

Polymer Communication

# Surface modification of epoxy resin by polyether–polydimethylsiloxanes–polyether triblock copolymers

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## Abstract

In order to reduce static friction coefficient ( $\mu_s$ ), polyether–polydimethylsiloxane–polyether triblock copolymers (PER–PDMS–PER) were incorporated into epoxy resins as surface modifiers. It was found that longer PDMS segments in PER–PDMS–PER and higher modifier contents led to lower  $\mu_s$  of modified epoxy resins upon stainless steel. The  $\mu_s$  of silicone rubber- and PTFE-side surfaces were evidently lower than that of stainless steel-side surface. ESCA investigations indicated that a longer PDMS block in modifier resulted in a flatter PDMS gradient at surface and the degree of PDMS accumulation on PTFE- and silicone rubber-side surfaces were much higher than that on stainless steel-side surface. © 2000 Elsevier Science Ltd. All rights reserved.

**Keywords:** Surface modification; Epoxy resin; Static friction coefficient

## 1. Introduction

For some practical applications, surface modification of solid polymer is desirable. It has long been recognized that incorporation of a small amount of surface-active additives during polymer fabrication can, at least partly achieve such a goal. Polydimethylsiloxane (PDMS)-containing copolymers are well known as such additives, the surface properties of conventional polymers that can be modified or improved by PDMS-containing copolymers include biocompatibility, hydrophobicity, surface finish and gloss, release properties, atomic oxygen resistance and reduction in friction [1–6].

Although PDMS-containing copolymers were usually introduced into epoxy resins [7,8], they were mainly used as toughness modifiers rather than surface modifiers. In other words, researchers seldom cared about the surface properties of the modified resins. In fact, sometimes the alteration of surface properties are also important to epoxy resins, for example, improving the oil and water repellency of epoxy resins coatings and lowering the friction of engineering parts cast by epoxy resins. Kasemura et al. have found that epoxy resins modified by aminopropyl-terminated PDMS had outstanding oil and water repellency [9]. But we found that aminopropyl-terminated PDMS were not

excellent modifiers for lowering the static friction coefficients ( $\mu_s$ ) of epoxy resins [10]. In this paper, polyether–polydimethylsiloxane–polyether triblock copolymers (PER–PDMS–PER) were added to epoxy resin matrices as surface modifiers, and it was expected to achieve a good result in the reduction of  $\mu_s$ . Effects of the structure and level of PER–PDMS–PER and the substrates used for casting and molding on the  $\mu_s$  and water contact angle were studied for both the air- and substrate-side surfaces. The enrichment of PDMS segments on the surfaces were characterized by ESCA measurement.

## 2. Experiments

### 2.1. Materials

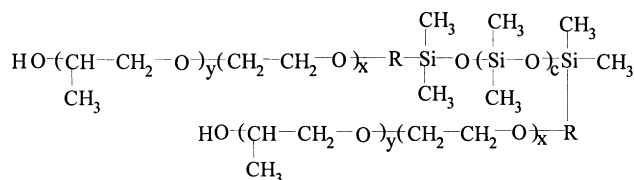
The epoxy resin used in this study was diglycidyl ether of bisphenol A (epoxy value 0.529), made by Shell Chemical Co. The curing agent was methylene dianiline (MDA). Allyl-terminated polyethers were the products of Nanjin Plastic Factory (P.R. China).

### 2.2. The synthesis of PER–PDMS–PER

PER–PDMS–PER was synthesized by hydrosilylation of bis-dimethylhydrogen siloxyl-terminated PDMS with allyl-terminated polyether. Its structural formula is shown in Scheme 1. In this paper, six kinds of PER–PDMS–PER

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Scheme 1. The structural formula of PER–PDMS–PER, R = C<sub>3</sub>H<sub>6</sub>.

are synthesized; their structural parameters determined by NMR are listed in Table 1.

### 2.3. Preparation of epoxy resin modified by PER–PDMS–PER

The PER–PDMS–PER/epoxy resin blend of a designed ratio was heated to 90–100°C and a stoichiometric amount of MDA was added. The mixture was stirred for 5 min to ensure complete dissolution of the curing agent, and then it was cast into the mold and cured at 100°C for 1 h and then at 150°C for 3 h. A sheet of resin having a size of 10 × 10 × 2 (thickness) was cast for water contact angle and ESCA measurements and a cylinder of 4 mm diameter and about 5 mm height was cast for  $\mu_s$  measurement. Three kinds of molds made of different substrates—stainless steel, silicone rubber and PTFE, respectively, were used. All the molds were washed by an ultrasonic washer in trichloromethane and dry in vacuum at 60°C for 1 h before casting, and all the samples were disposed by the same way before water contact angle,  $\mu_s$  and ESCA measurements.

### 2.4. Water contact angle measurement

Static water contact angles ( $\theta$ ) were measured at 20°C using a Contact Anglemeter CA-D (Kyowa Kagaku Co. Ltd.). Five drops of water were measured for each surface, and the average value was calculated.

### 2.5. Static friction coefficient measurement

The static friction coefficient ( $\mu_s$ ) of epoxy resin upon stainless steel was measured with the apparatus illustrated in Fig. 1. The surface asperity of stainless steel plate is about 0.1  $\mu\text{m}$ ; it was thoroughly rinsed with trichloromethane and vacuum dried before each test. The load ( $W$ ) weigh 1 kg and the driving rate was 10 mm per min. The driving force ( $F$ ) at the time when the sample started to move was recorded by

Table 1  
Structural parameters of PER–PDMS–PER

Code	Structural parameters calculated from NMR		
	$c$	$x$	$y$
Si-11	27 ± 3	25 ± 1	20 ± 1
Si-21	52 ± 3	25 ± 1	20 ± 1
Si-31	79 ± 4	25 ± 1	20 ± 1
Si-12	27 ± 3	12 ± 1	30 ± 2
Si-22	52 ± 3	12 ± 1	30 ± 2
Si-32	79 ± 4	12 ± 1	30 ± 2

force sensor, then  $\mu_s$  was calculated from  $F$  and  $W$ :  $\mu_s = F/W$ . Each sample was tested for five times, the average value of  $\mu_s$  was calculated.

### 2.6. ESCA spectra

ESCA spectra for modified epoxy resins were measured by an ES-300 photoelectron spectrometer (Kratos Co.) using a Mg K $\alpha$  X-ray source. The X-ray gun was operated at 15 kV and 10 mA and the analyser chamber pressure was  $1 \times 10^{-6}$  Pa. Two photoelectron take-off angles of 5 and 90° were used.

## 3. Result and discussion

### 3.1. Static friction coefficients and water contact angles

The static friction coefficients ( $\mu_s$ ) and water contact angles ( $\theta$ ) of epoxy resins modified by 5 phr PER–PDMS–PER and cast from stainless steel mold are shown in Table 2. For the air-side surfaces of modified resins,  $\mu_s$  were markedly lower and  $\theta$  were obviously higher than that of the unmodified sample. The structure of polyether blocks (the unit ratio of oxypropene/oxyethylene) had little influence on either  $\mu_s$  or  $\theta$  in this study, but the length of PDMS blocks had evident effect on  $\mu_s$ , a longer one led to a lower  $\mu_s$ .

Table 3 lists the atomic ratios of Si<sub>2p</sub> to C<sub>1s</sub> determined by ESCA of the air-side surfaces of samples modified by Si-12, Si-22 and Si-23 at 5 phr. At take-off angle of 5°, the atomic ratios of Si<sub>2p</sub> to C<sub>1s</sub> for the air-side surfaces of the above three samples had an almost identical value of ca. 0.45. This fact indicated that the length of PDMS block had little effect on the extent of PDMS enrichment of the topmost layer (ca.

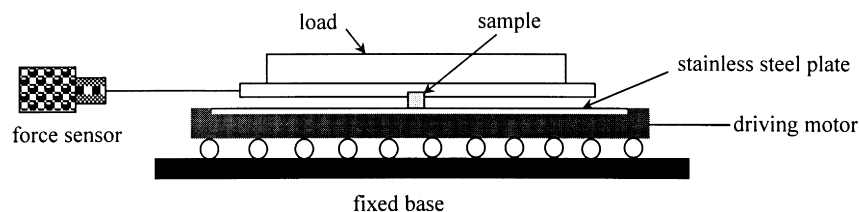


Fig. 1. The apparatus used to determine the static friction coefficient of epoxy resin.

Table 2  
Static friction coefficients ( $\mu_s$ ) and water contact angles ( $\theta$ ) of the epoxy resins modified by 5 phr PER–PDMS–PER

Modifier	Air-side surface		Stainless steel-side surface	
	$\mu_s$	$\theta$ (deg)	$\mu_s$	$\theta$ (deg)
Control	0.43	63	– <sup>a</sup>	– <sup>a</sup>
Si-11	0.22	86	0.32	72
Si-21	0.15	88	0.28	70
Si-31	0.12	88	0.25	71
Si-12	0.22	89	0.30	70
Si-22	0.14	87	0.27	70
Si-32	0.11	88	0.25	71

<sup>a</sup> The epoxy resin could not be demolded.

10 Å). At take-off angle of 90° (the sampling depth about 100 Å), the differences of the atomic ratios of Si<sub>2p</sub> to C<sub>1s</sub> among the air-side surfaces of the above three samples became evident, it suggested that PDMS block length influenced the PDMS gradient at surface. A longer PDMS block in the modifier led to a flatter gradient, and perhaps, this was the main reason why it led to a lower  $\mu_s$  of the modified epoxy resin as shown above.

The values of  $\theta$  suggested that PER–PDMS–PER were not excellent modifiers for improving oil and water repellency of epoxy resins compared with aminopropyl-terminated PDMS, probably because of a small difference in the enrichment extent of PDMS of the topmost layer between PER–PDMS–PER/epoxy blend and aminopropyl-terminated PDMS/epoxy resin blend [9]. However, the  $\mu_s$  of air-side surface of epoxy resin modified by 5 phr aminopropyl-terminated PDMS was 0.28 and it was obvious that PER–PDMS–PER were excellent modifiers for lowering the  $\mu_s$  of epoxy resins compared with aminopropyl-terminated PDMS so far as the air-side surfaces [10]. The reason was perhaps that the gradient of the accumulation extent of PDMS segment decreasing with the sampling depth in PER–PDMS–PER/epoxy blend was much flatter than that in aminopropyl-terminated PDMS/epoxy resin blend.

However, substrate-side surfaces are more important when epoxy resins are used for casting and molding rather than for coating. Unfortunately,  $\mu_s$  had much less decrease for stainless steel-side surfaces compared with that of air-

Table 3  
The atomic ratios of Si<sub>2p</sub> to C<sub>1s</sub> measured by ESCA of the air-side surfaces of epoxy resins modified by 5 phr PER–PDMS–PER

Modifier	Si <sub>2p</sub> /C <sub>1s</sub>	
	Take-off angle of 5°	Take-off angle of 90°
Si-12	0.447	0.225
Si-22	0.451	0.392
Si-32	0.445	0.423

Table 4  
Effect of substrates on the static friction coefficients ( $\mu_s$ ) and water contact angles ( $\theta$ ) of epoxy resins modified by 5 phr Si-22

Substrate	Air-side surface		Substrate-side surface	
	$\mu_s$	$\theta$ (degree)	$\mu_s$	$\theta$ (degree)
Stainless steel	0.14	86	0.27	70
Silicone rubber	0.14	87	0.13	87
PTEE	0.12	88	0.14	88

side surfaces as listed in Table 2. And stick-flip phenomena were usually observed during the tests for the unmodified sample and the stainless steel-side surfaces of modified resins, but never found for the air-side surfaces of the modified resins. Effect of the structure of PER–PDMS–PER on  $\theta$  and  $\mu_s$  for stainless steel-side surface was similar to that for air-side surface.

### 3.2. Effect of the substrates

The effect of the substrates used for casting and molding on  $\theta$  and  $\mu_s$  on the epoxy resins modified by 5 phr Si-22 is illustrated in Table 4. It was clear that  $\theta$  and  $\mu_s$  of the air-side surfaces hardly changed with the alteration of substrates. On the contrary,  $\theta$  and  $\mu_s$  of the substrate-side surfaces were greatly affected by the substrates, PTFE- and silicone rubber-side surfaces had lower  $\mu_s$  and higher  $\theta$  than stainless steel-side surface. The differences of  $\theta$  and  $\mu_s$  between air-side and substrate-side surface for PTFE and silicone rubber substrates were invisible, and stick-flip phenomena were not found for the PTFE- and silicone rubber-side surfaces of the modified resins during the tests.

Table 5 lists the atomic ratios of Si<sub>2p</sub> to C<sub>1s</sub> of air-, stainless steel-, silicone rubber- and PTFE-side surfaces of the above modified epoxy resins. Either photoelectron take-off angle was 5 or 90°, the atomic ratios of Si<sub>2p</sub> to C<sub>1s</sub> of the silicone rubber- and PTFE-side surfaces were almost equal to that of the air-side surfaces, and all of them were much higher than that of the stainless-side surface. This result probably can be explained by the apparent discrepancy of surface energy between stainless steel and PTFE or silicone rubber. It indicated that silicone rubber- and PTFE-side

Table 5  
Effect of substrates on the atomic ratios of Si<sub>2p</sub> to C<sub>1s</sub> by ESCA of epoxy resins modified by 5 phr Si-22

Surface	Si <sub>2p</sub> /C <sub>1s</sub>	
	Take-off angle of 5°	Take-off angle of 90°
Air-side	0.451	0.392
Stainless steel-side	0.187	0.156
Silicone rubber-side	0.433	0.386
PTEE-side	0.445	0.395

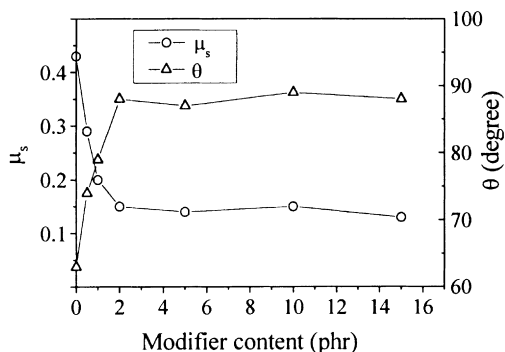


Fig. 2. Effect of the modifier content on the static friction coefficient ( $\mu_s$ ) and water contact angle ( $\theta$ ) of the silicone rubber-side surface of epoxy resin-modified by Si-22.

surfaces were enriched much more PDMS than stainless steel-side surface, and obviously, this led to the differences in  $\theta$  and  $\mu_s$  shown above.

The gradient of the enrichment extent of PDMS segments decreasing with the sampling depth seemed not to be influenced by the substrates as shown in Table 5.

### 3.3. Effect of the modifier content

Fig. 2 shows the effect of the modifier content on  $\theta$  and  $\mu_s$  of the silicon rubber-side surfaces of epoxy resins modified by Si-22 and cast from silicone rubber molds. When the modifier content was lower than 2 phr, an increase of modifier resulted in an abrupt reduction of  $\mu_s$  and an abrupt enlargement of  $\theta$ . The effect leveled off as the modifier content was above 2 phr.

Fig. 3 shows the relationship between the atomic ratios of  $\text{Si}_{2p}$  to  $\text{C}_{1s}$  of modified epoxy resins and the modifier contents. Here, we used atomic ratios that were obtained at the take-off angle of  $5^\circ$ . The relationship was similar to that between the modifier content and  $\theta$  and  $\mu_s$ . It suggested that PDMS enrichment arrived to the highest degree at 2 phr modifier.

## 4. Conclusions

PER–PDMS–PER were not promising surface modifiers for improving the oil and water repellency of epoxy resins, but they were excellent ones for reducing the  $\mu_s$  of epoxy resins upon stainless steel. A longer PDMS segment in

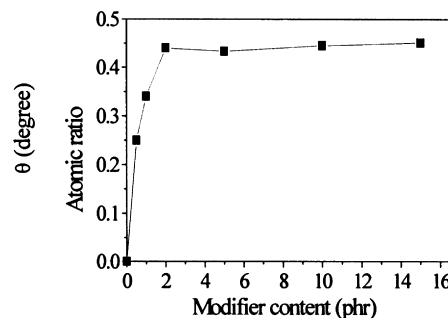


Fig. 3. Relationship between the atomic ratio of  $\text{Si}_{2p}$  to  $\text{C}_{1s}$  and the modifier content of the silicone rubber-side surface of epoxy resin modified by Si-22 at photoelectron take-off angle of  $5^\circ$ .

PER–PDMS–PER led to a lower  $\mu_s$ . An increase of modifier resulted in an abrupt reduction of  $\mu_s$  and the effect leveled off as the modifier content was above 2 phr. The substrates used for casting and molding have no effect on the  $\mu_s$  of the air-side surfaces but have evident effect on that of the substrate-side surfaces. The  $\mu_s$  of silicone rubber- and PTFE-side surfaces were evidently lower than that of stainless steel-side surface. ESCA investigation showed that a longer PDMS block in modifier resulted in a flatter gradient of the enrichment extent of PDMS segment decreasing with the sampling depth, and the degree of PDMS accumulation on PTFE- and silicone rubber-side surfaces were much higher than that on stainless steel-side surface.

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