

# Development of Polymer-Molding-Releasing Metal Mold Surfaces with Perfluorinated-Group-Containing Polymer Plating

Kunio Mori, Yaeko Sasaki, Hidetoshi Hirahara, Yoshiyuki Oishi

Department of Applied Chemistry, Iwate University, Ueda, Morioka 020-8551, Japan

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**ABSTRACT:** The polymer-molding-releasing properties of metal molds were found to be related to the following factors: (1) interfacial chemical bonding between the surfaces of polymers and metal molds and (2) a friction force or friction coefficient between polar substances and/or low-molecular-weight components in the polymers and physical factors on mold surfaces. We theoretically and experimentally confirmed that metal molds with good polymer-molding-releasing properties had very small surface free energies. We also proved that the surface free energies in the resulting polymer moldings were lower than before shaping. The molding releasing properties improved with decreasing friction force and friction coefficient between the

surface of polymers and metal molds and with decreasing surface free energy. To obtain metal molds with lower surface free energies, we developed a polymer plating method with perfluorinated-group-containing triazine dithiol. The metal mold treated by polymer plating had lower critical surface tension ( $7.5 \text{ mJ/m}^2$ ) than Teflon ( $18 \text{ mJ/m}^2$ ), indicating that the surface consisted of  $\text{CF}_3$  groups. The treated mold showed excellent durability in its releasing properties, which was better than that of the untreated mold. This technique was developed for the production of molds for the  $F\theta$  lens and the naturally bright focusing screen. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 2549–2556, 2003

## INTRODUCTION

Releasing properties have become a matter of interest for the production of polymer articles in molds. Marked improvements in releasing properties of polymer molds have resolved many problems associated with surface roughness, size precision, taper, noncontamination, and number of push-out pins, and abrasions. To obtain good conditions for release in polymer molds, one should know how the interface between the polymers and metals is formed during molding and how the chemical components of the obtained polymer surfaces are determined.<sup>1</sup>

Release is a phenomenon that is the opposite of adhesion because for release, the formation of as weak a force as possible at the interface is required during molding, and for adhesion, that of as strong an interfacial bond as possible is required between the polymers and metals. To obtain the weakest interfacial force during molding, one should experimentally investigate the formation process of the interface between the polymers and metals. When the weakest interfacial bonds for the metal molds are attained, the surface tension of the molds are made as small as possible. The stabilization theory of interface in the

adhesion between polymers and metals yields some information about this problem.<sup>2,3</sup> To produce molds with smaller surface tensions the polymer plating of perfluoroalkyl-group-containing triazine dithiols has been developed. This method allows a  $\text{CF}_3$ -group-coated surface to be produced on metal molds.

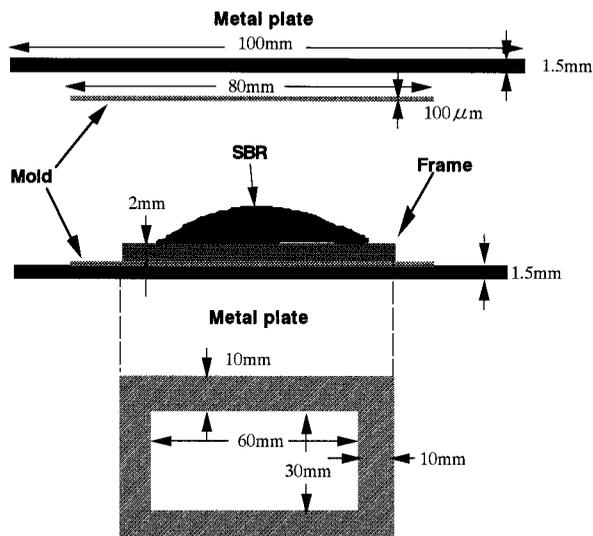
This article clarifies the relationship between the surface free energies on metal molds and molded products and the relationship between the adhesion force and friction force. These relationships are important to the processes of removing polymer products from molds and producing metal molds with the lowest surface free energies, and for checking the performance of releasing metal molds produced experimentally. Finally, examples of releasing metal molds for plastic lens molding are used to illustrate these relationships.

## EXPERIMENTAL

### Materials and reagents

Styrene–butadiene copolymer (SBR; styrene content = 25%) and nitrile–butadiene copolymers (NBR; nitrile content = 18–41%) were obtained from Japan Zeon Co., Ltd.<sup>4,5</sup> Polydicyclopentene (PDC) resin (Zeonex280) was supplied from Nippon Zeon Co., Ltd. Polymer additives, including sulfur, *N*-cyclohexyl-2-benzothiazyl disulfenamide (CBS), tetramethylthiuram disulfide (TMTD), *N*-isopropyl-*N'*-phenyl-*p*-phenylene diamine, ZnO, and

Correspondence to: K. Mori (kuni@wate-u.ac.jp).



**Figure 1** Diagram and dimensions of compression molds for the preparation of SBR or NBR vulcanizates.

stearic acid were commercially obtained. Steel plates (SKD-11,  $200 \times 2000 \times 0.3$  mm) were commercially obtained. 2-[2-(Perfluorooctyl)ethyl butyl]amino-1,3,5-triazine-4,6-dithiol monosodium (FBTDN) was prepared by the reaction of 2-(perfluorooctyl)ethyl butylamine, cyanuric trichloride, and sodium hydrosulfide according to a method described in a previous paper.<sup>6</sup> Metal compression molds [average surface roughness ( $R_a$ ),  $0.02 \mu\text{m}$ ] for the present experiment were prepared by polishing steel plates after being plated with electroless nickel plating (thickness:  $10 \mu\text{m}$ ) at  $40^\circ\text{C}$ .

### Preparation of vulcanizates

We produced SBR and NBR vulcanizates by hot-pressing rubber mixtures in a compression mold ( $30 \times 60 \times 2$  mm), as shown in Figure 1. The vulcanizates, with a  $150 \text{ mol}/\text{m}^2$  network concentration, were prepared with cure time (20–40 min) controlled at  $160^\circ\text{C}$ . The rubber mixtures were prepared by the roll-milling of elastomers (100 phr), FEF black (50 phr), sulfur (0.5 phr), CBS (1.5 phr), TMTD (1.5 phr), IPP (2 phr), ZnO (5 phr), and stearic acid (1 phr).

### Polymer plating<sup>7,8</sup>

The electrochemical polymerization of FBTDN, referred to here as polymer plating, was carried out with a potentiostat at/galvanostat at (Hokuto Denko HA-5080) with a linear scanner and a computer, as described previously.<sup>7</sup> The electrolytic cell was equipped with a working electrode (nickel-plated steel plates or metal molds), a counterelectrode (Pt plate), and a reference electrode (saturated calomel electrode) and was filled with an electrolytic solution containing FBTDN ( $0.001 \text{ mol}/\text{dm}^3$ ) and  $\text{Na}_2\text{CO}_3$  ( $0.1 \text{ mol}/\text{dm}^3$ ) in water. The

nickel-plated steel plates ( $R_a < 5 \text{ nm}$ ) were polished by finishing and were used after they were washed with hexane.

### Injection molding<sup>9</sup>

The injection molding ( $1 \times 20 \times 30$  mm) of the PDC resin (Nippon Zeon, Zeonex280) with a lower hygroscopicity for the producing lens was carried out with an injection-molding machine (Scale 120t, Sumitomo Juki Industry Co., Ltd.) after experimental molds were mounted to the machine. In this case, the dimensions of film gate were as follows: thickness-1 and 8 mm and length-6 mm. The injection-molding conditions were as follows: injection rate- $0.3 \text{ dm}^3/\text{s}$ , injection pressure-200 MPa, cylinder temperature- $260^\circ\text{C}$ , mold temperature- $105^\circ\text{C}$ , cooling time-10 s, and molding cycle time-30 s.

### Measurement

Fourier transform infrared (FTIR) spectra were measured with a Jasco IR-5500 (Jasco Co., Ltd.), by high-performance reflection absorption spectroscopy (RAS), and by transmittance absorption spectroscopy (KBr tablet method). The thickness of the polymer films was determined with an ellipsometer (Mizojiri Engineering Co, Ltd). The surface free energy was calculated by the substitution of contact angles with Wu's equation.<sup>4</sup> The respective contact angles of pure water and methylene iodide on the molds and vulcanizates were determined with an Elma goniometer-type contact angle measuring apparatus (Elma-type G-1) in the clean area. Droplet diameter was controlled at 0.08–0.1 mm. The surface tensions of water and methylene iodide were given by Matsumoto<sup>7</sup> Critical surface tension was determined with Zisman plots<sup>10</sup> after the contact angles of the aliphatic carbon hydride of octane from hexadecane were measured. ESCA spectra were obtained at a base pressure of  $10^{-10} \text{ Pa}$  with an X-ray photoelectron spectrometer (ESCA Lab-5, VG Scientific Co., Ltd). A Mg  $K\alpha$  X-ray was used as the excitation source (23,500 eV) at take-off angles of 15, 45, and  $90^\circ$ .  $R_a$  was determined with an atomic force microscope (Nanoscope III, Digital Instruments, Santa Barbara, CA) equipped with a  $10\text{-}\mu\text{m}$  piezocanner to investigate the degree of adhered resin on the mold surfaces.

### THEORY ON RELEASING PROPERTY

There is a inverse relationship between adhesion and releasing properties. The conditions of nonadhesion are those of releasing, and the conditions of nonreleasing are those of adhesion. The factors affecting the releasing properties of molds are primarily an interfacial chemical force between plastics and metals (first-

order bonds), an interfacial physical force between plastics and metals (second-order bonds), a friction coefficient and friction force between plastics and metals, the ingredients and oligomers in polymer and pinholes, and unevenness on the surface of the mold. In the direct adhesion between polymers and metal during curing, the formation of first-order bonds between the polymer and the metals is essential to obtaining good adherends with high adhesive strengths.<sup>1,2</sup> The presence of first-order bonds in the adherends leads to a marked contribution of second-order bonds to the adhesive strength. In the first period of molding, the second-order bonds contribute to the releasing properties between polymers and metal molds. Next, first-order bonds at the interface between adhered polymers and molds are formed. Therefore, the formation of second-order bonds in the releasing properties is discussed first.

Second-order bonds acting at the interface represent the work of adhesion ( $\Delta W$ ), as shown in eq. (1), where  $\gamma_p$ ,  $\gamma_M$ , and  $\gamma_{MP}$  are the surface tensions of the polymers and the molds and the interfacial tension between the polymer and molds, respectively:

$$\Delta W = \gamma_M + \gamma_p - \gamma_{MP} \quad (1)$$

The greater  $\Delta W$  is the greater the second-order bond force (adhesion force) is at the interface.  $\Delta W$  is high when  $\gamma_M$  is equal to  $\gamma_p$  and both  $\gamma_M$  and  $\gamma_p$  are greater. However, when  $\Delta W$  is 0, adhesion does not occur; this is a releasing condition. The condition  $\Delta W = 0$  is not realistic. Realistically, the releasing conditions occur when  $\gamma_M \neq \gamma_p$  and both  $\gamma_M$  and  $\gamma_p$  are very small.

The friction force ( $F$ ) between the polymers and metals is shown in eq. (2).<sup>1,12</sup>

$$F = \mu(L - PS) \quad (2)$$

where  $\mu$  is the friction coefficient,  $L$  is the load,  $P$  is the adhesive force, and  $S$  is the contact area of the load.  $F$  is proportional to  $\mu$  and  $P$ . This means that the releasing property is improved as friction decreases.

The pinholes and roughness of metal molds that are packed with polymers, polar ingredients, and oligomers also allow mechanical bonds to be generated between polymer products and mold surfaces. When the pinholes and roughness on metal molds have low surface tensions it becomes difficult to pack polymers, polar ingredients, and oligomers in the molds due to the releasing conditions. This means that the releasing properties can be markedly improved if the surface of the metal molds is finished with a very low surface free energy.

**TABLE I**  
**Relation Between Surface Free Energies ( $\gamma^a$ ) in Molds and Vulcanizates**

Mold	Mold and its surface free energy $\gamma(\gamma_p; \text{mJ/m}^2)$	Surface free energy of SBR vulcanizates		
		$\gamma$	$\gamma_p$	$\gamma_D$
TF	28.4 (0.4)	31.3	0.2	31.1
FP	41.5 (8.2)	35.6	1.5	34.1
KP	47.7 (13.0)	37.4	1.9	35.5
UP	48.5 (13.3)	37.9	2.1	35.8
PF	50.8 (14.5)	39.6	2.5	37.1

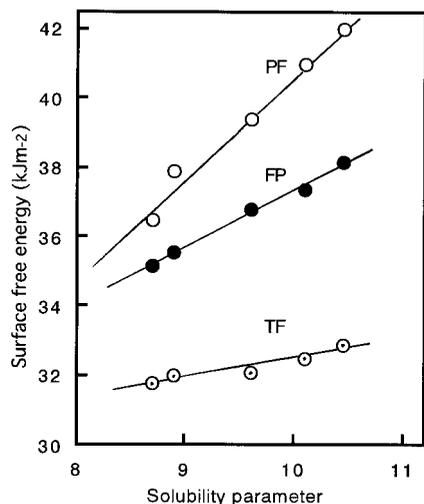
FP = ferrite plate; KP = polyimide film Toray Du Pont Co., Ltd. UP-polyimide film Ube Losan Co., Ltd.

<sup>a</sup>  $\gamma = \gamma_p + \gamma_D$  where  $\gamma_p$  is the polar component, and  $\gamma_D$  in the dispersion component of  $\gamma$ .

## RESULTS AND DISCUSSION

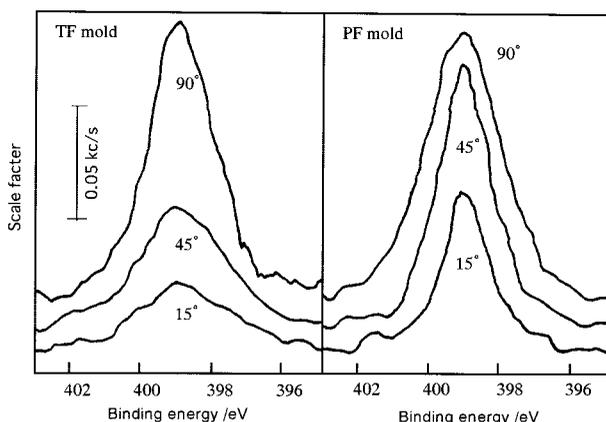
### Relationship between the surface free energies of the polymer products and metal molds

To investigate the theory that the surface components of polymer products must be influenced by that of the molds, SBR and NBR vulcanizates were prepared with molds of various surface energies (plates or films), and their surface free energies were determined. SBR and NBR were used because molds with various surface free energies are easily obtainable. Table I shows the surface free energies of molds and SBR vulcanizates prepared in various molds. The surface free energies of molds, which were determined from the contact angles of water and methylene diiodide, were in the range 28.4–50 mJ/m<sup>2</sup>. The surface free energies of the obtained SBR vulcanizates changed in a way that corresponded to the surface free energies of the molds, even though the same SBR was used. When the surface free energies of the molds were high, SBR vulcanizates with high surface free energies were obtained. When the surface free energies of molds were low, SBR vulcanizates with low surface free energies were obtained. The surface free energies in those cases greatly changed in the dispersion component. This was because the dispersion components of the top layer of vulcanizates changed by energy matching to those of molds. Figure 2 shows the relationship between the solubility parameters of nitrile rubbers and the surface free energies of various NBR vulcanizates prepared by three kinds of molds. The chemical component that increased the surface free energies in the NBR vulcanizates was a nitrile group (—CN), and those that decreased the surface free energies were a butadiene unit (—CH<sub>2</sub>CH=CHCH<sub>2</sub>—) and a vinyl group (—CH<sub>2</sub>CH=). The surface free energies of the NBR vulcanizates increased linearly with the surface free energies of the molds. In addition, the surface free energies of various NBR vulcanizates increased with the solubility parameter of nitrile rubbers, and



**Figure 2** Relationship between surface free energies and solubility parameters in NBR vulcanizates prepared by molds with various surface free energies. FP = ferrite plate.

the slope of the linear line increased with the surface free energies of molds. This result indicates that in the case of molds with high surface free energies, the concentration of nitrile groups in the NBR vulcanizate surfaces increased with the polar component of nitrile rubbers. In the case of molds with low surface free energies, the concentration of nitrile groups in NBR vulcanizate surfaces was low even when the nitrile content in the NBR vulcanizates was high. Figure 3 shows the N1 s peaks in the ESCA spectra of NBR vulcanizate surfaces prepared with Teflon film (TF) Pet film (PF) and PF molds, which were measured at various radiation angles (15, 45, and 90°). The chemical component of a very thin layer was observed when the radiation angles were small, and that of a very thick layer was observed when the radiation angles were large. NBR vulcanizates prepared with a PF mold had a clear N1 s peak even at the low radiation



**Figure 3** Peak intensities of the N1s peak and glancing angles in the ESCA spectra of NBR vulcanizates prepared in TF and PF molds.

**TABLE II**  
Initial Surface Free Energy ( $\gamma$ ) on the NBR Vulcanizates with 5-phr Aliphaticamide

Amide	Mold	$\gamma$ (mJ/m <sup>2</sup> )		
		$\gamma$	$\gamma_p$	$\gamma_D$
Palmitamide	TF	32.1	2.0	28.2
	FP	37.2	8.8	28.4
Stearamide	TF	31.8	1.8	30.0
	FP	37.8	8.2	29.6
Behenamide	TF	30.8	1.6	29.2
	FP	38.5	7.9	29.5

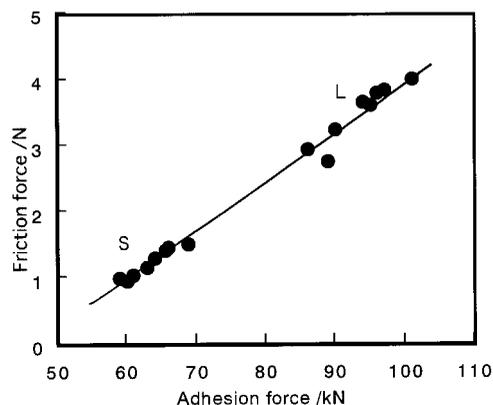
$\gamma_p$  = polar component;  $\gamma_D$  = dispersion component; FP = ferrite plate.

angle (15°), but this peak intensity was lower than those at the radiation angles of 45 or 90°. NBR vulcanizates prepared with a TF mold had a sufficiently high N1s peak at the 90° radiation angle; however, in these vulcanizates, the N1s peak intensity decreased with decreasing radiation angle. This means that in the top layer of the vulcanizate surface, many more  $-\text{CH}_2\text{CH}=\text{CHCH}_2-$  and  $-\text{CH}_2\text{CH}=\text{C}$  groups were present in comparison with  $-\text{CN}$  groups, corresponding to the results of surface free energy. Thus, molds had a great effect on the chemical component properties and on the physical properties of their surfaces to products.

Ingredients and oligomers contained in polymers are responsible for worsening the releasing properties in the molds. These substances remain on mold surface after they are packed into pinholes and irregularities. Table II shows the surface free energies of NBR vulcanizates that were prepared with two molds with different surface free energies. Uncured NBR contains alipharamides. During vulcanization, alipharamides separated on the NBR vulcanizate surfaces. TF molds with low surface free energies resulted in NBR vulcanizates with low surface free energies. FT molds with high surface free energies resulted in NBR vulcanizates with high surface free energies. NBR vulcanizates in FT molds had higher polar components in their surface free energy than those in TF molds. When the surface free energies of molds are small, the releasing properties should be maintained because bond forces between molds and polymer products are small and because mold surfaces come into contact with the nonpolar groups even if the polar substances in the polymers are present at the interface between the molds and polymer products. Higher polar components indicate the presence of polar chemical groups, and nonpolar components indicate the presence of nonpolar chemical groups.

#### Adhesion and friction forces

We estimated that the increase in adhesion force between the molds and polymer products worsened the



**Figure 4** Relationship between friction force and adhesion force in NBR and SBR vulcanizates. S indicates that both the vulcanizates and sliders had small surface free energies; L indicates that both the vulcanizates and sliders had large surface free energies.

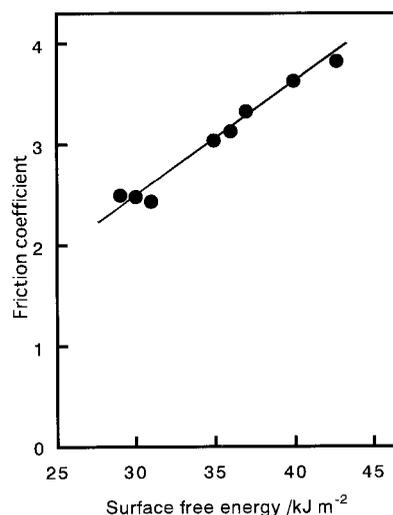
releasing properties of molds because the improvement or worsening of the releasing properties of molds is caused by the magnitude of the adhesion forces between the polymer and mold materials. The releasing properties of molds are also related to the friction force of molds. An increase in the friction force worsens the releasing properties of polymer products from molds. Molds with a large draft angle cause an increase in the number of inferior products when the friction force is high. In Figure 4, the relationship between the friction and the adhesion force, which was calculated from the surface tensions of vulcanizates and metals, is shown. A close correlation was observed between these surface tensions.<sup>13</sup> In the figure, the plots near an S mark are those for the vulcanizate surfaces with small surface free energies, which were tested by an indenter with a small surface free energy. Plots near an L mark indicate the case in which vulcanizate surfaces with large surface free energies were tested by an indenter with a large surface free energy. Surface free energies between both had to be small to reduce the friction and adhesion forces of the mold and polymer product surfaces. Figure 5 shows the relationship between the friction coefficient and surface free energy in vulcanizates. The friction coefficient in the molds decreased with decreasing surface free energy in the polymer products. The friction coefficient is particularly important when polymer products are removed from molds. When the polymer products are fished out from molds with a low friction coefficient, the scratching of polymer products is prevented, and release is facilitated.

#### Preparation of molds with low surface free energies

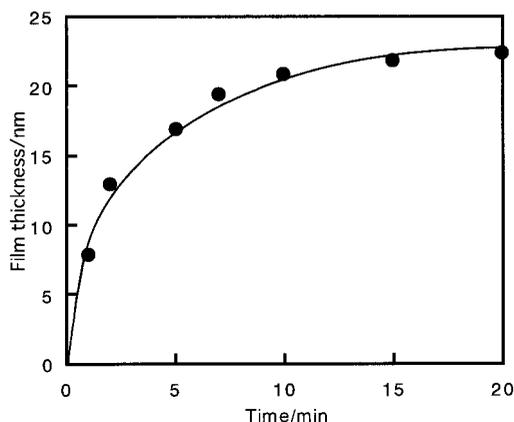
Molds with low surface free energies can be obtained by the close packing of a perfluoro group ( $\text{CF}_3-$ ),

which has the lowest surface free energy on the surface. Zisman showed that solid surfaces packed closely by the  $\text{CF}_3-$  group have a critical surface tension of  $6 \text{ mJ/m}^2$  at present, the lowest among all solid substrates. The Langmuir-Blodgett<sup>14</sup> method places  $\text{CF}_3-$ -group-containing molecules side by side, closely packed on the substrate surface, to accumulate a molecular film. Miyashita et al.<sup>15</sup> investigated the accumulation of a thin film of perfluoro-group-containing acrylamide polymers and obtained a critical surface tension of  $9.2 \text{ mJ/m}^2$ . This method, however, is unsuitable for the accumulation of closely packed molecular films on complicated and irregular surfaces on an industrial scale.

We reported the ability to accumulate polymer film surfaces covered by a  $\text{CH}_3-$  group on electrochemically treated steel plates with 6-dioctylamino-1,3,5-triazine-2,4-dithiol in a  $\text{Na}_2\text{CO}_3$  aqueous solution. This method is called polymer plating. Thus, we investigated whether metal surfaces were covered by the  $\text{CF}_3-$  group in the polymer plating of perfluoro-group-containing triazine dithiols as described later. Figure 6 shows the relationship between the thickness of polymer film and plating time in the polymer plating of perfluoro-group-containing triazine dithiols. Plating conditions of 10 min at  $40^\circ\text{C}$  yielded a film thickness of 20 nm. Figure 7 shows the FTIR spectra of a perfluoro-group-containing polymer film, perfluoro-group-containing polymer powders (KBr method), and perfluoro-group-containing triazine dithiols (monomer). The polymer powder was scraped from polymer-plated metal (KBr method). The perfluoro-group-containing polymer film (RAS method) and perfluoro-group-containing polymer powders were of the same sample. Those two samples and the monomer had different wavenumbers and absorption inten-

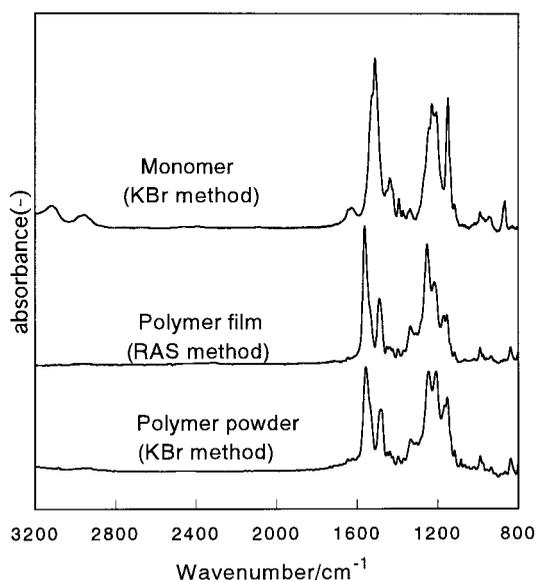


**Figure 5** Effect of surface free energy on the friction coefficient of NBR vulcanizates prepared by molds with various surface free energies.



**Figure 6** Relationship between film thickness and time in the polymer platings of perfluorinated-group-containing triazine dithiol in 0.1M  $\text{Na}_2\text{CO}_3$  aqueous solution at 40°C.

sities. The monomer changed to a polymer, as indicated by the two IR spectra. The polymer was considered to be a disulfide polymer due to the presence of a peak at  $542\text{ cm}^{-1}$ , which was assigned to a S-S bond<sup>8</sup> in the Raman spectrum measurement. The wavenumbers of absorption of the IR spectra obtained via the RAS (perfluoro-group-containing polymer film) and KBr methods were identical, but the absorption intensities for the corresponding wavenumbers were different. The KBr method prevented the transmission IR spectrum of an isotropic molecule assembly, where the RAS method yielded the reflection IR spectrum of an anisotropic molecule assembly. In particular, the absorption intensity at  $1254\text{ cm}^{-1}$  (stretch vibration), which was assigned to a  $\text{CF}_3$ - group, was not changed compared with the powder and film; however, that at



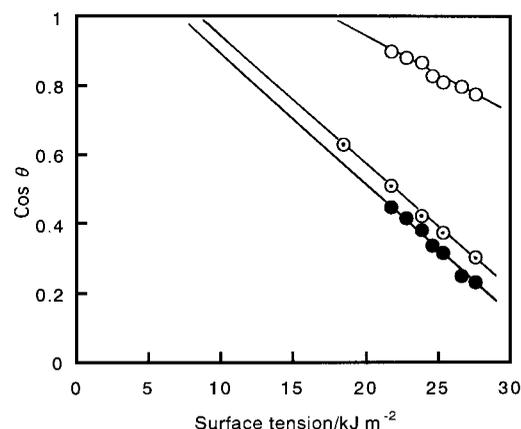
**Figure 7** FTIR spectra of triazinedithiol monomer prepared with the KBr method and its polymer prepared with the RAS and Johnson methods.

$1167\text{ cm}^{-1}$  (stretch vibration), which was assigned to a  $\text{CF}_3$ - group, decreased considerably. This indicates that the polymer film was anisotropic. The contact angles of pure water and methylene diiodide on the polymer film (the thickness of nickel plating) were  $120^\circ$  and  $108^\circ$ , respectively. The surface free energy of the polymer film was  $13.7\text{ mJ/m}^2$ , and the density of the polymer film was 1.92 (monomer-1.73).

Figure 8 shows the Zisman plots of the polymer film prepared by the polymer plating of a perfluoro-group-containing triazine dithiol, perfluoro-group-containing acrylamide polymer,<sup>15</sup> and Teflon. These values were reasonable because the Zisman plots on the treated surfaces were fitted linearly. Critical surface tension ( $\gamma_c$ ) on the polymer film was  $7.5\text{ mJ/m}^2$ . A perfluoro-group-containing acrylamide polymer film,<sup>15</sup> obtained by the LB method, had a critical surface tension of  $9.2\text{ mJ/m}^2$ . Teflon film had a critical surface tension of  $18\text{ mJ/m}^2$ , indicating that the surfaces were arranged by  $-\text{CF}_2\text{CF}_2-$  groups. Therefore, the polymer films obtained by the polymer plating of a perfluoro-group-containing triazine dithiol indicated that the surfaces were arranged in a closely packed manner by  $\text{CF}_3$ - groups ( $\gamma_c$ - $6\text{ mJ/m}^2$ ) as the  $\gamma_c$  was  $7.5\text{ mJ/m}^2$ .

#### Property of releasing molds

Model molds ( $10 \times 20 \times 0.2\text{ mm}$ ) for injection, which were obtained under the conditions described in Figure 6, were evaluated by the measurement surface roughness (PV) and the contact angle of water in the injection molding of norbornen resin, as shown in Table III. In the injection molding of PDC resin, the polymer-plated mold had markedly better surface properties than the untreated mold. PV is the difference between the highest and the lowest parts on the mold surfaces.  $R_a$  is the average roughness of the mold



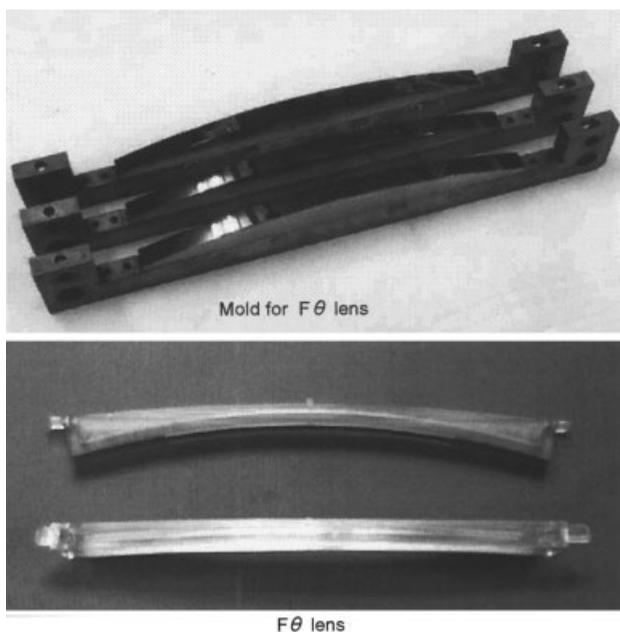
**Figure 8** Zisman plots of the polymer plating of (●) perfluorinated-group-containing triazine dithiol (○), an LB film of perfluorinated acrylamide polymer, and (○) Teflon.

**TABLE III**  
Changes in the Surfaces of Molds During Polynorborene Resin Treatment

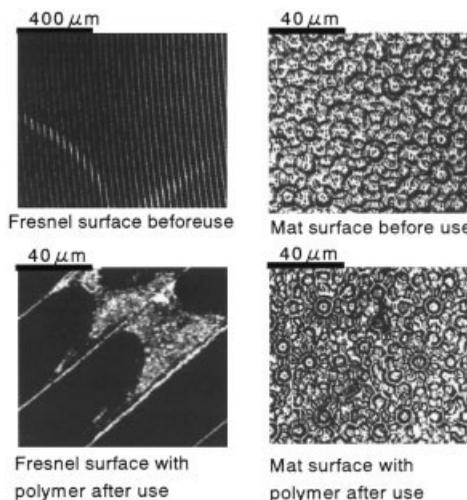
Molding shots	Surface roughness (nm)				Contact angle (°)	
	Untreated		Treated		Untreated	Treated
	PV	$R_a$	PV	$R_a$		
0	21	4	22	3	76	121
500	28	10	21	4	103	120
1000	284	86	18	4	101	119
3000	—	—	21	5	102	118
5000	—	—	23	4	102	119

surfaces. Untreated molds caused PV to increase suddenly with the increasing shot numbers, that is, the adhesion of PDC resin to the mold surface. Because PDC resin is water repellent, the adhesion of PDC resin to the mold surface caused an increase in the contact angle of water on the molds. In such cases, the contact angle was greater than 100° (CH<sub>3</sub>-covered surface-98–100°, CH<sub>2</sub>-covered surface 94°) because the mold surfaces on which the resin adhered were rough.<sup>16</sup> Up to this point, the polymer plated molds did not cause a change in the releasing properties of the molds, even at 5000 shots; the contact angle on the mold surface constant was maintained, indicating surfaces without PDC resin.

Figure 9 shows molds for the Fθ lens where F is the focus distance and θ is the incidence angle; the lens ideal image height (y) is shown by F tan θ<sup>17</sup> and the obtained Fθ lens produced by the previous data. Fθ



**Figure 9** Fθ lens mold plated by perfluorinated group-containing triazine dithiol and the Fθ lens plated by the molds.



**Figure 10** Fresnel and mat surfaces before and after use in the mold for the naturally-bright focusing screen.

lenses were obtained in injection molds with the injection machine. The PV of the molds was reflected in that of the Fθ lens. In the Fθ lens used for copy machines, a PV of more than of 50 nm causes laser light to reflect diffusely. Extreme flatness is required because the diffuse reflection of laser light causes the generation of spotted color in copy machines. Because the film thickness used in the polymer plating was in the range of 20–40 nm, the spotted color of pictures due to the PV of the molds was not a problem. The polymer plating was thus characterized by a thickness of less than 100 nm as a strong thin film.

Figure 10 shows the surface of the untreated molds of a naturally bright focusing screen. The naturally bright focusing screen consisted of mat and Fresnel surfaces. The mold of the mat surface was composed of the assembly of a small lens (1–10 nm), on which irregular patterns were inscribed. The Fresnel surface was composed of various patterns, on which a right triangle was inscribed in a circular shape. Such a mold for optical lenses can be produced with releasing agents, but the surfaces of optical lenses are contaminated during molding. The lens loses reasonable properties even in the presence of a few surface spots. As shown in Figure 10, the untreated Fresnel and mat molds became contaminated with an adhered resin, even after several shots. The resin appeared as residuals or as a black spot. These molds produced inferior lenses after several shots. With increasing shot number, the amount of resins adhered on the Fresnel and mat surfaces increased. The polymer-plated molds, however, did not yield inferior lenses until 3500 shots. Such high releasing properties were possible because the polymer-plated molds had a very low surface free energy.

## CONCLUSIONS

Molds with small surface free energies were found to produce polymer products with small surface free energies and excellent releasing properties in the molds themselves. The chemical components of the surfaces of polymer products injection-molded in molds were dominated by the chemical components of the mold surfaces. Molds with small surface free energies yielded surfaces with small surface free energies. Molds with large surface free energies result in surfaces with large surface free energies. The releasing properties of the molds were related to the friction force between the mold and polymer product surfaces. We showed this by making the friction force and coefficient between both smaller, which required both surface free energies to be decreased to the greatest extent possible. To produce molds with small surface free energies, the polymer plating of perfluoro-group-containing triazine dithiol to mold surfaces was developed. The polymer plating resulted in a  $\gamma_c$  of 7.5 mJ/m<sup>2</sup> on metal molds and coated the top surface of molds with a CF<sub>3</sub>-group. The treated metal molds, model molds, had excellent durability in the injection molding of the polymers. The molds were very effec-

tive for the releasing properties in the injection molding of a lens with complicated and small patterns on both surfaces.

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