

MODIFICATION OF EPOXY RESINS WITH PHENOLIC HYDROXYL- TERMINATED POLYSILOXANE

HOU Qingpu (侯庆普). HUANG Ying (黄英)** and YU Yunzhao (余云照)
(*Institute of Chemistry, Academia Sinica, Beijing 100080*)

ABSTRACT

Phenolic hydroxyl-terminated polysiloxanes were incorporated into epoxy resins to reduce the internal stress owing to the mismatch in coefficient of thermal expansion (CTE). Polysiloxane-epoxy resin block copolymers were made by a pre-reaction step prior to the curing. In the cured resin, the domain size of the polysiloxane phase depended on the structure of the phenolic hydroxyl-terminated polysiloxane. It was found that the modulus of the cured resin depended largely on the level of the modifier, while the CTE was affected greatly by the structure of the polysiloxane. By means of incorporating a few percent of methylphenylsiloxane unit into the polydimethylsiloxane chain, or by introducing more compatible end-capping groups, the compounds of more effective low stress modifiers were synthesized.

INTRODUCTION

Epoxy molding compounds are widely used in electronic encapsulation. "Low stress" is now emphasized in the development of epoxy encapsulants for the packaging of very large scale integrated circuits, because as the die size and the complexity of the device increase, the problem of internal stress becomes more and more critical [1].

Internal stress in semiconductor devices arises mainly from mismatch in thermal expansion coefficient between the silicon chip/lead frame and the plastic encapsulant. Therefore the thermal expansion coefficient in the glass state and the modulus are considered as the most important "stress factors" in molding compounds. Elastomeric additives have been introduced to epoxy resins with the purpose of lowering the modulus, while in some cases the thermal expansion coefficient of the resin can be reduced as well [2,3].

Polysiloxanes are the preferred "low stress agent" for their low glass transition temperature and excellent thermal stability. They have been incorporated into the resin matrix in many ways. RTV (room temperature vulcanized) silicone rubbers have been dispersed into epoxy resins with the

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* * To whom correspondence should be addressed

aid of compatibilizers [4]. However, there are many problems caused by bleeding out of the polysiloxane additive during the molding process. To increase the compatibility of silicone elastomer with epoxy resin functional groups, such as amine, epoxide, hydroxyl end-groups have been introduced on silicone elastomer. By means of functional group reactions soft segments were chemically bonded to the resin matrix. In this way great improvements have been achieved [5-7].

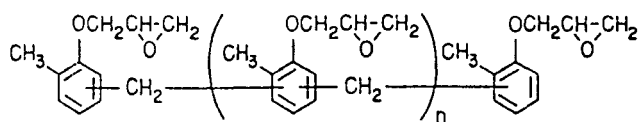
In the present research phenolic hydroxyl-terminated polysiloxanes were used as modifier for epoxy resins. Structural variables were investigated with the objective of illustrating the structure-property relationships in the polysiloxane-modified epoxy resins.

EXPERIMENTAL

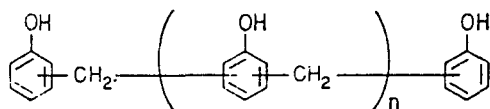
1. Materials

The epoxy resin used throughout this work was a polyglycidyl ether of o-cresol-formaldehyde-novolac (EOCN, epoxide equivalent 205 g/eq), and the curing agent was a phenol-formaldehyde novolac resin (PN, hydroxyl equivalent 107 g/eq). Their structures are shown below. Triphenyl phosphine (TPP) was employed as an accelerator. Phenolic hydroxyl-terminated polysiloxanes of average molecular structure shown in scheme 1 were synthesized in this laboratory. I, II, III were prepared by the addition reaction between H-Si-terminated polysiloxane and 2-allyl phenol. IV, V were prepared by the reaction between epoxy-terminated polysiloxane and p, p'-iso-propylidenediphenol and p, p'-dihydroxydiphenyl sulfone, respectively. They have a functionality of 2.0 according to the $^1\text{H-NMR}$ data.

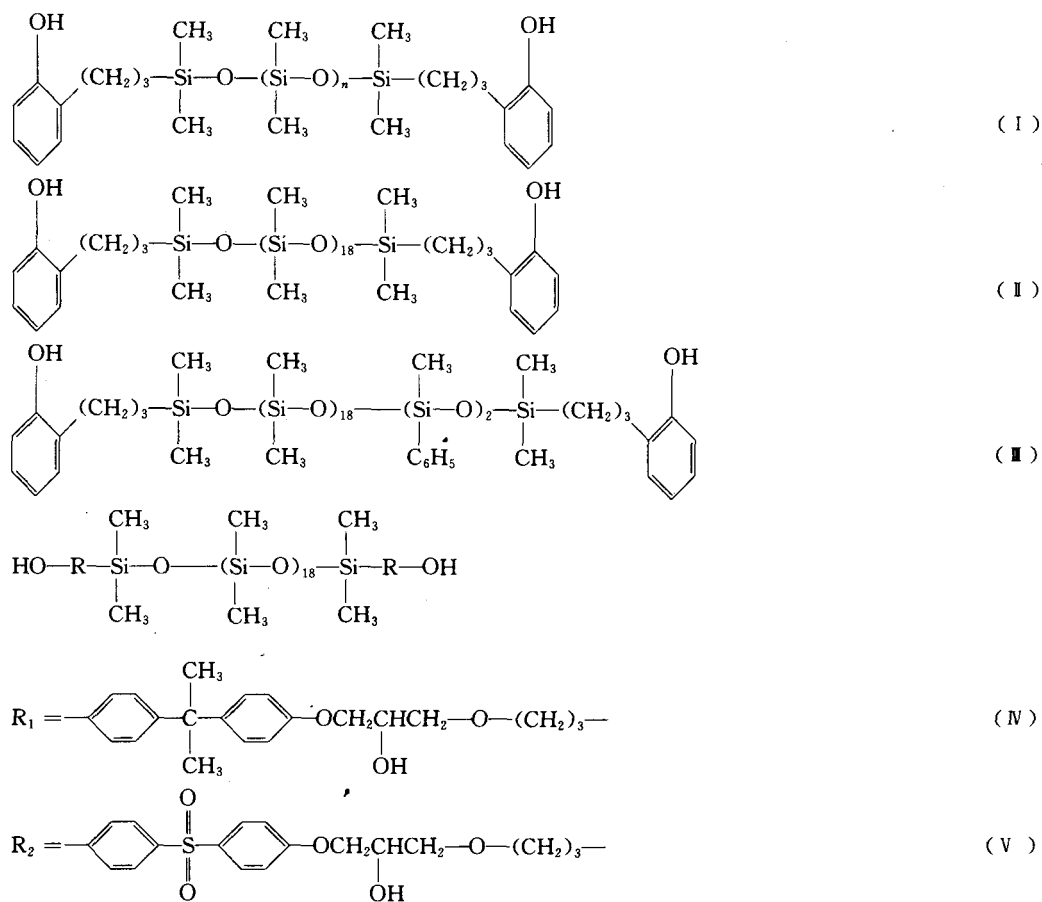
EOCN



PN



Molecular structures of EOCN and PN



Scheme 1 Molecular structures of phenolic hydroxyl-terminated polysiloxanes

2. Preparation of specimens

A two-step procedure was employed for the preparation of specimens. First polysiloxane-epoxy resin block copolymer were made by pre-reaction of phenolic hydroxyl-terminated polysiloxanes with EOCN. The reaction mixtures were heated in nitrogen at 150°C in the presence of TPP until the disappearance of the phenolic hydroxyl group of the product in the NMR spectrum. Then the blend of the polysiloxane-modified EOCN, PN and the accelerator TPP were kneaded at 70–80°C to prepare the molding compounds. Transfer-molding was carried out at 150°C under 10 MPa pressure for 15 min. The specimens were post-cured at 180°C for 8h, and then subjected to cooling down to room temperature at the rate 1°C/min. The mixed amounts were chosen so that the amount of epoxy functional groups was equal to the sum of phenolic hydroxyl on the modifier and hardener.

3. Measurements

Thermal mechanical analysis (TMA) was run on a Perkin-Elmer TMS-2 Thermomechanical Analyzer at a heating rate $10^{\circ}\text{C}/\text{min}$. The inflection of the expansion curves was taken as the glass transition temperature (T_g). The coefficient of thermal expansion below T_g (α_1) was calculated according to the expansion in the temperature range 80 – 100°C .

The modulus (E_f) was determined from flexural deformation of beams. Rectangular bars of size $55 \times 6 \times 4$ mm were used. Three point bending tests were run on an Instron-1122 testing machine at a span interval of 40 mm and a cross-head speed 2 mm/min.

Morphology of the materials was studied using a scanning electron microscope (Hitachi S-530 SEM). A thin layer of gold was sputtered onto the fracture surfaces before observation. A Quantimet 520 image analyzer was used for the analysis of the particle size distribution.

RESULTS AND DISCUSSION

1. Phenolic hydroxyl-terminated polydimethylsiloxanes as modifier

In our preliminary study the results of a published work by Ito et al.^[6] have been checked, since the conclusion on the structure-property correlation by the polydimethylsiloxane (PDMS) modifier was remarkable. It has been verified that molecular weight in the range from 1400 to 3000 was most favorable for PDMS used as low stress modifier. A PDMS oligomer of molecular weight 600 was found partially dissolved in the epoxy resin, so that the glass transition temperature of the cured resin was lowered for ca. ten degrees by inclusion of 5 parts of modifier per hundred parts of resin by weight (phr). A PDMS of molecular weight 10,000 was less effective on lowering the internal stress, expressed in terms of the product $\alpha_1 \cdot E_f$.

Based upon the results of the reference^[6] and our preliminary study, the polysiloxanes of average molecular structure II, III, IV and V (scheme 1) were synthesized for further study.

Since the PDMS-modified epoxy resins are two-phase materials, the interaction in the interphase will exert great influences on the material performance. Chemically bonding between the PDMS blocks and the epoxy resin was found necessary both for improving the mechanical strength and for lowering the coefficient of thermal expansion (CTE). A comparison of the properties of PDMS-modified epoxy resin is given in Table 1.

It can be seen that a significant impairing in the mechanical strength and

an increasing in CTE were caused by direct blending of 5 phr modifier II without the prereaction step. When the modifier II was first reacted with EO CN at 150°C for 3 h and then kneaded with PN and TPP, a lowering both in CTE and in modulus was achieved. Therefore, this two-step process was employed for the preparation of specimen throughout this work.

Table 1 Effect of pre-reaction on the properties of PDMS-modified epoxy resins cured with PN

Modifier	Control	Modifier I	Modifier II
Level(phr)	—	5	5
Pre-reaction	—	150°C/3h	no
Flexural strength (MPa)	96.2	89.4	76.3
Modulus (E_f , GPa)	2.79	2.27	2.30
Maximum deflection (mm)	2.66	2.49	2.20
CTE (α_1 , $10^{-5}/^{\circ}\text{C}$)	6.73	6.10	7.24
$T_g(^{\circ}\text{C})$	164	166	158
$E_f, \alpha_1 (10^5 \text{Pa}/^{\circ}\text{C})$	1.88	1.38	1.67

2. Phenolic hydroxyl-terminated poly[*dimethyl-co-methyl phenyl siloxane*] as modifier

A small proportion of methylphenyl siloxane units was introduced into the PDMS polymer chains to improve the compatibility with the epoxy resin. The copolymer of structure III was found to be a suitable modifier, with which the stress factors of the cured resins were improved greatly, while the thermal resistance was not impaired.

The effect of the methyl phenyl siloxane units on the morphology of the polysiloxane-modified epoxy resins was significant. Typical SEM micrographs of the fracture surfaces are given in Fig. 1. In Fig. 2 the particle size distributions of the polysiloxane domain in the cured resins modified with 10 phr II or 10 phr III are shown. The average diameter of the polysiloxane domain was 0.83 μm for the II-modified epoxy resin, and 0.31 μm for the III-modified epoxy resin.

Mechanical and thermal properties of the modified resins are given in Table 2. It can be seen that both polysiloxane I and III are effective at reducing the modulus and the CTE, and the copolymer III is more effective than the homopolymer I.

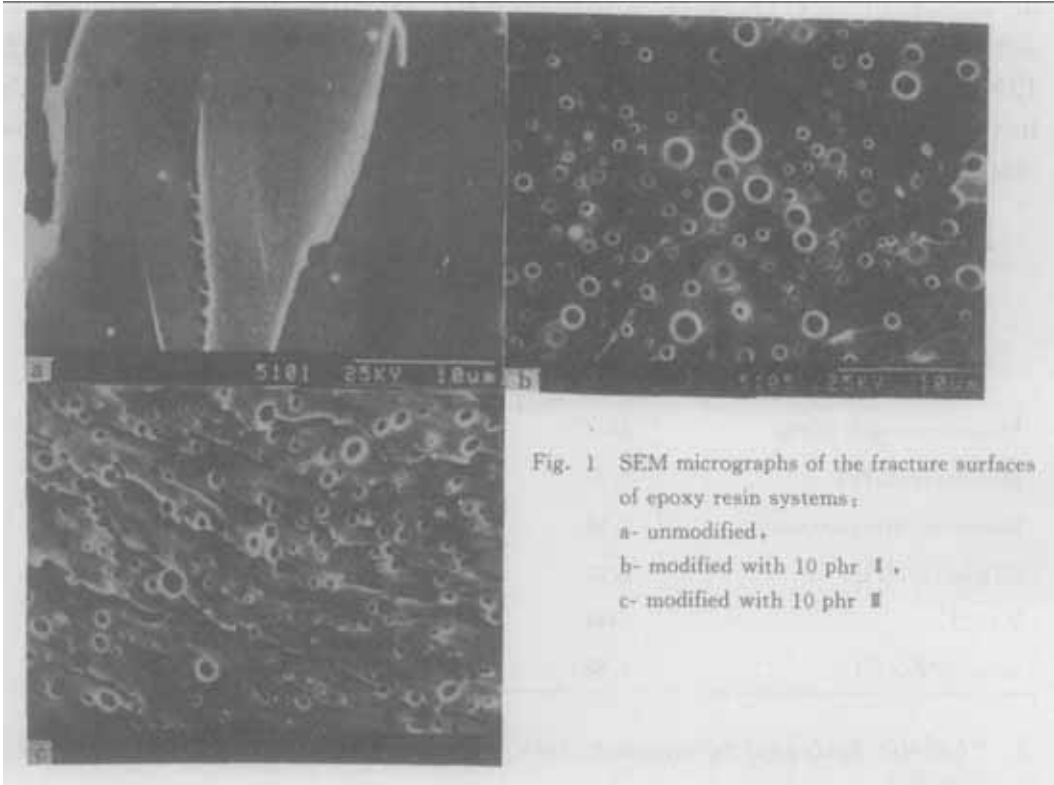


Fig. 1 SEM micrographs of the fracture surfaces of epoxy resin systems:
a- unmodified.
b- modified with 10 phr I ,
c- modified with 10 phr II

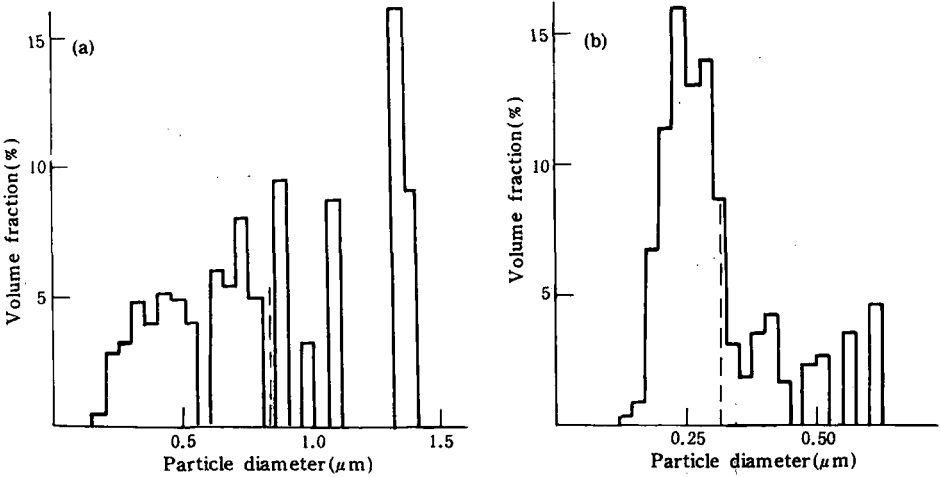


Fig. 2 Polysiloxane particle size distributions in the modified epoxy resin systems:
a- modified with 10 phr I , b- modified with 10 phr II

Table 2 Mechanical and thermal properties of polysiloxane modified epoxy resins

Modifier structure Level(phr)	I		II		Control
	5	10	5	10	
Flexural strength(MPa)	89.4	95.6	103.0	105.4	96.2
Modulus(E_t , GPa)	2.27	2.02	2.37	1.90	2.79
Maximum deflection(mm)	2.49	3.30	3.14	3.83	2.66
CTE(α_t , $10^{-5}/^{\circ}\text{C}$)	6.10	5.83	5.63	5.33	6.73
$T_g(^{\circ}\text{C})$	166	170	167	165	164
$E_t \cdot \alpha_t (10^5 \text{Pa}/^{\circ}\text{C})$	1.38	1.18	1.33	1.01	1.88

3. Effect of end capping group of the PDMS modifier

Since the preferred polysiloxane modifiers are low molecular weight substance, the end group should play a significant role in microphase formation of the polysiloxane-modified epoxy resins. As shown in Scheme 1, the PDMS oligomers of structures II, IV and V are endcapped with phenol group, bisphenol A group and bisphenol sulfone group respectively. The difference in particle size distribution of the polysiloxane phase was remarkable, when the same proportion of PDMS (5 phr) with different end group was used for the modification of epoxy resin (Fig. 3 and Fig. 4). The phenol-capped PDMS gave an average diameter of $0.61 \mu\text{m}$; bisphenol A-

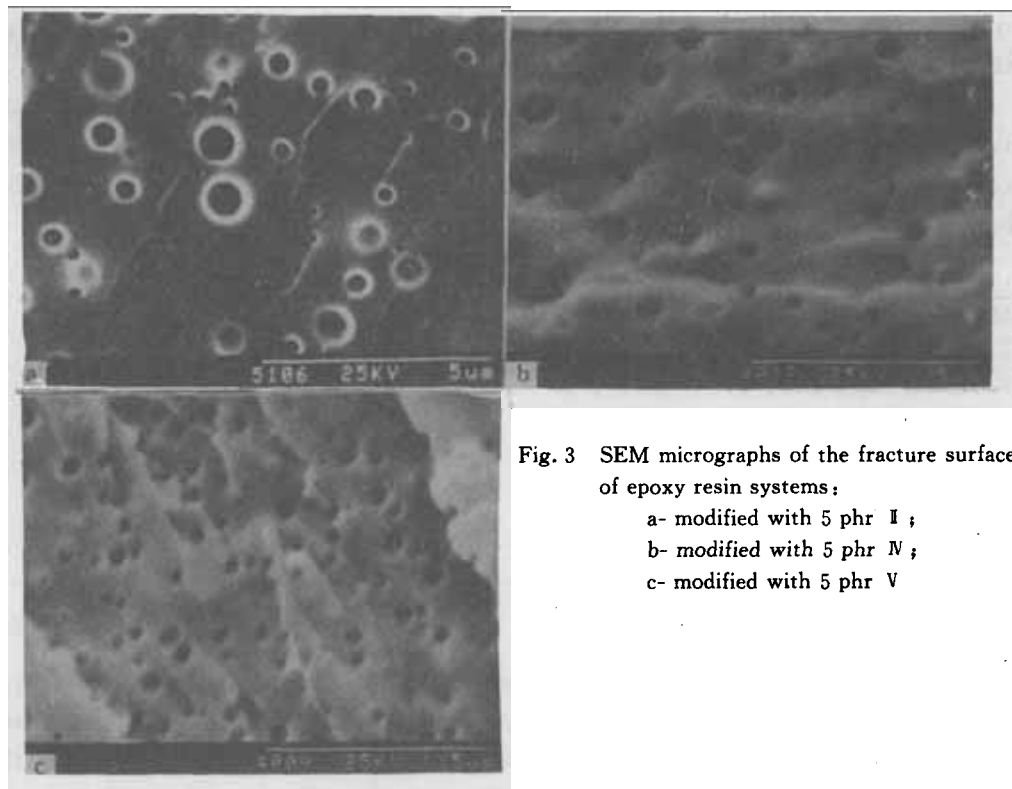


Fig. 3 SEM micrographs of the fracture surfaces of epoxy resin systems:

- a- modified with 5 phr II ;
- b- modified with 5 phr IV ;
- c- modified with 5 phr V

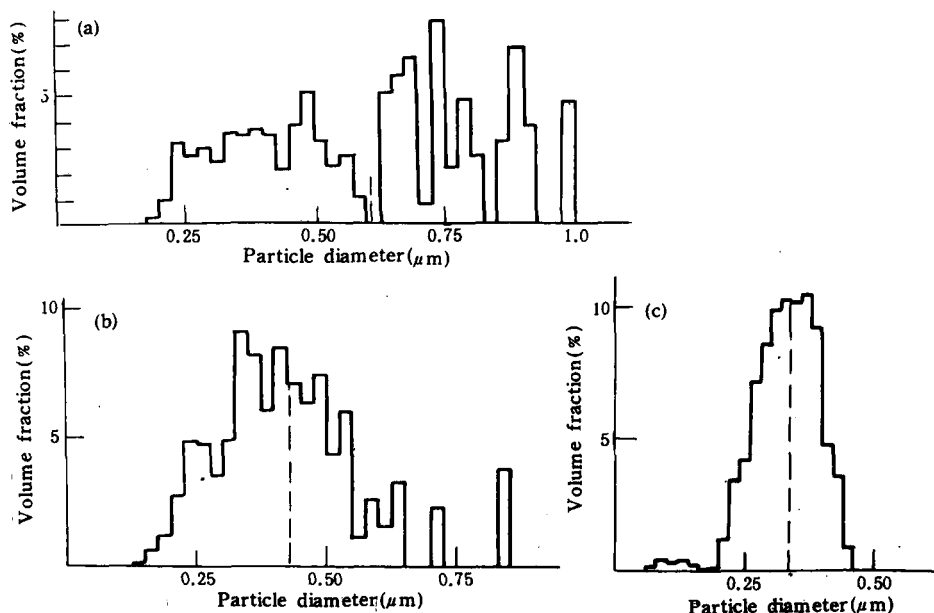


Fig. 4 Polysiloxane particle size distributions in the modified epoxy resin systems;
a- modified with 5 phr I; b- modified with 5 phr N; c- modified with 5 phr V

capped PDMS gave an average diameter of $0.43 \mu\text{m}$; the polysiloxane domain from the bisphenol sulfone-capped PDMS had the smallest average size ($0.33 \mu\text{m}$) and very narrow distribution.

The mechanical and thermal properties of the modified epoxy resin are given in Table 3. It can be seen that all these modifiers are effective on reducing the modulus. However, the PDMS IV and V are more effective than the PDMS I at reducing the CTE below T_g .

Table 3 Mechanical and thermal properties of epoxy resins modified with polysiloxanes.

Modifier structure	I	IV	V	Control
Level(phr)	5	5	5	—
Flexural strength(MPa)	89.4	93.2	85.3	96.2
Modulus(E_f , GPa)	2.27	2.31	2.26	2.79
Maximum deflection(mm)	2.49	2.86	2.31	2.66
CTE($\alpha_1, 10^{-5}/^\circ\text{C}$)	6.10	5.39	5.36	6.73
$T_g(^\circ\text{C})$	166	176	176	164
$E_f, \alpha_1(10^5\text{Pa}/^\circ\text{C})$	1.38	1.25	1.21	1.88

4. Final remarks

By incorporation of a polysiloxane phase, the modulus of epoxy resins was reduced. The effect was proportional to the level of the modifier, while the structure of the modifiers seems to exert only a minor influence on the modulus. The polysiloxane additives were also effective on reducing the

CTE below T_g . The effectiveness depended largely on the structure of the modifiers. By means of including methyl phenyl siloxane units into the PDMS polymer chains, or by introducing more compatible end-capping groups, PDMS modifiers became more compatible with the epoxy resin, so that smaller dispersed domains were formed in the resin matrix. It seems that small particle size of the PDMS phase and strong interaction between the phases favor the lowering of CTE below T_g . This can be accounted by the tentative mechanism given in the reference [3], according to which the free space in the interphase region plays the role for relieving the volume expansion as the temperature increases.

Keywords:

Epoxy resin; Polysiloxane; Internal stress

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