Influence of Crosslinking Degree of Silicone Rubber Particles on Properties of Epoxy Resin

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ABSTRACT: Silicone rubber particles with different degrees of crosslinking were prepared. Silicone oils containing Si—H groups and vinyl groups were reacted at various mol ratios in their composite emulsions. Epoxy resin was modified using these particles and the results indicated that the content of the silicone rubber particles, the crosslinking degree of the rubber particles, and the addition of a coupling agent affected the properties of the modified epoxy resins. The influence of the coupling agent depends on the crosslinking degree of the silicone rubber particles. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 69: 619–625, 1998

Key words: epoxy resin; silicone rubber; modification; crosslinking degree

INTRODUCTION

Epoxy resins have excellent performance, such as high strength and modulus, outstanding adhesion, and heat resistance. However, they are brittle and have low thermal shock resistance. The ability to increase their toughness and shock resistance with little decrease of their other properties is the key problem both in fundamental and application research.[1] Introduction of the rubber phase into epoxy resin is one of the most successful methods.[2] Compared with other elastomers (butadiene–acrylonitrile rubber and acrylate rubber), silicone rubber has demonstrated many advantages: low glass transition temperature and thermal and chemical stabilization. The factors influencing the properties of the modified epoxy resins, such as the volume fraction, the size of the rubber phase, and the interfacial interaction between the rubber phase and epoxy resins, have been studied.[3–5] It has been reported that the mechanical strength of the rubber was important in the toughening of nylon-6,[6] but few studies about the relationship between the crosslinking degree of the rubbers and the properties of toughened epoxy resins have been reported.

In this article, silicone rubber particles with different degrees of crosslinking were prepared and used to modify *o*-cresol novolac epoxy resin. To improve the interfacial adhesion, a coupling agent was added. The influence of the crosslinking degree of the silicone rubber particles, their content in the composite, and the interfacial adhesion on the mechanical and thermal properties of the modified epoxy resins are discussed.

EXPERIMENTAL

Materials

Hydrogen-containing silicone oils (SHC) and vinyl-containing silicone oil (SVC) were obtained from the Shin-Estu Chemical Co. Ltd. (Tokyo, Japan) *o*-Cresol novolac epoxy resin (ESCN-195), novolac resin (PN), and 1,8-diazobicyclo(5,4,0)-7-undecene (DBU) were obtained from the Shimadzu Chemical Co. The structures of SHC, SVC,

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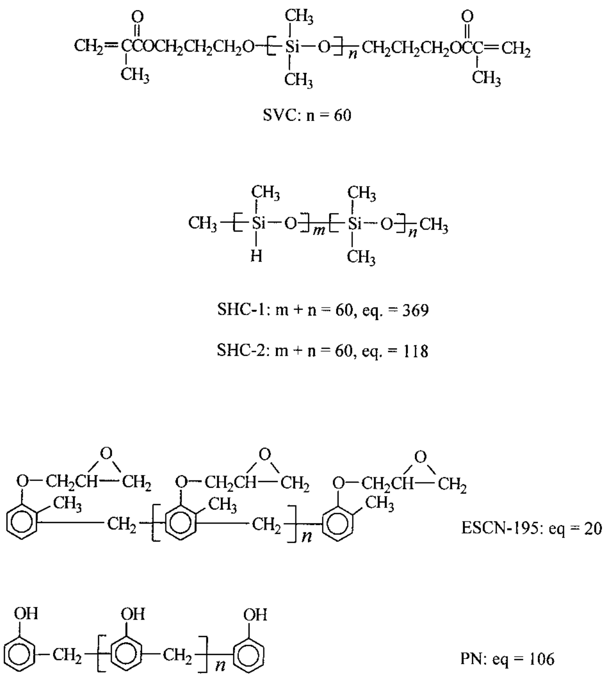

Scheme 1

ESCN-1, and PN are shown in Scheme 1. Octamethylenebenzyl poly(ethylene oxide)ether with a polymerization degree of 10 (OP-10) and γ-glycidylpropyloxy trimethyloxysilane (GPTMS) were analytical reagents. The catalyst for the addition of Si—H and the vinyl group was prepared according to the method described in ref. 7.

Preparation of Silicone Rubber Particles

The mixture of SHC and SVC with an equivalent ratio of 2 : 1 or 2 : 3 (50.0 g) was poured into a 1.5 wt % OP-10 aqueous solution (300 mL) and their stable latex was prepared using a homogenizer. Then, the catalyst (0.5 mL) was added and the latex was kept at 60°C for 12 h. The latex was deemulsified with anhydrous sodium sulfate and the silicone rubber particles were obtained by filtration, washing with distilled water, and drying under a vacuum at 70°C.

Characterization of Silicone Rubber Particles

For measuring the crosslinking degree of the silicone rubber particles, a series of samples of silicone rubbers were prepared by the reaction of SHC and SVC in the bulk with the same equivalent ratios to those in the latex. Then, they were immersed in petroleum ether at room temperature for 5 days. The volume of the silicone rubbers before (V_0) and after (V_1) swelling were measured and the volume swelling degree of the dry silicone rubbers (Q) were calculated according to eq. (1):

$$Q = V_1/V_0 \tag{1}$$

The obtained latex was irradiated under ^{60}Co γ-ray and a drop of it was placed on a piece of smooth glass. After the water was evaporated at room temperature and dried under a vacuum, the diameter and diameter distribution of the silicone rubber particles were determined on a Hitachi X-650 scanning electron microscope (SEM) and more than 200 particles were measured.

Measurement of Mechanical Properties of the Modified Epoxy Resin

After ESCN-195 (100 phr), PN (50 phr), DBU (5 phr), and silicone rubber particles (5–15 phr) were blended uniformly using a dual roller, an appropriate amount of the mixture was put into a mold, then heated at 150°C under 1 MPa for 15 min and postcured at 180°C at 0.1 MPa for 6 h. After cooling, the sample piece was cut into the test pieces with a dimension of 60 × 10.00 × 1.60 mm. Before the measurement, the test pieces were annealed at 100°C for 12 h.

A three-point bending test was used for measuring the mechanical properties of the modified epoxy resins on a Shimadzu AutoGraph DCS-5000 versatile testing machine with the displacement rate of 2 mm/min. The flexural strength (σ_f), flexural modulus (E_f), and elongation at break (ε) were calculated according to the method described in ref. 8. All the values were the average of five measurements. To improve the interfacial adhesion of the silicone rubber particles and epoxy resin, the particles were treated with GPTMS in advance. The typical procedure was as follows: Silicone rubber particles (6.0 g), ethanol (20 mL), and GPTMS (0.6 g) were mixed carefully and stood at 60°C for 6 h; then, the particles were dried under a vacuum.

Measurement of Thermal Properties of Modified Epoxy Resin

Thermal linear expanding coefficients of the modified epoxy resins in the glassy (α_g) and the rubbery state (α_r) were measured on an RJY-1 thermal mechanical analyzer (Shanghai Balance Factory) with a heating rate of 10°C/min, and then

Table I Preparation of Silicone Rubber Particles and Their Swelling Degree

Silicone Rubber Particle	Silicone Oil (Equiv Ratio)			Swelling Degree (Q)	$Q^{5/3}$
	SVC[a]	SHC-1[a]	SHC-2[a]		
HVC-1	1	0	2	2.93	6.00
HVC-2	2	0	3	3.45	7.88
HVC-3	1	2	0	4.07	10.38
HVC-4	2	3	0	4.40	11.81

[a] SHC-1: DP = 60, equiv = 369; SHC-2: DP = 60, equiv = 118; SVC: DP = 60.

the glass transition temperature (T_g) was obtained.

SEM Observation

The feature of the breaking surface of the modified epoxy resin was observed under a Hitachi X-650 SEM.

RESULTS AND DISCUSSION

Crosslinking Degree of Silicone Rubber Particles

The recipe for preparing the silicone rubber particles and their swelling degrees (Q) are listed in Table I. As reported in ref. 9, the average molecular weight between the crosslinking points (M_c) of the polymer network can be obtained from the following equation:

$$\overline{M_c}\,\frac{0.5-\chi}{\rho V} = Q^{5/3} \qquad (2)$$

where χ is the Flory–Huggins interaction parameter; ρ, the density of the crosslinked polymer; and V, the mol volume of the swelling solvent.

Recently, Rubinstein and Colby also deduced that the equilibrium modulus of the dry polymer network (G) is reversibly proportional to $Q^{5/3}$,[10] and it is well known that G is also reversibly proportional to M_c. Thus, $Q^{5/3}$ is proportional to $\overline{M_c}$ and can be used as a parameter for the crosslinking degree. The results are listed in Table I.

The swelling degree of the obtained silicone rubber particles decreased slightly with increase of the equivalent ratio of SHC to SVC for the same SHC (see Table I). A higher swelling degree of HVC-3 and HVC-4 prepared from the reaction of SVC with SHC-1 (lower equivalence of Si—H) was observed compared with HVC-1 and HVC-2 from SVC with SHC-2 (higher equivalence of Si—H) (see Table I). Thus, the crosslinking degree of these silicone rubber particles increased in the following order:

HVC-1 > HVC-2 > HVC-3 > HVC-4

The diameter and diameter distribution of the particles are listed in Table II and showed that those of the particles of different silicone rubbers were quite similar. Thus, the properties of the modified epoxy resins were decided mainly by other factors.

Effect of the Content of Silicone Rubber Particles

The σ_f, E_f, and ε of the epoxy resin modified with 5 phr HVC-1 and 5 phr HVC-4 are shown in Figure 1. The σ_f or the E_f of the modified epoxy resin was lower than that of pure epoxy resin and decreased with increase of the content of the silicone rubber particles. ε decreased with increase of the content of the rubber particles for both of the modified epoxy resin, although it was higher than that of the pure epoxy resin for the epoxy resin modified by HVC-1. It was reported in our previous article that the poor compatibility of the silicone rubber with the epoxy resin caused the aggregation of the particles.[7] As the content of the rubber particles increased, more serious aggregation of these rubber particles would be brought about. Therefore, the modified epoxy resin containing more particles might break easier under the same stress, which was confirmed by the fact that the fracture surface of the modified epoxy resin containing more silicone rubber particles was smoother (see Fig. 2).

Effect of Crosslinking Degree of Silicone Rubber Particles

Increment of the crosslinking degree of silicone rubber increases its strength and modulus and,

Table II Diameter and Diameter Distribution of the Particles

Silicone Rubber Particle	Number Percentage				
	0–1 μm	1–2 μm	2–3 μm	3–4 μm	>5 μm
HVC-1	57.6	24.1	12.3	5.2	0.8
HVC-2	61.2	23.4	10.7	3.8	0.9
HVC-3	58.5	21.2	14.1	6.2	0
HVC-4	56.2	27.1	11.7	4.9	0.1

on the contrary, decreases its flexibility. It would be interesting to study the influence of the crosslinking degree of the silicone rubber particles on the mechanical properties of the modified epoxy resin. Therefore, the silicone rubber particles with different degrees of crosslinking were prepared (Table I) and used to modified the epoxy resin. The results are shown in Figure 3.

The strength and modulus of the silicone rubber were lower than those of the pure epoxy resin and the introduction of silicone rubber particles into the epoxy resin would reduce both of them. It was clearly observed that the values of σ_f and E_f decreased with increase of $Q^{5/3}$, that is, when the crosslinking degree of the silicone rubber particles increased, both of σ_f and E_f increased. It is very interesting to note that ε also increased with increase of the crosslinking degree [see Fig. 3(c)]. The result might be related to the dispersion behavior of the particles during blending. The particles having a higher crosslinking degree were easier to mix homogeneously with the epoxy resin. However, the particles with a lower crosslinking degree were adhesive to some extent, so they aggregated more seriously in the matrix of the epoxy resin. The fracture surface of the epoxy resins modified with different silicone rubber particles was in accordance with the results above (see Fig. 2).

Effect of Addition of the Coupling Agent

GPTMS was grafted onto the surface of the particles by the reaction of Si—$(OCH_3)_3$ with Si—OH groups on the particle surface, which was produced from the reaction of Si—H with water during the reaction of SHC with SVC, and the compatibility between the particles and the matrix was improved. At the same time, glycidyl groups of GPTMS would participate in the crosslinking reaction of the epoxy resin and the interface interaction could be increased. The mechanical properties of the epoxy resins containing 15-phr silicone rubber particles treated with and without GPTMS are listed in Table III.

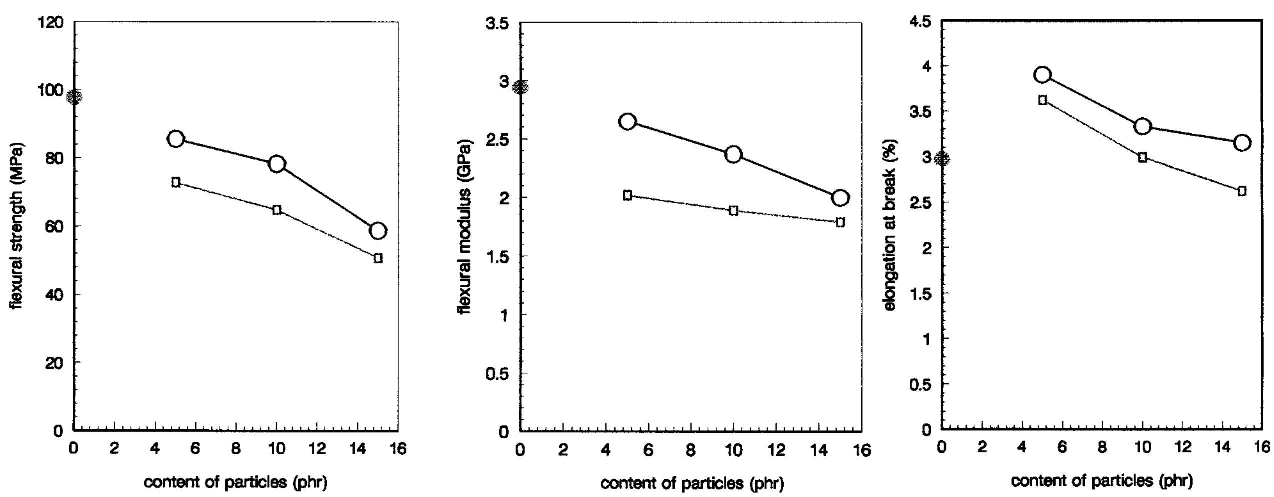

Figure 1 Mechanical properties of modified epoxy resins at different contents of the particles: (●) pure epoxy resin; (○) epoxy resin modified with HVC-1; (□) epoxy resin modified with HVC-4).

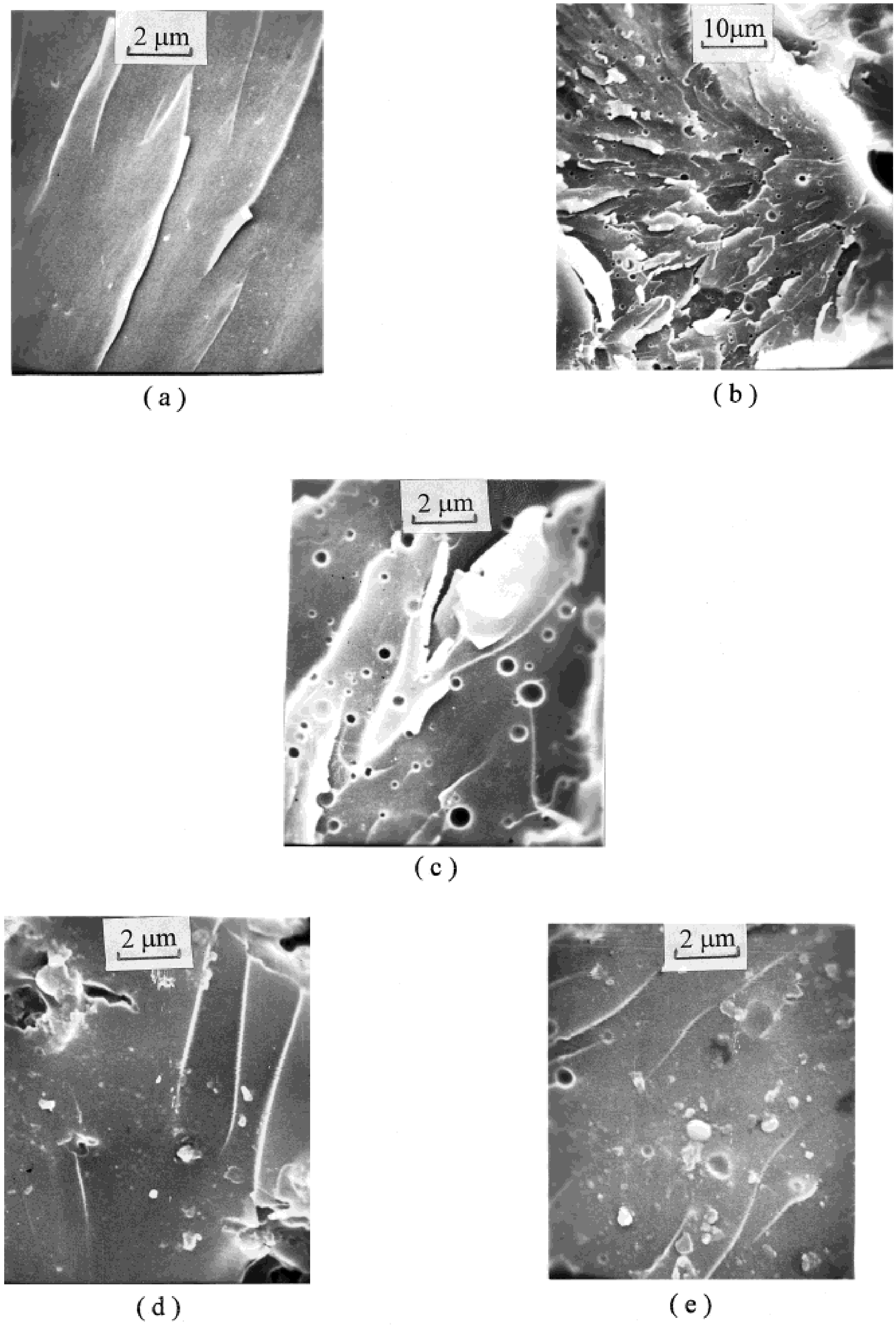

Figure 2 TEM photos of the fracture surface of epoxy resins: (a) pure epoxy resin; (b) epoxy resin modified with 5 phr HVC-1; (c) epoxy resin modified with 5 phr HVC-2; (d) epoxy resin modified with 5 phr HVC-3; (e) epoxy resin modified with 5 phr HVC-4.

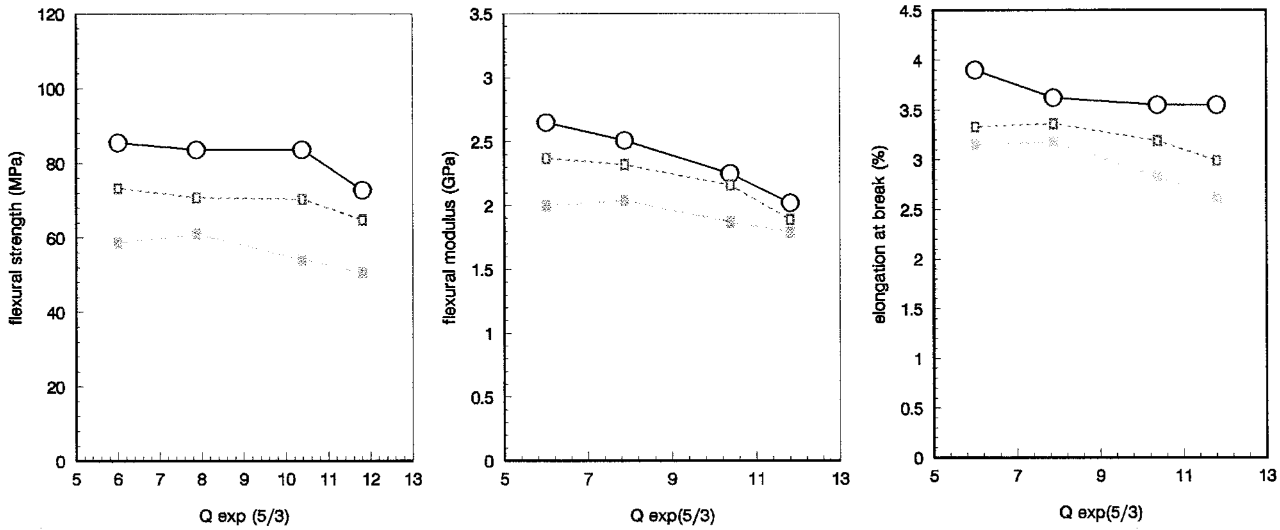

Figure 3 Mechanical properties of epoxy resins modified by rubber particles with different crosslinking degrees: (○) epoxy resin modified with 5 phr particles; (□) epoxy resin modified with 10 phr particles; (■) epoxy resin modified with 15 phr particles).

The treatment of GPTMS had little effect on the σ_f of the modified epoxy resins (see Table III). Its influences on E and E_f depended on the crosslinking degree of the silicone rubber particles. When the crosslinking degree was high (for HVC-1 and HVC-2), the E_f increased and ε decreased after the particles were treated with GPTMS. When the crosslinking degree was low (for HVC-3 and HVC-4), no change of E_f and an increase of ε were observed (see Table II). These results might be attributed to chemical bonding between the particles and the matrix and the dispersibility of the particles. When the crosslinking degree of the particles was high, the particles were hard and GPTMS could not permeate deep into them, so the number of glycidyl group on the particle surface was very large and it led to a strong interface interaction between the particles and the matrix, and little microcrack was induced by the rubber particles. Therefore, the modulus increased and the elongation decreased. By comparison, when the crosslinking degree of the particles was low, the particles were soft and it was convenient for GPTMS to enter into them. So, the content of the glycidyl group on the particle surface was low and the interface interaction was not too strong. Meanwhile, the dispersibility of the particles in the matrix improved. The modulus and strength did not change and the elongation increased. The influences of the factors mentioned above on the toughness and shock resistance of the modified epoxy resins are being studied and the results will be reported later.

Table III Influence of GPTMS on the Mechanical Properties of Modified Epoxy Resin

Silicone Rubber Particle	GPTMS[a] (Wt Ratio)	σ_f (MPa)	E_f (GPa)	ε (%)
HVC-1	None	58.7	2.00	3.15
HVC-2	None	61.0	2.04	3.18
HVC-3	None	54.1	1.87	2.83
HVC-4	None	50.7	1.79	2.62
HVC-1	0.1	59.8	2.45	2.45
HVC-2	0.1	53.9	2.28	2.62
HVC-3	0.1	55.2	1.80	3.92
HVC-4	0.1	51.3	1.81	3.47

[a] Weight ratio of GPTMS to silicone rubber particles.

Table IV Properties of Modified Epoxy Resins

Silicone Rubber Particle	σ_f (MPa)	E_f (GPa)	ε (%)	T_g (°C)
none	97.8	2.94	2.97	182.1
HVC-1 (5 phr)	85.5	2.65	3.90	181.9
HVC-2 (5 phr)	83.6	2.51	3.55	179.5
HVC-3 (5 phr)	83.6	2.25	3.55	178.0
HVC-4 (5 phr)	72.8	2.02	3.62	177.8
HVC-1 (15 phr)	58.7	2.00	3.15	176.7
HVC-2 (15 phr)	61.0	2.04	3.18	174.6
HVC-3 (15 phr)	54.1	1.87	2.83	171.5
HVC-4 (15 phr)	50.7	1.79	2.62	170.2

Thermal Properties of Modified Epoxy Resins

The glassy transition temperature (T_g) of the epoxy resins was determined on a TMA apparatus and the results are listed in Table IV.

The T_g of the modified epoxy resins was lower than that of the pure epoxy resin and declined with increase of the content of the silicone rubber particles. Moreover, the crosslinking degree of the particles had an effect on the T_g. The higher the crosslinking degree, the higher was the T_g of the modified epoxy resin.

CONCLUSIONS

Silicone rubber particles were prepared by the addition reaction of SHC and SVC in their latex. The crosslinking degree of the particles increased with decrease of the equivalence of SHC and slightly with increase of the equivalent ratio of SHC to SVC. Besides the content of silicone rubber particles in the blends, their crosslinking degree had a big effect on the properties of the modified epoxy resins. Additionally, the influence of GPTMS depended on the crosslinking degree of the particles.

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