

PHASE STRUCTURE AND PROPERTIES OF EPOXY RESIN MODIFIED BY POLYSILOXANE BEARING PENDANT AMINO GROUPS

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Abstract Polysiloxane-modified epoxy resins were prepared through the reaction of epoxy resin with polydimethylsiloxanes bearing pendant *N*-(β -aminoethyl)- γ -aminopropyl groups. The morphology and properties of the cured epoxy resins modified by the polysiloxanes were investigated. It was found that the phase structure and properties of the cured epoxy resins depend mainly on the amino group content in the polydimethylsiloxane and the level of the modifier. The change of phase structure in the cured epoxy resin systems was responsible for the dramatic change in their mechanical and surface properties.

Key words Phase structure, Polysiloxane, Epoxy resin, Mechanical property

INTRODUCTION

Based on the excellent flexibility and unique low surface energy, polysiloxanes were incorporated into epoxy resins to reduce their modulus and to improve their surface properties^[1-3, 10]. Owing to the great difference in the solubility parameter, it is difficult to disperse polysiloxane in epoxy resin by simple blending. Functional groups, such as amino, hydroxyl and carboxyl group, have been introduced into polysiloxane molecules to increase their compatibility with epoxy resin. By means of functional group reactions polysiloxane soft blocks were chemically bonded to the resin matrix. It has been found that the phase structure of the cured epoxy resin can exert a decisive effect on its properties^[4-6]. In the present work, the particularity in the phase structure and properties of epoxy resins modified with polydimethylsiloxanes bearing pendant *N*-(β -aminoethyl)- γ -aminopropyl groups was investigated.

EXPERIMENTAL

Materials

The epoxy resin (ER) 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). The polysiloxanes bearing pendant amino-groups (APS) were prepared by the base-catalyzed copolymerization and rearrangement of poly[methyl *N*-(β -aminoethyl)- γ -aminopropyl siloxane] oligomer with octamethylcyclotetrasiloxane and low molecular weight trimethylsiloxy-terminated polydimethylsiloxane. Each polysiloxane molecule contains 300 siloxane units on average.

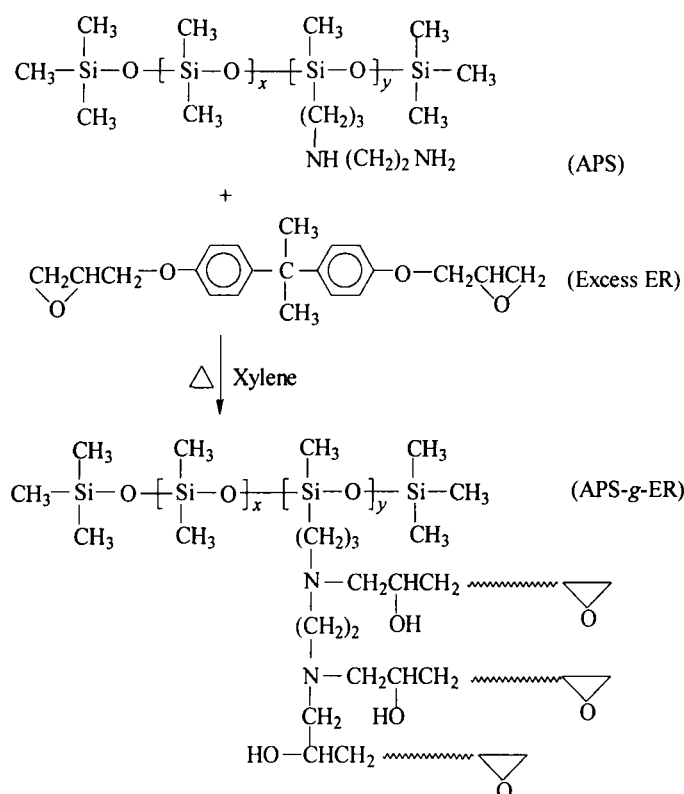
Preparation of Polysiloxane/Epoxy Resin Blends (APS/ER)

The polysiloxane-grafted epoxy resins (APS-g-ER) were prepared through the reaction of APS with a large excess of the epoxy resin, as shown in Scheme 1. The reaction mixtures were dissolved in xylene and refluxed for 4 h to effect the reaction. The completion of the reaction was verified by determining the epoxy group in the

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APS/ER blends. Finally, the solvent was removed by distillation under reduced pressure. The composition of the APS/ER blends is given in Table 1.



Scheme 1 Preparation of polysiloxane-modified epoxy resins (APS/ER blend)

Table 1. Composition of the APS/ER blends

No.	Amino group content in APS (mmol/g)	APS-g-ER content in the blend (wt%)	APS content in APS-g-ER (wt%)	APS content in the blend (wt%)
1	0.47	6.3	78.7	5
2	0.70	7.1	70.9	5
3	0.84	7.4	67.5	5
4	0.91	7.6	65.6	5
5	1.21	8.5	58.7	5
6	1.42	9.1	54.9	5
7	0.70	1.4	70.9	1
8	0.70	4.2	70.9	3

Preparation of Specimens

The APS/ER blend was heated to 90–100°C and a stoichiometric amount of MDA was added. The mixture was stirred for five min to ensure complete dissolution of the curing agent, and then it was cast into silicone rubber molds and cured at 150°C for 3 h.

Measurements

The phase structure of the cured resins was studied using a scanning electron microscope (Hitachi S-530 SEM). For the study of mechanical properties, three-point bending tests were conducted on an Instron 1122 test machine at a crosshead speed of 2 mm/min. The dimensions of the specimens were 55×6×4 mm, and the span of the supports was 40 mm.

The contact angle of the cured resins with water was measured on a Contact Anglemeter CA-D (Kyowa

Kagaku Co. Ltd.). The specimens were ground elaborately; the surface was rinsed with ethanol and dried at 60°C for 3 h.

RESULTS AND DISCUSSION

Compatibility of APS with the Epoxy Resin

Polydimethylsiloxanes without functional groups were not compatible with the epoxy resin. Their compatibility was improved by the introduction of amino groups. In No. 5 and No. 6 of Table 1, more methyl *N*-(β -aminoethyl)- γ -aminopropyl siloxane units were introduced into a polysiloxane molecule having 300 siloxane unit in the molecular chain. As the amino groups reacted with the epoxy resin, the formed graft copolymers became soluble in the resin before curing.

The solubility of the graft copolymers in the resin decreased as the curing of the epoxy resin progressed, and the polysiloxane separated to form micro domains dispersed in the resin matrix.

For the APS of No. 1 through No. 4 in Table 1, the content of the amino group was not high enough to make the graft copolymer soluble in the resin. However, they could disperse in the resin. The dispersions of APS in the epoxy resin showed very interesting rheological behavior and unique morphology after curing.

Rheological Behavior of the APS/ER Blends

A plot of viscosity vs. shear rate for the APS/ER blends is given in Fig. 1. In all these blends the APS concentration was held at 5 wt%, while the content of the amino group was variable. It is seen that the viscosity of the APS/ER blends prepared from the APS with an amino group content above 1.21 mmol/g did not change significantly with shear rate. In these cases APS/ER graft copolymers were dissolved in ER.

In contrast, the APS/ER blends obtained from APS with an amino group content of 0.91 mmol/g or less were strongly shear-thinning. In these cases APS/ER graft copolymers were dispersed in the epoxy resin. The high viscosity at low shear rates indicated that the dispersed phase occupies a large volume fraction.

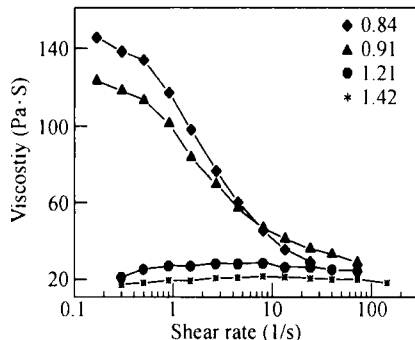


Fig. 1 Viscosity versus shear rate at 25°C for APS/ER blend, APS content 5 wt%, amino group content in APS: 0.84, 0.91, 1.21 and 1.42 mmol/g

Morphology of the Polysiloxane-modified Epoxy Resins

The SEM micrographs of the fracture surface of the cured APS/ER systems with different amino group content in APS are shown in Fig. 2. As seen in Fig. 2a, when the amino group content in APS was higher than 1.21 mmol/g, the dispersed phase was very fine and the average particle size was estimated to be 0.1 μ m. The obscure interface indicates a good adhesion between the two phases.

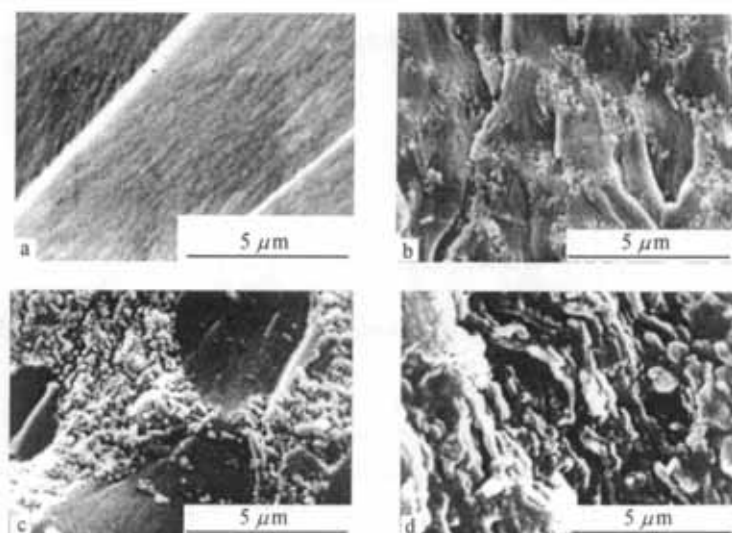


Fig. 2 SEM micrographs of the fracture surfaces of the cured APS/ER systems, APS content 5 wt%
The amino group content of APS in a, b, c and d is 1.21, 0.91, 0.84 and 0.70 mmol/g, respectively

Epoxy resins modified with APS having an amino group content below 0.91 mmol/g showed a complex morphology (Fig. 2b, c and d). Epoxy resin particles of diameter under $0.2\ \mu\text{m}$ were included in the APS domains, which occupied a very large volume fraction and formed the secondary continuous phase. The volume fraction of the epoxy continuous phase diminished and that of the second continuous phase expanded as the amino group content of APS became lower.

The graft copolymers APS-g-ER were good interfacial stabilizers when the amino group content of APS was appropriate, which stabilized the dispersion of epoxy resin in polysiloxane. Therefore, the second continuous phase in the APS/ER blends occupied a large volume fraction, although APS took up only 5% by weight.

Mechanical Properties of the Cured Resins

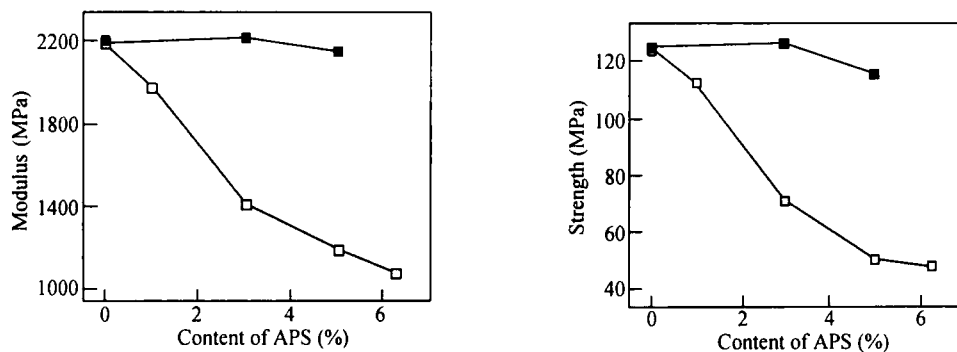


Fig. 3 Effect of the APS content on mechanical properties of the cured APS/ER systems, amino group content in APS: (■) 1.42 mmol/g and (□) 0.70 mmol/g

The mechanical properties of the polysiloxane-modified epoxy resin, in terms of flexural strength and modulus, depended on the APS level and the amino group content in APS. As can be seen in Fig. 3, the introduction of 5 wt% of APS with an amino group content of 1.42 mmol/g had a slight effect on the flexural strength and the modulus. On the contrary, the mechanical properties of the cured resin deteriorated dramatically when APS with an amino group content below 0.84 mmol/g was incorporated. Undoubtedly, the change in the mechanical

properties was due to the reduction of the volume fraction of the epoxy continuous phase of epoxy resin.

In Fig. 4 the influence of the amino group content of APS on the mechanical properties of APS/ER systems is shown. There is an inflection point at the amino group content 0.91 mmol/g both in the curve for the flexural strength and in the curve for the modulus. As described previously, at this point the resin begins to have a complex morphology.

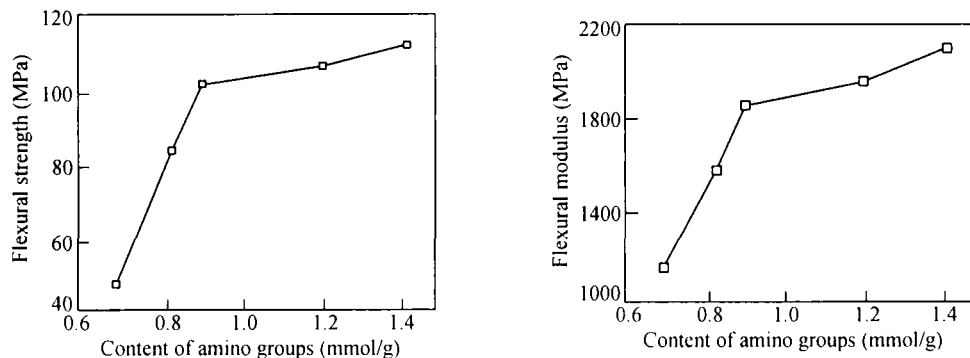


Fig. 4 Influence of the amino group content on the mechanical properties of APS/ER systems, APS content 5 wt%

Surface Properties of the Cured Resins

Polydimethylsiloxanes have low surface energy, therefore they have a high contact angle, usually from 100° to 110° [7], with water. The contact angle of the APS-modified epoxy resins with water was dependent upon the amino group content of the modifier (Fig. 5). Abnormally high contact angles were observed when the amino group content in APS was below 0.84 mmol/g. This seems to be related to the complex morphological structure, that would cause the development of capillaries or cavities in the surface [8, 9].

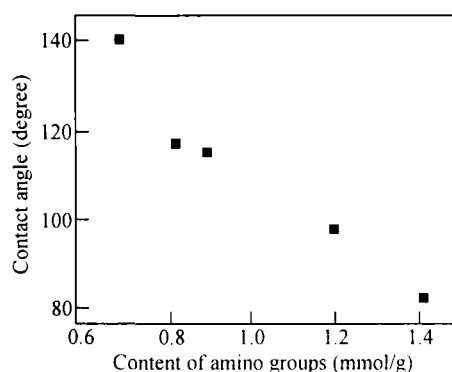


Fig. 5 The effect of amino group content in APS on the contact angle of the cured resins with water, APS content 5 wt%

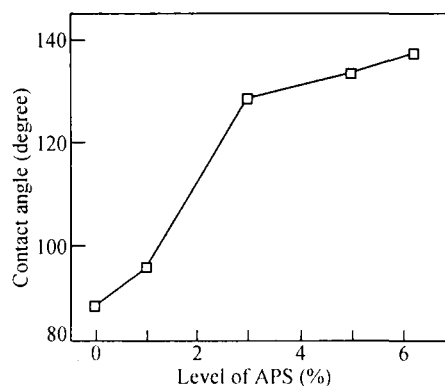


Fig. 6 Level of APS and contact angle of the cured APS/ER systems, amino group content in APS is 0.70 mmol/g

The contact angle with water rose with the content of APS in the blends at low concentrations, and then leveled off (Fig. 6). The coverage of the resin surface by polysiloxane chain seems to be saturated as the APS level reached 3 wt%.

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