Surface Modification of Epoxy Resin with Fluorine-Containing Methacrylic Ester Copolymers

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SYNOPSIS

To improve oil and water repellency, fluorine-containing block copolymers, which were composed of methyl methacrylate (MMA), glycidyl methacrylate (GMA), and 1H, 1H, 2H, 2H-heptadecafluorodecyl acrylate (PFA), were blended with an epoxy resin. It was expected that a glycidyl group would mesh with the epoxy resin by primary bonding, and the low surface energy fluorocarbon segment would absorb and orient to the exterior to fluorinate the surface. X-ray photoelectron spectroscopy, contact angle, and peel strength of pressure-sensitive adhesives for modified epoxy resin surface were determined. The amount of fluorine obtained via angular-dependent ESCA investigation in the modified resin surfaces increased with the shallowing of the sampling depth. With increasing modifier content, the amount of fluorine in the modified resin surface layer increased, and the critical surface tension of modified resin surfaces and the peel strength of a silicone pressure-sensitive adhesive affixed to the modified epoxy resin, decreased. A considerable amount of fluorine in the resin surface modified with GMA-containing block copolymers remained after Soxhlet extraction, whereas in the surface modified with copolymer without GMA, more fluorine was extracted. It was shown that these copolymers were good surface modifiers to improve oil and water repellency. © 1993 John Wiley & Sons, Inc.

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 other items. In particular, the applications of epoxy resins to anticorrosives are important, and they are also used for rust-preventing coatings on ships and 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 im-

provements could be made, epoxy resins could be more extensively applied.

Conversely, it is well known that fluororesins have an extremely low surface free energy and show high oil and water repellency. Therefore, it is hypothesized that surface properties of epoxy resins may be improved remarkably by fluorination. We[1-6] have already reported that the lower surface energy segment of multicomponent systems such as copolymers absorb and orient to polymer surfaces so as to minimize surface tension. If we can blend a fluorine-containing copolymer in an epoxy resin, a fluorinated segment will be predominant over the surface of the resin, and the resultant modified resin would have a high oil and water repellency. Furthermore, Oshibe et al.,[7,8] our co-workers, reported a new method for preparing block copolymers that contain both a perfluoroalkyl group and a certain functional group using a polymeric peroxide (PPO) as the initiator of polymerization. We have synthesized block copolymers that have both perfluoroalkyl and glycidyl groups with this technique and have attempted

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to blend these block copolymers into epoxy resin to improve its oil and water repellency. It is hypothesized that a glycidyl group will mesh epoxy resin by primary bonding and the fluorocarbon segment will absorb and orient to the exterior to fluorinate the resin surface when the copolymer is blended into the resin. In this paper, we report the experimental results on surface fluorination of epoxy resin with blending of these copolymers. We used X-ray photoelectron spectroscopy, contact angles, and peel strength of pressure-sensitive adhesives for the modified epoxy resin surfaces and discuss the viability of utilizing these copolymer as an epoxy resin surface modifier.

2. EXPERIMENTAL

2.1. Materials

Epikote 828 was used as the epoxy resin and bis(para-amino cyclohexyl) methane (PACM) as the curative. The composition data for the modifier copolymers under consideration in this study are shown in Table I. For the surface modifier, three types of block copolymers were used, consisting themselves of two blocks. One block was composed of a random copolymer of methyl methacrylate (MMA) and glycidyl methacrylate (GMA), and the other was a polymer of 1H,1H,2H,2H-heptadecafluorodecyl acrylate (PFA). All these block copolymers had the same PFA content, but MMA and GMA content differed. Therefore, GMA content was used for classification, using such nomenclature as MDF0, MDF10, and MDF40. The number following the MDF designation represents GMA content.

Methyl ethyl ketone (MEK) was used as the casting solvent. N-alkane and dialkylphthalate (DAP) homologous series were used as the standard liquids for determining contact angles. Surface properties of these liquids are listed in Table II. In a previous paper,[9] we reported that DAP homologous series were useful as standard liquids for determining contact angle. The silicone-containing pressure-sensitive adhesive (24 mm wide) used for the peeling test was supplied by Nichiban Corp.

Table I Composition of Modifiers (wt %)

Modifier	MMA	GMA	PFA
MDF0	75	0	25
MDF10	65	10	25
MDF40	35	40	25

2.2. Preparation of Modified Epoxy Resin

A certain amount of epoxy resin, curative, and modifier were dissolved together in MEK and the solution was poured into a square aluminum vessel, and the solvent was evaporated for 1 h at 80°C. Then, the mixture was cured for 1 h at 100°C.

2.3. Contact-Angle Measurement

Contact angle (θ) was measured at 20 ± 1°C using an Elmer Optics Ltd. Goniometer contact-angle measuring device. θ was measured at both the left and right sides five times for each drop of liquid. Five drops were measured, and the average value was calculated.

2.4. Peel Testing

The cured epoxy resin was cut into a 30 × 150 mm sheet, and the pressure-sensitive adhesive, conforming to JIS procedure C2107, was affixed using a 2 kg roller, and the 180° peel test was conducted using 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 Shimazu Manufacturing Ltd. ESCA 850 X-ray photoelectron spectrometer using a MgKα X-ray source. The X-ray gun was operated at 8 kV and 30 mA, and the analyzer chamber pressure was 10^{-6}–10^{-7} Pa.

Depth profiles were determined using both the variable photoelectron takeoff angle method and the argon ion-etching method. For the angular-dependent experiment, five types of sample holders, whose takeoff angles (ϕ) were 90°, 60°, 45°, 30°, and 15°, were used. The sampling depth for each takeoff angle $d(\phi)$ is described as follows:

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

where d is the sampling depth for takeoff angle ϕ = 90°.

For the argon ion-etching experiment, an ion gun was operated at 2 kV and 10 mA, and an argon ion was regulated by controlling the argon gas flow rate by adjusting the pressure in the analyzer chamber to 4×10^{-4} Pa. Very few papers have reported any experimental results obtained with ESCA, using the ion-etching method for polymers since it was difficult to obtain an exact depth profile because of inhomogeneous etching over the sample surface and se-

Table II   Surface Properties of Standard Liquids for Contact-Angle Measurement at 20°C

Standard Liquids	γ (dyn/cm)	γ^d (dyn/cm)	γ^p (dyn/cm)
n-Decane	23.9	23.9	0
n-Dodecane	25.4	25.4	0
n-Tetradecane	26.7	26.7	0
n-Hexadecane	27.6	27.6	0
n-Heptadecane	28.0	28.0	0
Dimethyl phthalate (DMP)	39.5	30.4	9.1
Diethyl phthalate (DEP)	36.6	31.3	5.3
Di-n-propyl phthalate (DPP)	34.4	31.0	3.4
Di-n-butyl phthalate (DBP)	33.1	30.9	2.2
Di-n-amyl phthalate (DAmP)	32.0	30.3	1.7
Di-n-heptyl phthalate (DHP)	30.0	28.9	1.1

lective etching of a certain atom. In a multicomponent system, containing a small amount of modifier in addition to a base polymer, the modifier may be oriented to the surface to make a thin film over the system. For surface analysis of such a system, the ion-etching method could be used. We measured the thickness of the surface film with this technique by determining the depth at which a signal of a certain atom disappeared due to etching.

sine of the takeoff angle (sin ϕ). The elemental ratios of F_{1S} to C_{1S} increased with a decrease in the sampling depth. These facts suggested that fluorines were not distributed homogeneously throughout the sampling region that was analyzed by ESCA with a takeoff angle of 90° (about 100 Å), but, rather, were localized within the outermost extremely thin layer (less than 30 Å) of the resin.
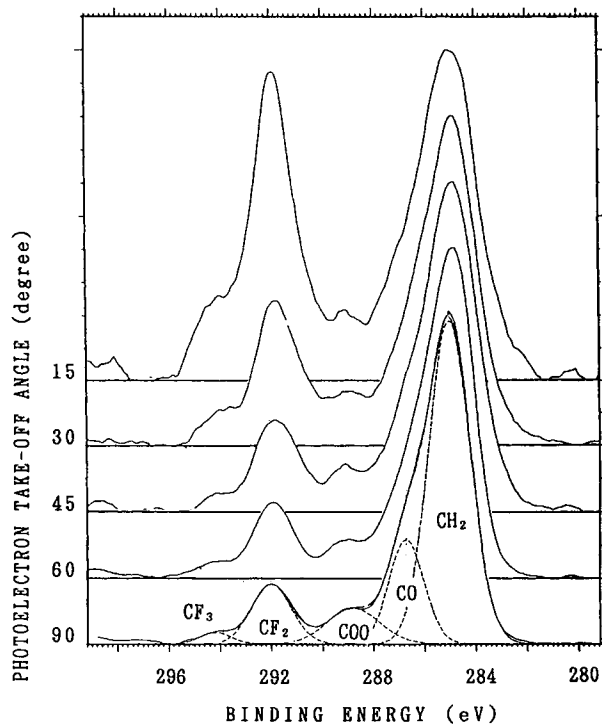
3. RESULTS AND DISCUSSION

3.1. ESCA Analysis of Modified Epoxy Resin

3.1.1. Surface Analysis with Variable Takeoff Angle Method

Figure 1 shows the change of ESCA spectrum of C_{1S} core-level depending on the takeoff angle for epoxy resins blended with MDF40 of 1 phr. As these spectra were very complex, they were curve-fitted, and the results were shown in a spectrum of $\phi = 90°$ as seen in the figure. The spectrum was divided into five component peaks at 294.1, 291.8, 289.3, 287.1, and 285.0 eV, respectively and these peaks were assigned to signals associated with CF_3, CF_2, COO, CO, and CH_2, respectively. The assigned binding energies were comparable to reported values[10] obtained in fluorine-containing plasma polymers. As observed in the figure, a decrease in takeoff angle (i.e., with shallowing of sampling depth) corresponded to an increase in the relative intensity of the component peak associated with CF_2 at 291.8 eV. In Figure 2, the elemental ratios of F_{1S} to C_{1S} for the epoxy resin, modified with MDF40 of a different modifier content, were plotted as a function of the

Figure 1   ESCA spectrum of C_{1S} core level for epoxy resin modified with MDF40 (modifier content, 1 phr).

Figure 3 shows the relationships between the elemental ratios of F_{1S}, O_{1S}, and N_{1S} to C_{1S} and takeoff angle (sin ϕ) for epoxy resin blended with MDF40 and MDF10 in 1 phr amounts. Although the tendency of the dependence of the elemental ratio on sin ϕ is the same as in the previous figure, a greater amount of F_{1S} in the MDF10-blended resin is detectable than in the MDF40 one, in spite of the same modifier content. Based on these facts, we surmise that MDF40, having more glycidyl groups than has MDF10, may be chemically bonded to the epoxy resin and may mesh the resin network in bulk during the curing process. Conversely, much of the MDF10 having relatively fewer glycidyl groups may be absorbed onto the surface via a PFA effect due to low surface free energy. The elemental ratio of O_{1S} to C_{1S} is independent of the take off angle. Oxygen is introduced through an ester group in the modifier and an ether group in the epoxy resin. Nitrogen is detected by the elemental ratio of 0.02–0.03 at a high takeoff angle ($> 30°$) but is not detectable in a low takeoff angle. Nitrogen is introduced through a curative amino group. Therefore, it is clear that the surface of the modified resin is covered by a thin layer (< 30 Å) of modifier.

Figure 4 shows the relationships between the elemental ratios of F_{1S} and O_{1S} to C_{1S} and the modifier content for the modified epoxy resin. Here, we use elemental ratios that were obtained with a sample holder having a $15°$ takeoff angle. Therefore, sam-
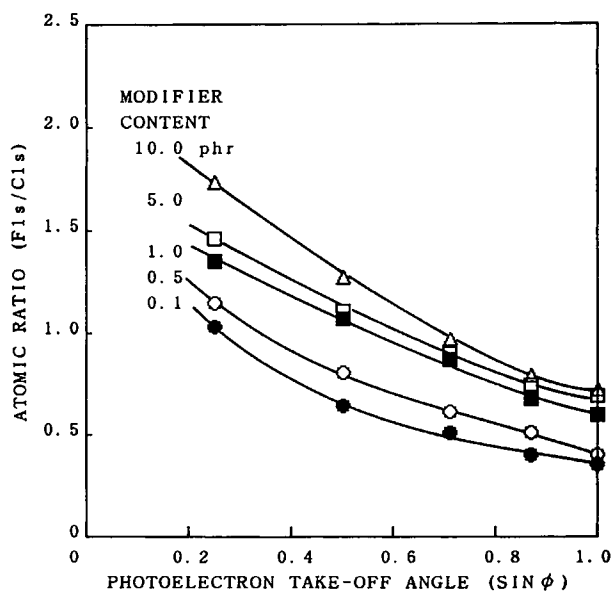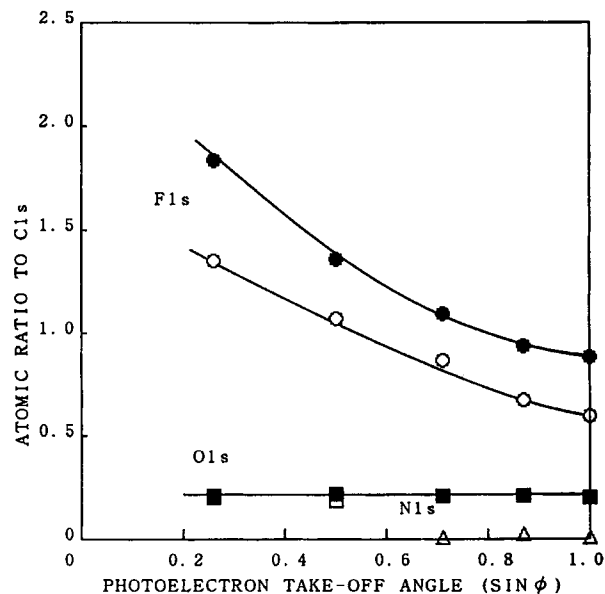
Figure 3 Atomic ratios of F_{1S}, O_{1S}, and N_{1S} to C_{1S} for epoxy resin modified with MDF40 and MDF10 (modifier content 1 phr) plotted against photoelectron takeoff angle: (O, ●), F_{1S}; ($\square$, ■) O_{1S}; ($\triangle$, ▲) N_{1S}; (solid) MDF10; (hollow) MDF40.

pling depth may be less than 30 Å. Elemental ratios of F_{1S} increase rapidly with an increase in modifier content. This is due to the adsorption and orientation of the low surface energy PFA segment of the
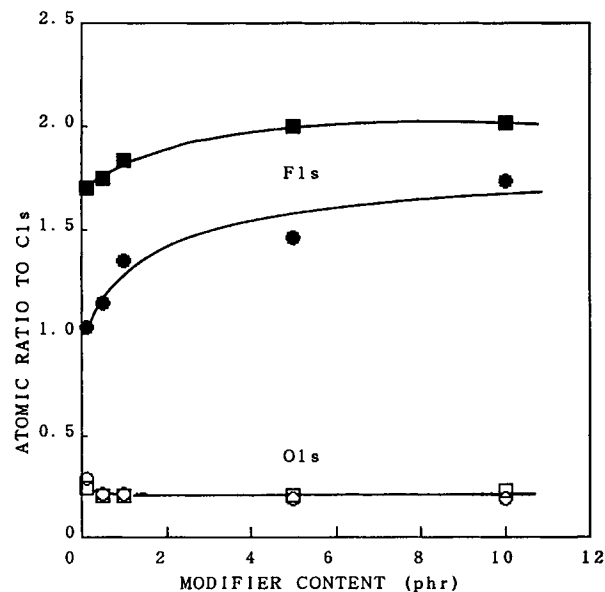
Figure 2 Atomic ratios of F_{1S} to C_{1S} for epoxy resin modified with MDF40 plotted against photoelectron takeoff angle (sin ϕ).

Figure 4 Atomic ratios of F_{1S} and O_{1S} for epoxy resin modified with MDF40 (circle) and MDF10 (square) plotted against modifier content at $15°$ takeoff angle: (solid) F_{1S}; (hollow) O_{1S}.

modifier to the resin surface. Elemental ratios of O_{1S} are independent of modifier content. Oxygen is introduced both by an ether group of the epoxy resin and by an ester group of the modifier. Elemental ratios of N_{1S}, introduced via the curative, but not plotted in the figure, are detectable in all samples in the amount of 0.01–0.04. The elemental ratio of F_{1S} for epoxy resin modified with MDF40 is less than that of MDF10, even though they have the same amount of O_{1S} and N_{1S}. Because the elemental ratio reaches 2 in a modifier content of 5 phr of MDF10, it is clear that the modified resin surfaces are covered completely with a PFA segment. However, in the MDF40-blended surface region whose elemental ratio of F_{1S} is less than 2, hydrocarbon segments could coexist with PFA segments.

3.1.2. Durability of the Modified Resin Surface

The length of time a modified surface of resin is kept in an actual application is important. To examine this durability, the modified epoxy resin (containing 1 phr of modifier) was extracted with MEK by a Soxhlet extractor and analyzed with ESCA. The results are listed in Table III.

After extraction for 0.5 h, 47% of the fluorine from MDF0-blended epoxy resin was extracted, and only 12% of the fluorine remained after 3 h. For MDF10- or MDF40-blended resin, 25% of fluorine was extracted at 0.5 h, and even after 3 h, 38% or 44% of the fluorine remained, respectively. Extraction for 3 h was a very severe test of the modified resin.

In the MDF0-blended epoxy resin, the modifier could be extracted relatively easily, because it could not bond chemically to the epoxy resin. However, in the MDF10- or MDF40-blended resins, the modifier could not be easily extracted because the gly-

cidyl group of the modifier was bonded to the epoxy resin.

3.1.3. Depth Profiles with Argon Ion-Etching Method

Figure 5 shows the change of ESCA spectra of C_{1S}, F_{1S}, O_{1S}, and N_{1S} depending on etching time for the epoxy resins blended with 10 phr of MDF40. The peak intensity of F_{1S} decreased rapidly with the progress of etching and disappeared after 4 min. The peak at 292 eV in the C_{1S} spectra associated with CF_2 also decreased. In the spectra of O_{1S}, and N_{1S}, no changes depending on etching time were observed. A depth profile diagram derived from the above XPS data is shown in Figure 6. The elemental percentage of C_{1S} increased with etching time and F_{1S} decreased; O_{1S}, and N_{1S} maintained approximately constant values during etching.

As the etching condition used in this experiment was very mild, it was concluded that PFA segments of modifiers were concentrated in the outermost extremely thin layer of resin surface. This behavior corresponded to the results determined using the angular dependent method described above.

3.2. Wetting Properties for Modified Epoxy Resin

3.2.1. Critical Surface Tension (γ_C)

Figure 7 shows the relationship between $\cos \theta$ determined with n-alkane and DAP for modified epoxy resin and the surface tension of the standard liquids (γ_C). A good linear relationship between $\cos \theta$ and γ_L was verified. Critical surface tensions (γ_C) obtained by the extrapolation of the straight line to $\cos \theta \rightarrow 1$ are listed in Table IV.

Figure 8 shows the relationships between critical

Table III Surface Composition of Modified Epoxy Resins before and after Soxhlet Extraction with MEK

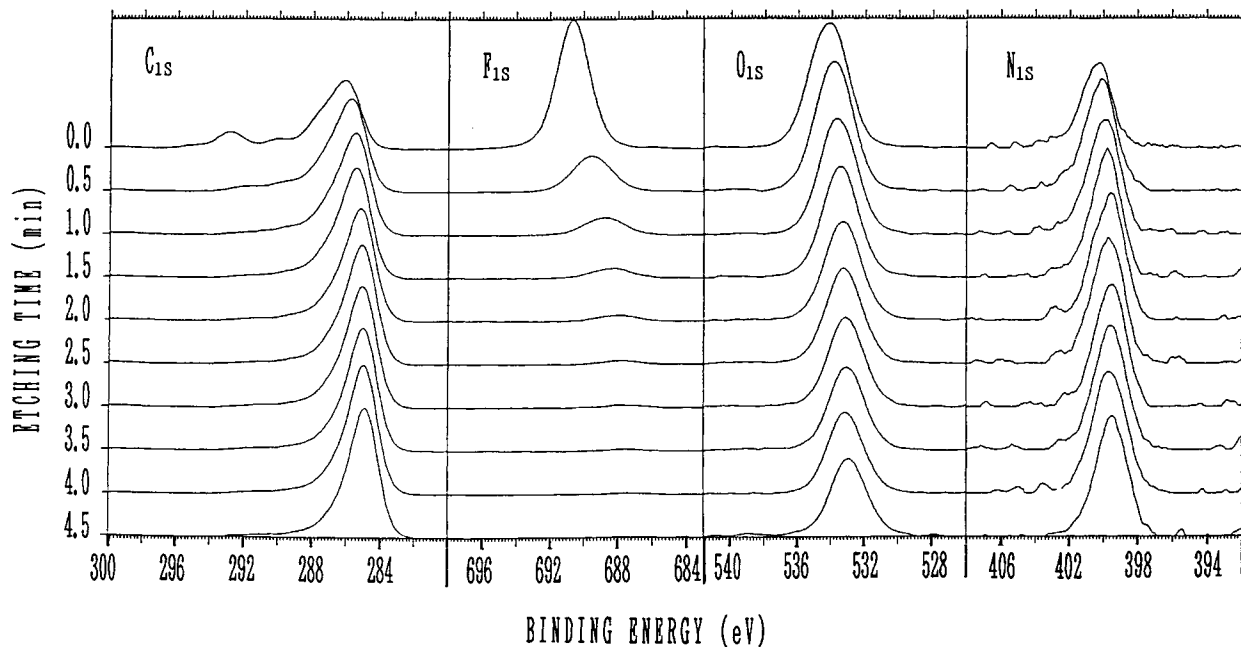| Modifier 1 phr	Extraction Time (h)	F/C Before a	F/C After b	F/C Extraction Rate (a − b)/a	O/C Before	O/C After	N/C Before	N/C After
MDF40	0.5	0.59	0.44	0.25	0.20	0.21	0.04	0.02
	3.0		0.38	0.35		0.17		0.03
MDF10	0.5	0.87	0.64	0.26	0.20	0.21	0.02	0.02
	3.0		0.44	0.49		0.23		0.02
MDF0	0.5	0.86	0.46	0.47	0.21	0.21	a	0.02
	3.0		0.10	0.88		0.19		0.03

a Undetectable.

Figure 5 Depth profiles of ESCA spectrums for epoxy resin modified with MDF40 (modifier content, 10 phr) obtained via argon ion-etching method.

surface tension (γ_C) for modified epoxy resin and modifier content. An increase in the modifier content resulted in a decrease in γ_C. Blending of MDF40 to the epoxy resin, as a whole, gave greater γ_C than did MDF10. Critical surface tensions obtained using nonpolar liquids (n-alkanes) for MDF10-blended
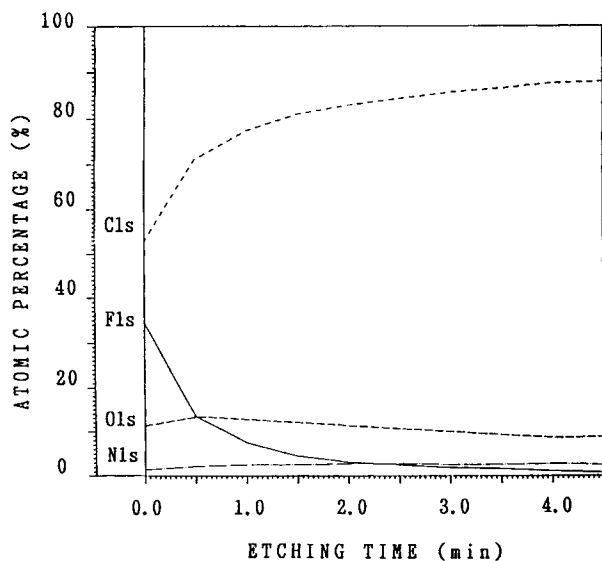

Figure 6 Depth profiles of surface composition for epoxy resin modified with MDF40 (10 phr) obtained via argon ion-etching method.

resin were approximately equal to those obtained using polar liquids (DAP), but in MDF40-blended resins, γ_C obtained with n-alkane was greater than with DAP when comparing the same modifier content surfaces. The differences in γ_C were as follows: Since the surfaces of MDF10-blended resins were covered entirely with PFA, as shown in ESCA analysis, they demonstrated both high oil and water repellency, whereas on MDF40-blended resin surfaces, because the covering with PFA was not so complete and because not only PFA segments existed but significant number of hydrocarbon segments also coexisted, modified resins did not show very high oil repellency, in spite of showing relatively high water repellency. Therefore, γ_C obtained with polar liquids (DAP) was lower than that in nonpolar liquids (n-alkane) of MDF40-blended resin. Kitazaki and Hata[11] reported the variability of γ_C depending on the polarity of the liquid series, measured by contact angle. They classified standard liquids into three type of series: nonpolar liquids (A); polar liquids (B); and hydrogen-bonding liquids (C), and gave the symbol γ_C^A, γ_C^B, and γ_C^C to the critical surface tension obtained using each liquid series, respectively. They showed that the nonpolar liquid series (A) gave a maximum value of γ_C and the hydrogen-bonding liquids (C) gave a minimum for a nonpolar solid such as n-hexatriacontane and polyethylene. These facts supported our hypothesis.
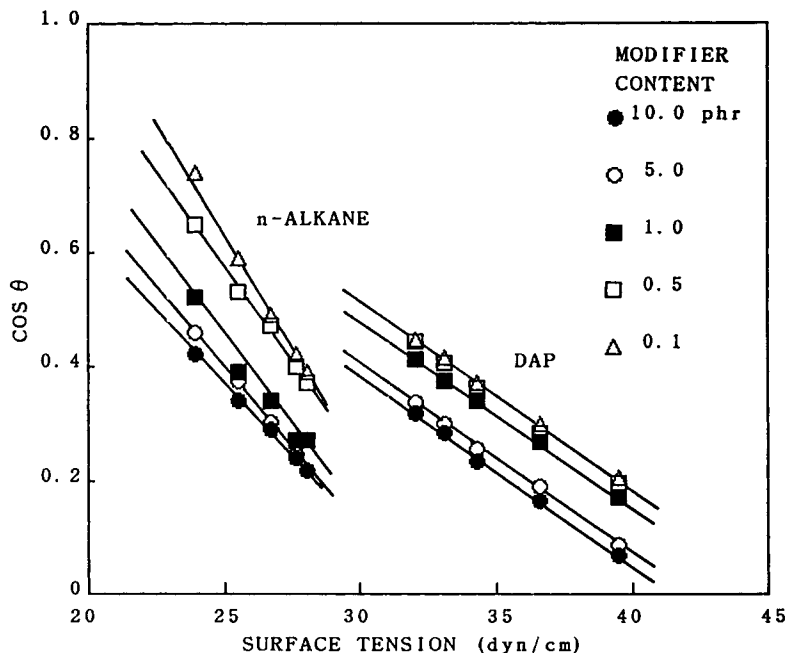
Figure 7 Zisman plots for epoxy resin modified with MDF40: (●) modifier content = 10 phr; (○) 5 phr; (■) 1 phr; (□) 0.5 phr; (△) 0.5 phr.

Figure 9 illustrates the relationships between γ_C obtained by contact-angle measurements and the elemental ratio of F_{1S} to C_{1S} (F_{1S}/C_{1S}) obtained via
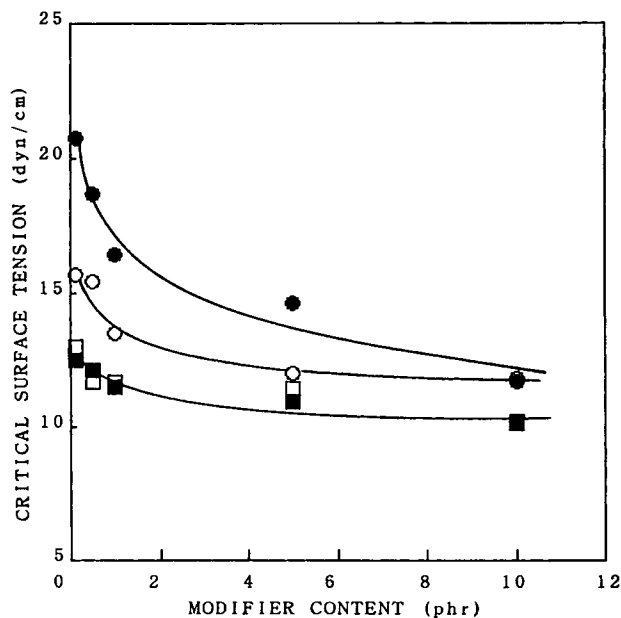

Figure 8 Critical surface tension for modified epoxy resin obtained with n-alkanes and dialkylphthalates (DAP) plotted against modifier content (phr): (circle) MDF40; (square) MDF10; (solid) with n-alkane; (hollow) with DAP.

ESCA analysis. γ_C decreases with an increase in fluorine. Base on these results, it is clear that γ_C is dependent mainly on the amount of fluorine introduced by the modifier.

3.2.2. Surface Tension (γ_S)

To quantitatively evaluate the surface tension (γ_S), and its dispersion force component (γ_S^d) and polar force component (γ_S^p), for modified epoxy resins, we employed Kaelble's[12] method as shown below.

It is well known that Young's eq. (2) between the contact angle (θ), solid surface tension (γ_S), solid/liquid interfacial tension (γ_{SL}), and surface tension of standard liquid (γ_L) is valid:

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

Conversely, assuming the additivity of intermolecular force, Fowkes[13] represented the surface tension by the sum of a contribution resulting from dispersion forces (γ^d) and a contribution resulting from polar forces (γ^p):

$$\gamma = \gamma^d + \gamma^p \qquad (3)$$

In addition, at the interface between a polar liquid

Table IV Surface Properties for Modified Epoxy Resins

Modifiers	Modifier Content (phr)	Critical Surface Tension (dyn/cm)		Surface Tension (dyn/cm)		
		n-Alkane	DAP	γ_S	γ_S^d	γ_S^p
MDF40	0.1	20.7	15.7	16.96	16.8	0.16
MDF40	0.5	18.7	15.4	16.76	16.6	0.16
MDF40	1.0	16.4	13.5	16.12	16.0	0.12
MDF40	5.0	14.6	12.0	15.00	15.0	0.00
MDF40	10.0	11.7	11.8	14.50	14.5	0.00
MDF10	0.1	12.5	13.0	15.92	15.8	0.12
MDF10	0.5	12.1	11.7	15.62	15.6	0.02
MDF10	1.0	11.5	11.7	15.20	15.2	0.00
MDF10	5.0	10.9	11.4	14.40	14.4	0.00
MDF10	10.0	10.1	10.2	14.10	14.0	0.00
FEP[9]			13.2	15.36	15.0	0.36

$(\gamma_1 = \gamma_1^d + \gamma_1^p)$ and nonpolar liquid $(\gamma_2 = \gamma_2^d)$ being in contact, he defined interfacial tension as follows:

$$\gamma_{12} = \gamma_1 + \gamma_2 - 2\sqrt{\gamma_1^d \gamma_2^d} \qquad (4)$$

For the interface between two polar liquids, Owens[14] and Kaelble[12] expanded Fowkes formula (4) to obtain the following equation:

$$\gamma_{12} = \gamma_1 + \gamma_2 - 2\sqrt{\gamma_1^d \gamma_2^d} - 2\sqrt{\gamma_1^p \gamma_2^p} \qquad (5)$$

Substituting Young's eq. (2) to this eq. (5) and dividing by $\sqrt{\gamma_L^d}$, we get the following:

$$\frac{\gamma_L(1 + \cos\theta)}{\sqrt{\gamma_L^d}} = 2\sqrt{\gamma_S^d} + 2\sqrt{\gamma_S^p}\frac{\sqrt{\gamma_L^p}}{\sqrt{\gamma_L^d}} \qquad (6)$$

This equation shows us that the linear relationship between $\gamma_L(1 + \cos\theta)/\sqrt{\gamma_L^d}$ and $\sqrt{\gamma_L^p}/\sqrt{\gamma_L^d}$ is valid. If contact angle (θ) is measured for various liquids having different values of γ_L, γ_L^d, and γ_L^p, we can plot $\gamma_L(1 + \cos\theta)/\sqrt{\gamma_L^d}$ as a function of $\sqrt{\gamma_L^p}/\sqrt{\gamma_L^d}$ to obtain a single straight line. From the gradient of this line, γ_S^p can be derived, and γ_S^d can also be defined from the extrapolated value of $\sqrt{\gamma_L^p}/\sqrt{\gamma_L^d} \rightarrow 0$. Figure 10 shows the relationships between $\gamma_L(1 + \cos\theta)/\sqrt{\gamma_L^d}$ and $\sqrt{\gamma_L^p}/\sqrt{\gamma_L^d}$ for the modified epoxy resins obtained with DAP. The data fell more or less on a straight line, lending validity to our eq. (6).

In Table IV, γ_s, γ_S^d and γ_S^p for modified epoxy resins calculated by this procedure are listed. Although we could not obtain γ_S of unmodified epoxy resin, because all standard liquids spread throughout the resin surface, it could have been larger than 40 dyn/cm. The data reported in a previous paper[9] on FEP are also listed in Table IV for comparison. Surface tension (γ_S) for modified resin decreases from 17 to 14 dyn/cm with an increase in modifier content. In the low content region, γ_S of MDF40-blended resin is only slightly larger than that of MDF10. In the region of content > 5 phr, γ_S for both MDF10 and MDF40 is lower than for FEP be-
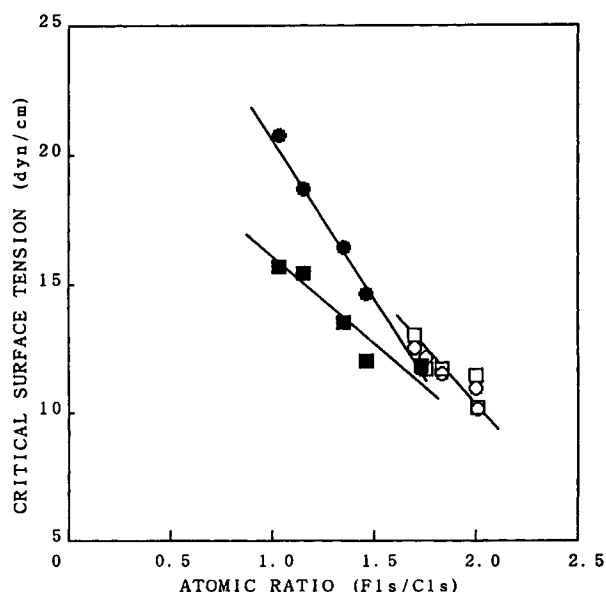

Figure 9 Critical surface tension for modified epoxy resin obtained with n-alkanes and dialkylphthalates (DAP) plotted against atomic ratio (F_{1s}/C_{1s}): (circle) with n-alkane; (square) with DAP; (solid) MDF40; (hollow) MDF10.
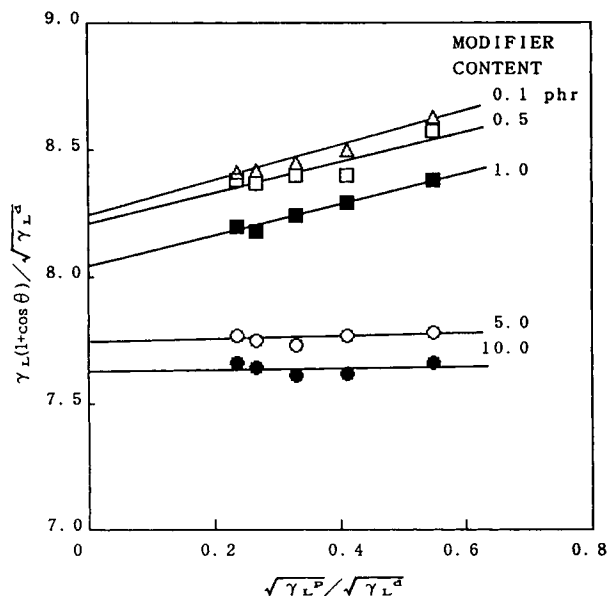
Figure 10 Relationships between $\gamma_L(1 + \cos\theta)/\sqrt{\gamma_L^d}$ and $\sqrt{\gamma_L^P}/\sqrt{\gamma_L^d}$ for modified epoxy resins obtained with DAP.

cause of the orientation of CF_3, which has a very low surface tension, to the resin surface. The dependency of γ_S^d on the modifier content demonstrates the same tendency as does γ_S. The value of γ_S^p is very low for both modifiers. These values appear to be lower than expected due to the amount of oxygen determined by ESCA ($O_{1S}/C_{1S} = 0.2$).

However, the outermost layer of modified resin is a thin film of PFA, and an ester group of the modifier is aligned under the film to form a subsurface. Even if ESCA is used, the sampling region reaches a significant depth (about 30–100 Å). Since the surface film of modified resin is thinner than the sampling depth, a considerable amount of oxygen is detected by ESCA analysis. Oxygen in the subsurface, however, does not affect contact angle, because the contact angle reflects the properties of the outermost molecular layers. Therefore, we must emphasize the importance of the contact-angle experiment in surface chemical studies in addition to instrumental analysis such as ESCA and SIMS.

3.3. Peel Strength

Recently, silicone pressure-sensitive adhesives have been developed and used extensively. These have very high adhesion characteristics, because of their good wettability due to the low surface free energy segment of silicone. Although silicone has been used

as a release agent for acrylic pressure-sensitive adhesives, it could not be used for silicone adhesive. Therefore, the development of a new release agent for these adhesives is desired. We have investigated the releasability of epoxy resin surface modified with fluorine-containing methacrylic ester copolymers having an extremely low surface free-energy segment PFA. Here, we define releasability as representing the performance of the release agent: how the agent can decrease the peel strength of a pressure sensitive adhesive affixed to the polymer surface by its interaction.

Figure 11 shows the relationship between the peel strengths of pressure-sensitive adhesives affixed to modified epoxy resins and the modifier content. The peel strength decreased with an increase in modifier content, and in the most effective case, it was $\frac{1}{3}$ of the unmodified case. From the results of the ESCA and contact-angle investigations, mentioned above, it was shown that the modified resin surfaces were covered with a thin layer of PFA and had lower critical surface tension than the reported surface tension of silicone, i.e., 19.9 dyn/cm.[15] Because of this, the wettability of the resin surface by the silicone adhesive could be decreased considerably by the addition of modifiers, and this reduction in wettability resulted in a decrease in the peel strength.

Thus, because these modifiers could decrease the peel strength of the silicone pressure-sensitive ad-
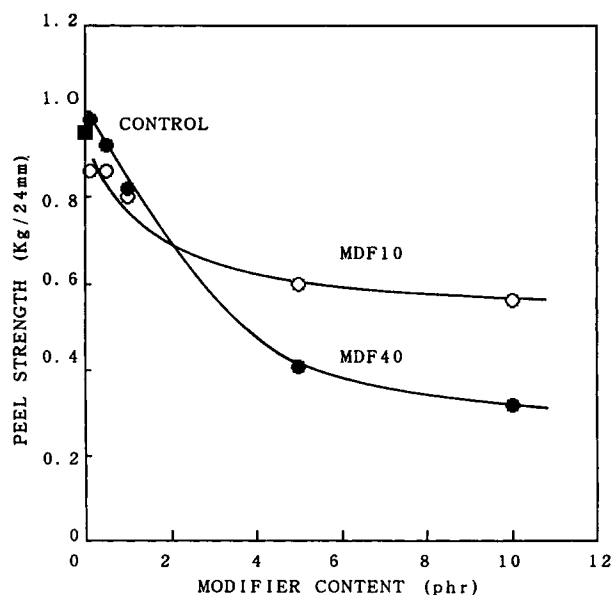

Figure 11 Peel strength of pressure-sensitive adhesive affixed to modified epoxy resins plotted against modifier content.

hesives affixed to the epoxy resin, it was clear that fluorine-containing methacrylic ester copolymers, used as a modifier of epoxy resin as illustrated in this study, could act as good release agents for silicone pressure-sensitive adhesives.

4. CONCLUSION

A modified fluorine-containing methacrylic ester copolymers was blended with an epoxy resin to enhance oil and water repellency.

1. The amount of fluorine in the modified epoxy resin surface layer increased with the shallowness of sampling depth and with an increase in modifier content.
2. The critical surface tension for modified epoxy resin decreased 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 silicone pressure-sensitive adhesives affixed to a modified epoxy resin decreased with an increase in the modifier. From this fact, it was shown that these modifiers could be effective as a release agent for silicone pressure-sensitive adhesives.
4. A considerable amount of fluorine in the resin surface modified with GMA containing block copolymers remained after Soxhlet extraction, whereas in the surface modified with a copolymer without GMA, more fluorine was extracted.

It was shown that these copolymers were good surface modifiers to improve the oil and water re-

pellency and could be used as a release agent for silicone pressure-sensitive adhesives.

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