

MODIFICATION OF EPOXY RESIN WITH POLYSILOXANE BEARING PENDANT QUATERNARY AMMONIUM GROUPS

Zuo-xin Huang, Ying Huang* and Yun-zhao Yu

*The State Key Laboratory of Engineering Plastics, Institute of Chemistry,
Chinese Academy of Sciences, Beijing 100080, China*

Abstract Polysiloxane bearing pendant quaternary ammonium groups (PSI) was used to modify the surface properties of epoxy resins. In the cured resin, PSI formed the dispersed phase. Remarkable enrichment and gradient distribution of polysiloxane on the surface region of the epoxy resins were demonstrated by XPS analysis. The composition and properties of the surface of PSI-modified epoxy resin, which is in contact with the mold, are dependent on the material of the mold. Through the incorporation of PSI, epoxy resins with low surface energy and low friction coefficient were obtained. Polysiloxane with lower ionic group content shows a higher degree of enrichment on the resin surface and leads to a higher contact angle against water, while the polysiloxane having optimum compatibility with the epoxy resin shows a greater effect in reducing the static friction coefficient of the resin against glass.

Key words Polysiloxane, Epoxy resin, Surface composition, Friction coefficient

INTRODUCTION

Epoxy resins are of great technical importance. They usually have relatively high surface energies and high friction coefficients. Therefore, surface modification of epoxy resin is desirable for many applications. In order to reduce their friction coefficient, polydimethylsiloxanes, because of their low surface energy, have been incorporated into epoxy resins^[1, 2]. However, owing to the great difference in their solubility parameter, it is extremely difficult to disperse polysiloxane in epoxy resin by simple blending. Functional groups, such as amino, phenolic hydroxyl and carboxyl groups, which can react with epoxy resin, have been introduced into the polysiloxane molecules^[3–7]. In this way the polysiloxane molecular chains were chemically bound to the network of the epoxy resin. The compatibility between the polysiloxane and the resin matrix was thus improved; but the enrichment of the polysiloxane on the surface region was hindered. It has been found that the polysiloxane-polyether block copolymers and graft copolymers without reactive group were effective for reducing the friction coefficient of the epoxy resin^[8].

It is usually the case that introduction of a small amount of ionic group will give rise to great changes in the properties of the parent polymer. Polymers with ionic groups can be used for improving the compatibility of polymer blends. In this work, we study the polysiloxane/epoxy resin systems, in which polysiloxanes bearing dimethyl-hydroxyethyl-silylpropyl ammonium chloride pendant groups were used as the modifier. The effects of the polysiloxane modifier on the morphology, surface composition and surface properties of the modified epoxy resins were investigated.

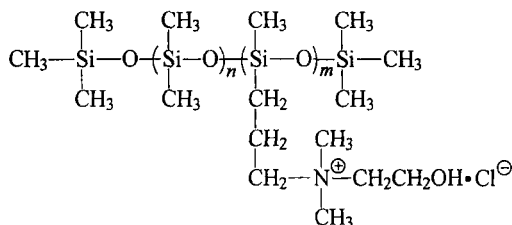
* Corresponding Author: Ying Huang (黄英), E-mail: Ying2Huang@yahoo.com.cn

Received January 17, 2002; Revised March 4, 2002; Accepted March 6, 2002

EXPERIMENTAL

Material

Polysiloxanes bearing quaternary ammonium groups (PSI) were prepared in this laboratory through the Menshutkin reaction^[9, 10]. The structure of PSI is shown in Scheme 1, and its structure parameters are listed in Table 1.



Scheme 1 Structural formula of PSI

Table 1. Structure parameters of PSI used in this study

Sample	<i>n</i>	<i>m</i>	Ionic group content (mmol/g)
PSI-1	74	4	0.76
PSI-2	73	8	1.09
PSI-3	64	13	1.66
PSI-4	75	20	1.96

The epoxy resin was the diglycidyl ether of bisphenol A (epoxy value 5.18 mmol/g) obtained from Shell Chemical Co. The curing agent, 4,4'-diaminodiphenylmethane (DDM), was supplied by Beijing Chemicals Factory, and purified by recrystallization from ethanol.

Preparation of PSI-Modified Epoxy Resins

Epoxy resin and PSI in designate ratios were mixed and heated to 90–100°C. A stoichiometric amount of DDM was introduced. The mixture was stirred vigorously for 5 min to ensure complete dissolution of the curing agent, and then evacuated to eliminate air bubbles. The blend was cast into molds and cured consecutively at room temperature for 24 h, 100°C for 24 h and 160°C for 5 h, respectively. After mold stripping the surface of the specimen was cleaned with ethanol to remove any contaminants, and dried at 50°C under vacuum (1.3 kPa) for 3 h before analysis and measurements.

Measurements

The elemental composition of the surfaces of the PSI-modified epoxy resins was determined by X-ray photoelectron spectroscopy with an ESCA 220I-XL spectrograph (VG Co.). The morphology of the fracture surfaces of the cured PSI-modified epoxy resins was studied by SEM microscopy using a Hitachi S-530 scanning electron microscope.

The contact angle of the resin surfaces against water was measured on a CA-D contact-anglemeter of Kyowa Kagaka Co. Ltd. The friction coefficient of epoxy resin against glass plate was measured under a load of 1 MPa using a home made set-up, in which the friction pair was moved at a speed of 10 mm/min and the applied force was recorded. The first peak in the force versus displacement curve was taken for the calculation of the static friction coefficient. Five measurements were made for each specimen.

RESULTS AND DISCUSSION

Morphology of PSI-modified Epoxy Resins

It is known that polydimethylsiloxanes are not compatible with the epoxy resin. A mixture of these two substances separates into two layers on standing. The compatibility was improved by the introduction of dimethyl-hydroxyethyl-silylpropyl ammonium chloride pendant groups so that stable dispersions of PSI in epoxy

resin can be obtained.

The SEM micrographs of the fracture surfaces of the epoxy resins modified with 2 phr (parts per hundred parts resin) PSI are shown in Fig. 1. It can be seen that the polysiloxane aggregates to form the dispersed phase, distributed randomly in the epoxy resin. The domain size of dispersed phase depends on the ion group content: it decreases from *ca.* 10–30 μm to *ca.* 2 μm as the ion group content of the polysiloxane increases from 0.76 mmol/g to 1.66 mmol/g. However, a further increase of the ion group content does not lead to a reduction in domain size of the dispersed phase; a slight rise was observed instead. The polysiloxane PSI-3 bearing 1.66 mmol/g ionic group is considered to have optimum compatibility with the epoxy resin.

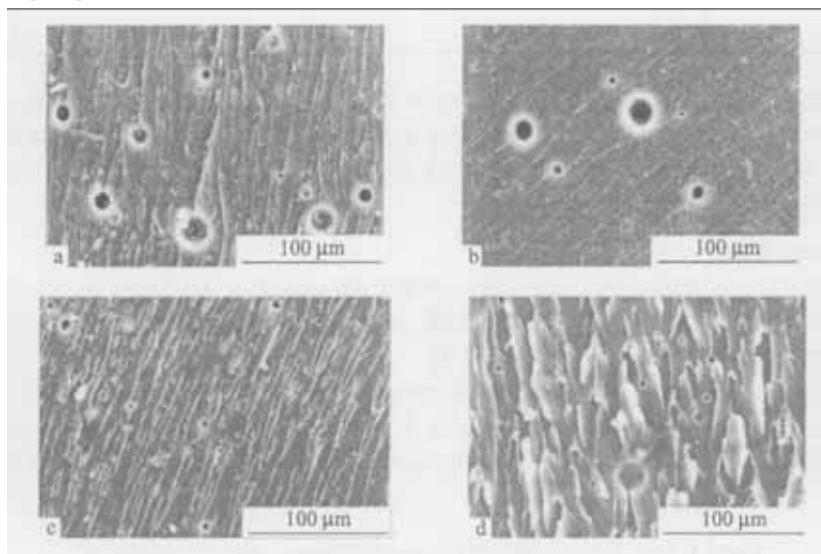


Fig. 1 SEM photographs for the PSI-modified epoxy resins

a) PSI-1; b) PSI-2; c) PSI-3; d) PSI-4

The concentration of polysiloxane was 2 phr.

Another important factor influencing the morphology of cured epoxy resin is the concentration of the polysiloxane modifier in the system. The domain size of the dispersed phase increased dramatically with the increase in the level of the polysiloxane. The average particle diameter of the dispersed phase was 0.3 μm for the resin containing 0.5 phr PSI-3. It became 2 μm and 35 μm as the concentration of PSI-3 increased to 2 phr and 4 phr, respectively. The large particles were unstable; they will bleed out to make the surface of the epoxy resin oily.

Surface Composition of the Modified Resins

The surface elemental composition of the cured resin surfaces within 10 nm depth was analyzed by XPS. The analysis results of the epoxy resin modified with 2 phr PSI-1 and PSI-3 are summarized in Table 2. It can be seen that the Si/C ratios in the surface region are much higher than that calculated according to the bulk composition. The polysiloxane tends to migrate to the surface of the resin and forms a polysiloxane-rich layer. This tendency was stronger in the system with PSI-1 as modifier, in which the ionic group concentration was lower.

The Si/C atomic ratio in the surface contacted with the mold depends on the kind of materials of which the mold is made. It is remarkable that polysiloxane was enriched on the surface contacted with mold of low surface energy (PTFE and silicone rubber) to a higher degree than on the surface contacted with mold of high surface energy (glass). This is reasonable based on thermodynamic principles: enrichment of polysiloxane at the interface contacted with surface of low energy will lower the free energy of the system. Enrichment on the surface contacted with glass is still significant, though to a lower degree. This may be attributed to the adsorption of the ionic group by the glass.

Table 2. Surface composition of the epoxy resin modified with 2 phr PSI

System	Material for mold	Si/C atomic ratio		
		Determined by XPS		Calculated according to the average composition
		Take off angle 45°	Take off angle 90°	
Epoxy/PSI-1	Silicone rubber	0.253	0.180	0.0034
Neat PSI-1	—	—	—	0.431
Epoxy/PSI-3	Silicone rubber	0.123	0.111	0.0028
Epoxy/PSI-3	Glass	0.087		0.0028
Epoxy/PSI-3	PTFE	0.144		0.0028
Neat PSI-3	—	—	—	0.339

By changing the take-off angle of photoelectrons in the XPS experiments, the gradient distribution of the polysiloxane modifier was demonstrated. The sampling depth for the take-off angle 45° was lower than that for the take-off angle 90°. Therefore, we can see that the polysiloxane concentration in the outermost surface is higher than that in the sub-surface region.

Contact Angle against Water

The contact angle of PSI-modified epoxy resin against water was used as a simple and direct criterion for surface energy. The contact angle for neat epoxy resin was 68°. Incorporation of the polysiloxane modifier resulted in remarkable rise of the contact angle (see Table 3 and 4).

The experimental values of contact angle for the epoxy resins modified with 2 phr PSI-3, which were cured in molds made of different materials, are given in Table 3. This difference in the value of contact angle could be attributed to the different degree of enrichment of polysiloxane modifier on the surface of the resins, as indicated by Table 2.

Table 3. The contact angles of PSI-modified epoxy resins against water^a

Mold material	Contact angle (°)
Stainless steel	78
Glass	78
Silicone rubber	93
PTFE	99

^a The epoxy resin was modified with 2 phr PSI-3.

The variation of contact angle with the concentration of PSI-3 is shown in Fig. 2. It can be seen that the contact angle rises rapidly with the increase of the concentration of the polysiloxane in the resin at the beginning, and then levels off when the concentration reaches about 2 phr. The coverage of the resin surface by polysiloxane segments seems saturated at this concentration of PSI-3.

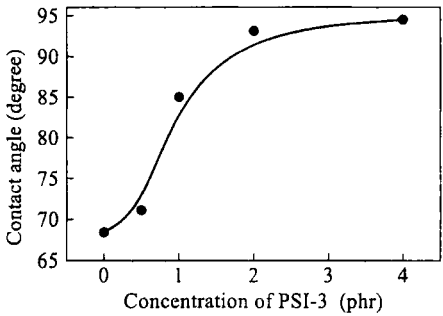


Fig. 2 Variation of contact angle with the concentration of PCI-3
The mold was made of silicone rubber.

Friction Coefficient of the Modified Resins

Enrichment of polysiloxane modifier on the surface resulted in a substantial reduction of friction coefficient. The static friction coefficient of neat epoxy resin against glass plate was 0.46. The static friction coefficient data of epoxy resin modified with 2 phr PSI are listed in Table 4. It is seen that all the polysiloxanes with different ionic group content are effective in enhancing the contact angle against water and reducing the static friction coefficient. However, the effects for enhancing the contact angle and for reducing the friction coefficient are not equivalent: PSI-1 with lower ion group content is more effective in enhancing the contact angle, while PSI-3, which has optimum compatibility with the epoxy resin, is more effective in reducing the friction coefficient. This is understandable since the contact angle is mainly dependent on the thermodynamic properties of the outermost surface, while the friction coefficient is affected by the mechanical propertoies of the surface as well.

Table 4. Surface properties of the epoxy resin modified with 2 phr PSI^a

PSI modifier	Ionic group content (mmol/g)	Contact angle against water (degree)	Static friction coefficient against glass
Control	—	68	0.46
PSI-1	0.76	105	0.29
PSI-2	1.09	101	0.29
PSI-3	1.66	93	0.23

^a The mold was made of silicone rubber.

CONCLUSIONS

The compatibility of polysiloxane with epoxy resin was improved by introduction of quaternary ammonium groups into the polysiloxane molecule. In the PSI-modified epoxy resins, polysiloxane formed the dispersed phase. Enrichment and gradient distribution of the polysiloxane on the surfaces of the cured resin were identified by XPS analysis. The degree of polysiloxane enrichment on the surface contacted with the mold depends on the surface nature of the mold. Polysiloxane with lower ion group content shows a higher degree of enrichment on the surface and leads to a higher contact angle against water. However, the polysiloxane of optimum compatibility with epoxy resin shows a greater effect in reducing the static friction coefficient of the resin against glass.

Acknowledgement The authors are grateful to the Dow Corning Corp., Midland, U.S.A. for its financial support.

REFERENCES

1 Hu, T.Y., Eiss, N.S., Yorkgitis, E.M., Wilkes, G.L., Tran, C., Yilgor, I. and McGrath, J.E., Polym. Mater. Sci. Eng., 1983, 49: 508

2 Eiss, N.S. and Szichos, Wear, 1986, 111: 347

3 Shieh, T.Y., Ho, T.H. and Wang, C.S., Angew. Makromol. Chem., 1997, 245: 125

4 Yilgor, E. and Yilogr, I., Polymer, 1998, 39(8–9): 1691

5 Meijerink, J.I., Eguchi, S., Ogata, M., Ishii, T., Numata, S. and Sashima, H., Polymer, 1994, 35(1): 179

6 Takahashi, T., Nakajima, N. and Saito, N., “Rubber Toughened Plastics”, Adv. Chem. 221, American Chemistry Society, Washington D.C., 1989, p.243

7 Kasemura, T., Kashima, Y. and Kawamoto, K., J. Adhesion, 1990, 33: 19

8 Huang, W., Yao, Y., Huang, Y. and Yu, Y., Polymer, 2001, 42: 1763

9 Huang, Z. and Huang, Y., Journal of Functional Polymers (in Chinese), 2000, 13(4): 367

10 Huang, Z., Yu, Y. and Huang, Y., J. Appl. Polym. Sci., 2002, 83(14): 3099