

# Surface Characteristics of Polydimethylsiloxane–Poly (methyl Methacrylate) Block Copolymers and Their PMMA Blends

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## Synopsis

To draw a relationship between surface concentration of the siloxane segment and adhesion performance, surface properties of the polydimethylsiloxane–poly (methyl methacrylate) block copolymers (PDMS-*b*-PMMA) prepared via poly (azo-containing siloxaneamide)s and their PMMA blends have been studied by measurements of FT-IR spectra, water contact angle, ESCA spectra and 180° peel strength toward pressure-sensitive adhesive tape. The water contact angles of the chloroform-cast blend films increased abruptly with siloxane bulk concentrations, or siloxane contents, particularly, on the air-side surfaces to reach almost 100° in low siloxane content. A marked increase of the contact angle was observed in the blends containing siloxane chain length (SCL) of longer than 2000. ESCA data evidently confirmed for these blend systems that the siloxane segments with low surface energy were accumulated or enriched mainly on the air-side surface, and that, on the other hand, polar PMMA segments with high surface energy were oriented to the glass-side surface and the inside of the films. This surface accumulation behavior of the siloxane segments reflected the 180° peel strength, as a measure of adhesion performance. The water contact angle and 180° peel strength were unequivocally correlated to the siloxane surface concentration estimated from ESCA data. Conversely, in the compression-molded blend films made by a hydraulic press between a Teflon and a stainless steel plate, the extent of surface accumulation of the PDMS segment was lower than that of the chloroform-cast films, suggesting lower degree of segment migration in hot-press films, probably due to substrate surface energy and lower relaxation in the blend melts.

## INTRODUCTION

Surface properties of solid polymers are of very much importance in many application fields, such as adhesion, coating, printing, friction, and biocompatibility. In most of the cases, they are controlled by the overlayer materials on surfaces. In block copolymers having more than two blocks, one block or segment is in preference to the others on the surface, depending on surface energy. Accordingly, it is generally known that the block copolymers exhibit characteristic surface structure and composition different from the bulk ones based on micro phase separation phenomena, essentially, influencing surface properties.

Siloxane polymers, typically, polydimethylsiloxanes (PDMS) are widely used for industrial and consumer applications to impart low surface energy characteristics. The block copolymers having polysiloxane chains are known to

manifest interesting surface behavior that the polysiloxane segments are accumulated or enriched, particularly, on air-side surfaces because of their low surface energy.

For the PDMS–polycarbonate (PC) block copolymers, Gaines et al.<sup>1</sup> found from contact angle measurements that the air-side surfaces of both the solution-cast and compression-molded films were almost composed of the PDMS blocks and the contact angles were affected by the substrates used for film preparation. Based on electron spectroscopy for chemical analysis (ESCA), also named X-ray photoelectron spectroscopy, Dwight et al.<sup>2–4</sup> confirmed surface segregation phenomena of the PDMS blocks in the PDMS–PC block copolymers and their blends for both the  $\text{CHCl}_3$ -cast and bulk-pressed films over a critical siloxane bulk concentration. More interestingly, the effect of siloxane block size, or siloxane chain length in molecule weight (SCL), not carbonate block size was found to be significant on the surface accumulation of the siloxane blocks. Also the effect of casting solvents on siloxane surface concentration was emphasized.<sup>5,6</sup> Schmitt et al.<sup>7,8</sup> proposed the models for the morphology of top 50 Å of the PDMS–PC block copolymers by means of ion scattering spectroscopy in combination with ESCA.

ESCA studies on PDMS–urethane copolymers<sup>9</sup> revealed that the PDMS blocks were preferentially oriented toward the surface and nitrogen in the urethane linkage was barely detected on the surfaces. In addition, for their blends with segmented polyether–urethanes, increasing the concentration of PDMS segments in the bulks resulted in reducing the presence of urethane segments and formed topmost PDMS layers.

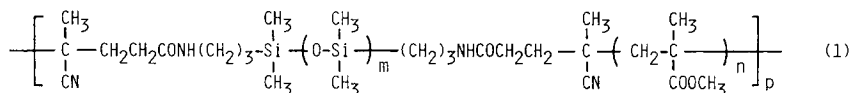
Contact angle and ESCA studies of the PDMS–polystyrene (PS) block copolymers also indicated that the overlayer of the surface region comprised of the PDMS segments with a thickness ranging from approximately 13 to greater than 40 Å, depending on the preparation method of copolymer films.<sup>10</sup> For the PDMS–poly(methyl methacrylate) (PMMA) block copolymers, a study on the surface activity of their blends films was performed by contact angle measurements, suggesting that a very low bulk concentration of the block copolymer (ca 0.1 wt %) was sufficient to produce the PDMS surfaces.<sup>11</sup>

McGrath et al., recently studied surface and bulk phase separation in PDMS–polysulfone block copolymers and their blends with polysulfone by means of ESCA and transmission electron spectroscopy.<sup>12</sup> It was noted in their works that the domain size increased with increasing block length, and the siloxane block length determined the extent of siloxane enrichment of the overlayer while the polysulfone block length influenced the gradient of surface composition or the degree of phase mixing.

As was reported previously,<sup>13</sup> macroazo initiators containing polysiloxane segments, i.e., poly(azo-containing siloxaneamide)s, were found to be interesting intermediates useful for synthesis of silicone–vinyl block copolymers, typically, PDMS–poly(methyl methacrylate) block copolymers (abbreviated as PDMS-*b*-PMMA, hereafter). A preliminary work on surface properties of the PDMS-*b*-PMMA thus prepared was done with contact angle and ESCA measurements.<sup>14</sup> Our results evidently supported the surface accumulation of the PDMS segments with relatively long SCL in spite of intervention of amide linkage between PDMS and PMMA segments, depending on siloxane bulk concentration, or siloxane content, and solvents utilized for film preparation. Similar surface information was also obtained from the MMA-based silicone

graft copolymers derived from macromonomers.<sup>15-18</sup> Relationships among molecular weight of macromonomers, siloxane surface concentration and morphology were reported for PMMA-PDMS graft copolymers.<sup>17</sup> Critical surface tension and peeling force of [2,2-bis { 4 (2-hydroxy-3-methacryloxy-propyloxy-phenyl) } -propane]/methacrylate end-capped PDMS systems crosslinked by electron beam irradiation were measured and explained in terms of surface modification.<sup>18</sup>

In this study, we have intensively investigated surface accumulation behavior of the PDMS segments for PDMS-*b*-PMMA prepared via macroazo-initiators and their PMMA blends and, furthermore, its effect on adhesion toward pressure-sensitive adhesive tape to draw a relationship between siloxane surface concentration and adhesion properties.



(PDMS-*b*-PMMA)

SCL = 250, 770, 2100, 4000

## EXPERIMENTAL

### Materials

The PDMS-*b*-PMMA used here were prepared as described in the previous paper,<sup>13</sup> and are listed in Table I. A commercial extrusion grade poly(methyl methacrylate) (PMMA) for blend was successively purified by reprecipitation from a chloroform-methanol system, and Soxhlet extraction with petroleum ether to remove, particularly, silicone-type impurity.  $M_n = 63,000$ ,  $M_w = 134,000$ ,  $M_w/M_n = 2.13$  (GPC). Reagent-grade chloroform and other solvents were used without further purification.

### Film Preparation

Two procedures, i.e., solution casting and compression molding, were applied to prepare the films for surface analysis as follows:

Mixtures of PDMS-*b*-PMMA and PMMA in given compositions were dissolved in chloroform in 5% concentration. The solutions were cast on clean glass culture dishes, and allowed to stand for almost two days. The cast films

TABLE I  
Block Copolymer Samples

Sample no.	SCL	<i>m</i>	GPC			Siloxane content <sup>a</sup> (wt %)
			$M_n$	$M_w$	$M_w/M_n$	
M-20	4000	52	70 000	251 000	3.58	14.20
23	2100	26	47 000	83 000	1.77	4.40
M-36	770	8	37 000	65 000	1.76	5.30
6	250	1	88 000	173 000	1.97	0.43

<sup>a</sup> Measured by <sup>1</sup>H-NMR spectra.

of 0.45 mm thickness were dried further at 40°C under reduced pressure for more than one day, after detachment from the glass surface.

Also, the compression-molded films with a thickness of 0.5 mm were made interposing some cast films between a stainless steel plate and a Teflon plate by the use of a hydraulic press at 180 to 190°C (for 3 min at 2 kgf/cm<sup>2</sup> gauge pressure, and then for 15 min at 50 kgf/cm<sup>2</sup>) followed by cooling with a cold press.

### Analysis and Measurements

A Shimadzu double beam spectrophotometer UV-180 was employed to measure the percent transmission of the films in a range of 300 to 800 nm.

Fourier transform infrared spectroscopy (FT-IR) of the films was performed with a JEOL FTIR spectrometer JIR-AQS 20 attached to an attenuated total reflection (ATR) apparatus, using a germanium prism with an incident angle of 45°.

Water contact angles of the blend films were measured with an Erma contact anglemeter Model II at 23°C and 50% RH. All measurements on both the air-side and glass-side surfaces were conducted within 1 min after placing water drops on the film surfaces.

Electron spectroscopy for chemical analysis (ESCA) or X-ray photoelectron spectroscopy of the films was done with a Shimadzu X-ray photoelectron spectrometer ESCA 750 accompanied by a data processor ESCAPAC 760. A Mg anode was used as a X-ray source under vacuum at  $2 \times 10^{-7}$  torr (6 kV-30 mA). A take-off angle for film samples was 90°. The aliphatic carbon 1s peaks were assigned to a binding energy of 285.0 eV to correct the energy shift due to electrification. The ESCA peak intensity was corrected by dividing the integrated numbers of photoelectron counts by relative strength factor, i.e., photoelectron cross-section.

A testing method for 180° peel strength as a measure of adhesion performance was almost based on JIS Z 0237. The films were adhered with a Scotch pressure-sensitive adhesive tape #250 (Sumitomo 3M Co.) with a width of 19 mm under a load of 5 kg roller. Then the 180° peel testing was done with a Shimadzu Autograph S-500-D of a 100 mm/min crosshead speed. The peel data were averaged for two specimens.

## RESULTS AND DISCUSSION

Chloroform used here as a casting solvent is a good solvent not only for PMMA but also for PDMS. However, the solubility parameter of chloroform ( $\delta = 9.3$  [cal/cm<sup>3</sup>]<sup>1/2</sup>)<sup>19</sup> more closely resembles that of PMMA ( $\delta = 9.1$  [cal/cm<sup>3</sup>]<sup>1/2</sup>)<sup>19</sup> than that of PDMS ( $\delta = 7.4$  [cal/cm<sup>3</sup>]<sup>1/2</sup>)<sup>19</sup>. Therefore, slow evaporation in a glass culture dish will lead to a gradient effect with most soluble material, PMMA, coming out last near the glass-polymer interface, as suggested previously.<sup>14</sup> The use of chloroform accelerates surface accumulation of the siloxane segments and also makes it possible to prepare the polymer films with a variety of surface siloxane concentration for this study. Several PDMS-*b*-PMMA/PMMA blend films were prepared by mixing a block copolymer and a PMMA homopolymer in chloroform and casting the resulting polymer solution onto a glass dish. The siloxane contents of these blend films were less than those of the block copolymers shown in Table I, i.e., less than 14 wt %.

It is noticed that appearance of the films for block copolymers and their blends thus obtained was visibly varied from transparent to opaque, depending on SCL of the block copolymers in spite of similar siloxane contents. The films having SCL of higher than 2100 were opaque, while those having SCL of lower than 770 were transparent. Typical dependence of siloxane content on transparency of the films are shown in Figure 1.

This evidently suggests existence of phase separation between the PDMS and the PMMA segments for the block copolymer blends having higher SCL, as already reported.<sup>14</sup> By the use of differential scanning calorimetry, the MMA homopolymer was confirmed to be miscible with the PMMA segments in the PDMS-*b*-PMMA used here, different from the case of blends of PS and styrene-dimethylsiloxane diblock copolymers having low molecular weight block.<sup>20</sup>

Both the air- and glass-side surfaces of the  $\text{CHCl}_3$ -cast films were first characterized by means of ATR FT-IR analysis. Figure 2 shows typical ATR FT-IR spectra of both the sides in PDMS-*b*-PMMA/PMMA blend films having SCL of 4000 and 770, and their difference spectra. The spectrum subtraction of the air-side surface from glass-side surface was made to compensate for the C—O stretching absorption of the MMA ester group of the blends at  $1150\text{ cm}^{-1}$  as fully as possible.

The difference spectrum of the blend having a SCL of 4000 surely indicates the excess of PDMS segments on the air-side surface in preference to those on the glass-side surface, even in very low siloxane bulk concentration or siloxane content (1.4 to 1.5 wt %), because of low energy PDMS surface. On the contrary, the difference spectrum of the blend having a SCL of 770 exhibited little appearance of PDMS segments. These ATR FT-IR analytical conditions, i.e., germanium prism with an incident angle of  $45^\circ$ , suggest the structural information taken from the surface layer of  $0.6\ \mu\text{m}$ . Therefore, even in this depth

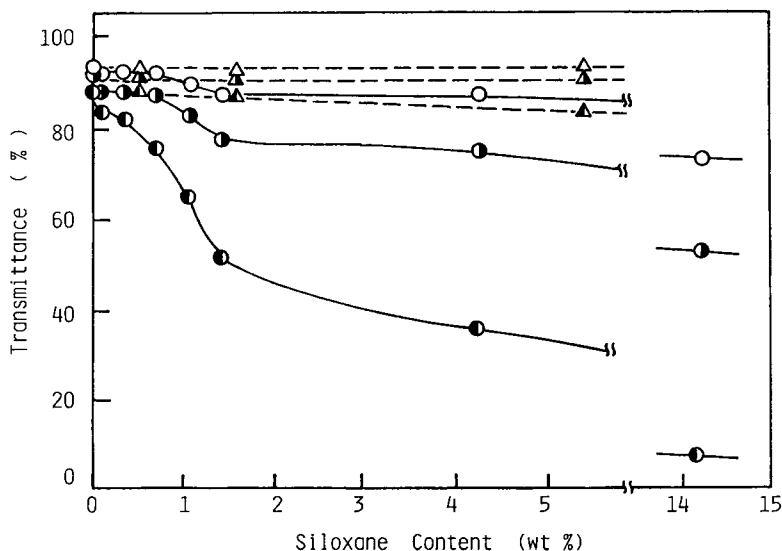


Fig. 1. Visible light transmittance for solution-cast PDMS-*b*-PMMA/PMMA blend films having SCL of 4000 and 770. 800 nm: (○) SCL 4000, (△) SCL 770; 600 nm: (●) SCL 4000, (▲) SCL 770; 400 nm: (●) SCL 4000, (▲) SCL 770.

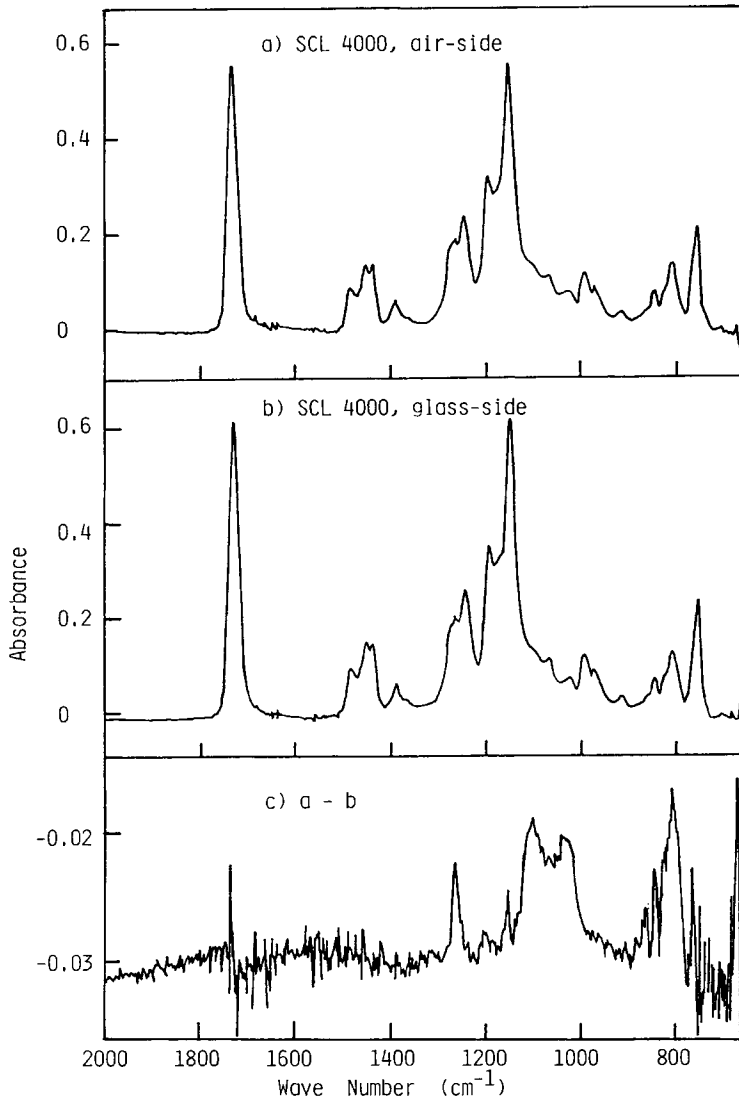


Fig. 2. ATR FT-IR spectra of PDMS-*b*-PMMA/PMMA blend films. Prism Ge, 45°, scan 100 times. SCL 4000, siloxane 1.4 wt %: (a); air side, (b); glass side, (c); (a)–(b). SCL 770, siloxane 1.5 wt %: (d); air side, (e); glass side, (f); (d)–(e).

region, preferential accumulation of PDMS segments on the air-side surface was confirmed in the case of blends with longer SCL.

More useful information to adhesion phenomena can be obtained from contact angle and ESCA data. Surface properties are generally said to be affected by the surface constitution of the top 10 Å or less. Accordingly, contact angle and ESCA data may afford more important surface information rather than ATR FT-IR data, in this case, with regard to topmost molecular layer and quantitative surface composition in the top 50 Å region, respectively.

The water contact angle,  $\theta$ , for the PDMS-*b*-PMMA/PMMA blend films were plotted against siloxane contents of the blends, as shown in Figure 3.

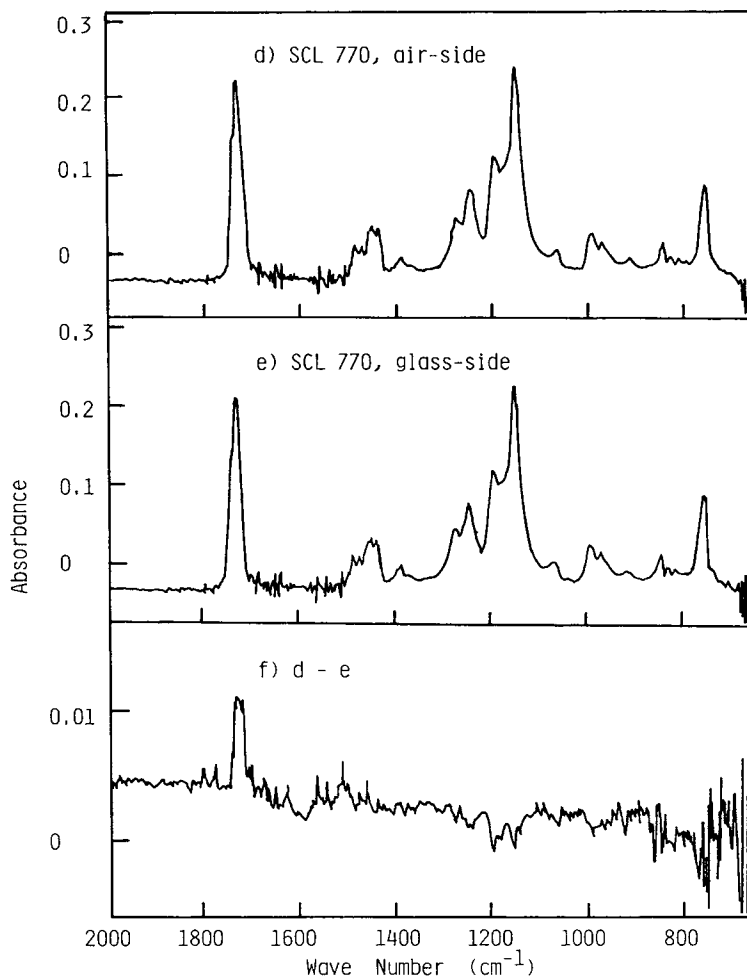


Fig. 2. (Continued from the previous page.)

A quite different surface behavior between the air- and glass-side surfaces was observed similar to the FT-IR results. The water contact angles were distributed from 60 to 100° for the PMMA homopolymer to the block copolymer. The water contact angles of air-side surfaces for the blends having a SCL of 4000 steeply increased to almost 100° in a very low siloxane content, suggesting an abrupt increase of hydrophobicity, while the glass-side surfaces were still hydrophilic because polar PMMA segments oriented to the glass surface. A commercial PDMS (Shin-Etsu KF-96, 500 cs) exhibited a water contact angle of almost 100°. Therefore, the overlayers of the air-side surfaces for the block copolymers having a SCL of 4000 and their blends were comprised mostly of the lower energy PDMS segments. Conversely, on the air-side surfaces of the PDMS-*b*-PMMA/PMMA blend system having a SCL of 770, the water contact angle gradually increased with siloxane content, indicating lower extent of surface accumulation of the PDMS segments. Furthermore, the difference of water contact angles between air- and glass-side surfaces of these films became smaller,

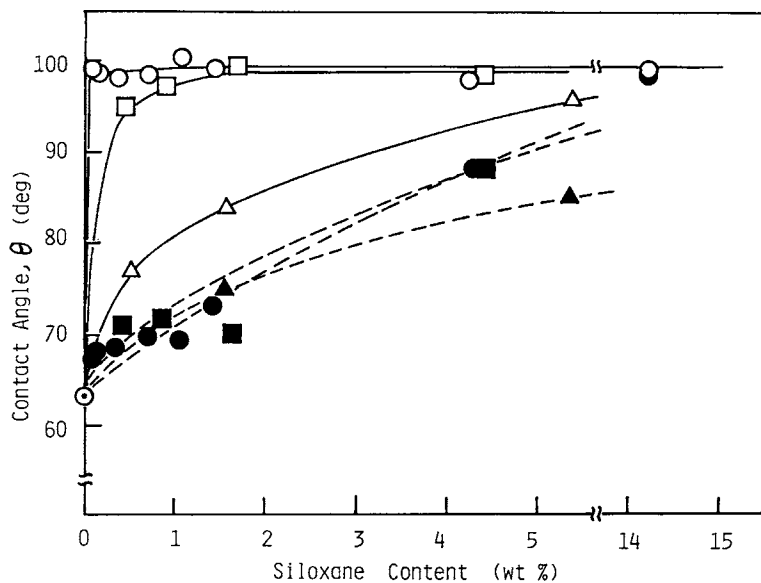


Fig. 3. Relationship between water contact angle and siloxane content. Air side: (○) SCL 4000, (□) SCL 2100, (△) SCL 770; Glass side: (●) SCL 4000, (■) SCL 2100, (▲) SCL 770.

as miscibility of two segments increased. Significant dependence of SCL on the water contact angles reflects an importance of phase separation behavior of the segments in block copolymer blends.

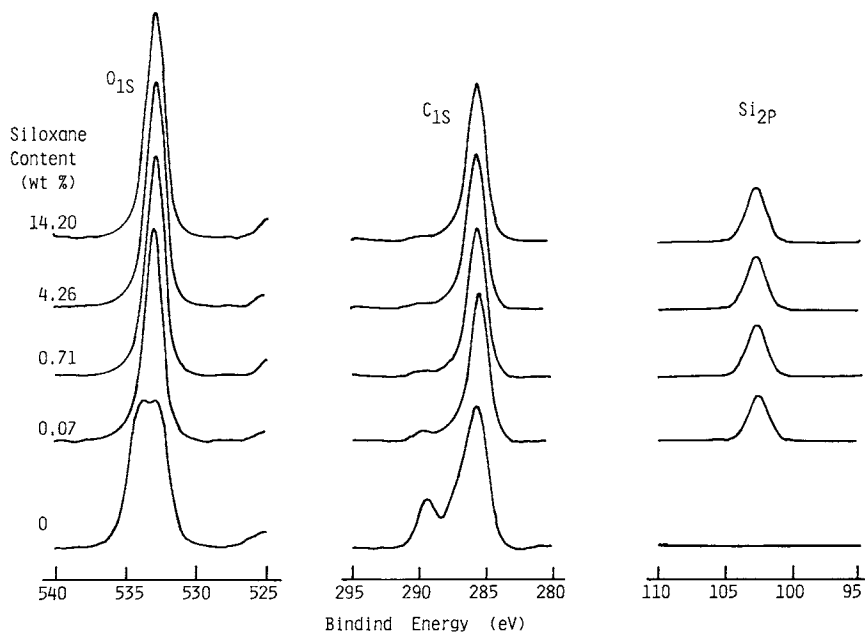


Fig. 4. ESCA spectra of air-side surfaces for PDMS-*b*-PMMA/PMMA blend films. SCL 4000.



ESCA data may offer more quantitative information on surface structure and composition not only in topmost surface, but also in subsurface up to a depth of 50 Å, in preference to contact angle data.

Figure 4 shows typical ESCA spectra of core-level photoelectrons on the air-side surface for the PDMS-*b*-PMMA/PMMA blend films having a SCL of 4000.

While no  $N_{1s}$  peak appeared in the blend films of a SCL of 4000,  $O_{1s}$ ,  $C_{1s}$  and  $Si_{2p}$  peaks were clearly identified and remarkably changed their peak patterns with an increase of siloxane content. Contrary to this, in the blend films having SCL of 770 and 250, a weak  $N_{1s}$  peak in addition to  $O_{1s}$ ,  $C_{1s}$ , and  $Si_{2p}$  peaks could be detected, particularly, on their glass-sides, indicating the occurrence of amide group on the surface. The spectral change in Figure 4 is attributed to an abrupt increase of the PDMS segments on the air-side surfaces. It is revealed that more than mono-molecular layers were well analyzed by this technique.

Plots of ESCA  $Si_{2p}/C_{1s}$  intensity ratio corrected by relative strength factor against siloxane content are shown in Figure 5.

As can be seen from this figure, ESCA  $Si_{2p}/C_{1s}$  ratios increased with the siloxane content, especially, on the air-side surface, depending on the SCL. The SCL dependence, and substrate effect on the surface accumulation of PDMS segments were noticed from this ESCA results, similarly to contact angle data. For the PMMA film, there was little difference in ESCA data between the air- and glass-side surfaces, although the methyl group is known to orient to the topmost surface by ion scattering spectroscopy.<sup>21</sup>

Generally, it is known that polysiloxane-containing block and graft copolymers are phase-separated on the basis of surface energy difference between two constituents, and three basic morphological structures. That is, spheres, rods,

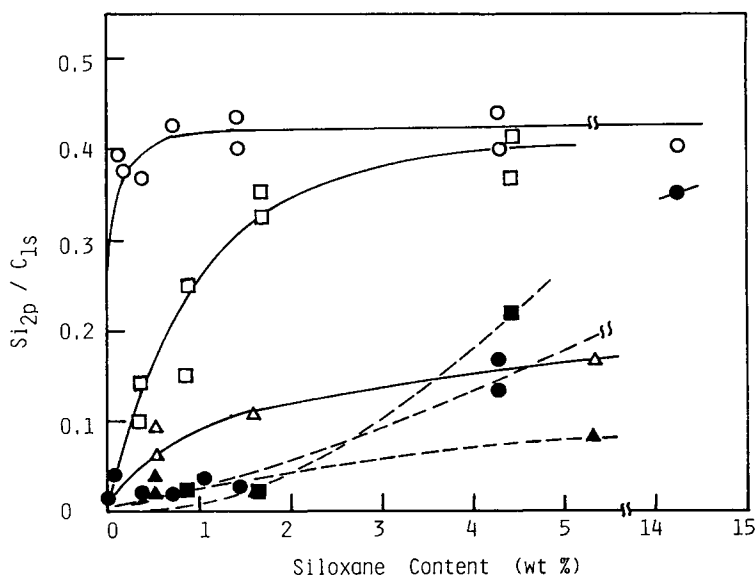


Fig. 5. Relationship between  $Si_{2p}/C_{1s}$  ratio and siloxane content. Air side: (○) SCL 4000, (□) SCL 2100, (△) SCL 770; Glass side: (●) SCL 4000, (■) SCL 2100, (▲) SCL 770.

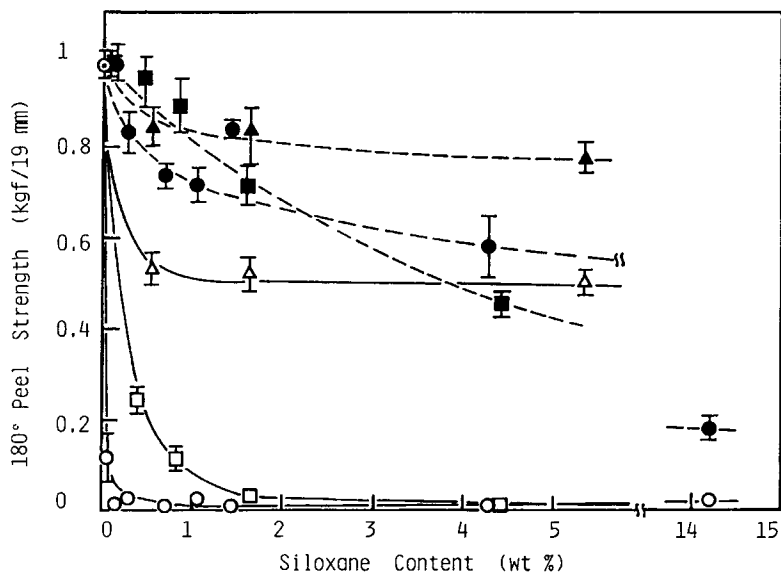


Fig. 6. Relationship between 180° peel strength and siloxane content. Air side: (○) SCL 4000, (□) SCL 2100, (△) SCL 770; Glass side: (●) SCL 4000, (■) SCL 2100, (▲) SCL 770.

and lamellae are generated depending on siloxane content, block length, solvent and so on, similar to styrene-isoprene block copolymers.<sup>22</sup> In those copolymers and their polymer blends, minor components form spherical domains, as revealed by transmission electron microscopy.<sup>12,17,18,23-29</sup> Also it is noted that the domain sizes are increased as a function of molecular weight of block or side chains from 10 to 50 nm.

In the present systems, the siloxane contents are less than 14 wt %, therefore, suggesting that the PDMS segments would form spherical domains in PMMA matrices of the block copolymers and the homopolymer. The domain sizes of the PDMS segments will increase with SCL. Correspondingly, high levels of surface accumulation of siloxane segments will be induced even at relatively low siloxane bulk concentrations due to diffusion of those microphases to the surfaces, particularly, air-side surfaces. Even in solvent-cast PS/PMMA diblock copolymers, the surface composition of PS blocks was reported to be in excess of their bulk value of 50% and also increased with the molecular weights of the copolymers.<sup>30</sup>

Surface structure and composition may significantly affect adhesion phenomena. The effect of surface accumulation of the PDMS segments on adhesion in this work was evaluated by 180° peel strength test using pressure-sensitive adhesive tapes.

Figure 6 shows the results of 180° peel strength of PDMS-*b*-PMMA/PMMA blend films adhered with pressure-sensitive adhesive tapes.

It is noted from this figure that 180° peel strength, particularly, for the PDMS-*b*-PMMA/PMMA blends having high SCL as adherends abruptly decreased with an increase of siloxane content. The air-side surfaces of the blends with SCL of 4000 were recognized to be almost adhesion-proof to pressure-sensitive adhesive tapes. It was interesting that the peel strength depended not

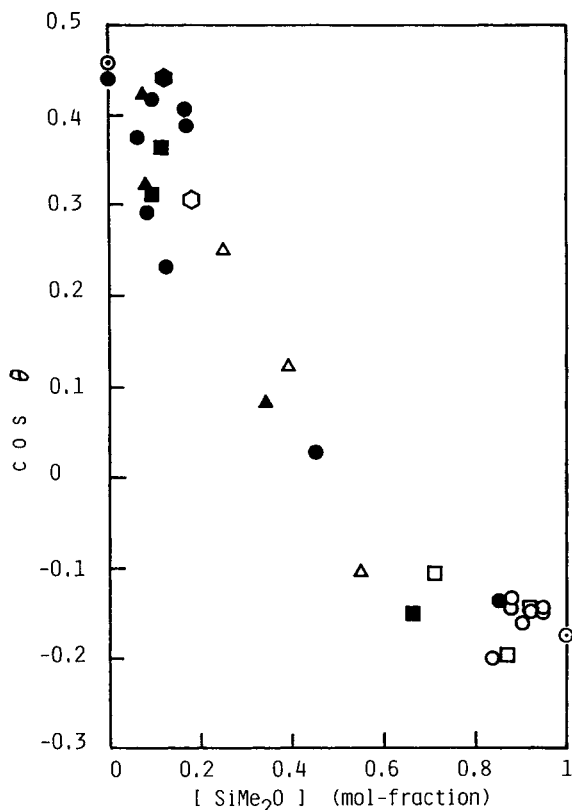


Fig. 7. Relationship between  $\cos \theta$  and  $\text{SiMe}_2\text{O}$  surface composition. Air side: (○) SCL 4000, (□) SCL 2100, (△) SCL 770, (◊) SCL 250; Glass side: (●) SCL 4000, (■) SCL 2100, (▲) SCL 770, (●) SCL 250.

only on siloxane content but also on SCL of the block copolymers as well as water contact angle and ESCA data.

Important information can be obtained from the relationship between adhesion properties, i.e., water contact angles and peel strength, and siloxane surface concentration.

Estimation of siloxane surface concentration is based on ESCA data. However, ESCA sampling depth is roughly dependent on escape depth and take-off angle. In the present work, the ESCA spectra were measured at  $90^\circ$  take-off angle, accordingly, affording structural and compositional information of  $50 \text{ \AA}$  surface layers from a simple escape-depth model, and therefore, enabling us to roughly determine siloxane surface concentration in mol % or mol-fraction by the use of ESCA  $\text{Si}_{2p}/\text{C}_{1s}$  ratios. It is necessary to utilize PDMS surface area fraction rather than surface concentration to discuss adhesion phenomena. However, there was no means to estimate the PDMS surface area fraction at the present stage of study. Therefore, in this study, the siloxane surface concentration at ESCA sampling depth in mol-fraction,  $(\text{SiMe}_2\text{O})/[(\text{SiMe}_2\text{O}) + (\text{MMA})]$  on the basis of monomeric units, was estimated from the corrected  $\text{Si}_{2p}/\text{C}_{1s}$  ratios as a simple approximation to obtain relationship between surface composition and contact angle or adhesion performance in these blend films.

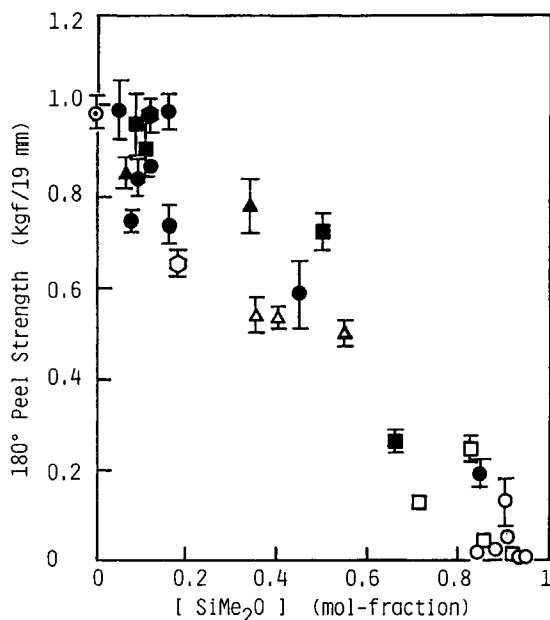


Fig. 8. Master curve for 180° peel strength and SiMe<sub>2</sub>O surface composition. Air side: (○) SCL 4000, (□) SCL 2100, (△) SCL 770, (○) SCL 250; Glass side: (●) SCL 4000, (■) SCL 2100, (▲) SCL 770, (●) SCL 250.

In Figure 7, the  $\cos\theta$  of PDMS-*b*-PMMA/PMMA blends is plotted against the siloxane surface concentration, involving the data concerning with both side of the films.

A certain relationship deviated from linear one between the  $\cos\theta$  and the siloxane surface concentration was observed in this figure. Cassie proposed a linear relationship between  $\cos\theta$  and surface area fraction for heterogeneous surfaces composed of two components.<sup>31</sup> Figure 7 suggests that these systems do not obey the Cassie's contact angle, although some problems, such as estimation of surface area fraction and validity of Cassie's model applying to microphase-separated surfaces, still remain open. However, it should be emphasized that the contact angle of these systems can unequivocally be estimated from the siloxane surface concentration using this relationship, regardless of SCL.

Also, plots of 180° peel strength against siloxane surface concentration are illustrated in Figure 8.

The peel strength for the blend films having some kind of SCL was found to be roughly correlated to the siloxane surface concentration estimated from ESCA data. This figure clearly reveals that the adhesion performance, in this case peel strength toward pressure-sensitive adhesive tape, was found to be expressed as a function of siloxane surface concentration on the monomer unit basis, regardless of SCL difference in the block copolymers. Thus, it is emphasized that there exists a rough master curve to describe a relationship between the peel strength and the siloxane surface concentration. Surface roughness of adherends should also be considered to govern adhesion performance. However, it was impossible to find significant difference of topography and structural

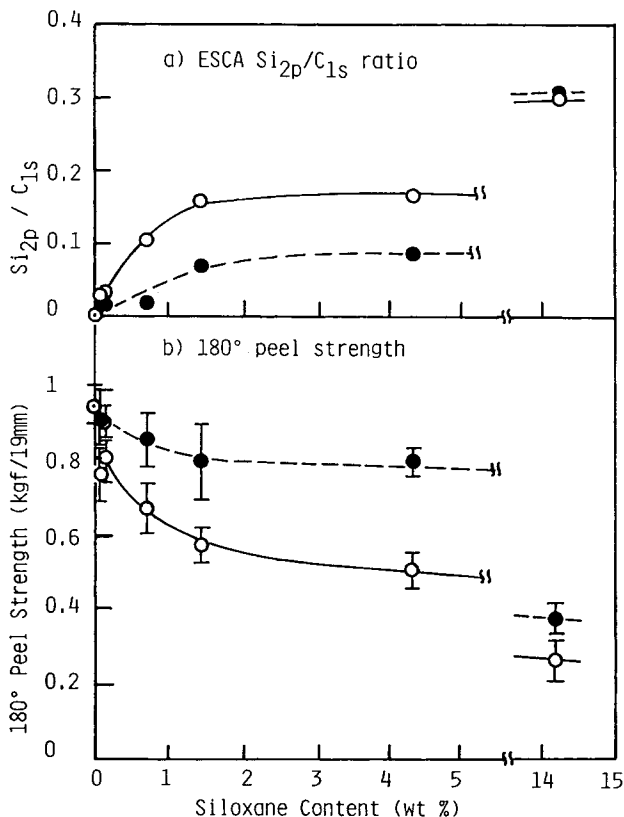


Fig. 9. ESCA  $\text{Si}_{2p}/\text{C}_{1s}$  ratio and  $180^\circ$  peel strength for hot-pressed PDMS-*b*-PMMA/PMMA blend films. PDMS-*b*-PMMA SCL 4000: (○) Teflon side, (●) stainless steel side.

details in the films between PMMA and PDMS-*b*-PMMA (sample no. M-20 in Table I), in spite of surface analysis by scanning electron microscopy. It is, therefore, concluded that the siloxane surface concentration increases with siloxane content and SCL, significantly, correlating with adhesion performance of the surfaces of block copolymers and their polymer blends. A reasonable explanation of this relationship must be delayed until the experimental data are accumulated.

Incidentally, for hot-pressed film specimens prepared by compression molding using a Teflon plate and a stainless steel plate, ESCA analysis and peel test were performed to compare with those of the solution cast films. In this study, Teflon and stainless steel were chosen as representatives of hydrophobic plate (critical surface tension  $\gamma_c = 19 \text{ dyn/cm}$ )<sup>32</sup> and hydrophilic plate ( $\gamma_c > 36$  as iron),<sup>33</sup> respectively. ESCA  $\text{Si}_{2p}/\text{C}_{1s}$  ratio and  $180^\circ$  peel strength of the hot-pressed blend (SCL 4000) films were plotted against siloxane content as shown in Figure 9.

In the ESCA spectra for some hot-pressed films, the Teflon-side surfaces exhibited existence of small amounts of lower molecular weight fluoro-compounds because of migration from the Teflon plate to the blend films. However, the migration of fluoro-compounds was found to be too small to affect on silox-

ane surface accumulation and adhesion phenomena. In the figure, some difference of siloxane surface concentration and peel strength between two surfaces was observed due to the surface energy difference of two substrates for compression molding. The hot-pressed films of the block copolymer and its PMMA blends showed relatively low siloxane surface concentration compared with  $\text{CHCl}_3$ -cast films substantially phase separated. Even in the Teflon-side surfaces,  $180^\circ$  peel strength was reduced to about one-half its initial value at 5 wt % of siloxane content, while that of the cast films decreased to almost zero at 1 wt % of siloxane content. This is explained in terms of substrate effect, segment migration and relaxation.<sup>1,34,35</sup> The polar group, in this case, MMA ester group, orients and adsorbs to the stainless steel surface depending on rate of molecular migration, and on the other hand nonpolar and low surface energy PDMS segment was in contact with the Teflon plate. However, both surfaces were still in nonequilibrium, and there was a great room for thermodynamic relaxation by segmental motion depending on temperature. Therefore, marked surface accumulation of PDMS segments was not observed in the hot-pressed films in comparison with that of  $\text{CHCl}_3$ -cast films.

In conclusion, PDMS-*b*-PMMA were found to be effective even at very low level for surface modification of PMMA, when SCL was practically longer than 2000. The extent of surface accumulation of the PDMS segments was found to depend not only on siloxane content but also on SCL, and substrates and solvent for film preparation. The peel strength of the PDMS-*b*-PMMA/PMMA blend films toward pressure-sensitive adhesive tape as a measure of adhesion performance was unequivocally correlated with the siloxane surface concentration estimated from ESCA data, affording a master curve between them. This surface information suggests that the PDMS-*b*-PMMA are practically useful for surface modification of some polymers, especially as release agents.

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