## Release Mechanisms for Pressure Sensitive Adhesive Tape on Silicone-Coated Glass

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## PLEASE SCROLL DOWN FOR ARTICLE

# Release Mechanisms for Pressure Sensitive Adhesive Tape on Silicone-Coated Glass*

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Regarding the function of the silicone release agent, the following two mechanisms, that is, the low energy surface of a cross-linked methyl hydrogen polysiloxane (MHPS) resin and the separation of a non-cross-linkable dimethyl polysiloxane (DMPS) oil itself have been compared. The 180° peel strength of the glass plate/silicone release agent/pressure sensitive adhesive (PSA) tape laminates decreased in the following order: un-coated>MHPS-coated>DMPS-coated glasses. ATR, ESCA and SEM observations of the PSA and glass surfaces after the peel test showed that no MHPS transferred from the glass surface to the PSA but a part of the DMPS transferred. From these results, it was concluded that, for decreasing peel strength, the separation of silicone oil (DMPS) itself is more effective than the low energy surface of the silicone resin (cross-linked MHPS).

KEY WORDS silicone release agent; mechanism of release; methyl hydrogen polysiloxane (MHPS); dimethyl polysiloxane (DMPS); peel strength of pressure sensitive adhesive (PSA) tape; superposition of peel strength; observation of fracture surface with ATR, ESCA, and SEM.

## 1. INTRODUCTION

Silicones have been widely used as release agents for pressure sensitive adhesive (PSA) tape but only a few papers have been published on the effect or the function. Therefore, the details have not been clear.

Commercially, the magnitude of the force required for unrolling a PSA tape (*i.e.*, whether the peel strength is high or low) is of great importance to both the tape maker and user.

A "sunny-side-up" egg is easily released from a fry-pan by not only finishing the pan with a fluoro-resin but coating it with fat. It seems that the releasing mechanism of the former is based on the low energy surface of the fluoro resin and that of the latter, on the separation of the fat itself.

In general, it is thought that the releasing function of the silicone release agents used for PSA tape results from their non-adhesive property, based on the low energy surface of silicones.[1,2] In practice, however, silicone oil (not as low surface energy) has also been used as a release agent.

In the present work, the following two mechanisms regarding the function of the silicone release agent have been compared: (1), the non-adhesive property originating from the low energy surface of silicone resin and (2), the separation (due to low cohesive strength) of silicone oil itself.

Now, it is said that the rubber-like, cross-linked polysiloxanes obtained by the reaction of methyl hydrogen polysiloxane (MHPS) and dimethyl polysiloxane (DMPS) having a reactive group such as silanol or vinyl are mainly used as silicone release agents.[1,3]

In this work, MHPS, a silicone resin, and DMPS, a silicone oil, have been selected as model release agents. The chemical structures of these two polysiloxanes are shown below. They are terminated with inactive trimethyl silyl groups.
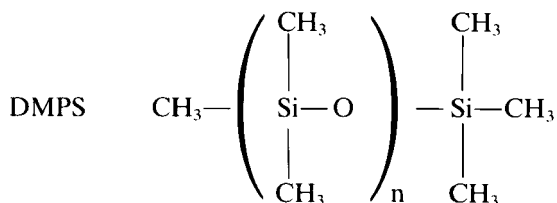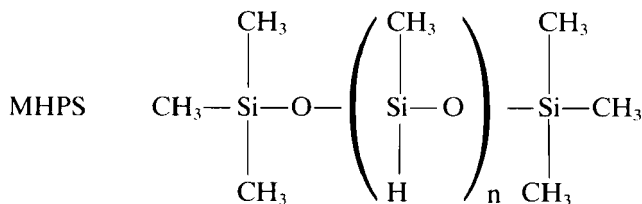


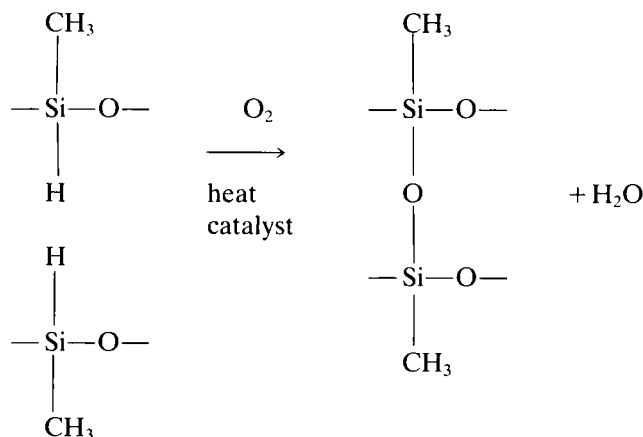MHPS is oil-like at room temperature and the contact angle for water on a thin film coated on a glass plate is about 45°. On baking the film at relatively low temperature, however, a thin cross-linked silicone resin film is formed. This film gives a water contact angle of about 90°.[4,5]



Initially, therefore, MHPS was used exclusively as a silicone release agent for paper. Because the cross-linked film obtained from MHPS is hard and strongly adheres to

glass, the peeling of this film from a glass surface is almost impossible. Therefore, it is clear that the releasing property of MHPS is based on its low energy surface. On the contrary, the contact angle of water on the glass plate surface coated with DMPS is about 45° even after baking at high temperature below about 200°C, because DMPS is stable to high temperature and remains oil-like.[4,5] A contact angle of 90°–100° is obtained only by heating over about 200°C with a catalyst. However, a cross-linking reaction at such high temperature cannot be used for preparing release paper. Therefore, it seems that the releasing property of DMPS is due to the cohesive separation of the oil-like material, so that on peeling PSA tape, some DMPS is expected to be transferred to the surface of the PSA but no MHPS (Fig. 1).

## 2. EXPERIMENTAL

### 2.1. Materials

As silicone release agents, a cross-linkable silicone oil, MHPS (KF-99, Shin-etsu Chemical Industry Co.) and a non-cross-linkable one, DMPS (KF-96) were used.
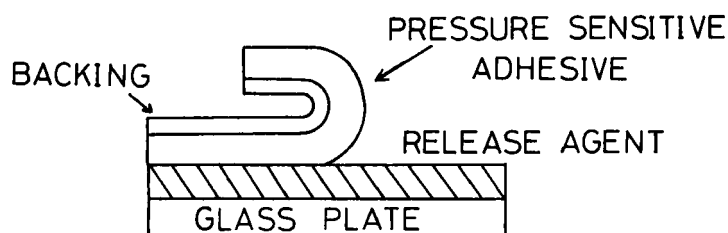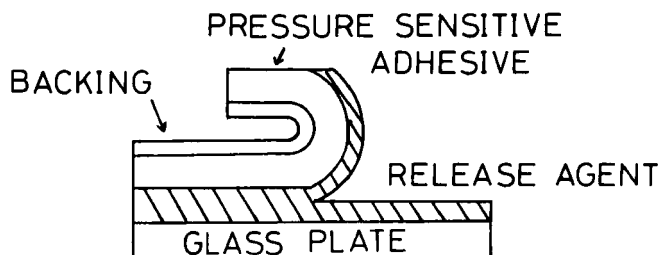


FIGURE 1  Schematic diagram of two expected mechanisms for release.

As the catalyst for hardening MHPS, a zinc salt of 2-ethyl-hexylic acid (Maruwaka Chemical Industry Co.) was used. As an adherend, a glass plate (Pyrex 7740, Corning Glass Works) was selected and, before bonding, it was cleaned thoroughly by treating with a solution of NaOH/methanol/distilled water. The contact angle of water on the pretreated glass was measured to be $0°$.

The Pyrex glass was chosen for the following reasons: (1), the adherend must be completely smooth to prevent the mechanical interlocking of the PSA resulted from micro-cracks or holes in the surface; (2), the surface cleaning is relatively easy; (3), there is only a trace amount of alkaline compounds in the Pyrex. In the case of common alkaline glass, the cross-linking reaction of MHPS occurs even at room temperature due to the catalytic action of alkali in the glass. In the case of the Pyrex, such a cross-linking reaction does not occur because there is so little alkali present. In the presence of alkali, Si—H becomes Si—OH by hydrolysis with the evolution of $H_2$ gas, the latter then produces Si—O—Si cross-links by condensation. In general, steel or phenolic resin plates are widely used as adherends for peel testing of PSA tape. However, these two plates are not the preferred adherends for this experiment. The reasons are that, in such work, the effects of contaminants, weak boundary layers (WBL) and micro-holes or crazes on the surface of the adherend should be eliminated as much as possible. The chemical composition and the topography of the surface of these two adherends are very complicated and will vary with each surface treatment for cleaning.

The cleaned glass plate was immersed in trichloroethylene solutions (1% wt) of MHPS containing the catalyst (5% wt for MHPS) and DMPS only, respectively, and dried at room temperature. Then, the glass plate coated with MHPS was baked at 150°C for 30 min to cross-link the MHPS. The specimens coated with DMPS were baked at 90°C for 30 min to remove completely the remaining solvent. A PSA tape was then laminated on the glass plates coated with MHPS and DMPS.

The 180° peel strength of these PSA tape/glass plate laminates was measured under various conditions using an Autograph DCS-100 (Shimadzu Corp.). A commercial PSA tape, 3M's Scotch Tape No. 250 (width: 25 mm), was chosen. It was confirmed by ESCA (Shimadzu Corp., 750) that no silicone release agent is contained in this PSA tape. The surface of the PSA, after the peel test, was observed with IR-ATR (Japan Spectroscopic Co.) and ESCA and the surface of glass plate, after the peel test, with SEM (JEOL, JSM-T20).

## 3. RESULTS AND DISCUSSION

### 3.1. Peel Strength

The peel strength of the laminates using un-coated (control, Fig. 2), MHPS-coated (Fig. 4), and DMPS (1,000 cs)-coated (Fig. 6) glasses as adherends was measured. The peel strengths of all of these laminates increased with decreasing temperature or with increasing peel rate, except for a few instances. They were superposed as a function of temperature and peel rate (standard temperature: $-15°C$), so that three master curves were obtained (Figs. 3, 5, 7). These master curves are displayed
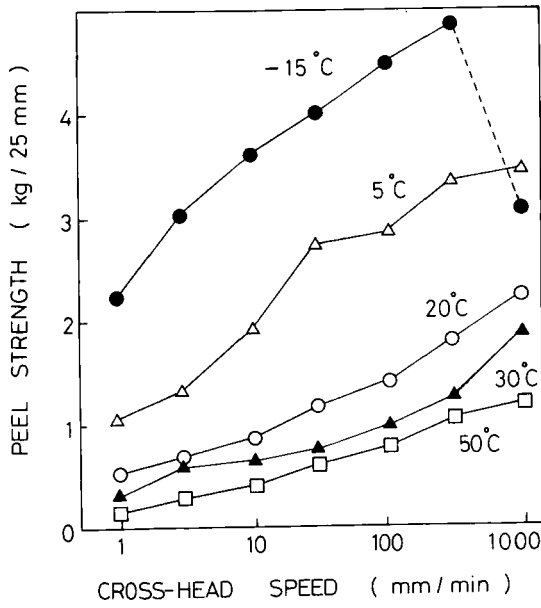
FIGURE 2   Effects of cross-head speed and temperature on peel strength of PSA tape from un-coated glass (control).
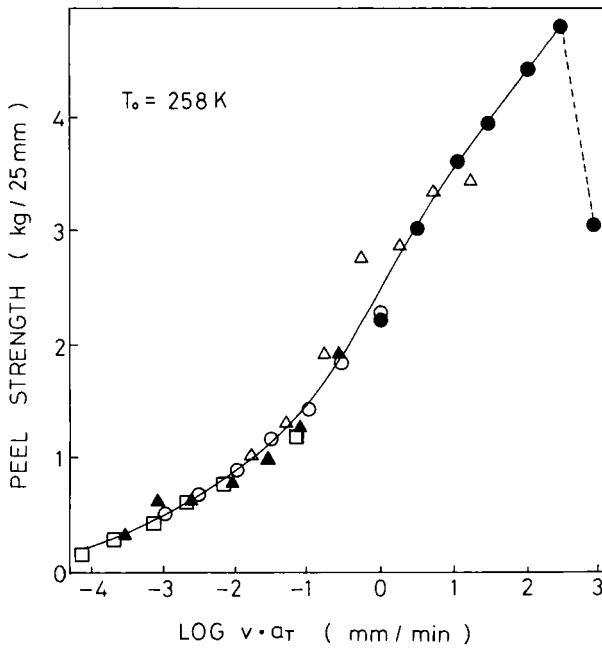


FIGURE 3   Master curve of peel strength from un-coated glass (control).
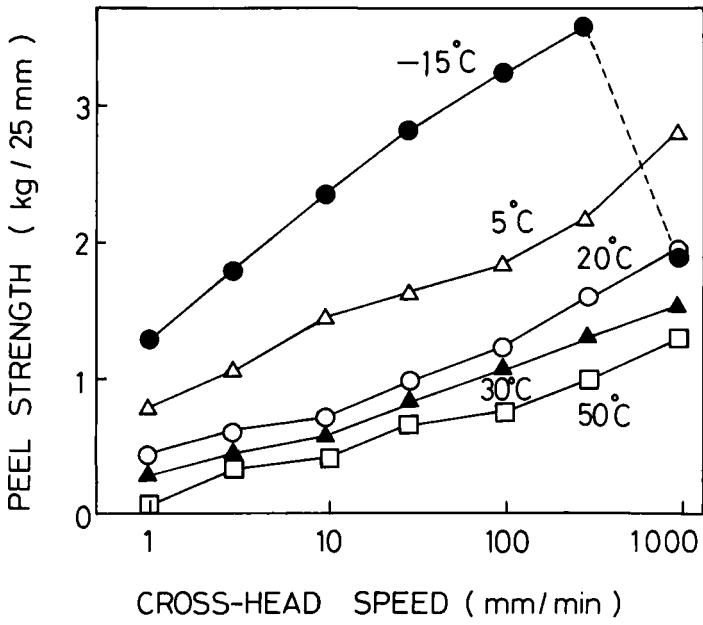
FIGURE 4  Effects of cross-head speed and temperature on peel strength for MHPS-coated glass (1% solution).
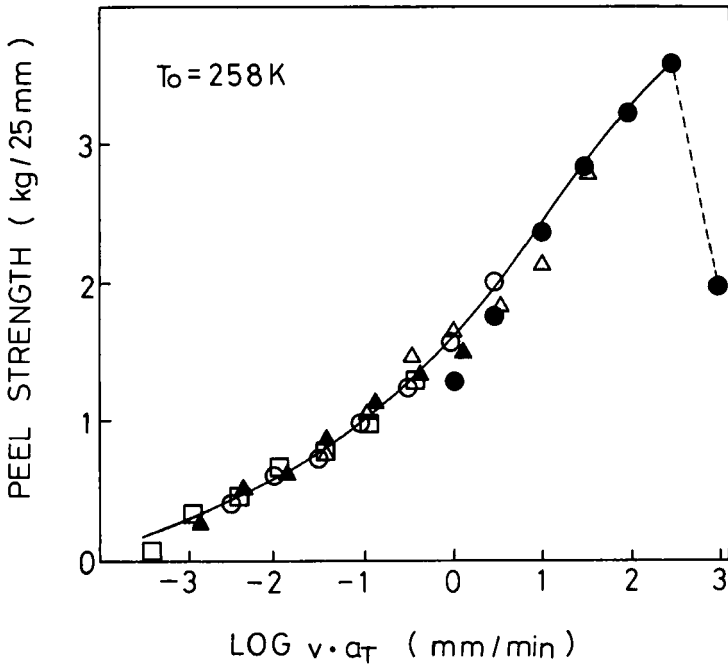
FIGURE 5  Master curve of peel strength for MHPS-coated glass.

FIGURE 6 Effects of cross-head speed and temperature on peel strength for 1,000 cs DMPS-coated glass (1% solution).



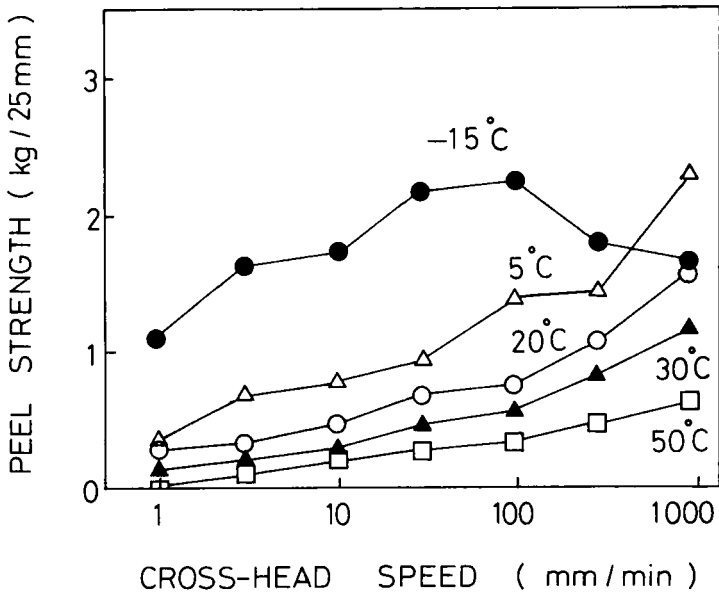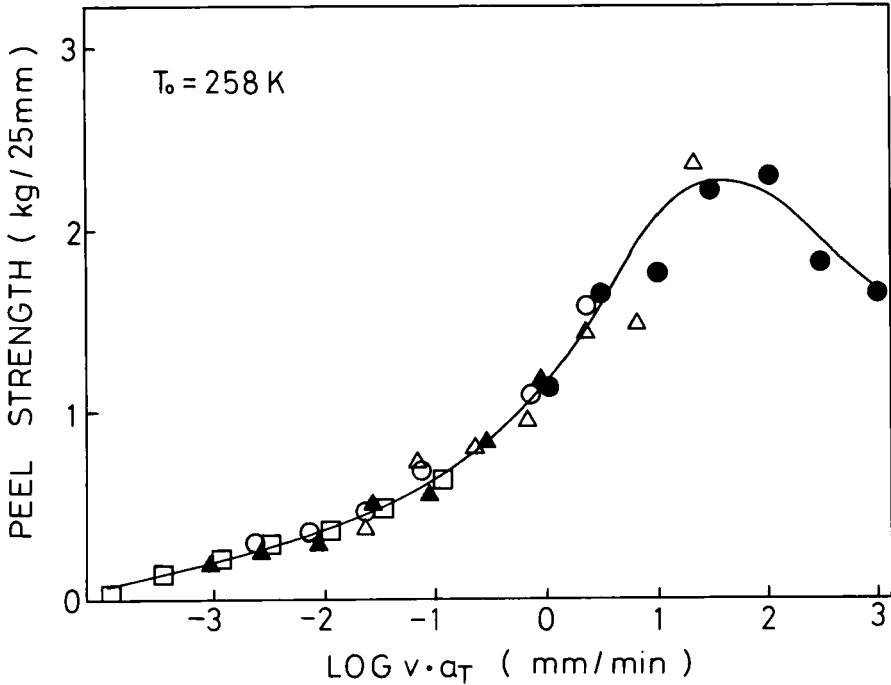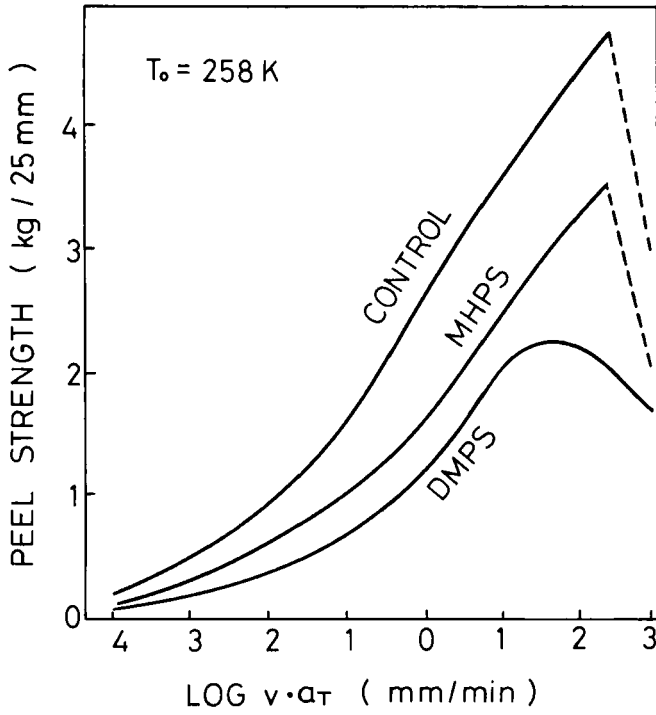FIGURE 7 Master curve of peel strength for 1,000 cs DMPS-coated glass.

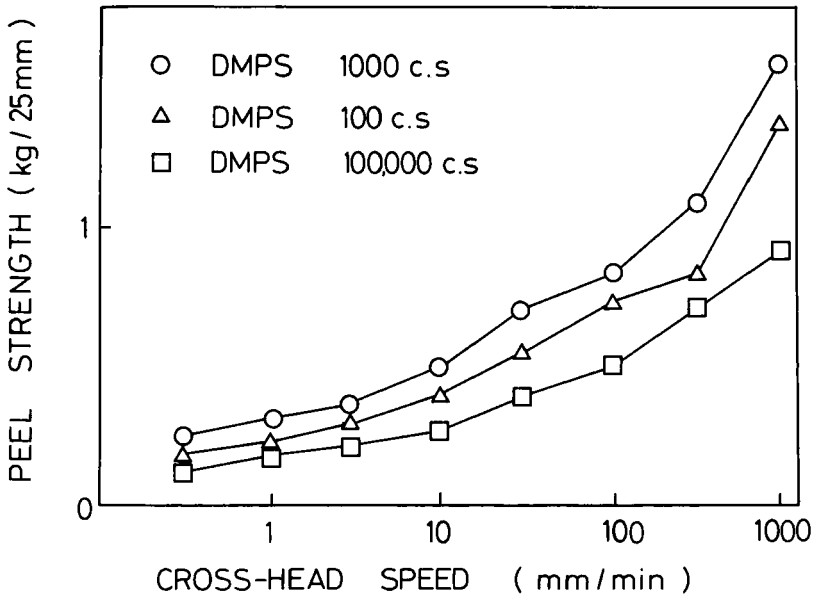FIGURE 8   Master curves of peel strengths for un-coated and MHPS- and DMPS-coated glasses (1% solution).



FIGURE 9   Effects of cross-head speed and viscosity of DMPS (1% solution, 20°C) on peel strength.

together in Figure 8. From these results, it is clear that the peel strength decreased in the following order: un-coated>MHPS-coated>DMPS-coated glass.

The rapid decrease in the peel strengths at $-15°C$ and the cross-head speed of 1,000 mm/min in Figures 2 and 4 is due to the breaking of the backing paper. According to visual observation, the loci of fracture were all at the interface between PSA and glass, except for the case of $-15°C$ and 1,000 mm/min. As shown in Figure 6, the peel strength decreased slowly when the cross-head speed exceeded 100 mm/min at $-15°C$. In this range, the modes of fracture were all slip-stick. Except for this range, the modes of fracture, as mentioned above, were all the interface between PSA and glass.

The effect of the molecular weight (here, expressed as viscosity in cs) of DMPS on the peel strength was examined. In Figure 9, the peel strength at 20°C for DMPS of 100, 1,000 and 100,000 cs is given.

The peel strength decreased in the order: 1,000 cs>100 cs>100,000 cs. The loci of fracture were all at the interface between PSA and glass, according to visual observation. The effect of the molecular weight of DMPS on the peel strength is not clear from this examination only. According to Perkel and Ullman,[6] the amount of equilibrium adsorption of DMPS on glass from a solution of a given concentration and at a given temperature increases with increasing molecular weight. In this experiment, solutions having the same concentration (1% wt in trichloroethylene) were used for all three DMPS. In the results shown in Figure 9, both the effect of the molecular weight and of the thickness of DMPS layer adsorbed on the glass surface are included. The measurement of the thickness of the adsorbed DMPS was attempted by ellipsometry but it was not successful. The number average $(\overline{M_n})$ and weight average molecular weights $(\overline{M_w})$ of DMPS are 26,000 and 40,000 for 1,000 cs and 94,000 and 203,000 for 100,000 cs, according to Perkel and Ullman.[6]

Next, the effect of the thickness of adsorbed DMPS was examined using DMPS (1,000 cs) solutions of various concentrations (Fig. 10). These results show that the peel strength at 20°C decreases with increasing concentration of DMPS, that is, increasing thickness of adsorbed DMPS.

### 3.2. Observation with IR-ATR

Figure 11 shows the IR-ATR spectra of the PSA surface after the peel test (20°C, 30 mm/min, 1% wt solution). For the un-coated glass (control) and MHPS-coated glass, the two spectra are essentially identical and show no characteristic absorption band of methyl polysiloxane (Si—CH₃: about 1260 cm⁻¹ and Si—O—Si: 1080–1020 cm⁻¹). Even so, it cannot be concluded that no MHPS transfers from the glass surface to the PSA surface. Trace amounts of MHPS, undetectable with ATR, may transfer. Therefore, it can, at most, be concluded that no transfer of MHPS occurs in the range of sensitivity of ATR.

On the contrary, in the case of DMPS (1,000 cs and 100,000 cs), the absorptions of methyl polysiloxane were clearly observed. The large absorption in the case of the 100,000 cs material indicates the presence of a considerable amount of DMPS. From these results, it is clear that some DMPS transfers from the glass surface to the PSA surface.
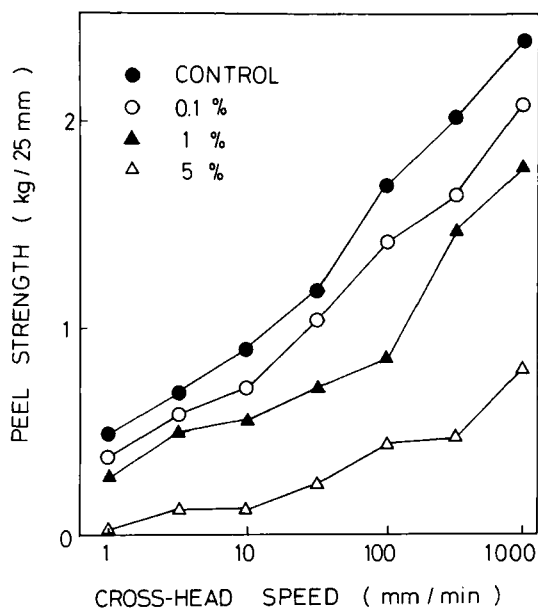
FIGURE 10   Effects of cross-head speed and concentration of 1,000 cs DMPS solution on peel strength (20°C).
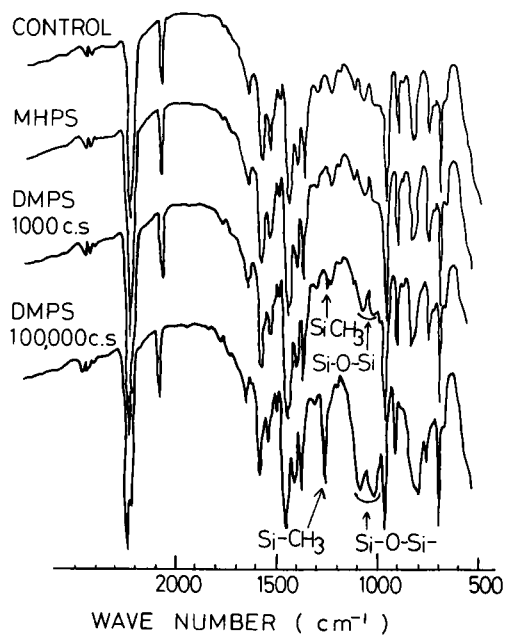


FIGURE 11   ATR spectra of PSA surface after peel test (1% solution, 20°C, 30 mm/min).

## 3.3. Observation with ESCA

Figure 12 shows ESCA spectra of Si (2p) on the PSA surface after the peel test (20°C, 1% solution). From these results, the following can be concluded:

(1) In the cases of the un-coated glass (control) and MHPS-coated glass, the faint peaks of Si (2p) having a similar shape were observed at 102.5 eV regardless of the peel rate (cross-head speed). In both cases, however, no transfer of any polysiloxane from the glass surface to the PSA surface can occur, because there is no polysiloxane on the glass surface for the un-coated glass, and because it is impossible to peel off the completely cross-linked MHPS resin from the MHPS-coated glass surface. Therefore, these faint peaks of Si (2p) may be due to a trace of inorganic silicon compounds such as mineral filler contained in the PSA. From the above considerations, therefore, it seems that the release function of the MHPS resin is based on its low energy surface.

(2) In the case of DMPS, the very intense peak of Si (2p) was observed at every peel rate. The peak for the 100,000 cs DMPS was higher than that of 1,000 cs. It is apparent that the difference depends upon the amount of coated DMPS, since the amount of the equilibrium absorption of DMPS from a solution increases with increasing molecular weight (here, viscosity). In addition, the height of the peak depends on the peel rate, and this is particularly remarkable at the peel rate of 1 mm/min for both 1,000 cs and 100,000 cs materials. From these results, it is clear that the release function of DMPS originates from the cohesive separation of DMPS itself.

While this work[7] was going on, the transfer of silicone from a tape backing surface to the PSA surface was confirmed with ESCA by Duel and Owen[8] using several commercial silicone release agents, though their compositions were not disclosed.
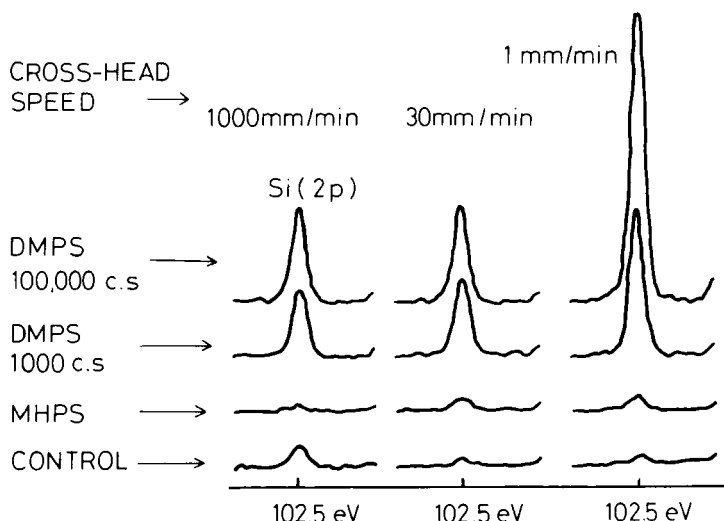


FIGURE 12    ESCA spectra of PSA surface after peel test (1% solution, 20°C).

### 3.4. Observation with SEM

The glass surface after the peel test (20°C, 1,000 mm/min, 1% wt solution) was observed by SEM. In the case of the un-coated glass, a number of fragments of the PSA were scattered all over the surface of glass (Fig. 13). This shows that a part of the PSA is fractured and deposited on the glass surface on peeling. In the case of MHPS-coated glass, many micro-fragments of the PSA were scattered here and there, and not all over, on the glass surface (Fig. 14). In the case of DMPS (1,000 cs and 100,000 cs) coated glass, a few fragments of the PSA or dust were observed (Figs. 15 and 16). These results agree with those obtained by ATR and ESCA. That is, the DMPS layer is fractured on peeling, a part of the DMPS transfers to the PSA surface and the remainder is left on the glass surface. Therefore, it is expected that no fragments of PSA remain on the glass surface. These observations by SEM agree well with the results of peel strength.
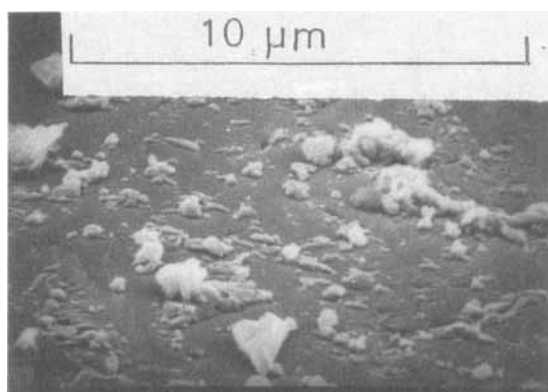


FIGURE 13    SEM of surface of un-coated glass (control) after peel test (20°C, 1,000 mm/min).
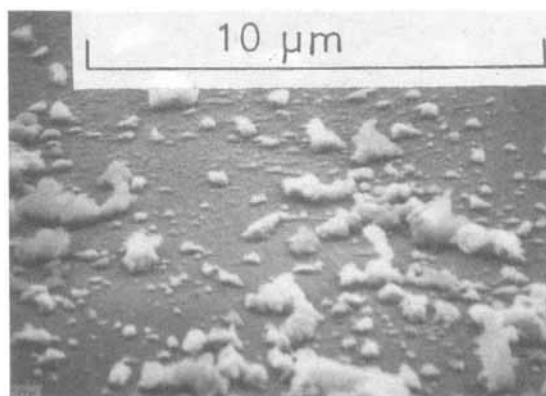


FIGURE 14    SEM of surface of MHPS-coated glass after peel test (1% solution, 20°C, 1,000 mm/min).
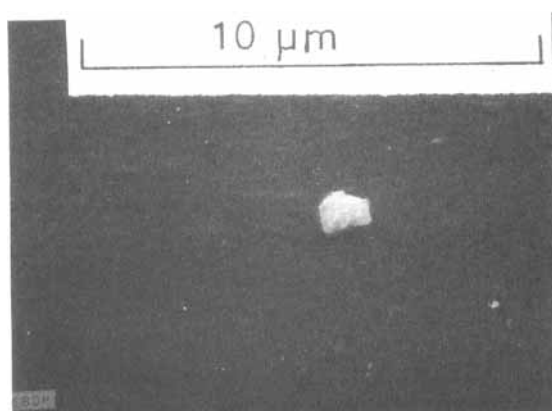
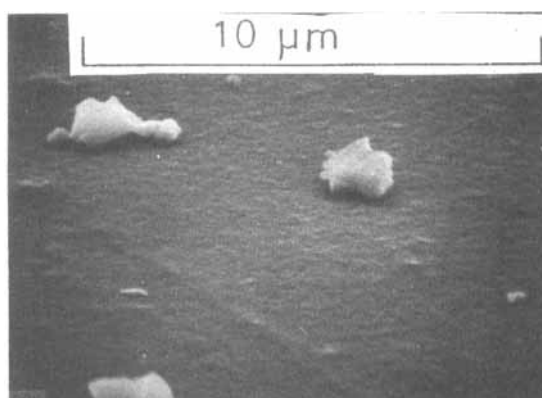FIGURE 15    SEM of surface of 1,000 cs DMPS-coated glass after peel test (1% solution, 20°C, 1,000 mm/min).



FIGURE 16    SEM of surface of 100,000 cs DMPS-coated glass after peel test (1% solution, 20°C, 1,000 mm/min).

## 4.  CONCLUSIONS

With respect to the function of silicone release agents, the following two mechanisms have been compared: (1) The non-adhesive property based on the low energy surface of a silicone resin; (2) The cohesive separation of a silicone oil itself. A cross-linkable methyl hydrogen polysiloxane (MHPS) was used as the silicone resin and a dimethyl polysiloxane (DMPS) as the silicone oil.

A commercial PSA tape having no silicone was laminated to glass plates coated with MHPS and DMPS. The peel strength of these laminates was measured. The PSA surface after the peel test was observed by IR-ATR and ESCA and the glass surface after the peel test by SEM.

From the results, the following conclusions were reached: (1) The peel strength of the laminates decreased in the order: un-coated glass>MHPS resin-coated> DMPS oil-coated. (2) Observation of the PSA surface after the peel test, by ATR and ESCA, showed that no silicone was present for the un-coated and the MHPS-coated glasses but a certain amount of silicone was found for the DMPS-coated glass. (3) When the surface of the glass plate after the peel test was observed by SEM, a relatively large number of fragments of the PSA was found on the surface of the un-coated glass, a small number of fragments on the MHPS-coated glass and only a few fragments on the DMPS-coated glass.

From these results, it was revealed that the cross-linked MHPS on the glass surface does not transfer to the PSA surface but a part of DMPS oil transfers and that, for decreasing peel strength, the cohesive separation of silicone oil (DMPS) itself is more effective than the non-adhesive property originating in the low energy surface of the silicone resin (cross-linked MHPS).

## Acknowledgements

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