

Preparation and Characterization of Polysiloxane-Modified Epoxy Resin Aqueous Dispersions and Their Films

Li Ding,^{1,2} Gui You Wang,^{1,2} Chun Pu Hu,^{1,2} Shu Sen Wu²

¹Key Laboratory for Ultrafine Materials, Ministry of Education, Shanghai 200237, People's Republic of China

²School of Materials Science and Engineering, East China University of Science and Technology, Shanghai 200237, People's Republic of China

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ABSTRACT: Polysiloxane-modified epoxy resin aqueous dispersions were prepared by the reaction of amino-polysiloxane (APS) with a graft epoxy resin that was synthesized with a diglycidyl ether of bisphenol A type epoxy resin and styrene/acrylic acid. The measurements of the epoxy values and FTIR spectra confirmed that this reaction really took place. The modified aqueous dispersion exhibits high viscosity, small particle size, and nearly the same surface tension as the unmodified one. Therefore, this indicates that the siloxane segments could be encapsulated into graft epoxy resin particles during the water dispersion process. For APS-modified films, the thermal stability and water resistance are

remarkably enhanced. Furthermore, lowering of the hardness and surface tension for these films was also observed and the surface composition was measured by X-ray photoelectron spectroscopy. The experimental data indicate that the siloxane segments easily migrate onto the surface during the film formation process and finally enrich on the surface of the APS-modified film. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 98: 880–885, 2005

Key words: epoxy resin; polysiloxane; aqueous dispersion; surface; thermal property

INTRODUCTION

Epoxy resins are widely used as coatings and adhesives because of their good adhesion for a number of substrates; however, they are easily contaminated by oil, grease, dirt, or other impurities resulting from their high surface energy.¹ It is well known that polysiloxane has an extremely low surface energy and exhibits excellent performance for oil and water repellency. Other attractive features for this kind of material include good thermal stability, oxidation resistance, weatherability, cryogenic properties, and high dielectric strength.² Modification of an epoxy resin by polysiloxane is an effective way to enhance the hydrophobicity, toughness, and heat resistance for a highly crosslinked epoxy resin system. Various research works on polysiloxane modification of epoxy resin have been published. Lin and Huang³ prepared a siloxane-incorporated epoxy copolymer with hot-melt polycondensation of bisphenol A type epoxy resin and hydroxy-terminated poly(dimethylsiloxane) (PDMS) or methoxy-terminated poly(methylphenyl siloxane), which caused the increase of the impact strength and

thermal stability when increasing the polysiloxane content. Huang et al.⁴ incorporated polyether-PDMS-polyether triblock copolymer (PER-PDMS-PER) into an epoxy resin to improve its surface properties. It was found that a long PDMS block in PER-PDMS-PER and a high content of block copolymer in the epoxy resin led to a low static friction coefficient of modified epoxy resins upon stainless steel. Shieh et al.⁵ reported that amine-terminated PDMS could be used to increase the toughness of a cresol-formaldehyde novolac epoxy resin cured with a phenolic novolac resin for an electronic encapsulation application. Kasemura et al.⁶ found that epoxy resins modified by aminopropyl-terminated PDMS showed good oil and water repellency. Up till now, with increasing environmental criteria, the importance of waterborne epoxy resins has been increased, especially in the modern coating industry; but the hydrophilic groups existing in the macromolecular chains deteriorate the water resistance of the final cured resin film. Therefore, it is thought that the water resistance of the film formed by a waterborne epoxy resin could be enhanced by introducing siloxane segments. Thus far, however, there are few reports on a polysiloxane-modified epoxy resin aqueous dispersion. In a previous article⁷ we reported an epoxy resin/silica sol hybrid aqueous dispersion and found that the water resistance of the cured hybrid system was appreciably enhanced. In this study an amino-terminated polysiloxane-modi-

Correspondence to: C. P. Hu (cphu@guomai.sh.cn).

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fied epoxy resin aqueous dispersion is prepared and characterized. Furthermore, the surface properties of the film formed by this kind of modified aqueous dispersion are reported.

EXPERIMENTAL

Materials

Diglycidyl ether of bisphenol A (DGEBA) type epoxy resin (E-03, epoxy value = 0.03 mol/100 g) was obtained from Shanghai Resin Factory and methoxylated melamine (R747) was purchased from Solutia Inc. Methacrylic acid (MAA, AR) was obtained from Shanghai Reagent Academe. Styrene (St, analytical reagent grade) and benzoyl peroxide (BPO, analytical reagent grade) were produced by Shanghai Lingfeng Chemical Reagent Co. Triethylene amine (chemically pure) and butanol (chemically pure) were made by Shanghai Feida Industry and Trade Co. Propylene glycol monobutyl ether (PGMBE, chemically pure) was obtained from Shanghai Coating Sales Co. Amino-polysiloxane (APS, 2-8822A, amino percentage = 0.65%) was kindly supplied by Dow Corning Co. BPO was refined by recrystallization (i.e., dissolution using chloroform and then precipitation using ethanol). Other materials were used as received.

Preparation of graft epoxy aqueous dispersions

A 500-mL four-necked round-bottomed flask equipped with a mechanical stirrer, condenser, nitrogen inlet, and thermometer was charged with E-03 and a small amount of mixed solvent (PGMBE/butanol = 2, w/w) and heated at around 110°C until the epoxy resin was dissolved. Then, the mixture of MAA, St, and BPO was added dropwise. After that it was reacted at this temperature for 3 h to attain the graft epoxy resin. The product was cooled to 60°C and neutralized with triethylene amine. Finally, water was added to disperse the graft epoxy resin under high speed agitation. The solid content for such water dispersion is 33%. The detailed preparation and characterization of the epoxy resin aqueous dispersion were described elsewhere.⁷

Preparation of polysiloxane-modified epoxy resin aqueous dispersions

APS was added into the graft epoxy resin prepared as mentioned above and reacted at 120°C for 4 h. Then, the reaction product was cooled to 60°C and neutralized with triethylene amine. After that water was added to obtain the polysiloxane-modified epoxy resin aqueous dispersion (solid content = 30–33 wt %).

TABLE I
Physical Properties of Epoxy Resin Aqueous Dispersions with Various Amounts of Amino-polysiloxane

Samples	APS/graft epoxy resin (w/w)	Viscosity (mPa s)	Particle diameter (nm)	γ_1 (mN m ⁻¹) 25°C
GE	0	63	121	27.4
SiGE-1	1.9/100	180	111	27.2
SiGE-2	3.8/100	190	107	27.2
SiGE-3	7.7/100	225	108	27.1
SiGE-4	11.5/100	245	101	27.0
SiGE-5	19.2/100	340	91	26.9

Preparation of films

The modified or unmodified graft epoxy resin aqueous dispersion was mixed with methoxylated melamine as a curing agent stoichiometrically, coated on a glass panel, and cured at 160°C for 20 min. The film was then dried under a vacuum at 60°C to reach constant weight.

Characterization

The epoxy value of the specimen taken from the reaction process was measured using the hydrochloric acid and acetone method according to HG2-741-72. The FTIR spectra of the aqueous dispersion were obtained with a Nicolet Magna-IR550 spectrometer. The viscosity of the aqueous dispersion was measured by an NDJ-79 rotation viscometer at 25°C. The particle size and distribution of the aqueous dispersion were tested by means of a Microtrac UPA 150 particle size analyzer. A QBY type pendulum durometer was employed for the measurement of the hardness of the film surface according to GB/T 1730-93. The contact angle of the liquid on the film was measured using a JC2000A contact angle measurer. Thermogravimetric analysis for the film was performed on a WRT-1 type thermogravimetric analyzer from 50 to 500°C at a heating rate of 10°C/min. X-ray photoelectron spectroscopy (XPS) analysis of the film surface was carried out using a PHI 5000C ESCA system and a monochromatic Al K α X-ray source operating at 250 W.

RESULTS AND DISCUSSION

Polysiloxane-modified epoxy resin aqueous dispersions

The polysiloxane-modified epoxy resin aqueous dispersions prepared with different APS contents are listed in Table I. Taking SiGE-3 as an example, the epoxy values at the end point of the synthesis of the graft epoxy resin and the end point of the synthesis of the polysiloxane-modified graft epoxy resin were measured and are listed in Table II. The table shows

TABLE II
Epoxy Value of Products During Preparation
Process of SiGE-3

Type of product	Epoxy value (mol/100 g)	
	Calcd	Found
Grafting reaction	0.0105	0.0092
Polysiloxane modification	0.0081	0.0062

that the determined epoxy value was a bit lower than the calculated value when the grafting reaction of the epoxy resin with MAA/St was stopped. It is clear that some epoxy groups in the system can react with the carboxyl groups existing in MAA during the grafting reaction. After adding APS in this system, the determined epoxy value dropped further to 0.0062, which was also lower than the calculated one. This indicates that not only all of the primary amino groups can react with epoxy groups, but also around 30% of the secondary amino groups created can further react with epoxy groups, as shown in Figure 1.

Figure 2 provides the FTIR spectra of the APS-modified epoxy aqueous dispersion and a comparable specimen. A weakened characteristic absorption peak of the epoxy group at 906 cm^{-1} for the modified specimen was observed as a result of the reaction between the amino groups and the epoxy groups. Furthermore, the absorption peak of hydroxy group was found to widen and shift from 3403 to 3368 cm^{-1} after the modification process, because the absorption peak of N—H also existed in this wavenumber range and the hydrogen bond between the unreacted secondary amino group and the hydroxy group in epoxy resin could form. All of these experimental results show that the reactions between the amino and epoxy groups really take place to form block and graft copolymers during the process for preparing the polysi-

loxane-modified epoxy resin aqueous dispersions (see Fig. 1).

Table I shows that the particle size of the modified aqueous dispersion decreases with increasing content of APS, but its viscosity increases. As described, polysiloxane exhibits strong hydrophobicity. Thus, during the dispersion process of the block and graft copolymers composed of polysiloxane and graft epoxy resin into water, the siloxane segments should have been wrapped by the graft epoxy resin chains containing hydrophilic groups and were inside of the particles. In this case, the formation of hydrogen bonds between the secondary amino group in the siloxane segments and the hydroxy groups in the epoxy resin could be expected to decrease the particle size as the water swollen volume of the particle decreases.⁷ In general, for a water dispersion the relationship between the distance of particles (h) and the particle diameter (d) can be described as follows⁸:

$$h = \left[\left(\frac{0.74}{\Phi} \right)^{1/3} - 1 \right] \times d \quad (1)$$

Thus, for a definite volume fraction (Φ) the distance between two small particles decreases, leading to strong interactions among particles and therefore the high viscosity of the system. At the same time, the electrical density on the particle surface is enhanced by reducing the particle size, also giving rise to the increase of the viscosity of the system.

The surface tension of different APS-modified epoxy resin aqueous dispersions was tested, and the values are listed in Table I. It shows that they are nearly the same as that of the unmodified epoxy resin aqueous dispersion and far from the surface tension of polysiloxane (21 mN/m) reported in the literature.⁹ These experimental data clearly indicate that the siloxane segments should be wrapped inside the graft epoxy resin particles.

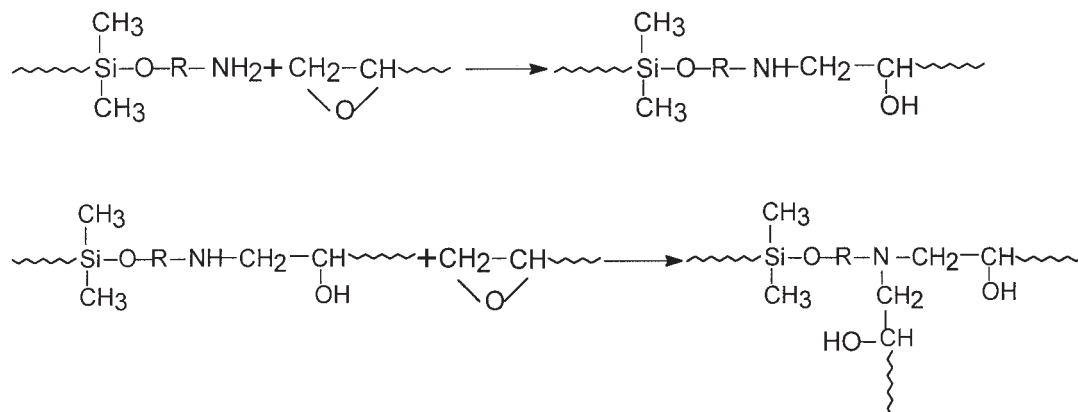


Figure 1 A schematic diagram of the reaction between the amino group and epoxy group during the modification of graft epoxy resin with amino-polysiloxane.

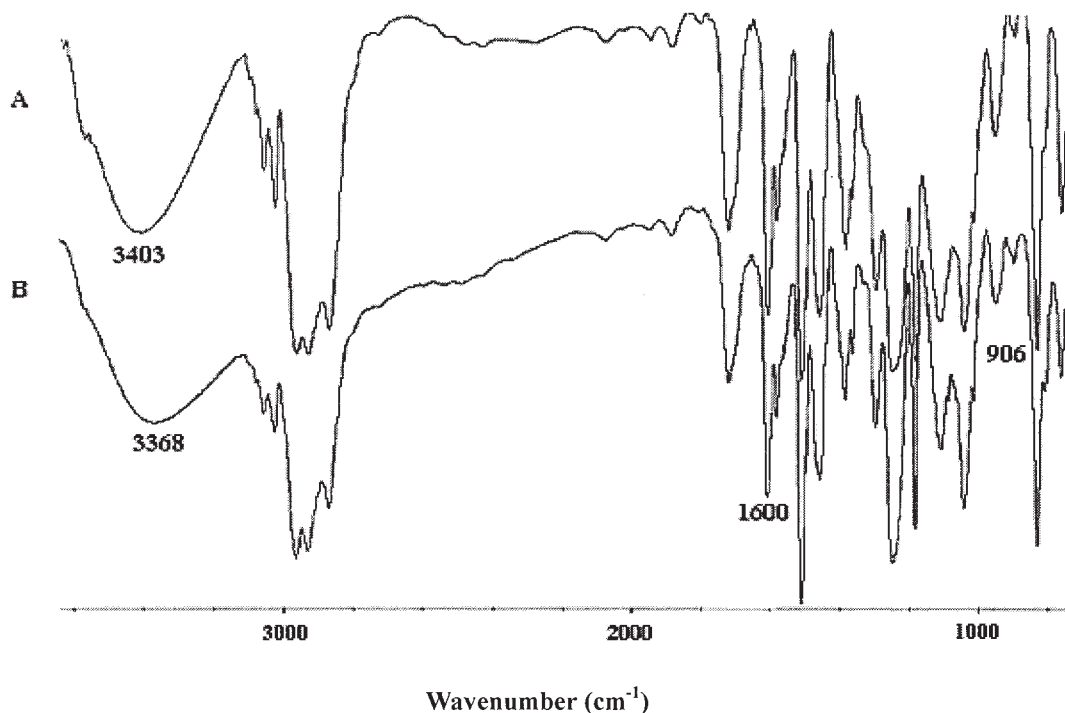


Figure 2 FTIR spectra of GE (spectrum A) and SiGE-2 (spectrum B).

Physical properties of films

The hydrophobicity and hardness of the films formed by the APS-modified epoxy resin aqueous dispersion were examined and the results are provided in Table III. It indicates that the contact angle of the water on the modified film surface evidently increases with increasing APS content, resulting from the migration of hydrophobic siloxane segments onto the film surface. For the most hydrophobic film of SiGE-5 in Table III and the comparable film of GE, the contact angles of water and ethylene glycol on these film surfaces were measured (contact angles of ethylene glycol on GE film and SiGE-5 film surfaces = 55 and 86°, respectively) and used to calculate their surface energy according to the following equations provided by the harmonic-mean method¹⁰:

$$(1 + \cos \theta_1)\gamma_1 = 4\left(\frac{\gamma_1^d \gamma_s^d}{\gamma_1^d + \gamma_s^d} + \frac{\gamma_1^p \gamma_s^p}{\gamma_1^p + \gamma_s^p}\right) \quad (2)$$

$$(1 + \cos \theta_2)\gamma_2 = 4\left(\frac{\gamma_2^d \gamma_s^d}{\gamma_2^d + \gamma_s^d} + \frac{\gamma_2^p \gamma_s^p}{\gamma_2^p + \gamma_s^p}\right) \quad (3)$$

where the subscripts 1 (water) and 2 (ethylene glycol) represent two kinds of standard liquids with known surface energy and the superscripts *d* and *p* stand for the dispersion and polar parts of the surface energy, respectively. The calculated results are listed in Table IV. They show that the surface energy of the SiGE-5 film, including the dispersion part and the polar part, decreases remarkably compared with that of the GE film.

Furthermore, the surface composition of SiGE-5 film was measured by XPS (Table V). It is obvious that the contents of silicon and oxygen elements on the surface are much higher than the calculated values, but they decrease quickly along the lines of thickness (i.e., 7- and 15-nm depth underneath the

TABLE III
Physical Properties of Polysiloxane Modified Epoxy Films

Samples	Contact angle of water on film (°)	Hardness of film surface
GE	86	0.94
SiGE-1	94	0.93
SiGE-2	98	0.93
SiGE-3	103	0.92
SiGE-4	103	0.92
SiGE-5	104	0.88

TABLE IV
Surface Energy of SiGE-5 and GE Films at 25°C

Samples	γ_s^d (mN m ⁻¹)	γ_s^p (mN m ⁻¹)	γ_s (mN m ⁻¹)
GE	17.3	12.2	29.5
SiGE-5	7.4	10.1	17.5

TABLE V
Surface Element Composition of SiGE-5 Film

Treatment condition	Element composition ^a (wt %)			
	C	O	Si	N
Without Ar ⁺ etching	67.6	20.5	9.0	2.9
After Ar ⁺ etching				
15 min ^b	82.3	9.6	5.2	2.9
30 min ^c	86.0	7.5	3.8	2.8

^a The calculated values for C, O, Si, and N are 74.9, 16.3, 5.5, and 3.3 wt %, respectively.

^b Around 7-nm depth.

^c Around 15-nm depth.

surface). These experimental data should be attributed to the enrichment of —Si—O— groups on the surface as consistent with the calculated surface energy of this specimen. In this case, the lowering of the carbon content on the surface of this film could be expected. However, it should be pointed out that in the system the nitrogen element mainly came from the neutralizer (triethylene amine) and the curing agent (methoxylated melamine) and the nitrogen element coming from the APS was very low. Thus, the enrichment of siloxane segments on the surface should have little effect on the distribution of nitrogen along the thickness of the sample.

It is of interest to note in Table III that the hardness of all modified film surfaces is lower than that of a comparable film (GE) surface and it gradually decreases with the increase of polysiloxane content as a result of the enrichment of flexible siloxane segments on the surface. Figure 3 shows the thermogravimetric

TABLE VI
Heat Resistance of Polysiloxane Modified Epoxy Films

Samples	Temperature at weight loss percentages (°C)			
	10%	20%	50%	60%
GE	263	339	386	397
SiGE-2	284	340	386	396
SiGE-3	309	351	400	427

curves for the GE film. The temperature values at different weight loss percentages are listed in Table VI. It exhibits that the heat resistance of SiGE-2 and SiGE-3 films is enhanced by increasing the content of polysiloxane, resulting from the higher bond energy for Si—O (477 kJ/mol) than that for C—C (334 kJ/mol).¹¹

CONCLUSION

A new kind of polysiloxane-modified epoxy resin aqueous dispersion was prepared by the reaction of APS with a graft epoxy resin. The viscosity of the modified aqueous dispersion increased and the particle size decreased, but the surface tension of the aqueous dispersion remained almost constant. The hydrophobicity and thermal stability of the films formed by such modified aqueous dispersions enhanced the hardness, and the surface tension of these films decreased as a result of the enrichment of siloxane segments on the surface of the film.

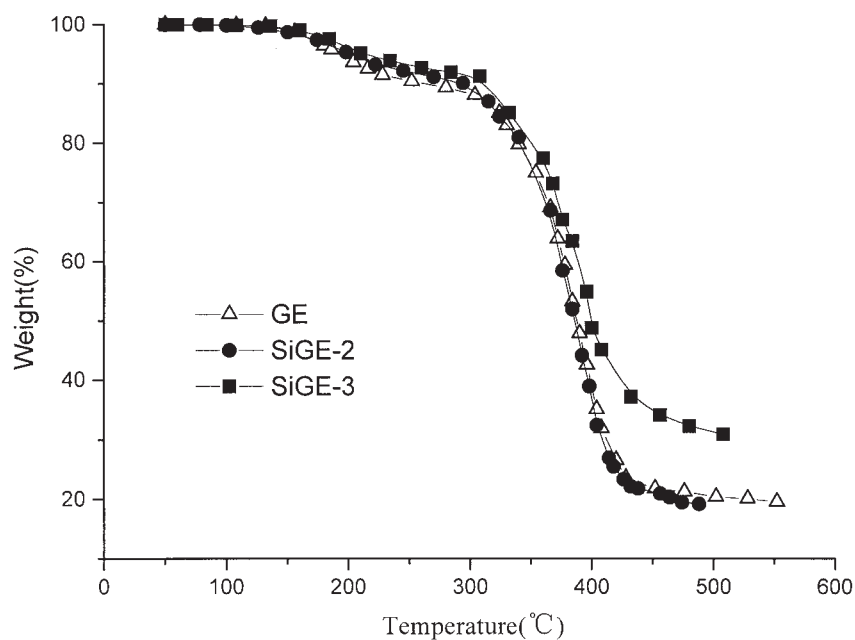


Figure 3 Thermogravimetric analysis of modified films (SiGE-2 and SiGE-3) and a comparable film (GE).

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