

Flexibility Improvement of Epoxy Resin by Using Polysiloxanes and Their Derivatives

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SYNOPSIS

A study of increasing the flexibility and lowering the internal stress of the cured epoxy resin was carried out by using polysiloxanes capped with functional groups and premaking polysiloxane particles with $d = 1.1 \mu\text{m}$ and narrow distribution. Polysiloxanes capped with functional groups were prepared by the reaction of X-22-163B with bisphenol-A, hexanedioic acid, and decanedioic acid. Poly(dimethylsiloxane-*b*-arylester) was synthesized by the reaction of poly(dimethylsiloxane) (X-22-162C) with arylester oligomers. Polysiloxane particles were obtained by cycling the mixture of polysiloxanes containing a vinyl group and a $\equiv\text{Si-H}$ group, respectively, emulsifier, and water in homogenizer. When oily polysiloxanes were used to improve the flexibility of epoxy resin, good compatibility of polysiloxanes with epoxy resin, and high molecular weight capped with epoxy group favor the formation of small-sized particles and homogeneous dispersion in the cured matrix. Comparisons were made among the epoxy resin modified with oily polysiloxanes capped with different functional groups. The results indicate that lightly crosslinked polysiloxane particles with $d = 1.1 \mu\text{m}$ and narrow distribution have the greatest increase of elongation and biggest decrease of internal stress. The reason for this is discussed. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Extensive investigation on the improvement in flexibility of epoxy resin has resulted in the understanding of structure-properties relationships. Many investigations have concentrated on the flexion and lowering of the internal stress of epoxy resins using elastomers. It is known that factors influencing the flexibility of modified epoxy resin are the size and distribution of elastomer structures and the contents in the epoxy resin matrix.¹⁻⁴ In the past, polysiloxane elastomer used as to improve flexibility attracted great attention due to its thermal stability. In order to improve the compatibility of polysiloxanes with epoxy resin, the modified polysiloxanes, such as capped with functional groups,⁵ poly(sulfone-*b*-dimethylsiloxane),⁶ and core-shell particles,⁷ were used to improve flexibility. Different results on flexibility improvement and lowering the

internal stress were observed. In this work, polysiloxanes capped with epoxy, carboxylic acid, poly(dimethylsiloxane-*b*-arylester) and phenolic groups, and silicone rubber particles were used to improve the flexibility of the epoxy resin. The differences in their flexing ability are investigated. The factors influencing flexibility are discussed.

EXPERIMENTAL

Materials

Bisphenol-A (A.R), decanedioic acid (A.R), *p*-benzenedicarboxylic acid (A.R), polysiloxane containing vinyl group (SVB) obtained from Bengbu Organic Siloxane Factory, polysiloxanes capped with epoxy group (X-22-163B,C,E,F), capped with carboxy group (X-22-162C) and containing $\equiv\text{Si-H}$ (KF-99) from Shintsu Company were used without further purification. The catalyst for the addition reaction of $\equiv\text{Si-H}$ and vinyl group was prepared by reflexing the mixture of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ and tet-

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ramethyl divinyl siloxane at 120°C for 1 h and washing the reaction mixture with distilled water to a neutral reaction. *o*-Cresol novolac epoxy resin, phenol novolac (hardener), and DBU (accelerator) were obtained from Hitachi Chemical Co. Ltd.

Preparation of X-22-163B Capped with Bisphenol-A (II)

X-22-163B (15.4 g, 4.4 mmol) was put into a solution of bisphenol-A (3.1 g, 13.3 mmol) in the presence of sodium hydroxide. The reaction mixture was heated at 160°C for 24 h with stirring. Neutralization was carried out by adding diluted hydrochloric acid into a reaction solution which was cooled to room temperature. The water in the reaction mixture was removed under reduced pressure. The precipitates occurred by adding *n*-heptane (20 mL) into the residue. After filtration and distillation of *n*-heptane, the product (7.4 g, 42%) was obtained.

Preparation of X-22-163B Capped with Decanedioic Acid (IIIa) or Hexanedioic Acid (IIIb)

X-22-163B (5.1 mmol) was put into a solution of diacids (16 mmol) in 3 mL of DMF. The mixture was refluxed at 150°C for 30 h. After the reaction

was completed, DMF was removed at reduced pressure. The unreacted acids were filtrated after adding *n*-heptane (20 mL). The products were obtained after distilling *n*-heptane in vacuum.

Preparation of Polyarylester Oligomers

A solution of *p*-phenylenedicarbonyl chloride (5.343 g, 26.3 mmol) in methylene dichloride (30 mL) was added dropwise into a solution of bisphenol-A (7.052 g, 32.9 mmol) in methylene dichloride (140 mL) and triethyl amine (10 mL) in 30 min. The reaction was carried out at room temperature for 3.5 h. The reaction mixture was washed with 5% NaHCO₃ aqueous solution. After drying over anhydrous magnesium sulfate, the precipitation was carried out by adding methanol into the reaction solution. The obtained white powder (yield: 99%) was dried in a vacuum. The polymerization degree (*n*) was around 4. The poly(arylester) with *n* = 2 was prepared with the same procedures except a 1:2 (mole ratio) of dicarbonyl dichloride to bisphenol-A was used.

Preparation of Poly(siloxane-*b*-arylester) (IVa When Polyarylester *n* = 2; IVb When *n* = 4)

The mixture of acetyl chloride (10 mL) and poly-siloxane (X-22-162C) capped with carboxy group

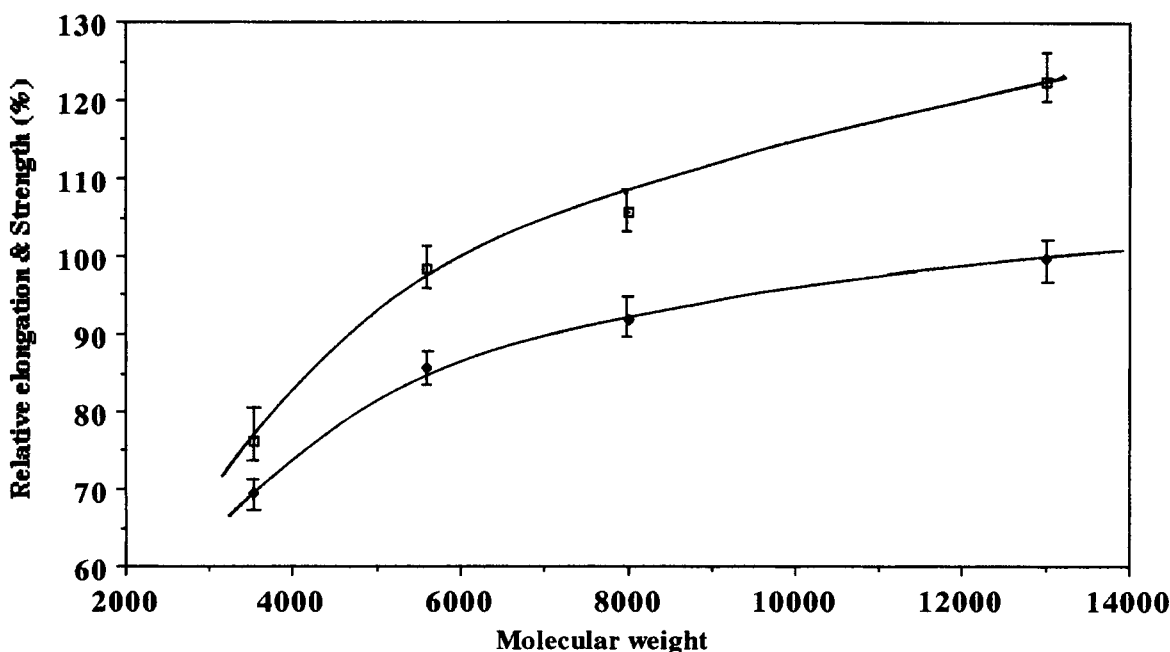
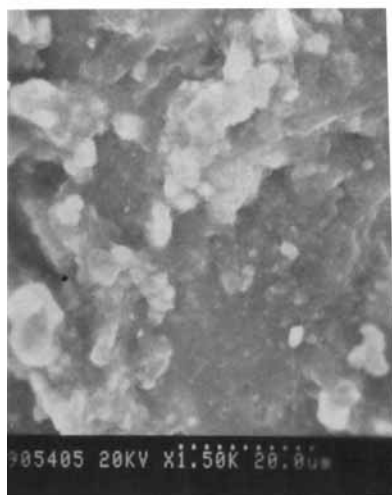
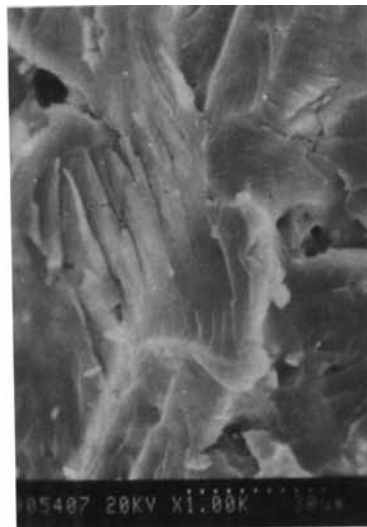


Figure 1 Influence of molecular weight of X-22-163 on flexural strength and elongation. Size of test pieces: 60 × 10 × 2; others see experimental part: (■) flexural strength; (□) elongation.



a



b

Figure 2 Fractured surfaces of the modified epoxy resin with polysiloxane, X-22-163B ($M_n = 3520$): (a) upper side; (b) lower side.

(8.9 mmol) was heated at 70°C for 2.5 h. The unreacted acetyl chloride was removed under reduced pressure. The obtained polysiloxane capped with $-\text{COCl}$ was dropwise added into a solution of poly(arylester) (4.45 mmol) in chlorobenzene (170 mL). The reaction mixture was refluxed at 132°C for 24 h. The precipitates occurred by adding methanol into the reaction solution. A pale white solid (yield: 30%) was obtained after filtering, washing, and drying *in vacuo*.

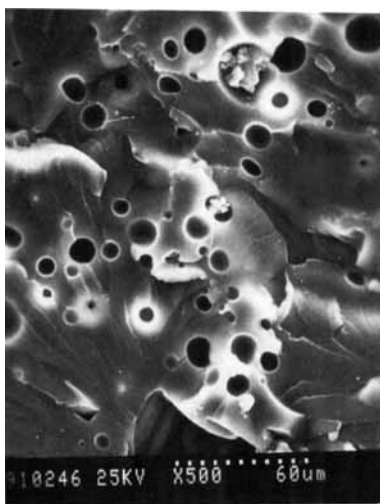


Figure 3 Fractured surface of the modified epoxy resin with polysiloxane ($M_n = 13,000$).

Preparation of Polysiloxane Particles (S_0 and S_1)

A suspension of SBV (210 g) and KF-99 (30 g) in water (300 mL) containing Tween 80 (40 g) was poured into a homogenizer. After additional water (1700 mL) was put into the homogenizer, the suspension solution was cycled two times at 400 atm, and a stable latex was obtained. After 40 drops of catalyst were put into the obtained latex at 50°C while stirring, the reaction mixture was allowed to stand for another 6 h. Particles were precipitated by adding anhydrous sodium sulfate (40 g) while stirring. Products (S_0) were obtained by filtration, washed with water, and dried in vacuum at 70°C. S_1 particles were obtained by mechanical stirring (2000 rpm) with the same ingredients as S_0 .

Measurement of the Modified Polysiloxane Structure, Particles Size, and Distribution

The infrared (IR) and nuclear magnetic resonance (NMR) measurements of the obtained polymers were performed on a Nicolet SX-170 IR spectrometer and EM-360L NMR instrument, respectively. The size and distribution of the particles produced by emulsion polymerization or existing in the matrix were measured by Hitachi X-650 scanning electron microscopy (SEM) and H-80 transmission electron microscopy (TEM).

Property Measurement of the Modified Epoxy Resin

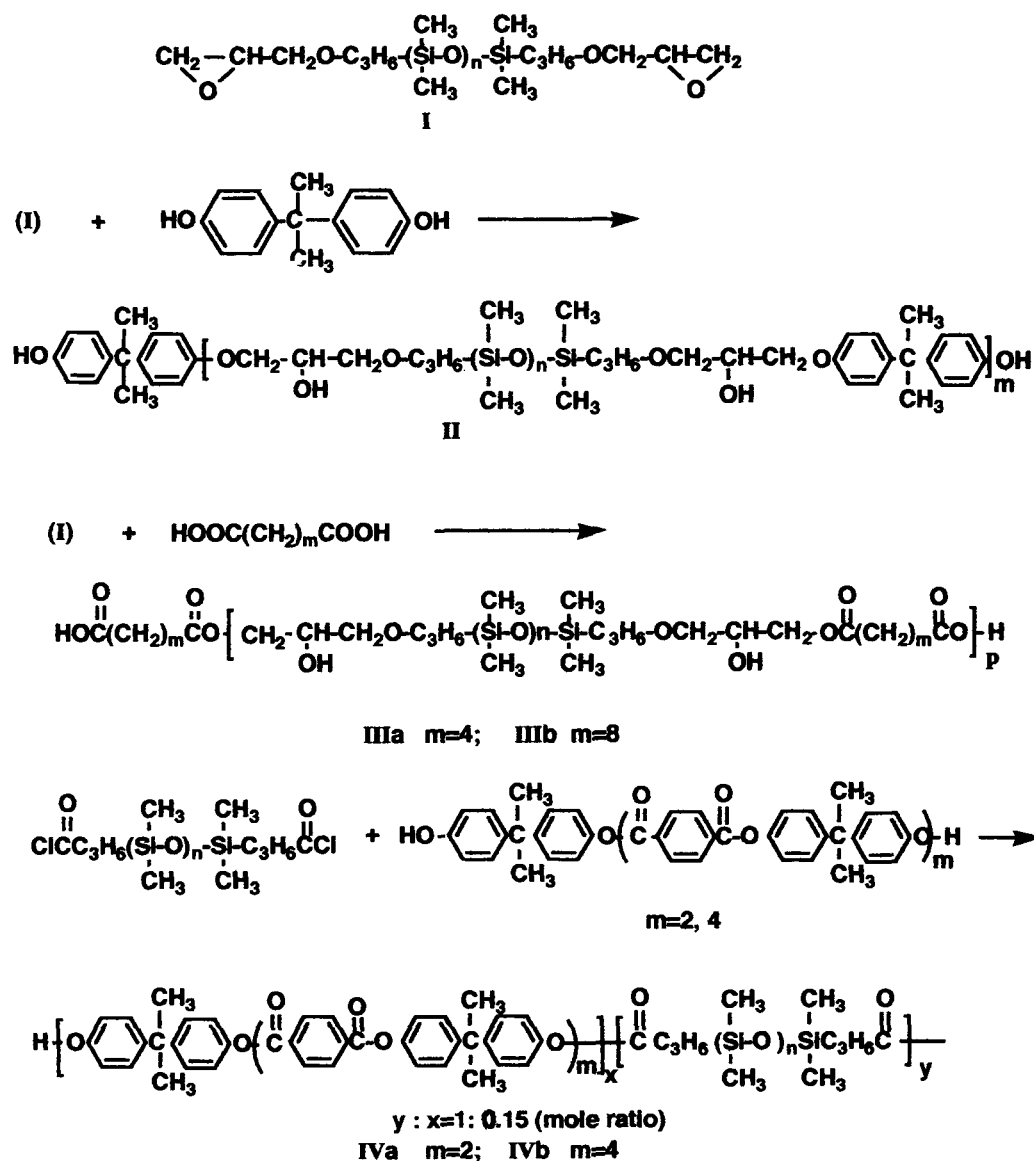
Making of Test Pieces

Epoxy resin (100 parts, weight), accelerator (5 parts, weight), phenolic resin (50 parts, weight), and the modified polysiloxanes were mixed by using a dual-roller machine while presetting the front roller at 90°C and the back roller at 30°C. After the mixture was homogeneously blended, a suitable amount was put into the mold. When small amounts of bubbles were excluded in the molten viscous fluid, the molten

material was pressured at 100 atm and 150°C for 15 min. After cooling the test samples were taken out from the mold and then treated at 180°C for 6 h. Test pieces of dimension 60 × 10 × 2 mm were obtained by cutting.

Property Measurement

Bending tests were performed on a Shimadzu mechanical test machine. The flexural strength, flexural modulus, and elongation were calculated according to the equations described in the literature.⁸ Each point was the average value of five measurements.



Scheme 1

Table I Influence of the Modified Polysiloxane Structure on Properties of the Cured Epoxy Resin^a

No.	Elastomer		Content of Elastomer in Epoxy Resin (phr) ^d	Relative Flexural Strength (%) ^e	Relative Flexural Modulus (%) ^e	Relative Elongation (%) ^e
	Modifier ^b	Mole Ratio of Si to Modifier ^c				
x-22-163B	—	—	8	69	92	76
II	BPA	1 : 3	8	96	80	120
IIIa	HD	1 : 1.4	8	83	78	107
IIIb	DD	1 : 2.53	8	86	78	114
IVa	AEO2	2 : 0.30	8	90	74	115
IVb	AEO4	2 : 0.30	8	100	84	121

^a The composition of test pieces: epoxy resin, 100 pt; phenol resin, 50 pt.

^b BPA: bisphenol A; HD: hexanedioic acid; DD: decanedioic acid; AEO2, AEO4: arylester $n = 2, 4$, respectively.

^c Calculated based on the proton NMR data.

^d phr = (weight of elastomer/weight of epoxy resin) \times 100%.

^e Relative to the corresponding values of epoxy resin.

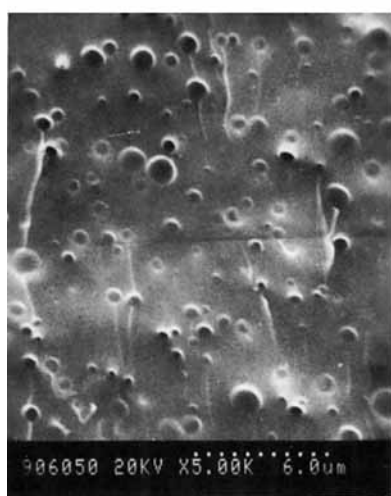
Measurement of Internal Stress

The internal stress (σ) was measured according to the method proposed by Nakamura and Inoue.^{3,9,10} Epoxy resin was coated to about 0.1 μm of coating layer on the surface of an aluminum alloy plate with dimension of $90 \times 10 \times 0.2$ mm which was preheated to 120°C. Bending of the coated plate occurred during the process of heating at 180°C for 6 h, then cooling to room temperature. The internal stress could be calculated using the bending radius of the

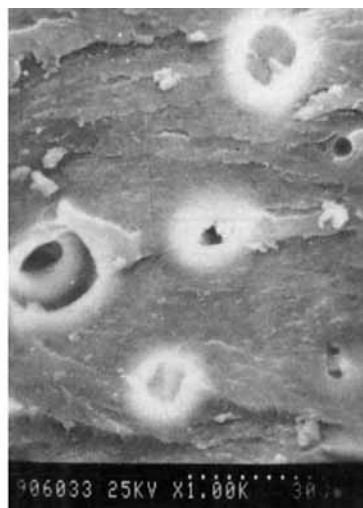
aluminum alloy according to the equation described by Nakamura.³

RESULTS AND DISCUSSION

Poor compatibility of polysiloxane oil with epoxy resin favors the complete phase separation to form an "island" structure in the matrix of the epoxy resin but does not favor the homogeneous blend of the



a



b

Figure 4 Fractured surfaces of the modified epoxy resin using II and IBv to improve flexibility: (a) II; (b) IIIb.

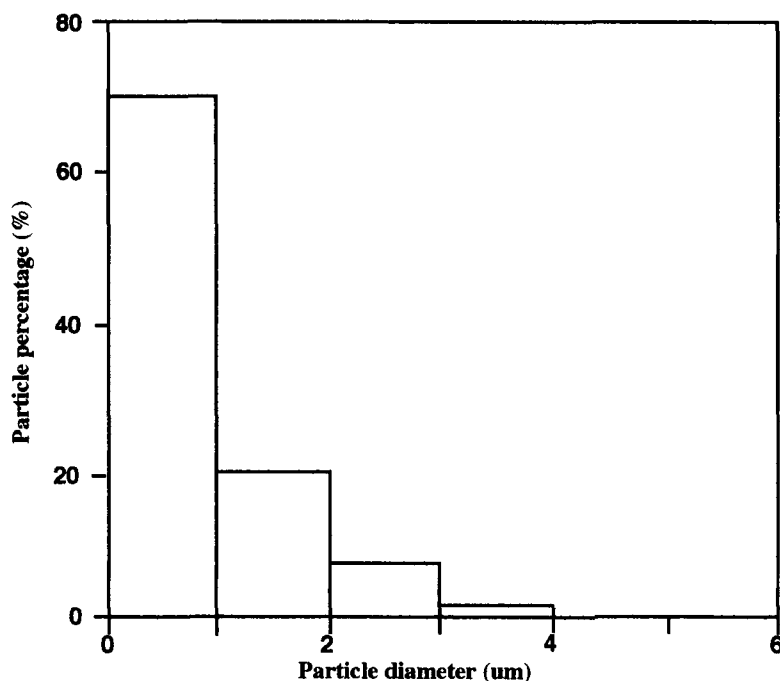


Figure 5 Distribution and size of particles (S_0) made by homogenizer. Conditions: see experimental part.

two components. Therefore, it is important to improve the compatibility of polysiloxanes with epoxy resin to enhance its flexibility.¹¹ The addition of surface-active agent into the blend system could improve the homogeneous mixing of epoxy resin and

polysiloxanes.^{11,12} We studied the influence of the molecular weight of polysiloxanes capped with epoxy group I on the flexibility. The results show that flexural strength and elongation increase as the molecular weight of polysiloxanes increases (see Fig. 1).

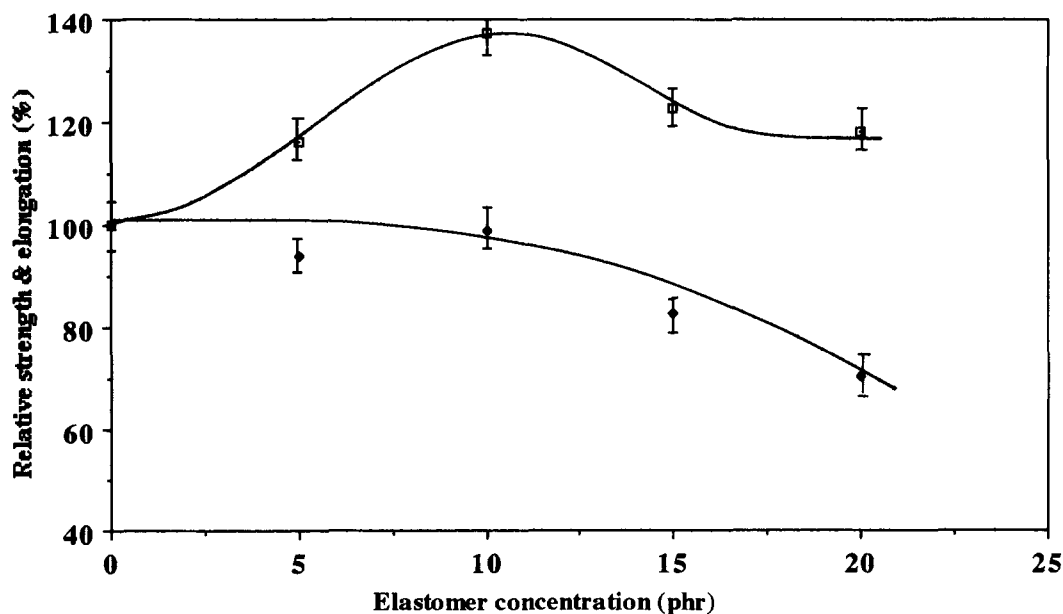


Figure 6 Influence of elastomere (S_0) particle content on the properties of the modified epoxy resin: (■) flexural strength; (□) elongation.

Table II Effect of Rubber Particle Size on Properties of the Modified Epoxy Resin^a

Flexibilizer	Domain Size (μm)	Elastomer Content (phr) ^b	Relative Strength (%) ^c	Relative Modulus (%) ^c	Relative Elongation (%) ^c
S ₁	16.1	8	83.7	79.7	105.8
II	0.3–3	8	96	80	120
IVb	0.3–6	8	99	84	121
S ₀	1.1 ^d	8	99	85	137

^a Same as for note a in Table I.

^b Same as for note c in Table I.

^c Same as for note d in Table I.

^d Average diameter.

It is interesting to study the electron microscopic pictures of the fractural section of the cured epoxy resin modified with polysiloxane ($M_n = 3250$). It was found that phase separation occurred on the upper side of the fractural section [see Fig. 2(a)]; almost only epoxy resin matrix appeared on the lower side [see Fig. 2(b)]. This fact indicates that oily polysiloxane rises up in the viscous epoxy resin while making the test pieces. Slow migration of polysiloxane with high molecular weight ($M_n = 13000$) and reaction of more epoxy groups with epoxy resin during the curing process caused a comparatively homogeneous distribution of polysiloxane particles with d values of 1–10 μm in the matrix (see Fig. 3). It might be an important factor for improving the flexibility with less decrease of flexural strength. Therefore, increasing the length of the chain segment compatible with epoxy resin and molecular weight could favor the further improvement of flexibility. In order to verify this assumption, polysiloxane X-22-163B ($M_n = 3520$) was modified with bisphenol-A, hexanedioic acid, and decanedioic acid to form II, IIIa, and IIIb, respectively, the reaction of polysiloxane X-22-162C ($M_n = 5220$) with arylester oligomers to produce IVa and IVb according to Scheme 1.

The structures and composition of the modified polysiloxanes were confirmed by IR and ¹H NMR spectra, as discussed elsewhere.¹³ The epoxy resin was mixed with these modified polysiloxanes on the dual rolling machine. Then test pieces were made and properties were measured. Results listed in Table I demonstrate that all the modified polysiloxanes could improve the flexibility of epoxy resin, the most effective modifiers being bisphenol-A and arylester oligomers. It is attributed to the kinetics of phase separation of silicone rubber from epoxy resin matrix. The modifiers containing benzene rings probably favor homogeneous distribution of particles in the epoxy matrix and formation of relatively small

particles (see Table I). In the case of II and IVb elastomers, the diameter of particles ranged from 0.3 to 20 μm [see Figs. 4(a) and 4(b)]. This is why II and IVb had higher improvement in flexibility to epoxy resin.

It was reported that particle size affected the efficiency of improving flexibility.^{2,14} The result is similar with our observation. However, it is difficult to control the phase separation process, which affects the particle size and distribution. This problem might be solved by premaking particles with small particle size and narrow distribution. Therefore, polysiloxane rubber particles (S₀) with narrow distribution and small size were prepared by cycling the mixture of SVB, KF-99, and emulsifier in the homogenizer at 400 atm and room temperature. The crosslinking reaction proceeded in the presence of catalyst. The size and distribution of particles are shown in Figure 5. The average diameter of the par-

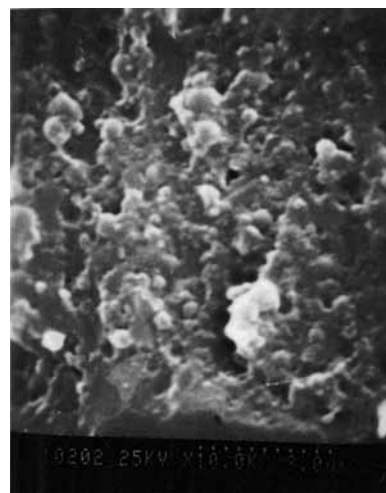


Figure 7 Fractured surface of the modified epoxy resin with elastomer particle S₀.

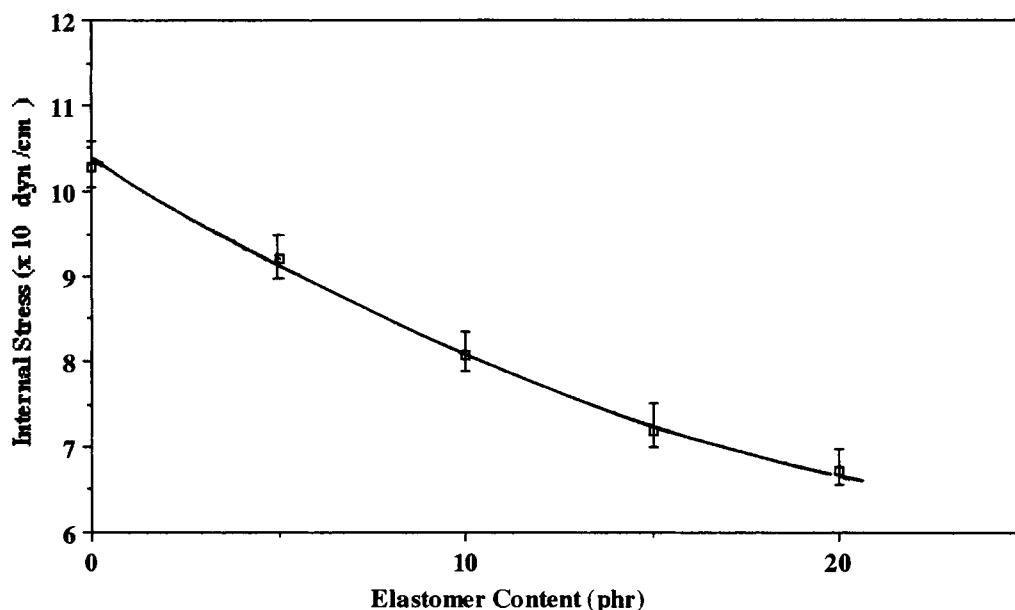


Figure 8 Relationship between internal stress and content of elastomer (S_0) in the curved epoxy resin.

ticles was $1.1 \mu\text{m}$. When silicone rubber particles were used in making the test pieces, the properties of modified epoxy resin at various rubber particle concentrations are shown in Figure 6. A maximum value of elongation appeared at 10 phr. This may be related to a low decrease of flexural strength. Further investigation of the reason as well as how to improve the method is in progress.

In comparison with S_1 and II, S_0 is shown to be better in improving flexibility (see Table II), attributed to its small domain size and homogeneous distribution in the matrix. In general, the smaller the particles, the more particles per volume there are. Therefore, since small-size particles have higher probability of inducing and terminating sliver cracks, much fracture energy was consumed. In addition, the small particles have a greater surface area; thus they have better interaction between the domain and matrix. It can be confirmed by SEM photographs. In the case of I, II, and IV as modifiers, the domain-matrix interfaces were smooth and clear (see Fig. 4); in the case of S_0 as modifier, a fuzzy and irregular interface between matrix and domain can be seen (see Fig. 7). As a result, less decrease of fractural strength and more elongation were observed (see Table II). Studying the internal stress in the modified matrix, it could be found that the higher the S_0 content, the lower the stress (see Fig. 8). The reason for this is that higher particles con-

tents would consume much fractural energy, and therefore lower stress was observed.

CONCLUSION

The results of this study indicate:

1. Comparing polysiloxanes having different molecular weights, or among the polysiloxanes with various functional groups, better toughness of epoxy resin was obtained by using high-molecular-weight polysiloxane or polysiloxanes capped with bisphenol-A and arylester oligomers.
2. For toughness improvement of epoxy resin, lightly crosslinked polysiloxane particles with $d = 1.1 \mu\text{m}$ and narrow-size distribution have the greatest increase of elongation and biggest decrease of internal stress.

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