

Flexibility Improvement of Epoxy Resin by Using Polysiloxane–PGMA (MMA) Composite Particles

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SYNOPSIS

A study on the increase of the flexibility and decrease of the internal stress of cured epoxy resins by addition of polysiloxane rubber particles grafted with and without glycidyl methacrylate (GMA) or methyl methacrylate (MMA) is reported. Polysiloxane latex was obtained by cycling a mixture of polysiloxane containing a vinyl group and a $\equiv\text{Si}-\text{H}$ group, respectively, emulsifier, and water in a homogenizer. Graft polymerization of GMA (or MMA) on these rubber particles was performed in the latex under γ -ray irradiation of ^{60}Co . The rubber particles were used to improve the flexibility of the epoxy resin. The particles grafted with GMA showed a homogeneous distribution in the matrix, better inducing and terminating craze. Comparisons were made among the particles grafted with MMA and various MMA–GMA or a series of GMA; the results indicated that the particles grafted with GMA (graft ratio = 10%) showed the greatest increase of elongation and decrease of internal stress. The factors influencing the toughness of the epoxy resin matrix are discussed.

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INTRODUCTION

The flexibility improvement of epoxy resin by the addition of elastomers has been extensively studied. It is known that several factors influence the flexibility of the modified epoxy resin such as the composition and structure of the elastomer, size and distribution of the domain in the matrix, and the content of elastomers in the epoxy resin.^{1–5} In recent years, polysiloxane elastomers as a flexibilizer have attracted great attention due to their thermal stability. Different results on flexibility improvement and lowering the internal stress were observed. However, only a very few of articles reported that polysiloxane rubber particles were used to toughen epoxy resin.⁶ The particles with poly (butyl acrylate) as the core and poly (methyl methacrylate) (PMMA) as the shell were prepared and used in studying the effect of the rubber particles' structure and the interaction between domain and matrix on the tough-

ness of epoxy resin. The results indicated that the core–shell structure of the particles had the functions of improving the homogeneous distribution of particles in the matrix and enhancing the interaction between the domain and matrix.⁶

In analyzing the investigation on the toughness of epoxy resin by using polysiloxane elastomers, the domains could be attributed to three types of structures: (1) There is no crosslinkage within domains and no chemical bonds between the domain and matrix, as shown in Figure 1(a). This domain was formed by phase separation of linear elastomers from a homogeneous mixture of epoxy resin and elastomer during the curing process. (2) As shown in Figure 1(b), there are chemical bonds between the domain and matrix, but no crosslinking within the domains. When linear elastomers with functional groups are used in toughening epoxy resin, the chemical bonds are formed by the reactions of elastomer with epoxy resin during the curing process. (3) No chemical bonds between the matrix and crosslinked domains exist, as shown in Figure 1(c). These domains are formed by adding rubber particles with or without the core–shell into the epoxy

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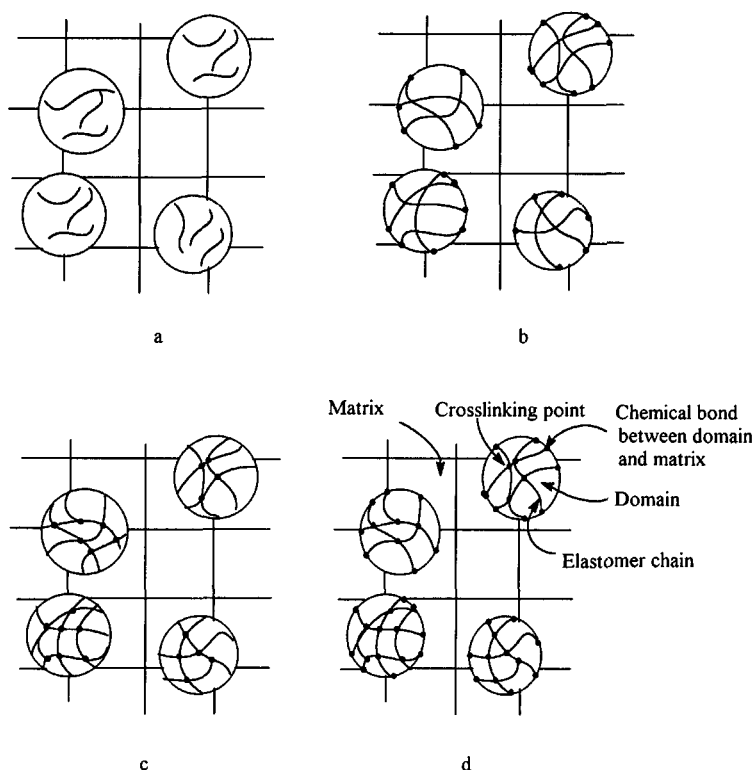


Figure 1 Diagram of domain structures in the matrix.

resin. It was thought interesting to study the cross-linked domains which have chemical bonds with the matrix as shown in Figure 1 (d).

In this study, we report the preparation of cross-linked polysiloxane rubber particles grafted with glycidyl methacrylate (GMA) which could react with epoxy resin. The particles were used as a flexibilizer; the effects of the particles' composition and structure and the chemical bonds between the domain and matrix on the flexibility and internal stress are discussed.

EXPERIMENTAL

Materials

Polysiloxanes containing a vinyl group (SVB) and $\equiv\text{Si}-\text{H}$ (KF-99) purchased from Benbu Organic Siloxane Co. and Shintsu Co., respectively, were used without further purification. The catalyst for the addition reaction of $\equiv\text{Si}-\text{H}$ and the vinyl group was prepared according to the procedure described in the literature.⁷ *O*-Cresol novolac epoxy

Table I Conditions and Results of the Surface Modification for S10

Elastomer	Irradiation Dose (Mrad)	Salt and Conc'n (mol/L)	Monomer and Amount ^a	Yield ^b (%)	Graft Ratio (%)	Graft Efficiency (%)
S10-M	0.68	NaBr (1)	MMA (73%)	83	36.5	48.8
S10-G5	0.61	NaCl (3)	GMA (5%)	90	5.0	99.9
S10-G10	0.61	NaCl (3)	GMA (10%)	88	10.0	99.0
S10-G20	0.61	NaCl (3)	GMA (20%)	88	18.5	92.5
S10-G30	0.61	NaCl (3)	GMA (30%)	85	27.0	90.0

^a Weight ratio of monomer added/rubber particles.

^b Weight percentage of grafted product/rubber particles and monomer added.

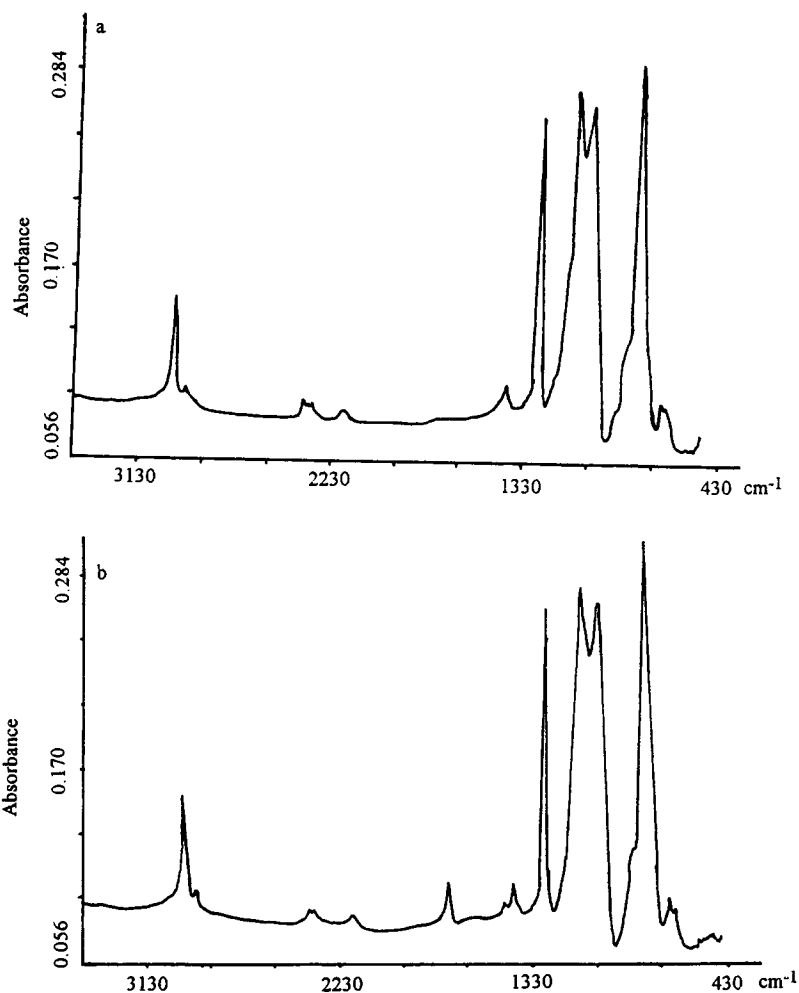


Figure 2 The IR spectra of (a) polysiloxane rubber particles S10 and (b) S10 grafted with MMA.

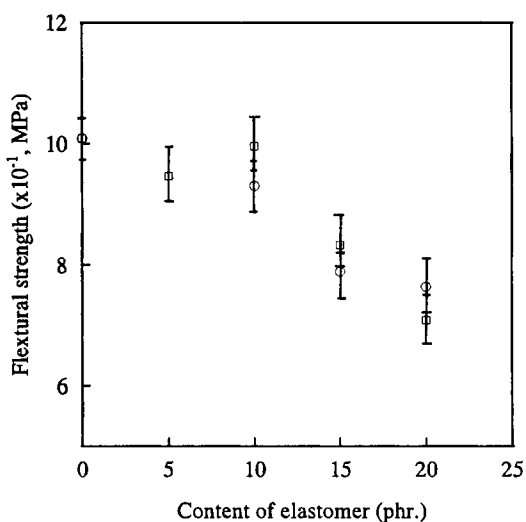


Figure 3 The effect of elastomer content on the flextural strength of the matrix: (□) S10; (○) S10-G10.

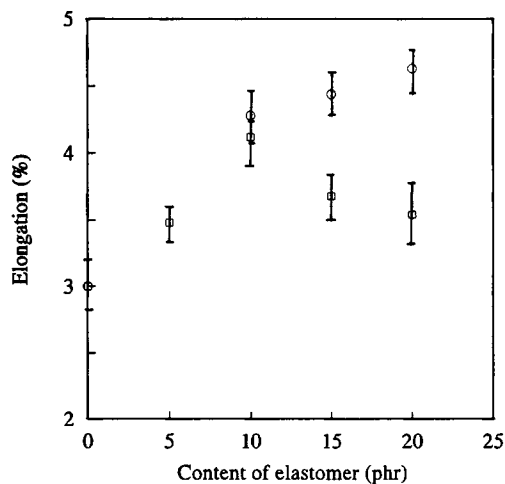


Figure 4 The effect of elastomer content on elongation of the matrix at break: (□) S10; (○) S10-G10.

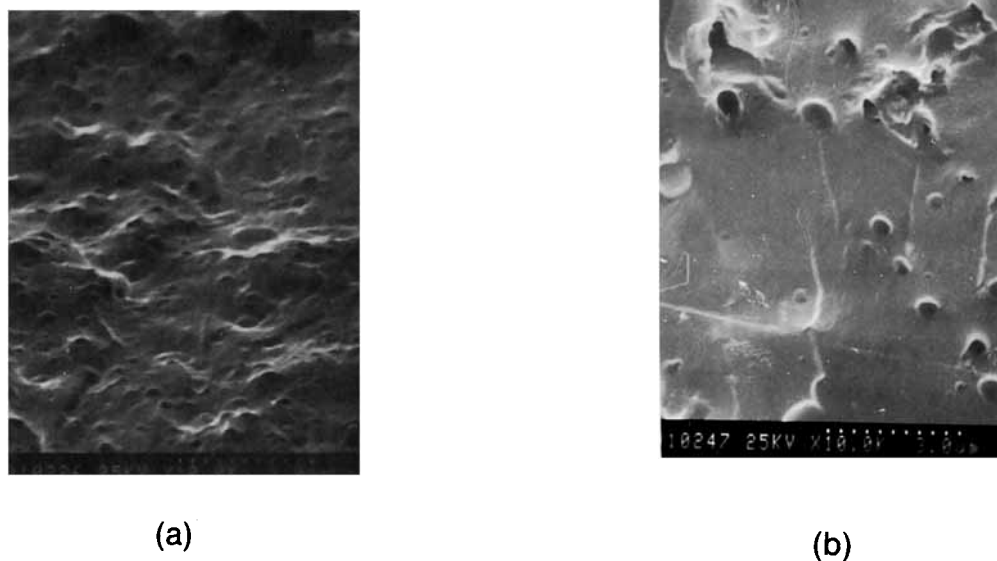


Figure 5 SEM photographs of the fracture section of the epoxy resin modified with S10 or S10-G10: (a) S10; (b) S10-G10.

resin, phenol novolac (hardener), and DBU (accelerator) were obtained from Hitachi Chemical Co.

Preparation of Polysiloxane Particles (S10)

Polysiloxane particles (S10) were prepared with the same method described in our previous article.⁸

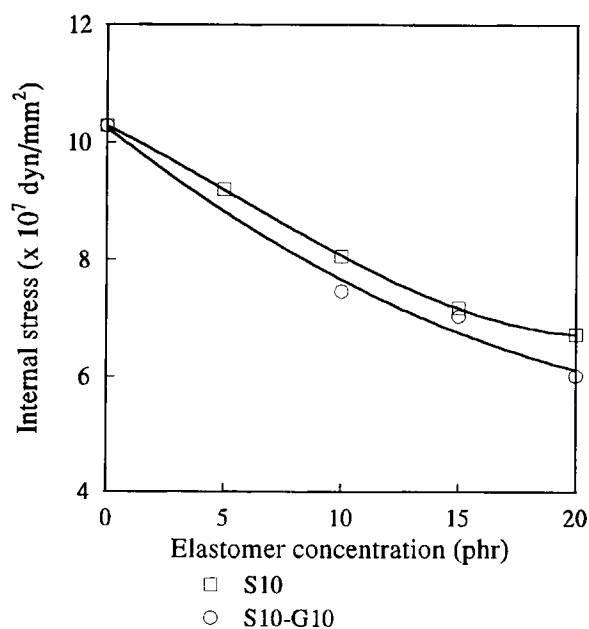


Figure 6 The relationship between internal stress and elastomer content: (□) S10; (○) S10-G10.

Surface Modification of Particle S10

Sodium bromide (10.2 g) was proportionally added into a 150 mL flask containing S10 latex (100 mL, 10.3 g rubber particles) while stirring. After sodium bromide was completely dissolved, GMA (1.03 g) was added dropwise. The mixture was stirred overnight, then irradiated by a γ -ray of ^{60}Co at 154.2 rad/s for 67 min under a nitrogen atmosphere. Particles were precipitated by adding anhydrous sodium

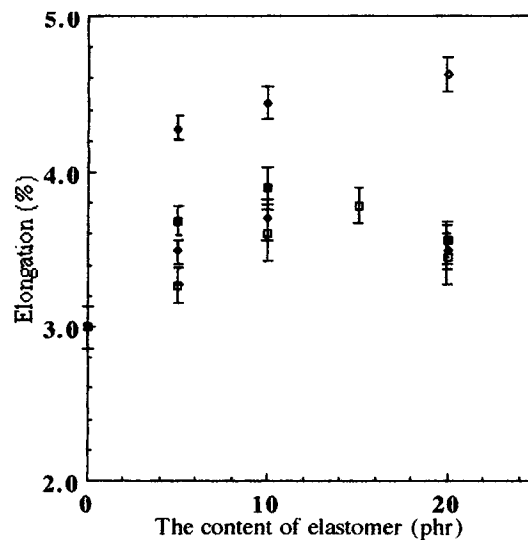


Figure 7 The effect of GMA content in the mixture of the grafted monomers on elongation of the matrix at break: (□) S10-M; (◆) S10-MG1; (■) S10-MG2; (◇) S10-G10.

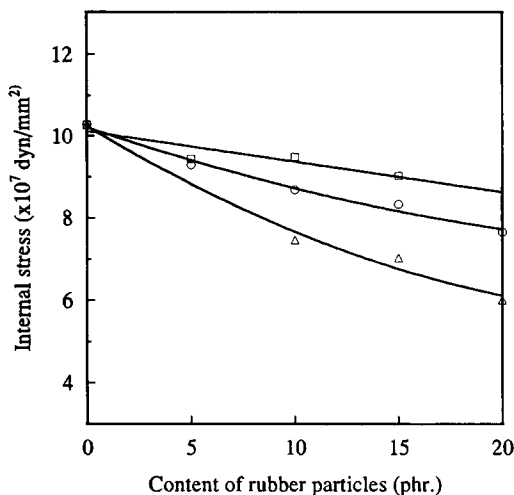


Figure 8 The effect of GMA content in the grafted rubber particles on internal stress of the matrix: (□) S10-M; (○) S10-MG2; (△) S10-G10.

sulfate (10 g) at 70°C while stirring. A white powder (S10-M; yield: 85%) was obtained by filtration, washed with water, and dried in a vacuum at 70°C. The conditions and results of the surface modification for particles S10 are listed in Table I.

Measurement of Graft Ratio and Graft Efficiency

The methods of measuring the graft ratio and graft efficiency were described in a previous article.⁸

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

The IR spectra of the grafted particles were performed on Nicolet SX-170 IR spectrometer. The size and distribution of the particles produced by emulsion polymerization or existing in the matrix were measured by Hitachi X-650 SEM and H-80 TEM instrument.

Making of Test Pieces

Epoxy resin (100 part, weight), accelerator (5 parts, weight), phenolic resin (50 parts, weight), and the modified polysiloxanes were mixed 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, the molten mixture in the mold was pressed at 100 atm and 150°C for 15 min, then treated at 180°C for 6 h. The test pieces with a dimension of 60 × 10 × 2 (mm) were obtained by cutting.

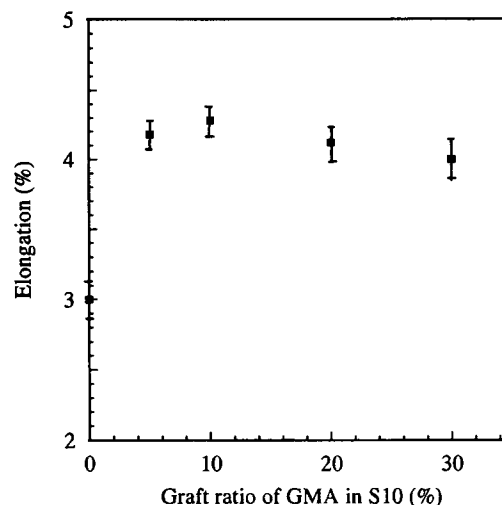


Figure 9 The effect of graft ratio of GMA in S10 on elongation of the matrix at break. Composition: epoxy resin/S10-G = 100/10 (weight ratio). Conditions: see Experimental part.

Measurement of Mechanical Properties

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.⁹ Each point was the average value of five measurements.

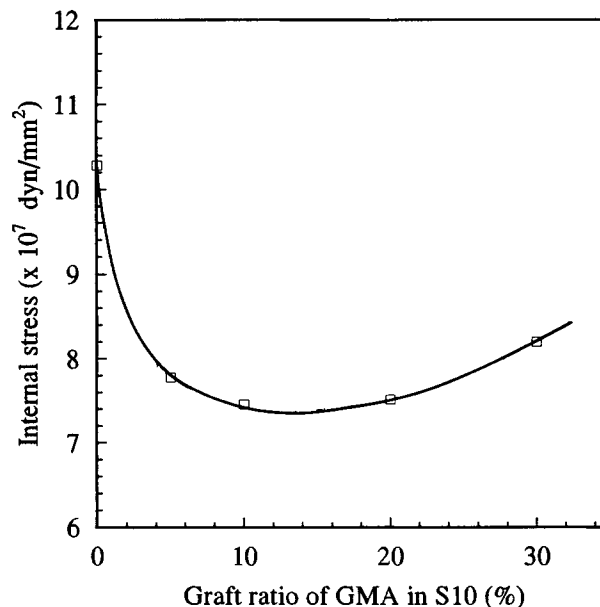


Figure 10 The effect of graft ratio of GMA in S10 on internal stress of the matrix. Composition: epoxy resin/S10-G = 100/10 (weight ratio). Conditions: see Experimental part.

Measurement of Internal Stress

The internal stress (σ) was measured according to the method proposed by Nakamura et al.³ Epoxy resin was coated on the surface of an aluminum alloy plate with a dimension of $90 \times 10 \times 0.2$ (mm), which was preheated at 120°C , until approx. $0.1 \mu\text{m}$ of the coating layer thickness was fulfilled. 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 on the value of the bending radius of the aluminum alloy according to the equation described by Nakamura et al.³

RESULTS AND DISCUSSION

In general, the graft ratio was measured based on the weight of the samples before and after extraction in a Soxhlet apparatus. It was difficult to avoid the loss of the grafted rubber particles during extraction because the particles with $1.1 \mu\text{m}$ of the average diameter were used in this study. Therefore, the graft ratios were measured by the IR method. The peak at $\nu 1730 \text{ cm}^{-1}$ appeared in the IR spectrum of S10 grafted with GMA (or MMA) after being extracted in benzene (see Fig. 2) and, correspondingly, for the IR spectrum of S10, no peak at $\nu 1600\text{--}1800 \text{ cm}^{-1}$ was observed [see Fig. 2(a)]. Since the peak at $\nu 1280 \text{ cm}^{-1}$ representative of the Si—C bond did not change during graft polymerization, it was used as an internal standard. The standard curves were obtained by, respectively, measuring the peak height at $\nu 1730$ and 1280 cm^{-1} on the IR spectra of the mixtures of S10 and PGMA (or PMMA) at a series of weight ratios. The graft ratio (g) could be obtained directly from the corresponding standard curve. The graft efficiency (Ge) was obtained according eq. (1):

$$Ge = \frac{\text{Weight of the monomer grafted with S10}}{\text{Weight of the monomer added}} \times 100\% \quad (1)$$

Graft polymerization of the rubber particles S10 was carried out in the emulsion polymerization solution after the crosslinking reaction was performed. The conditions and results are listed in Table I. The results in Table I demonstrate the occurrence of the grafting reaction on the surface of the particles. The addition of salt into the emulsion solution prevents the formation of PMMA particles and increases the graft efficiency. The homopolymerization possibility of GMA increased when more GMA was added into

the emulsion system. Thus, a slight decrease of Ge values as the amount of GMA used increased was observed (see Table I). The grafting mechanism in the emulsion system was discussed in another article.⁸

A few papers have reported on the flexibility improvement of epoxy resin using polysiloxane rubber particle.⁶ Homogeneous distribution of the rubber particles in the epoxy resin matrix is one of the factors improving flexibility.¹⁰ Poor compatibility of polysiloxane rubber particles and their strong tendency to aggregate did not favor a homogeneous blend of the two components. Therefore, it is very important to improve the surface properties of the rubber particles. The purpose of this study was to graft GMA (or MMA) onto the surface of the particles and to analyze the influence of the grafting on the modification of the epoxy resins. Siloxane rubber particles grafted with and without PGMA were used as a flexibilizer, and their flexural strength and elongation of the modified epoxy resin at various particle contents were measured. The results are shown in Figures 3 and 4, respectively. A maximum value of elongation appeared at 10 phr (see Fig. 4). Simultaneously, a decrease of flexural strength at an elastomer content higher than 10 phr is observed (see Fig. 3). The possible reasons for better flexibility improvement of S10-G10 particles (See Fig. 4) are (1) better compatibility of the surface of the S10-G10 rubber particles with the epoxy resin matrix and (2) formation of chemical bonds between the matrix and particles because the epoxy groups of GMA could react with the epoxy resin during the curing process. The SEM photograph of the epoxy resin modified with S10-G10 demonstrated that inducing and terminating the craze can take place even for very small rubber particles [see Fig. 5(b)], thus, much fracture energy was consumed (see Fig. 5). As a result, the modified matrix with S10-G10 should be of lower internal stress. This was confirmed by studying the internal stress in the modified matrix as shown in Figure 6. When 20 phr of rubber particles were used, the internal stress of the matrix modified with S10-G10 reduced to 58% of the original value. As a comparison, the corresponding value for the matrix modified with S10 was 65%.

To verify further that the formation of chemical bonds between the domain and matrix affect the flexibility improvement, the modified rubber particles grafted with PMMA (S10-M), PMMA (68 wt % of S10)-PGMA (5 wt %) (S10-MG1), PMMA (63 wt %)-PGMA (10 wt %) (S10-MG2), and PGMA were prepared; then, these various particles were used in making the test pieces. Their elonga-

tions at break were measured and are reported in Figure 7. The curves indicate that rubber particles grafted with more GMA showed more flexibility improvement. In general, the higher the content of GMA in the particles, the more bonds formed between the domain and the matrix. However, only a suitable amount of GMA grafted in the particles would help in inducing and terminating the craze, which consumed the fracture energy and reduced the internal stress of the matrix produced from the curing process and cooling from cure temperature to room temperature. Measuring the internal stress in the modified matrix led to the conclusion that the higher the content of GMA grafted onto S10 the lower the internal stress (see Fig. 8).

It was interesting to study the influence of the contents of GMA grafted onto the silicone particles on the properties of the modified epoxy resin. A series of rubber particles grafted with different amounts of GMA (S10, S10-G5, S10-G10, S10-G20, and S10-G30) were used to make the test pieces. The elongation and internal stress of epoxy resin modified with these particles were measured. Figures 9 and 10 present the elongation and internal stress as a function of the contents of GMA in S10, respectively. The maximum value of elongation and the smallest value of internal stress appeared at 10% of the graft ratio. This finding indicates that the formation of too many bonds between the domain and matrix does not favor the reduction of internal stress. In fact, each chain of grafted GMA contained some amount of epoxy groups which took part in the crosslinking reaction with the epoxy resin during the cure process. When too much GMA was grafted in the rubber particles, a shell with a high density of crosslinkage around the particles could be formed. This structure might not favor the induction and termination of the craze. The length of the grafted chain and the density of grafting points on the surface of rubber particles should influence the structure of the matrix around the particles, thus affecting the efficiency of the flexibility improvement. This study is in progress.

CONCLUSION

The graft polymerization of GMA or MMA on the polysiloxane particles was carried out under γ -ray

irradiation of ^{60}Co . The toughness of the epoxy resin could be obtained by addition of these polysiloxane rubber particles grafted with or without GMA as the flexibilizer. Reducing the aggregation of the particles during the curing process and increasing the interaction between the matrix and domain led to improvement of the flexibility. This purpose can be afforded by modifying the surface structure and properties of the particles. The monomer GMA has an epoxy group and better compatibility with the matrix. The particles grafted with GMA improves the homogeneous distribution of particles in the matrix and form the chemical bonds between the domain and matrix. An appropriate amount of these bonds would favor the induction and termination of the craze, thus increasing the toughness of the modified epoxy resin and reducing the internal stress.

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