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T. Kasemura^a; C. Komatu^a; H. Nishihara^a; S. Takahashi^a; Y. Oshibe^b; H. Ohmura^b; T. Yamamoto^b

^a Department of Applied Chemistry, Faculty of Engineering, Gifu University, Gifu-shi, Japan ^b Fine Chemicals and Polymers Research Laboratory, NOF Corporation, Chita-gun, Aichi, Japan

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Surface Modification of Epoxy Resin with Silicone-containing Block Copolymers*

T. KASEMURA, C. KOMATU, H. NISHIHARA, S. TAKAHASHI

*Department of Applied Chemistry, Faculty of Engineering, Gifu University,
1-1 Yanagido Gifu-shi 501-11, Japan*

Y. OSHIBE, H. OHMURA and T. YAMAMOTO

*Fine Chemicals and Polymers Research Laboratory, NOF Corporation,
Taketoyo-cho, Chita-gun, Aichi, 470-23 Japan*

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In order to improve oil and water repellency, silicone-containing block copolymers, composed of methylmethacrylate (MMA), glycidylmethacrylate (GMA), and polydimethylsiloxanemethacrylate (SMA), were blended in an epoxy resin. It was expected that the low surface energy dimethylsiloxane segments would adsorb and orient at the exterior of the resin to make a thin surface phase and the glycidyl groups would mesh with the epoxy resin by primary bonding. The techniques of X-ray photoelectron spectroscopy (ESCA), dynamic contact angle (DCA) and peel strength measurements of pressure sensitive adhesives were used to characterize the modified epoxy resin surface phases. The amount of Si_{2p} obtained *via* angular dependent ESCA investigation in the near surface region of the modified resin increased with decreasing sampling depth. With an increase in modifier content, both the amount of Si_{2p} and O_{1s} also increased. Both advancing and receding contact angles for an aluminum plate coated with modified resin, measured by dipping into and out of water, increased with the addition of these modifiers. The peel strength of a pressure sensitive adhesive tape affixed to the modified epoxy resin decreased dramatically with increasing modifier content. It was found that these copolymers were good surface modifiers to improve oil and water repellency and that they acted as release agents.

KEY WORDS surface modification; epoxy resin; silicone; dynamic contact angle; ESCA; peel strength; oil and water repellency; pressure sensitive adhesive; PSA; release agent.

1. INTRODUCTION

Epoxy resins, because of their exceptional properties such as strength, heat resistance and adhesion, have been extensively used in paints, electronic parts, matrices of composite materials, adhesives and others. In particular, the applications of epoxy resins as anticorrosives are important and they are also used for rust-preventive coatings on ships and large structures. However, they are not always considered good materials for coating agents. Epoxy resins easily adsorb organic materials

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because they have a relatively high surface free energy. Therefore, the surfaces of coatings made of epoxy resins are easily contaminated. Moreover, they are easily affected by water, because they inevitably have a hydroxyl group in their molecular structure. If improvements could be made, epoxy resins could be more extensively applied.

Conversely, it is well known that silicones have a very low surface free energy and show high oil and water repellency. Therefore, it can be hypothesized that surface properties of epoxy resins may be improved remarkably by the introduction of silicones. We¹⁻⁷ have already reported that the lower surface energy segment of multicomponent systems, such as copolymers, adsorbed and oriented on polymer surfaces so as to minimize surface tension. If we can blend a silicone-containing copolymer into an epoxy resin, a dimethyl siloxane segment will be predominant over the surface of the resin and the resultant modified resin would have high oil and water repellency.

Oshibe *et al.*,^{8,9} our coworkers, have reported a new method for preparing block copolymers using a polymeric peroxide (PPO) as the initiator of polymerization. We have synthesized block copolymers which contain both polydimethylsiloxane methacrylate and glycidymethacrylate using this method, and have attempted to blend these block copolymers into an epoxy resin to improve its oil and water repellency. It is hypothesized that a glycidyl group will be connected to the epoxy resin by primary bonding and that the dimethyl siloxane segment will adsorb and orient at the surface to siliconize the resin surface when the copolymer is blended into the resin.

In this paper, we report the experimental results on surface improvement of an epoxy resin blended with these copolymers. We use X-ray photoelectron spectroscopy, dynamic contact angle measurements and the peel strengths of pressure sensitive adhesive tapes for the modified epoxy resin surfaces to characterize the epoxy coatings and we discuss the validity of utilizing these copolymers as epoxy resin surface modifiers.

2. EXPERIMENT

2.1 Materials

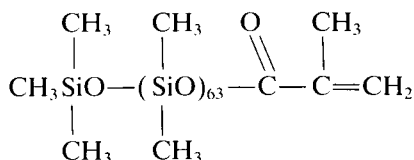
Epikote 828 (Shell) was used as the epoxy resin and bis(para-amino cyclohexyl) methane (PACM) as the curative.

For the surface modifiers, three types of block copolymers were synthesized, which contained two blocks. One block of the copolymers was composed of a random copolymer of methylmethacrylate (MMA) and glycidymethacrylate (GMA) and the other block was a copolymer of polydimethylsiloxane methacrylate (SMA) and MMA. We have already confirmed that a block copolymer which has a MMA/GMA block of molecular weight about 10000 and a MMA/SMA block of M_w of 10000~15000 is obtained under the same conditions as used in this study. The monomer contents of the modifier copolymers under consideration in this study

TABLE I
Composition of silicone-containing block copolymers

Copolymer		MMA	GMA	SMA
MGS-0	Feed	75	0	25
	NMR	86.5	0	13.5
MGS-10	Feed	65	10	25
	NMR	73.5	12.5	14
MGS-30	Feed	45	30	25
	NMR	51.5	33.5	15

are shown in Table I. All of these block copolymers had approximately the same SMA content, but the MMA and GMA content was different. Therefore, the GMA content was used for our classification, using such nomenclature as MGS-0, MGS-10 and MGS-30. The number following the MGS designation represents the GMA content.



Scheme 1 Polydimethylsiloxane methacrylate (SMA)

Methylethylketone (MEK) was used as the casting solvent. Water and dimethylphthalate (DMP) were used as the standard liquids for measuring dynamic contact angles.

An acrylic pressure sensitive adhesive tape (25 mm wide polyester tape #31B) used for the peeling test was supplied by Nitto Denko Corporation.

2.2 Preparation of Modified Epoxy Resin

A certain amount of epoxy resin, curative and modifier were dissolved together in MEK, the solution was poured into a square aluminum vessel and the solvent was evaporated for 1 hour at 80°C. Then, the mixture was cured for 1 hour at 100°C. For the DCA specimen, an aluminum plate (25 mm wide, 50 mm long and 0.3 mm thick) was dipped into the solution. The coating on the plate was then cured under the same conditions as mentioned above.

2.3 Dynamic Contact Angle Measurement

For dynamic contact angle measurement, we employed an instrument made by Orientec Corporation (DCA20), applying the Wilhelmy plate technique used for measuring the surface tension of a liquid.

2.4 Peel Testing

The cured epoxy resin was cut into a 30 × 150 mm sheet and the pressure sensitive adhesive tape, conforming to JIS C2107 procedure, was affixed using a 2 kg roller, then stored in a desiccator for 24 hours at 20°C. Subsequently, the 180° peel test was conducted with a crosshead speed of 300 mm/min at 20°C.

2.5 ESCA Spectrum Measurement

ESCA spectra for modified epoxy resins were measured by a Shimadzu Manufacturing Ltd. ESCA 850 X-ray photoelectron spectrometer, using a MgK α 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. Depth profiles were determined using a variable photoelectron take-off angle method. For the angular dependent experiment, five types of sample holders, whose take-off angles (ϕ) were 90°, 60°, 45°, 30°, and 15°, were used. The sampling depth for each take-off angle $d(\phi)$ is described as follows:

$$d(\phi) = d \cdot \sin \phi \quad (1)$$

where d is the sampling depth for take-off angle $\phi = 90^\circ$

3. RESULTS AND DISCUSSIONS

3.1 ESCA Analysis of Modified Epoxy Resin

Figure 1 shows the elemental ratios of Si to C of the epoxy resins modified with MGS-30, at different modifier contents, plotted as a function of the sine of the take-off angle ($\sin \phi$). The elemental ratios of Si to C increase with a decrease in the sampling depth and approach 0.5, which is the value for polydimethyl siloxane. These facts suggest that the silicones are not distributed homogeneously throughout the sampling region analyzed by ESCA with a take-off angle of 90° (about 100 Å) but, rather, were localized within the outermost extremely thin layer (less than ~30 Å) of the resin. The end-to-end distance of polydimethyl siloxane in SMA whose degree of polymerization is 64, as measured by NMR, is 26.9 Å. This is calculated based on a bond angle of Si—O—Si = 110°, and O—Si—O = 160°, and an interatomic distance = 1.76 Å. This value is comparable with the thickness of the surface layer for a modified resin obtained *via* ESCA.

Figure 2 shows the relationships between the elemental ratios of O and Si to C and the modifier content for the modified epoxy resin. Here, we used elemental ratios obtained with a sample holder having a 15° take-off angle. Therefore, the sampling depth may have been less than 30 Å. Elemental ratios of O and Si to C increase rapidly with an increase in modifier content. This was due to the adsorption and orientation of the low surface energy silicone segment of the modifier at the resin surface.

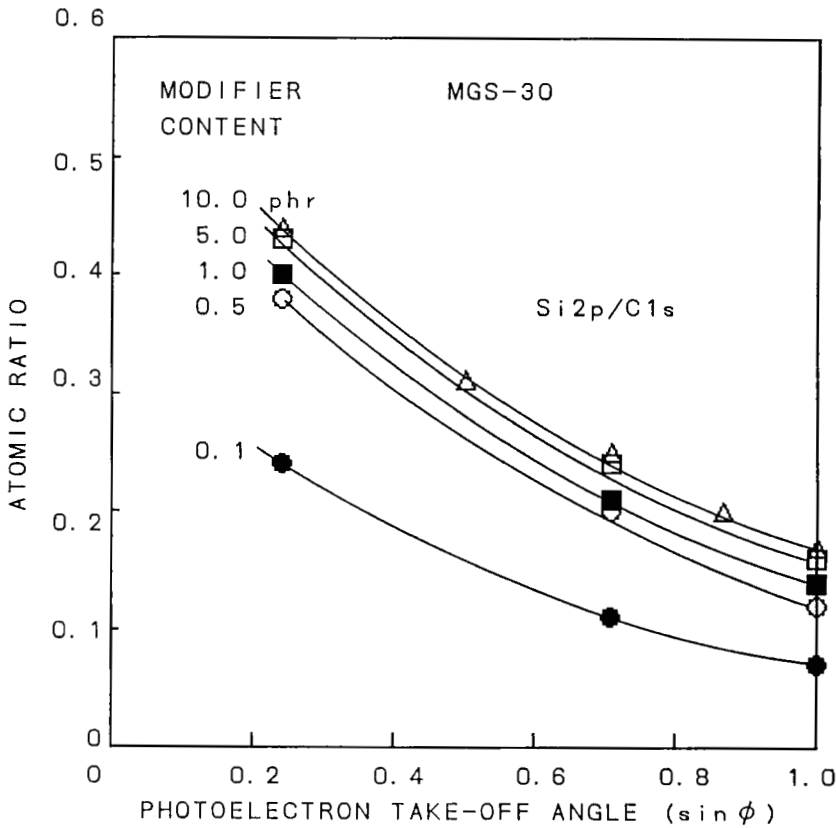


FIGURE 1 Atomic ratio of Si_{2p} to C_{1s} for modified epoxy resin as a function of photoelectron take-off angle ($\sin \phi$). Modifier content: ●, 0.1 phr; ○, 0.5; ■, 1.0; □, 5.0; △, 10.0.

3.2 Dynamic Contact Angles of Modified Epoxy Resin

Epoxy resin exhibits a relatively high advancing contact angle but a low receding contact angle; therefore, it shows a large contact angle hysteresis. An undesirable property of epoxy resin, that it is easily affected by water, has been shown by the fact that it has a low receding contact angle and a large hysteresis to water. Therefore, a dynamic contact angle measurement is a useful method to evaluate the effect of a surface modification. Here we describe briefly the principle of the Wilhelmy method.¹⁰

In Figure 3, the principle of the Wilhelmy method is shown. A sample plate (about 20 mm wide, 50 mm long and 1 mm thick), hanging on a load cell, is dipped into and out of a standard liquid to allow measurement of the contact angle. The force (F) applied to the load cell, when the bottom of the plate just comes into contact with the liquid surface, can be described as follows:

$$F = P\gamma_L \cos \theta, \quad (1) \quad 2$$

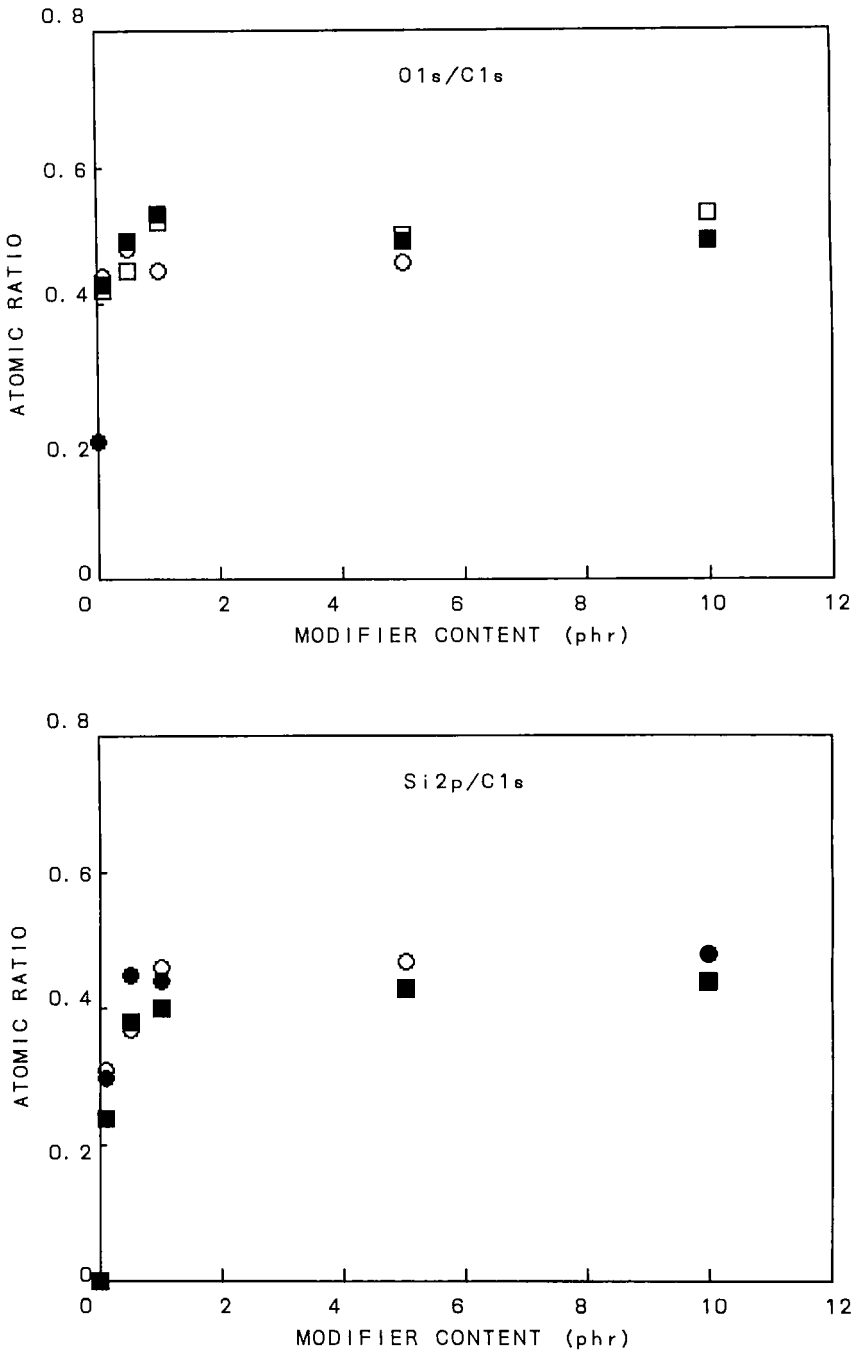


FIGURE 2 Atomic ratio of Si_{2p} and O_{1s} to C_{1s} for modified epoxy resin as a function of modifier content: ●, MGS-0; ○, MGS-10; ■, MGS-30.

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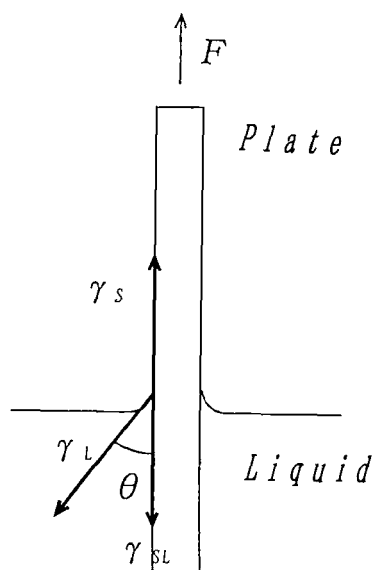


FIGURE 3 Illustration of the principle of dynamic contact angle measurement (Wilhelmy method).

where P is the perimeter of the sample plate, γ_L is the surface tension of the liquid and θ is the contact angle. Here, the mass of the plate is neglected. Young's equation is also described as follows:

$$\gamma_L \cos \theta = \gamma_s - \gamma_{SL} = \frac{F}{P}, \quad (2)$$

where γ_s is the surface free energy of the sample plate and γ_{SL} is the interfacial tension between the sample plate and the liquid. If γ_L is known, we can calculate the contact angle (θ) by measuring F and P . The contact angles in the dipping in and out processes are called the advancing contact angle and receding contact angle, respectively. The procedure is performed as follows: first, the sample plate is mounted so that the bottom of the plate is 5 mm over the liquid surface; then it is lowered 20 mm at a certain constant velocity and immediately returned to its original starting point, *i.e.*, 5 mm above the surface of the liquid.

Figure 4 shows the relationships between the dynamic contact angles, dipping into and out of water and DMP, and the modifier content for the modified epoxy resin. Both advancing and receding contact angles increase with an increase in modifier content for both standard liquids. This is due to the adsorption and orientation of the low surface free energy silicone segments at the surface of the resin. Based on this fact, it can be seen that the water and oil repellency of the epoxy resin can be improved by these modifications. In particular, the disadvantage of the epoxy resin, that is easily affected by water, was improved remarkably due to the modification, since the increase in receding angle to water was very large.

Figures 5 and 6 show relationships between the contact angle hysteresis (CAHy)

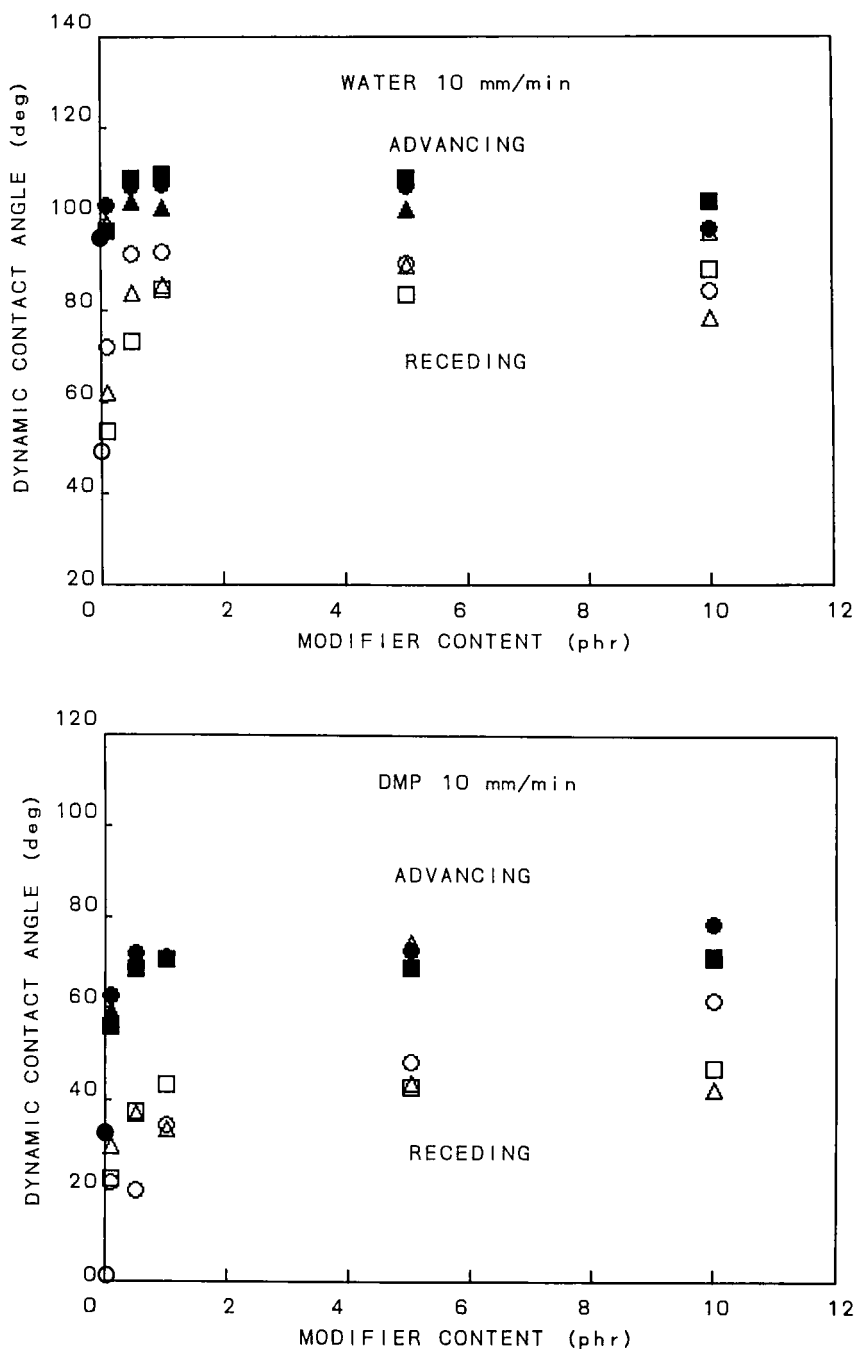


FIGURE 4 Dynamic contact angles for modified epoxy resin dipping into and out of water and DMP, as a function of modifier content: ○, ●, MGS-0; □, ■, MGS-10; △, ▲, MGS-30; solid, advancing contact angle; open, receding contact angle.

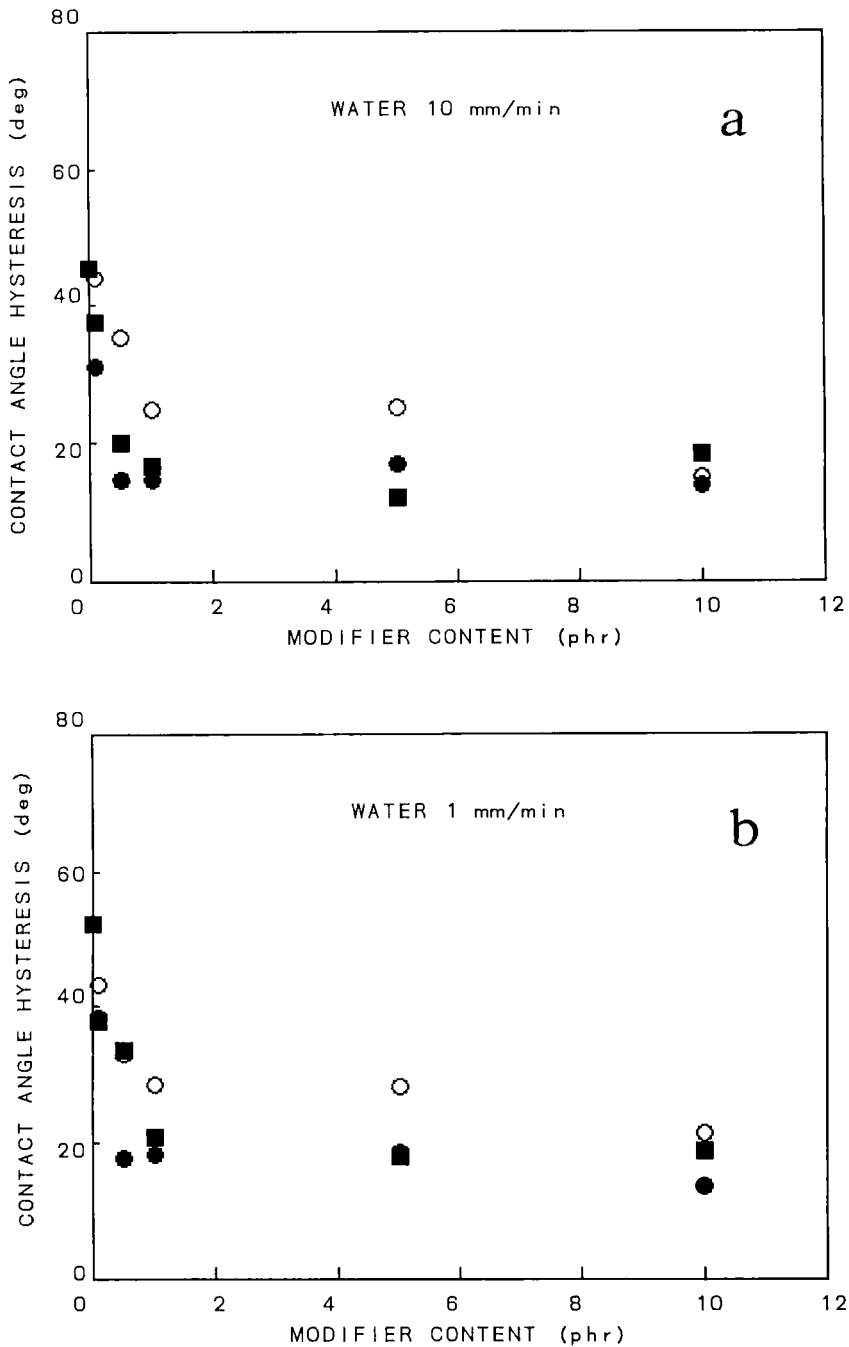


FIGURE 5 Contact angle hysteresis for modified epoxy resin dipping into and out of water as a function of modifier content: (a) dipping velocity 10 mm/min, (b) 1 mm/min; ●, MGS-0; ○, MGS-10; ■, MGS-30.

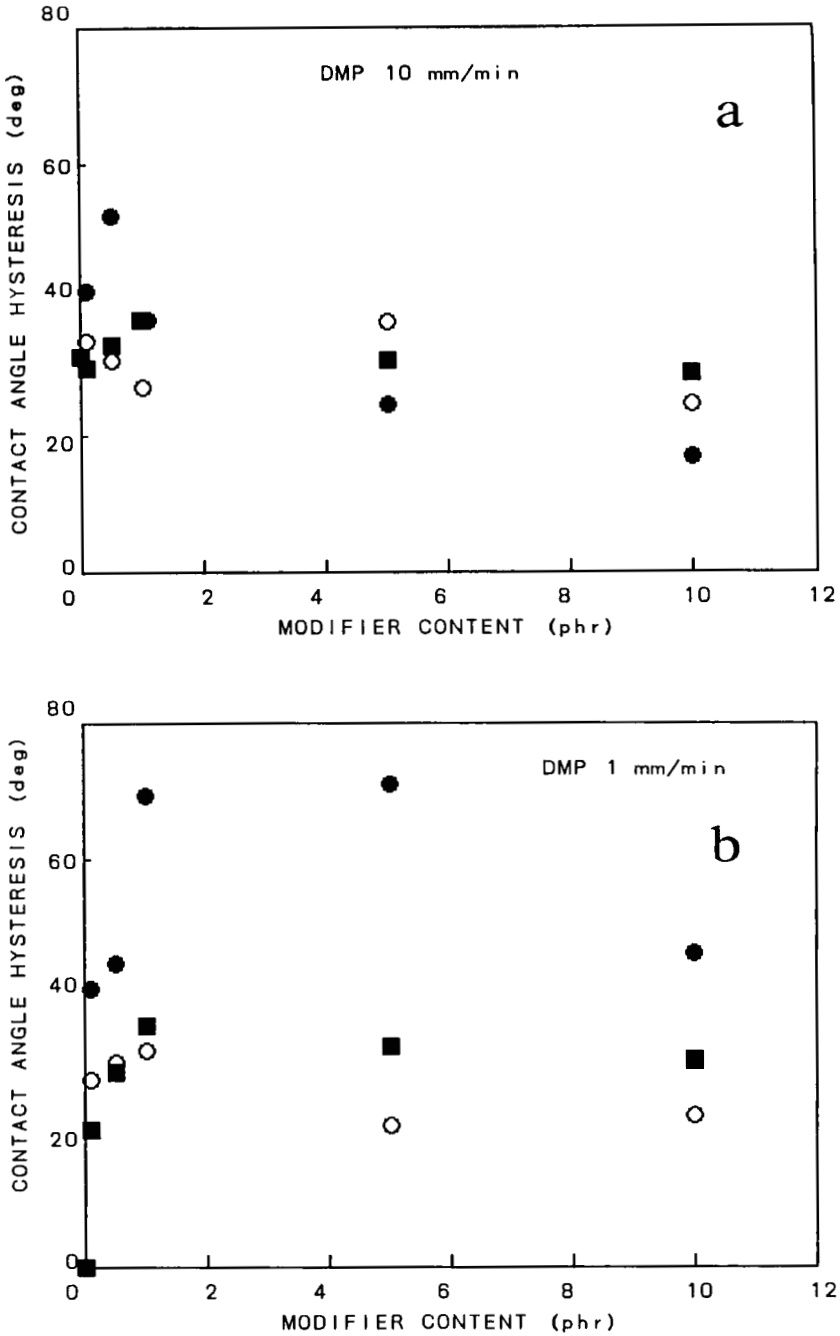


FIGURE 6 Contact angle hysteresis for modified epoxy resin, dipping into and out of DMP, as a function of modifier content: (a) dipping velocity 10 mm/min, (b) 1 mm/min; ●, MGS-0; ○, MGS-10; ■, MGS-30.

and modifier content for the modified resin to water and DMP, respectively. These angles also display differences due to the change in the dipping velocity. CAHy to water decreases with an increase in modifier content for both velocities. Also, from these results, it is clear that the resin surface attained water repellency. In contrast, CAHy with DMP shows a different behavior depending on the dipping velocity. For fast dipping, CAHy initially increases with an increase in modifier content, except for MGS-10, reaches a maximum value at 0.5 or 1.0 phr modifier, and then it decreases at higher modifier contents. The cause may be as follows. In the low content region, as the resin surface could not be covered entirely with the silicone segments, the receding angle still maintained a relatively low value, while the advancing angle increased. Johnson and Dettre^{11,12} have shown that if water is used for the standard liquid, a hydrophobic component contributes predominantly to the advancing contact angle, causing an increase, and a hydrophilic component contributes to the receding contact angle, causing a decrease. Because we used DMP (a polar organic liquid) as the standard liquid in this study, the adsorbed silicone segment, which is not soluble in DMP, may contribute mainly to the advancing contact angle in the low modifier content region, causing an increase in advancing contact angle. However, a hydrocarbon segment of the epoxy resin may principally contribute to the receding contact angle and may maintain it at a low level. Consequently, CAHy displays a high value. In the high modifier content region, the resin surface may be entirely covered with silicone segments to make a thin overlayer film; therefore, the receding angle also may have attained a large value, resulting in a decrease in CAHy. Therefore, although CAHy in a low modifier content region displays approximately the same value as in the high modifier content region, there is a significant difference between the low and high contact angle hysteresis regions.

For slower (1 mm/min) dipping into DMP (Figure 5 (b)), an interesting behavior was observed. CAHy with coatings containing MGS-0, which does not have a glycidyl group, increased rapidly with an increase in modifier content. However, coatings containing the other two modifiers (MGS-10 and MGS-30), which have a glycidyl group, displayed the same behavior as seen in the case of faster dipping. We⁷ have already reported on the surface modification of epoxy resin with block copolymers consisting of MMA, GMA and perfluoroalkyl methacrylate. In that study, it was shown that a considerable amount of fluorine in the resin surface modified with GMA-containing block copolymers remains after Soxhlet extraction with MEK, whereas in the surface modified with copolymer without GMA, almost all of the fluorine is extracted. Therefore, the increase in CAHy for MGS-0 could have been due to a dissolution of MGS-0 into DMP. That is to say, during the receding process, as MGS-0 without a glycidyl group could dissolve in DMP, the modifier was removed from the resin surface, exposing a subsurface under the silicone surface layer. Since the new exposed surface, which was composed of an MMA segment, developed a relatively high surface tension (γ_s in eq. 2), the receding contact angle had a low value, causing an increase in CAHy. On the other hand, in the MGS-10 and MGS-30 blended resins, the modifier could not easily dissolve in DMP because their glycidyl group was bonded to the epoxy resin network. Therefore, the CAHy exhibited the same behavior as in the other cases.

3.3 Peel Strength of Pressure Sensitive Adhesive Tape Affixed to Modified Epoxy Resin

Figure 7 shows the relationship between the peel strengths of pressure sensitive adhesive tapes affixed to modified epoxy resins and the modifier content. The peel strength decreases dramatically with an increase in modifier content. The peel strength for unmodified resin is 2.1 Kg/25 mm and, in the most effective case, the peel strength was reduced to 1/100 of the unmodified case.

As can be seen from the results of ESCA and dynamic contact angle measurements, it is clear that the modified resin surfaces were covered with an overlayer of silicone segments and have a very low surface tension. Because of this, the wettability of the resin surface by a pressure sensitive adhesive could be decreased considerably with the addition of modifiers, and this reduced wettability could result in a decrease in peel strength.

Thus, because these modifiers can decrease the peel strength of the acrylic PSA tape affixed to the epoxy resin, it is clear that silicone-containing methacrylic ester copolymers, used as modifiers of an epoxy resin as illustrated in this study, are able to act as release agents for pressure sensitive adhesives.

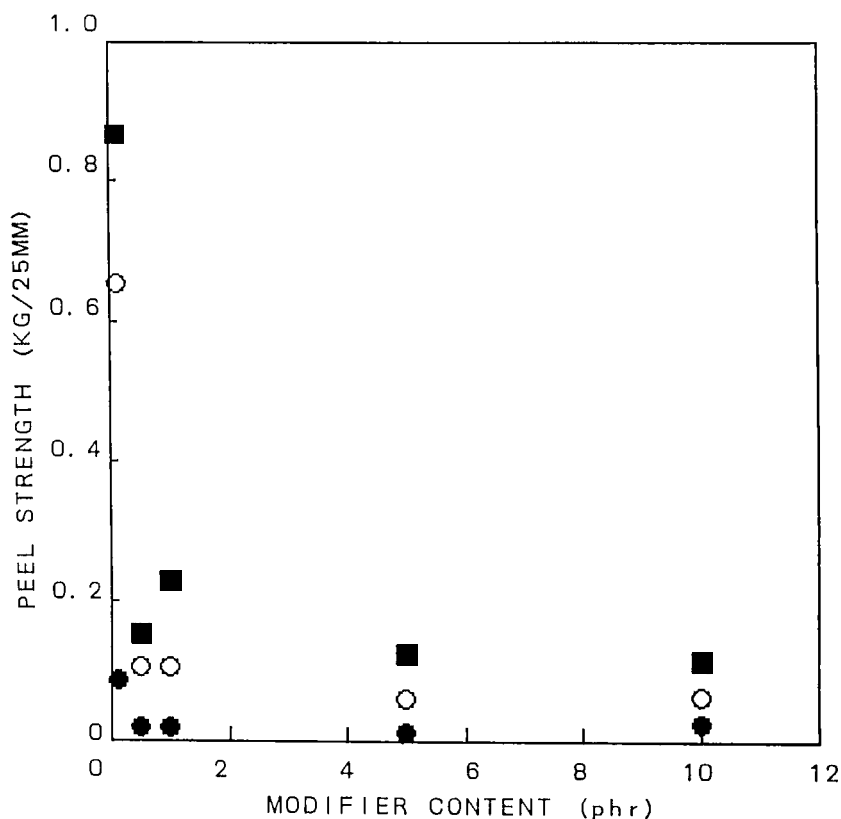


FIGURE 7 Peel strength of pressure sensitive adhesive tape affixed to modified epoxy resin as a function of modifier content: ●, MGS-0; ○, MGS-10; ■, MGS-30.

4. CONCLUSION

A modifier of silicone-containing methacrylic ester copolymers was blended with an epoxy resin to enhance oil and water repellency.

1. The amount of Si in the modified epoxy resin surface layer increased with decreasing sampling depth and with an increase in modifier content.
2. Both advancing and receding contact angles for the modified epoxy resin increased with an increase in modifier content. It was clear that the oil and water repellency could be enhanced by blending the modifiers with the epoxy resin.
3. The peel strengths for pressure sensitive adhesive tapes affixed to a modified epoxy resin decrease with an increase in the modifier content. From this fact, it was shown that these modifiers are effective as release agents for pressure sensitive adhesives.

It was shown that these copolymers are good surface modifiers to improve oil and water repellency and can be used as release agents for pressure sensitive adhesives.

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