Surface modification of epoxy resin with telechelic silicone

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In order to improve oil and water repellency, amino-terminated poly(dimethylsiloxane)s were blended in an epoxy resin. It was hypothesized that the low surface energy poly(dimethylsiloxane) segment will absorb and orient to the exterior of the resin to make a thin surface film. Results from an ESCA investigation showed that both the amount of Si_{2p} and O_{1s} in the modified resin surface increased with an increase in the modifier content, and reached 0.5. Both advancing and receding contact angles for an aluminium plate coated with modified resin dipping into and out of water and dimethylphthalate increased by the addition of these modifiers. The peel strength of a pressure-sensitive adhesive affixed to the modified epoxy resin decreased dramatically.

(Keywords: surface modification; telechelic silicone; dynamic contact angle)

INTRODUCTION

Epoxy resins have been extensively used in paints, electronic components, matrices of composite materials, adhesives, etc., because of their exceptional properties such as strength, heat resistance and adhesion. In particular, the applications of epoxy resins to anticorrosives are important, and they are also used for rust-proof coatings on ships and other large structures. However, they are not always considered good materials for coating agents. Epoxy resins easily absorb organic materials because they have a relatively high surface free energy. Therefore, the surfaces of coating films 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 the properties of epoxy resins could be improved, they could be more extensively applied.

Conversely, it is well known that poly(dimethylsiloxane) (PDMS) has an extremely low surface free energy and exhibits high oil and water repellency. Therefore, it is thought that the surface properties of epoxy resins may be improved remarkably by the introduction of such a low energy segment. We[1–7] have already reported on lower surface energy segments of multicomponent systems, such as copolymers, absorbed and oriented to polymer surfaces so as to minimize surface tension. If we can blend a PDMS in an epoxy resin, the low energy segments will predominate over the surface of the resin, and the resultant modified resin would have a high oil and water repellency.

An aminopropyl-terminated poly(dimethylsiloxane) (ATPS) could be a good modifier. It is thought that an amino group will mesh the epoxy resin by primary bonding, and the dimethylsiloxane segment will absorb and orient to the exterior of the resin to lower the surface tension when these polymers are blended into the resin. In this paper, we report the experimental results on surface modification of an epoxy resin blended with ATPS. We use X-ray photoelectron spectroscopy, and measure the static and dynamic contact angles, and peel strength of pressure-sensitive adhesives for the modified epoxy resin surfaces and discuss the validity of utilizing these as an epoxy resin surface modifier.

EXPERIMENTAL

Materials

Epikote 828 was used as the epoxy resin and bis(*p*-amino cyclohexyl)methane as the curative. For modifiers, five kinds of ATPSs, with degrees of polymerization as given by the manufacturer of 10, 20, 40, 50 and 100, were used. These modifiers were denoted by ATPS-10, ATPS-20, etc. with the number indicating the degree of polymerization (n) of the PDMS. The value of n was obtained by n.m.r. from the ratio of the signal area of the proton of Si–CH_3 to the terminal CH_2 (see *Table 1*). The ATPSs were supplied by ShinEtsu Corporation.

In order to investigate the effect of a casting solvent on the modified surface properties, three kinds of solvent having approximately the same solubility parameter (s.p.) but different surface tension (s.t.), i.e. methyl ethyl ketone (MEK) (s.p. = 9.3 $cal^{1/2}\ cm^{2/3}$, s.t. = 24.6 dyn cm^{-1}), benzene (s.p. = 9.2, s.t. = 28.8) and chlorobenzene (s.p. = 9.5, s.t. = 33.2), were used as the casting solvents.

Water and dialkylphthalate (DAP) homologues were used as the standard liquids for determining contact angles. The surface properties of these liquids are listed in *Table 2*. In a previous paper[8], we reported that DAP homologues were useful as standard liquids for determining contact angles.

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Table 1 Characterization of ATPS

ATPS	Degree of polymerization Manufacturer	Degree of polymerization N.m.r.
ATPS-10	10	8 ± 1
ATPS-20	20	22 ± 2
ATPS-40	40	34 ± 3
ATPS-50	50	53 ± 3
ATPS-100	100	89 ± 5

Table 2 Surface properties of standard liquids (dialkylphthalates for contact angle measurement at 20°C

Standard liquids	γ (dyn cm^{-1})	γ^d (dyn cm^{-1})	γ^p (dyn cm^{-1})
Dimethylphthalate (DMP)	39.5	30.4	9.1
Diethylphthalate (DEP)	36.6	31.3	5.3
Di-n-propylphthalate (DPP)	34.4	31.0	3.4
Di-n-butylphthalate (DBP)	33.1	30.9	2.2
Di-n-amylphthalate (DAmP)	32.0	30.3	1.7
Di-n-heptylphthalate (DHP)	30.0	28.9	1.1

γ^d and γ^p, dispersion and polar components of surface tension, respectively

Preparation of modified epoxy resin

A known amount of epoxy resin, curative and modifier were dissolved together in a solvent, and the solution was poured into a square aluminium vessel and evaporated for 1 h at 80°C. Then, the mixture was cured for 1 h at 100°C. For the dynamic contact angle measurement specimen, an aluminium plate (25 mm wide, 50 mm long, and 0.3 mm thick), which was washed by an ultrasonic washer in trichloroethylene, was dipped into the solution. The plate was then cured under the same conditions as stated above.

ESCA spectra

ESCA spectra for modified epoxy resins were measured by an ESCA 850 X-ray photoelectron spectrometer (Shimadzu Manufacturing Ltd) using a Mg Kα X-ray source. The X-ray gun was operated at 8 kV and 30 mA, and the analyser 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 holder, with take-off angles (ϕ) of 90, 60, 45, 30 and 15°, were used. The sampling depth for each take-off angle, $d(\phi)$, was described by:

$$d(\phi) = d \sin \phi \qquad (1)$$

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

Contact angle measurement

Static contact angle. The static contact angle (θ) was measured at 20 ± 1°C using a goniometer (Elmer Optics Ltd). θ was measured on both the left and right sides, five times for each drop of standard liquid. Five drops were measured, and the average value was calculated.

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

Peel testing

The cured epoxy resin was cut into a 30×150 mm sheet, and the pressure-sensitive adhesive, conforming to JIS C2107, was affixed using a 2 kg roller. The 180° peel test was conducted using a crosshead speed of 300 mm min^{-1} at 20°C.

RESULTS AND DISCUSSION

ESCA analysis of modified epoxy resin

Figure 1 shows the relationship between the atomic ratios of Si_{2p}, O_{1s} and N_{1s} to C_{1s} for the epoxy resin modified with ATPS-100 with 10 phr modifier content and the sine of the take-off angle ($\sin \phi$). The atomic ratios of Si_{2p} and O_{1s} to C_{1s} increased with a decrease in the sampling depth. At $\phi = 15°$ ($\sin \phi = 0.26$), both Si_{2p}/C_{1s} and O_{1s}/C_{1s} were nearly equal (0.5). The value of 0.5 corresponded to a calculated value from the molecular structure of PDMS. In the deeper sampling region, more oxygen was detected than silicon, since oxygen was introduced to the resin by an ether group of the epoxy resin and by dimethylsiloxane, while silicon was introduced via the modifier only. These facts suggested that PDMS was not distributed homogeneously throughout the sampling region analysed by ESCA with a take-off angle of 90° (~ 100 Å), but were localized in the outermost extremely thin layer (< 30 Å) of the resin. From these results, it was shown that a low surface free energy dimethylsiloxane segment absorbed and oriented to the resin surface to make a thin surface film. Nitrogen was not detected in the region of $\sin \phi < 0.7$ but a trace was in a deeper region ($N_{1s}/C_{1s} = 0.01 \sim 0.02$). Although not shown in the figure, N_{1s}/C_{1s} at $\phi = 90°$ for an epoxy resin with 10 phr of ATPSs decreased with an increase in n from 0.04 ($n = 10$) to 0.02 ($n = 100$). Nitrogen was introduced via the terminal amino groups and curative. As the amino groups of both terminals of ATPS could mesh to the resin by primary bonding, the molecular chain absorbed to the resin surface could form a loop. Therefore, nitrogen detected via ESCA was oriented to the subsurface under the absorbed PDMS film. The

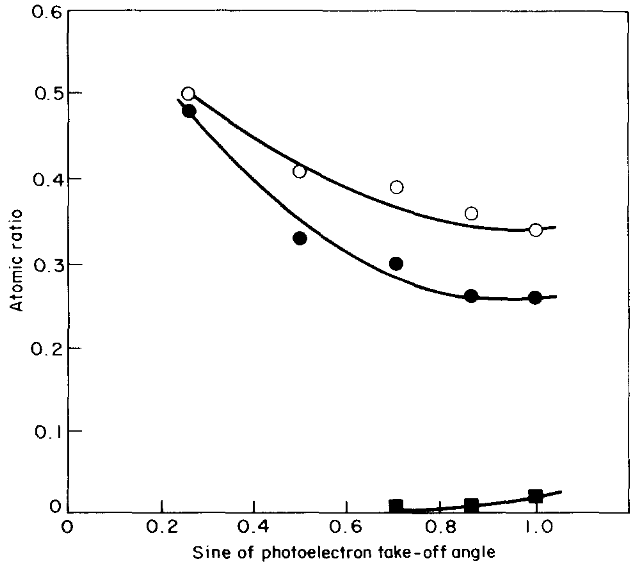

Figure 1 Atomic ratio of (○) O_{1s}, (●) Si_{2p} and (■) N_{1s} to Cl_s plotted against the sine of the photoelectron take-off angle for epoxy resin modified with ATPS-100 (10 phr modifier content)

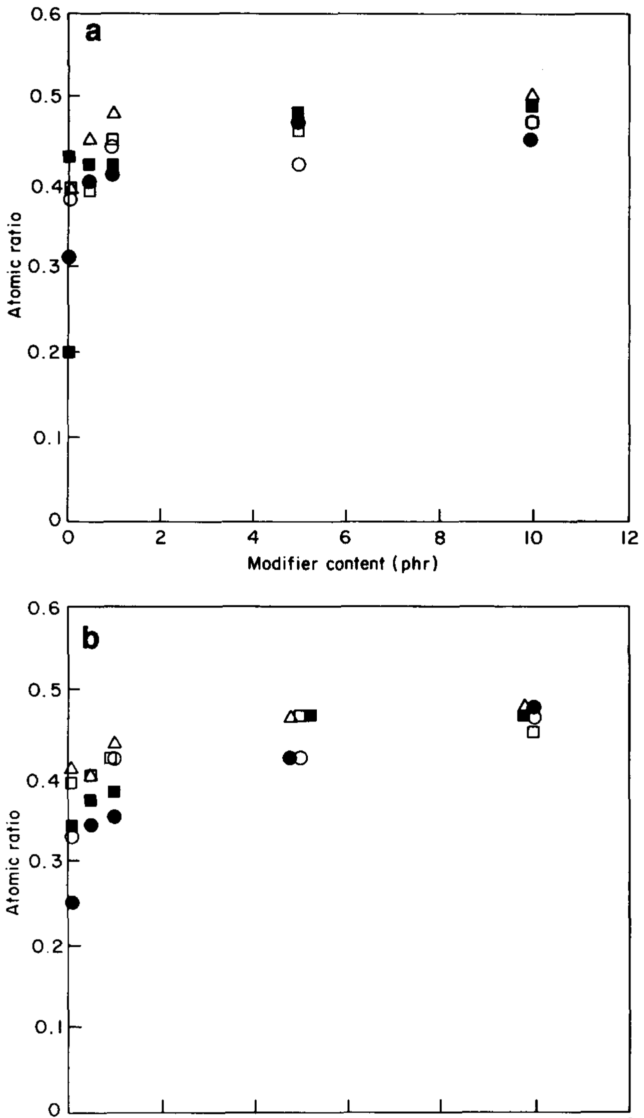

Figure 2 Atomic ratio of (a) O_{1s} and (b) Si_{2p} to C_{1s} for modified epoxy resins as a function of the modifier content: (●) ATPS-10; (○) −20; (■) −40; (□) −50; (△) −100

thickness of the surface film of the resins inevitably was dependent on the *n* value of ATPS.

Figure 2 shows the relationship between the atomic ratios of Si_{2p} and O_{1s} to C_{1s} and the modifier content of the modified epoxy resin. Here, we use atomic ratios which were obtained with a sample holder having a 15° take-off angle. Therefore, the sampling depth may be <30 Å. Atomic ratios of Si_{2p} and O_{1s} to C_{1s} increase rapidly with an increase in modifier content and approach 0.5. This is due to the absorption and orientation of the low surface energy PDMS segment of the modifier to the resin surface as described above. As can be seen in the figure, increasing the *n* value of ATPS tends to increase the atomic ratios of Si_{2p}/C_{1s} and O_{1s}/C_{1s}. This is due to the longer chain length of ATPS which can create a larger absorbed loop on the resin surface and a thicker surface for the PDMS film.

Wetting properties of modified epoxy resin

Static contact angle. Figure 3 shows the relationship between the cosine of the contact angle of DAP and its surface tension (Zisman plot) for the epoxy resin modified with ATPS-10. The effect of the solvent which was used for casting on the wetting property is also shown. The linear relationships were observed independent of the modifier content. Although there was some scattering of data and influence of the solvent in the low modifier content region, in the resin with 10 phr ATPS, the scattering and solvent influence were eliminated and all the data fell on a single straight line. For the low modifier content resin, the surface could not be covered entirely with a PDMS segment and a hydrocarbon segment could coexist in the resin surface. This heterogeneity of the resin surface could be changed subtly by altering the casting conditions, such as concentration, curing temperature, etc., and could result in scattering the data. For a resin with a modifier content of <1 phr, systematic data could not be obtained, since the contact angle changed during the measurement, possibly because of reorientation of a segment at the liquid/solid interface so as to minimize interfacial tension. Thus, because the effect of the casting

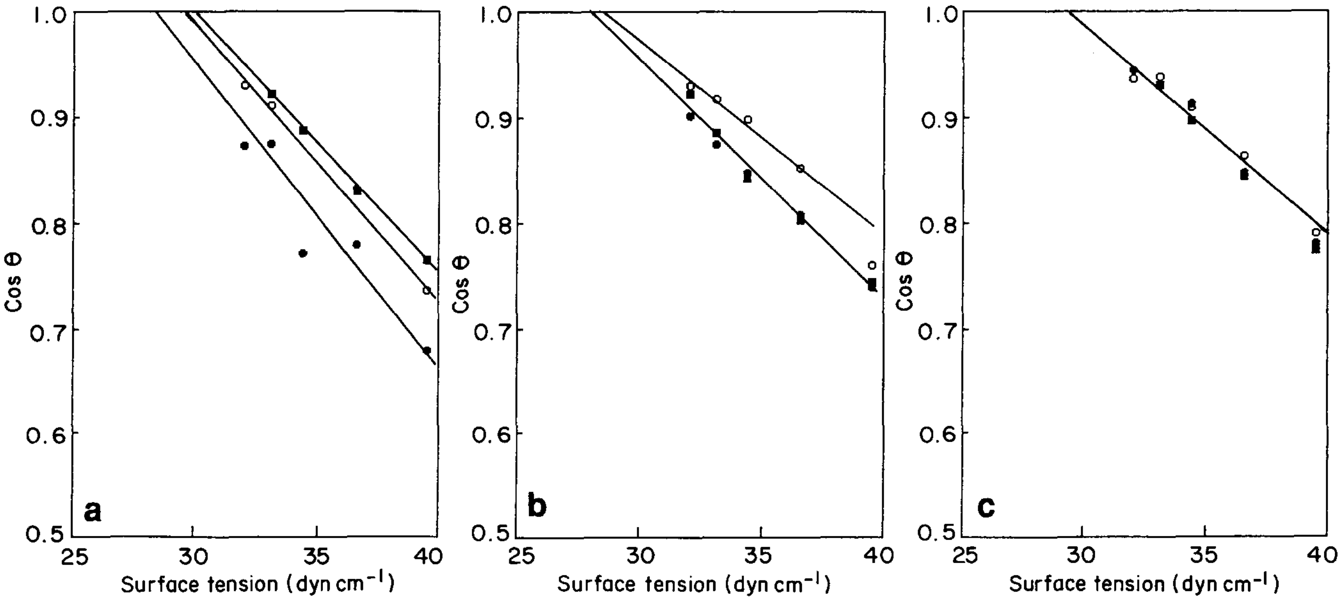

Figure 3 Cosine of the contact angle (cos θ) as a function of the surface tension of standard liquids (DAP) for epoxy resin modified with ATPS-10 using three types of solvent: (●) MEK; (○) benzene; (■) chlorobenzene. Modifier content: (a) 1 phr; (b) 5 phr; (c) 10 phr

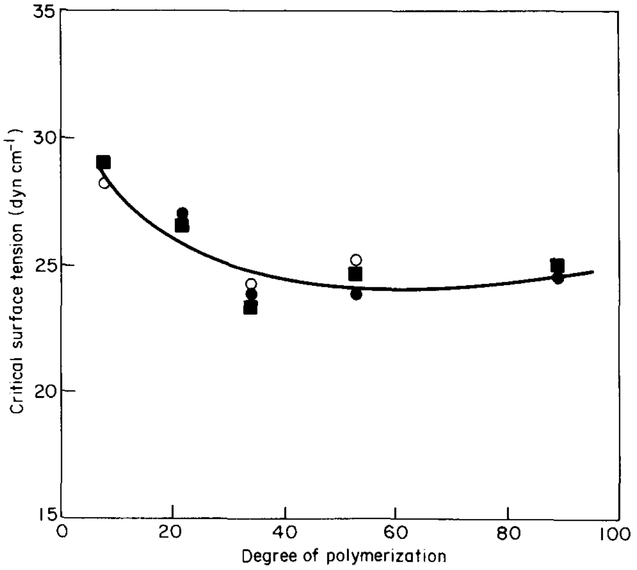

Figure 4 Critical surface tension as a function of the degree of polymerization of ATPS for modified epoxy resins. Modifier content: (●) 1 phr; (○) 5 phr; (■) 10 phr

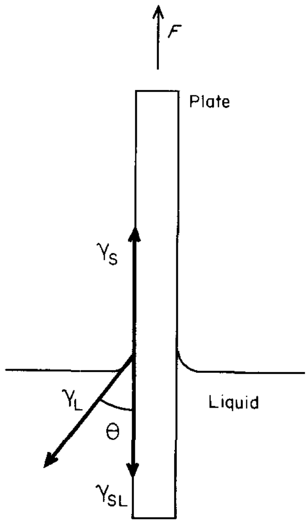

Figure 5 Principle of the Wilhelmy method for dynamic contact angle measurement

solvent was not observed, subsequent experiments were carried out using MEK only.

Figure 4 shows the relationship between the critical surface tension (γ_c) which was obtained by the extrapolation of the line to $\cos\theta \rightarrow 1$ and the n value of the modifiers for the modified resin. γ_c decreased with the n value of ATPS.

Dynamic contact angle. A dynamic contact angle measurement is a useful method to judge the effect of a surface modification. Here we describe briefly the principle of the Wilhelmy method[9].

Figure 5 shows the principle of the Wilhelmy method. A sample plate (~20 mm wide, 50 mm long, 1 mm thick) hanging onto a load cell is dipped into and out of a standard liquid giving the contact angle to be measured. A 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:

$$F = P\gamma_L \cos\theta \qquad (1)$$

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 described as follows:

$$\gamma_L \cos\theta = \gamma_S - \gamma_{SL} = \frac{F}{P} \qquad (2)$$

where γ_S is the surface tension of the sample plate and γ_{SL} is the interfacial tension between the sample plate and the liquid. If γ_L is known, θ can be obtained by measuring F and P. The contact angles in the dipping into and out of processes are called the advancing and receding contact angles, respectively.

Figures 6 and *7* show the relationships between the dynamic contact angles when 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 increase in modifier content for both standard liquids. This is due to the absorption and orientation of the low surface free energy segments, PDMS, to the exterior of the resin. Based on this, it can be shown that the water and oil repellency of the epoxy resin can be improved by these modifications. In

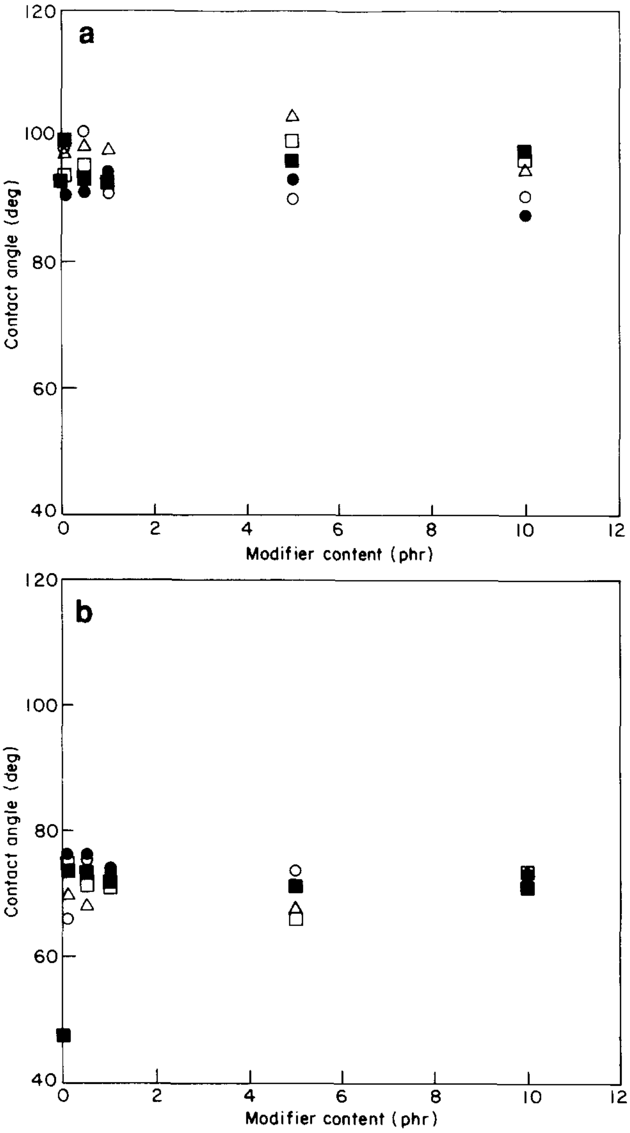

Figure 6 Dynamic contact angles dipping (a) into and (b) out of water as a function of modifier content for modified epoxy resin at 10 mm min^{-1} dipping velocity: (●) ATPS-10; (○) −20; (■) −40; (□) −50; (△) −100

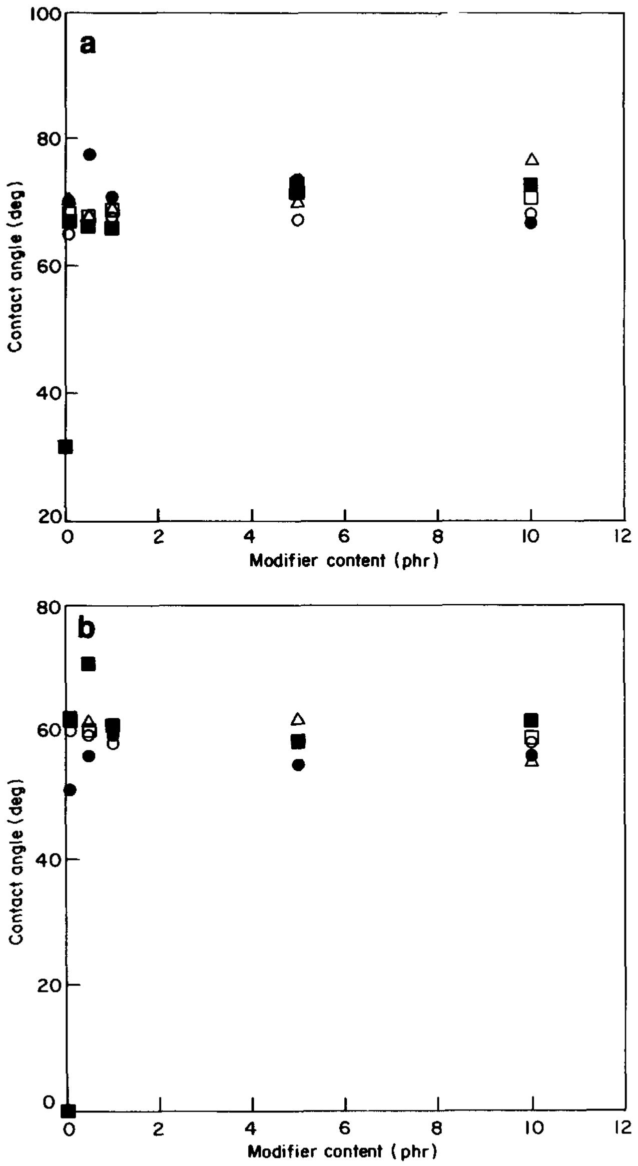

Figure 7 Dynamic contact angles dipping (a) into and (b) out of DMP as a function of modifier content for modified epoxy resin at 10 mm min^{-1} dipping velocity: (●) ATPS-10; (○) −20; (■) −40; (□) −50; (△) −100

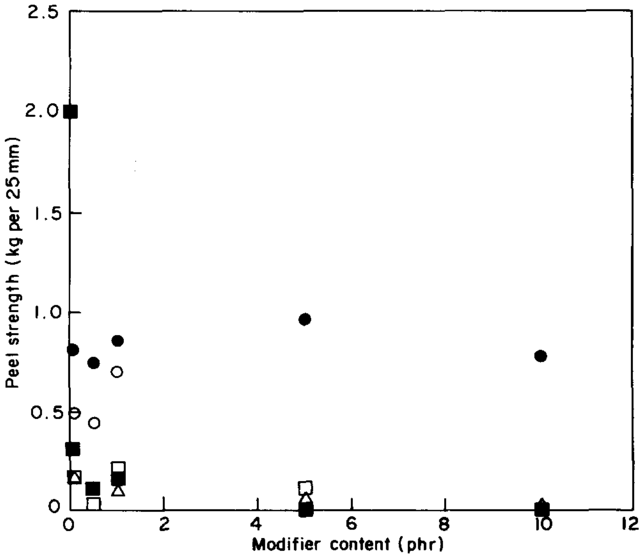

Figure 8 Peel strength of pressure-sensitive adhesive affixed to modified epoxy resin as a function of modifier content: (●) ATPS-10; (○) −20; (■) −40; (□) −50; (△) −100

particular, the disadvantage of poor repellency for water was improved remarkably by modification, since the increase in the receding angle was substantial.

Peel strength of pressure-sensitive adhesive affixed to modified epoxy resin

Figure 8 shows the relationship between the peel strengths of pressure-sensitive adhesives affixed to modified epoxy resins and the modifier content. The peel strength decreased drastically with an increase in modifier content except for ATPS-10. In some cases, peel strength could not be measured in a high modifier content region (> 1 phr), because the adhesive could be easily removed from the resin surface.

As could be seen from the results of ESCA and dynamic contact angle measurements, it was clear that the modified resin surfaces were covered with a thin film of PDMS segments and had a very low surface tension. Because of this, the wettability of the resin surface by a pressure-sensitive adhesive could be decreased considerably by the addition of modifiers, and this reduction in wettability resulted in a decrease in peel strength.

Thus, because these modifiers could decrease the peel strength of the pressure-sensitive adhesives affixed to the epoxy resin, it was clear that ATPS, used as a modifier of epoxy resin as illustrated in this study, could act as a good release agent for pressure-sensitive adhesives.

CONCLUSIONS

A modifier of ATPSs was blended in an epoxy resin to enhance oil and water repellency.

1. The amount of Si in the modified epoxy resin surface layer increased with a decrease in the sampling depth and with an increase in modifier content.
2. Both advancing and receding contact angles for 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.
3. The peel strength for pressure-sensitive adhesives affixed to a modified epoxy resin decreased with an increase in the modifier. From this, it was shown that these modifiers could be effective as release agents for PDMS pressure-sensitive adhesives.

It was shown that ATPSs were good surface modifiers to improve oil and water repellency and could be used as release agents for pressure-sensitive adhesives.

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