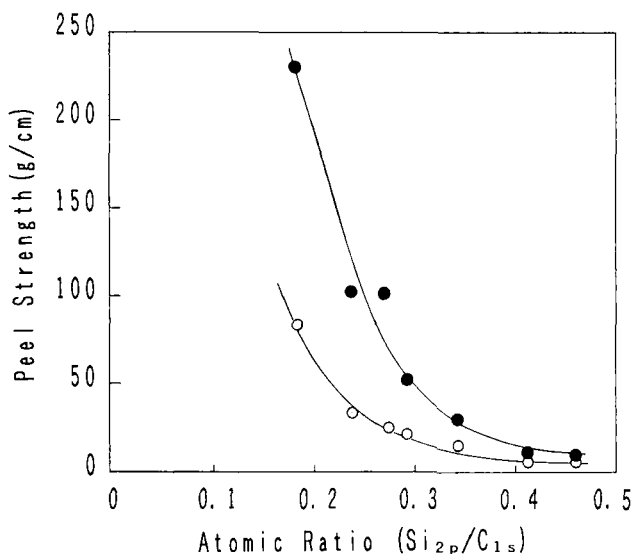

FIGURE 8   Relationship between peel strength and siloxane content on the surface of the adhesives.
○: initial; ●: after 72 hrs. at 60°C.

SUS 304 was found to be a function of PDMS concentration on the surface. The Si_{2p}/C_{1s} ratio from 0.30 to 0.35 was found to be acceptable to maintain the adhesive function and to keep a low and constant peel strength.

3.4. Relationship between Peel Strength and Surface Contamination of the Substrate

Table IV shows the Si_{2p}/C_{1s} ratio of the adhesives blended with three kinds of modifiers, before and after contact with SUS 304. Also, O_{1s} spectra on SUS 304 before and after contact with adhesive, modified with I and II, are shown in Figure 9.

On the surface of the adhesives, the Si_{2p}/C_{1s} ratio decreased slightly after removing SUS 304 in every case. The surface composition on SUS 304 changed with this decrease. Namely, the peak at ca. 532.3 eV, which consisted of C=O(2) and Si—O(7), increased, and the peak of M—O(1) at 531 eV decreased, with a decrease in the Si_{2p}/C_{1s} ratio on the surface of the adhesives. This tendency was accelerated with an increase in the blending amount of I, although these adhesives showed an excellent low peel strength performance. It was found from the results that PDMS contamination occurred by contact with the adhesives and, at the same time, the above results suggested that the low peel strength was mainly achieved by the cohesive failure of the PDMS layer on the top surface of the adhesive. As a result of cohesive failure, PDMS contamination occurred. As described above, the change of peel strength in the case in which modifier II was used (Si_{2p}/C_{1s} on the adhesives was 0.18) was larger than that of the case in which modifier I was used (Si_{2p}/C_{1s} was 0.33). This tendency of increasing peel strength corresponded to the peak height of C—O(3), which originated from a polar group of the adhesive, i.e., the lower the Si_{2p}/C_{1s} ratio, the higher the peak height of C—O(3). This result indicated that the enrichment layer of PDMS on the adhesive surface worked as a barrier to prevent the orientation of polar groups in the bulk of the adhesives.

On the other hand, the change in the Si_{2p}/C_{1s} ratio on the surface of the adhesives, which accompanied the removal of the SUS 304, was relatively small in the case in which the initial Si_{2p}/C_{1s} ratio was lower than 0.2 or higher than 0.3, when compared with the case when it was between 0.2 and 0.3, as shown in Table IV. These results

TABLE IV
Surface composition of adhesives blended with modifiers

Modifier					Si_{2p}/C_{1s} ratio on adhesives		
Composition						After removal of SUS 304	
M_n of SiMA	P(MMA-co-SiMA)		SiMA	Addition (%)	Before touching	0 hr[a]	24 hrs[a]
1000	70	20.1	9.9	3	0.19	0.17	0.19
2000	70	18.0	12.0	1	0.27	0.20	0.23
				3	0.33	0.31	0.31
5000	70	21.6	8.4	3	0.23	0.20	0.25

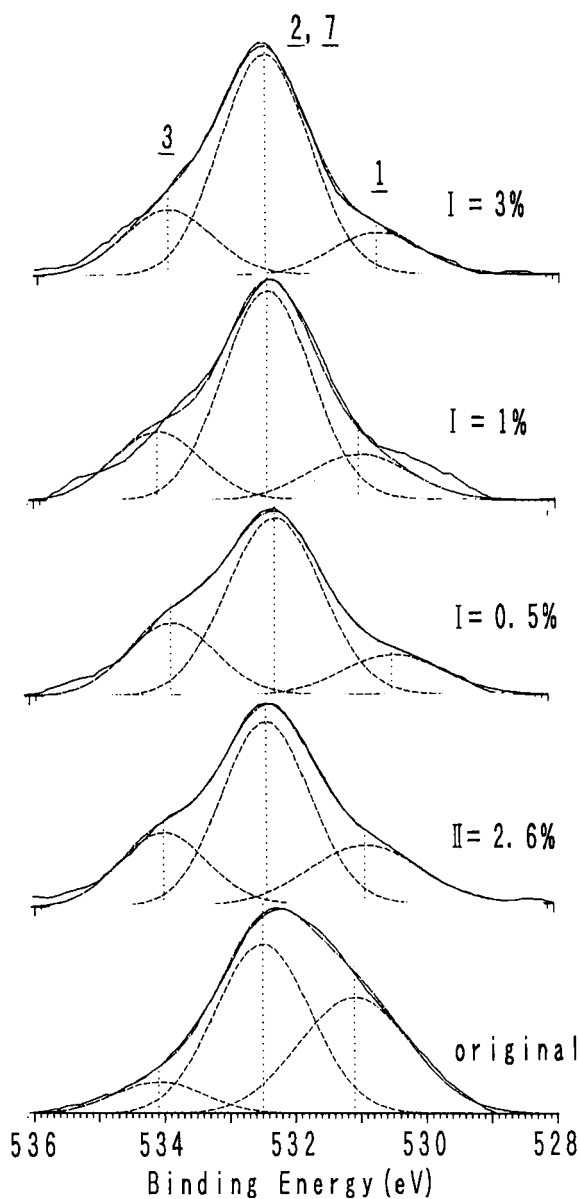[a]Holding time after removal of SUS 304.

FIGURE 9   ESCA spectra of SUS 304 surface before and after contact with adhesive blended with surface modifier. I: P(MMA-co-SiMA) and SiMA [70/18/12]; II: P(MMA-co-SiMA) [70/18].

meant that the cohesive failure of PDMS was relatively small when PDMS segments existed as phase-separated islands at the top surface of the adhesive matrix, also, that a PDMS layer remained after cohesive failure because the initial PDMS layer was rather thick. The Si_{2p}/C_{1s} ratio recovered to its initial value within 24 hours in every case. Thus, the reorientation of PDMS segments in bulk was suggested and their behavior was interesting from a practical point of view.
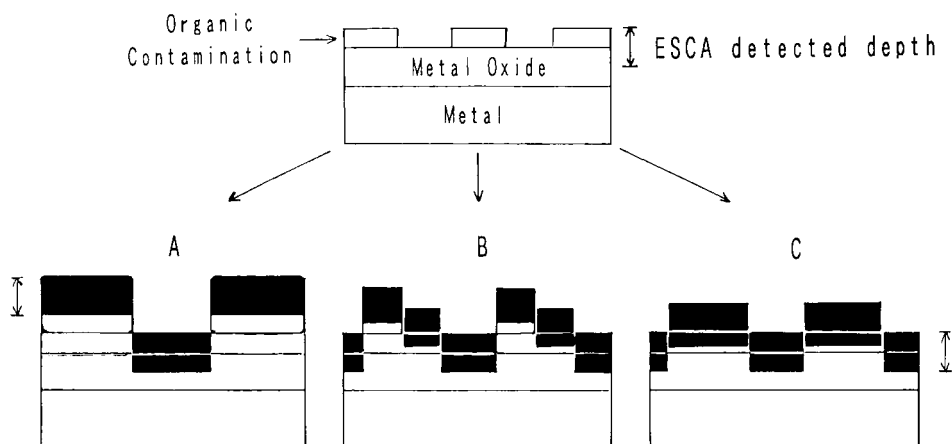
FIGURE 10 Schematic representation of the occurrence of contamination on SUS 304.

Figure 10 shows a schematic representation of the occurrence of contamination on SUS 304. "A" represents the contamination on SUS 304 from adhesives having no modifiers, "B" represents the case in which PDMS segments existed as phase-separated islands on the adhesive and "C" is in the case in which a PDMS overlayer was formed on the adhesive. The amount of contamination is estimated to be largest in case "A" by comparing ESCA spectra as shown in Figures 3 and 9. Meanwhile, the amount of contamination in case "B" is smaller than that of the others, although contamination by both adhesive and PDMS occurred. A suitable modifier could be selected to keep unchanged peel strength or to minimize the contamination on the substrate.

4. CONCLUSIONS

We made clear the cause of the increase in peel strength of adhesives during contact, and investigated how to modify adhesives so as to keep low and constant peel strength for a long time. Based on the above investigations, we can conclude the following:

1. The polar groups in the adhesive oriented toward the interface between the adhesive and SUS 304 so as to minimize interfacial free energy during adhesion.
2. The orientation of polar groups increased affinity between the adhesive and the metal. The orientation caused cohesive failure when the adhesive film was removed from SUS 304. As a result, the peel strength of the adhesive increased.
3. The use of a modifier which contained both P(MMA-co-SiMA) and PDMS showed an excellent effect in producing low and constant peel strength, although modification with PDMS or P(MMA-co-SiMA) was not sufficient.
4. It was hypothesized that PDMS which migrated to the surface was extended

uniformly over the surface by PDMS segments of P(MMA-co-SiMA) and the enriched layer of PDMS on the adhesive surface worked as a barrier to prevent the orientation of polar groups in the bulk. Therefore, low and constant peel strength could be achieved.

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