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Yeong-Soon Gal[a]; Hee-Chul Kang[a]; Byung-Yeol Park[a]; Hyoung-Geun Kim[a]; Sang-Kii Chung[a]; Tae-Kyeong Hwang[a]; Bal Jung[a]
[a] Agency for Defense Development, Taejeon, Korea

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THE EFFECT OF STYRENE ON EPOXY RESIN FORMULATIONS FOR FILAMENT WINDING

YEONG-SOON GAL,* HEE-CHUL KANG, BYUNG-YEOL PARK,
HYOUNG-GEUN KIM, SANG-KII CHUNG, TAE-KYEONG HWANG, and
BAL JUNG

Agency for Defense Development, 4-4-5
P.O. Box 35, Yuseong 305-600, Taejeon, Korea

ABSTRACT

The effect of styrene on epoxy resin formulations for filament winding were studied from the viewpoints of processing, mechanical, and thermal properties. Five epoxy blends with different compositions of epoxy resin, hardener, and styrene were made and evaluated. The addition of a small amount (maximum 10%) of styrene to the epoxy formulations decreased the resin viscosity from 605 to 160 cP and increased the pot life of the mixed resin system. The tensile and flexural properties were found to be similar, regardless of styrene content. The thermal properties (heat deflection temperature, glass transition temperature, etc.) of the resulting thermoset blends decreased as the styrene content increased. From the viewpoints of resin viscosity, pot life, and mechanical and thermal properties, it was found that the addition of a small amount (5–10%) of styrene to an epoxy resin was adequate for an epoxy matrix system used for filament winding.

INTRODUCTION

Due to the extensive uses of epoxy resins in the areas of electrical laminates, molding compounds, aerospace composites, and sporting goods, the interests of academic and industrial researchers have been particularly focused on these epoxy resin systems and fiber-reinforced composites [1–4].

Filament winding is a process for the fabrication of reinforced composites in which a series of resin-impregnated continuous filaments are applied to a mandrel according to a predetermined geometrical relationship [5, 6]. Its main use is to make tube- and pipe-shaped objects, such as chemical storage tanks, liners for smokestacks, golf club shafts, aerospace missiles, and drive shafts [3, 7–9]. To date, various epoxy resin formulations have been used for the filament winding fabrication of high performance composite structures [10–13].

There are some handling criteria that are unique for filament winding: 1) viscosity should be 1500 cP or lower, 2) pot life should be as long as possible (preferably more than 6 hours), 3) toxicity should be low, and 4) the thermomechanical property of the cured matrix should be considered.

In order to satisfy the above criteria (especially viscosity and pot life), a number of diluents have been used for epoxy resin formulations [1, 12]. Small amounts of low-molecular weight diluents, particularly difunctional ones, do not seriously degrade the properties of a cured matrix.

In most cases, mono- and diglycidyl compounds have been used as the reactive diluents of epoxy resin formulations for filament winding [12].

Polymeric blends consisting of an unsaturated polyester and the styrene monomer are standard commercial products and widely used [14, 15]. Resin systems from epoxy-maleic anhydride, vinyl monomer, and aromatic nitrophenol were developed for coating and impregnating large motor and generator insulation and other insulated electrical components [16, 17]. Heat-curable epoxy resin formulations containing styrene have been developed for use as casting materials, adhesives, coatings, and polymer concrete [18–24]. The styrene-modified diglycidyl ether of bisphenol A (DGEBA) epoxy system cured with trimellitic anhydride has been investigated to explore processing and structure relationships [25, 26]. However, to our knowledge, there have been no reports on systematic studies of resin formulations for filament winding in which the styrene monomer is used as the reactive diluent to reduce the viscosity of the resin system and to increase the pot life through chemical, physical, and mechanical properties.

We now report on the effect of styrene monomer on an epoxy resin formulation composed of a basic DGEBA-type epoxy resin and a modified aromatic amine hardener.

EXPERIMENTAL

Materials

The properties of a DGEBA-type epoxy resin (YD-128, Kukdo Chemical Industry Co. Ltd.) and a curing agent (KH-100, Kukdo Chemical Industry Co. Ltd.) are listed in Table 1. Styrene (Oriental Chemical Co. Ltd., 99%) was used after simple distillation. E43 release agent (Chem-Trend Incorporated) was used.

Specimen Preparation

Resin mixing was performed using a mechanical stirrer at high rotation speeds for about 3 minutes. Specimens were prepared by casting the mixture into a steel (SCM 4) mold prepared according to JIS K6911. The mold was coated with E43

TABLE 1. Properties of Epoxy YD-128 and Hardener KH-100

Properties	YD-128	KH-100
Epoxy equivalent (g/equiv)	184–190	–
Amine equivalent (g/equiv)	–	44.6
Viscosity (cP at 20°C)	11,500–13,500	180
Color (Gardner)	0.5 max	13 max
Specific gravity (g/cm^3)	1.17	1.022
Chlorine content (%)	0.05 max	–
Flash point (°C)	–	>135
Specification	DGEBA-type epoxy resin	Aromatic amines with aliphatic chains

release agent before use. A standard cure cycle was as follows: 80°C (2 hours) + 120°C (2 hours) + 155°C (6 hours). Five epoxy blends, labeled A, B, C, D, and E, with different compositions of YD-128, KH-100, and styrene were prepared as shown in Table 2.

Apparatus and Procedures

The viscosities of the resin mixtures were measured with a Brookfield viscometer (Model RVT) according to ASTM D2393. Tensile tests were performed on an Instron 1335 at room temperature at a stroke rate of 1.3 mm/min. Test specimens was made according to the JIS K6911 standard. Elongation measurements were taken using an Adamel-Chomargy EX10 extensometer. Young's modulus was computed from the linear part of the curve; elongation and stress at break were also recorded.

Compression tests were made using the same testing machine at a stroke rate of 1.3 mm/min according to ASTM D790-81. The specimens (12.7 × 10 × 4 mm) were deformed in a compression ring between steel plates, and the support span-to-depth ratio was 16.

The tests of heat deflection temperature were done with a heat deflection tester (Tinus Olsen Testing Machine Company) according to ASTM D648-82.

TABLE 2. Compositions of Five Epoxy-Styrene Blends

	Component, wt%		
Code	YD-128	KH-100	Styrene
A	100	25	0
B	100	25	3
C	100	25	5
D	100	25	7
E	100	25	10

Dynamic mechanical properties were measured using DuPont DMA 982 modules coupled to the DuPont 9900 thermal analysis system for data acquisition and analysis. The heating rate for the DMA experiments was 5°C/min from ambient to 250°C.

Differential scanning calorimetry (DuPont 910) was used to measure the glass transition temperatures. The thermal stabilities of the cured epoxy matrix systems were characterized using a Thermogravimetric Analyzer (DuPont 951) at a heating rate of 10°C/min.

RESULTS AND DISCUSSION

Formulations and Chemical Properties

In order to understand the formulation and basic properties of the present epoxy-styrene resin systems, GPC and NMR spectroscopies were measured. The basic processing properties, such as initial viscosity of the resin mixture, viscosity change with time, and pot life, were also measured.

As described in Table 2, five epoxy-styrene thermoset blends containing different amounts of styrene were formulated and tested.

Figure 1 shows GPC chromatograms of YD-128 alone and of the YD-128-styrene (100/7 by weight) formulation. The characteristic peaks of styrene (elution count: 30.27), which were absent in the chromatogram of YD-128 alone, were observed in the YD-128-styrene formulation.

Figures 2 and 3 show the ^{1}H-NMR and the ^{13}C-NMR of the YD-128-styrene (100/7 by weight, Code D) formulation. In the ^{1}H-NMR spectrum, characteristic peaks (δ, ppm: 5.17, 5.20, 5.68, 5.75, 6.61-6.73, 7.20-7.37) of styrene were newly observed besides the peaks of the basic epoxy resin, YD-128. The ^{13}C-NMR spectrum (Fig. 3) of YD-128-styrene (100/7 by weight) also shows the small characteristic peaks of styrene at chemical shifts of 113.4, 125.8, 127.4, 128.1, 137.1, and 136.4 ppm.

Figure 4 shows the viscosity profiles of the present epoxy resin formulations composed of YD-128-styrene and hardener KH-100 (aliphatic alkyl substituted aromatic amines). The test temperature was 40°C, which has been used frequently as the resin bath temperature for filament winding. The initial viscosities of the present resin systems were notably decreased from 605 cP for Formulation A (having no styrene moiety) to 160 cP for Formulation E (styrene/YD-128 = 10/100). This phenomenon indicates that the styrene monomer lowers the viscosity of the resin system considerably and thus increases the wettability of the reinforcement fiber in the matrix resin. The tendency of the viscosity of mixed resin systems to increase was similar regardless of the styrene content of the resin system. The final viscosities after 9 hours at 40°C were 1500 cP for Formulation A and 260 cP for Formulation E. In regard to resin viscosity and pot life, the addition of 3-10 wt% styrene monomer was found to be adequate for the filament winding fabrication of variable composite structures.

Because the styrene monomer is a volatile compound, a considerable amount of styrene can be emitted in the curing process of thermoset matrices, resulting in volume shrinkage of cured matrices. Therefore, studies on the reduction of styrene emissions in unsaturated polyester and vinyl ester resins were carried out [15].

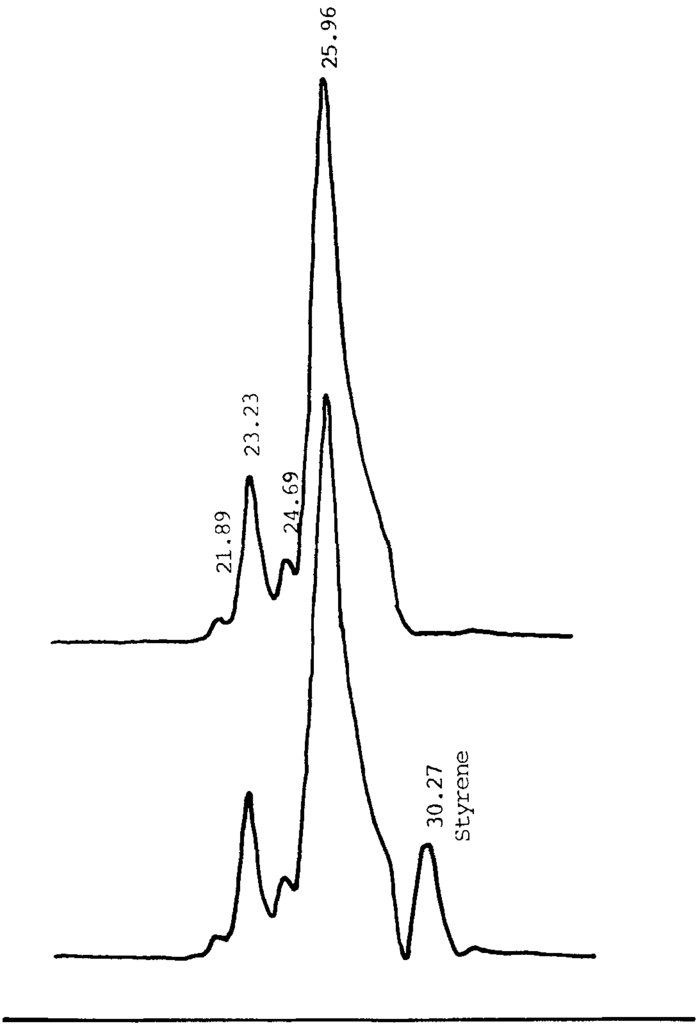

FIG. 1. GPC chromatograms of YD-128 and YD-128-styrene.

In order to determine the extent of styrene emissions in epoxy-styrene thermoset blends, volatile emissions were measured by the "open-cup method" with 200 g resin mixtures. The weight loss of cured matrix systems compared to the initial uncured matrix system are shown in Fig. 5. It is seen that the weight loss of the present matrix systems (from Formulation A to Formulation E) increased as the styrene content increased. As the styrene content in the formulations increased, the weight loss percentage (the styrene emitted during the curing process/the initial styrene of the resin mixture) increased from 13.7% for Formulation B to 25.23% for Formulation E. From these experiment results, even in the case of Formulation

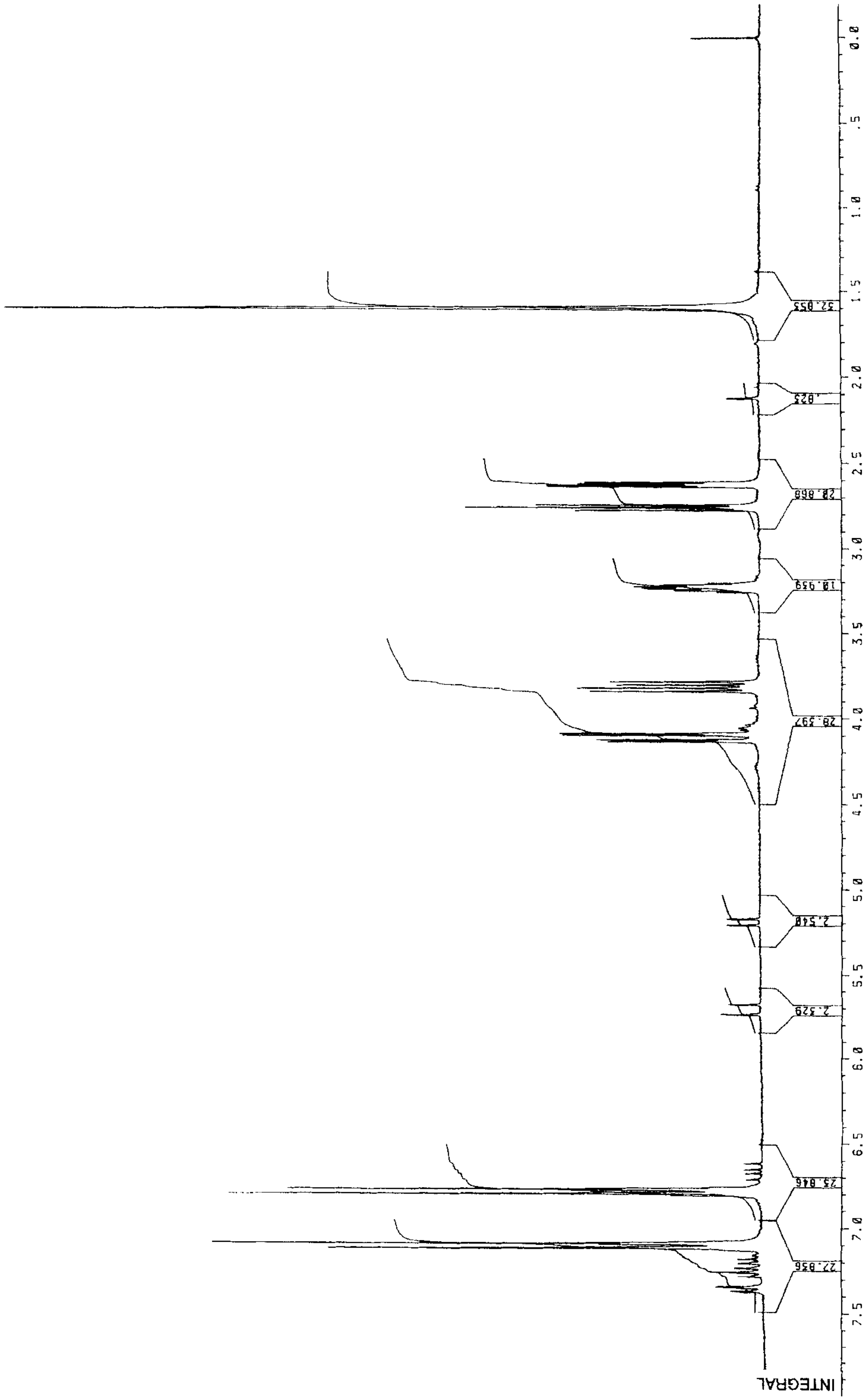

FIG. 2. ^{1}H-NMR spectrum of YD-128–styrene formulation (100/7 by weight).

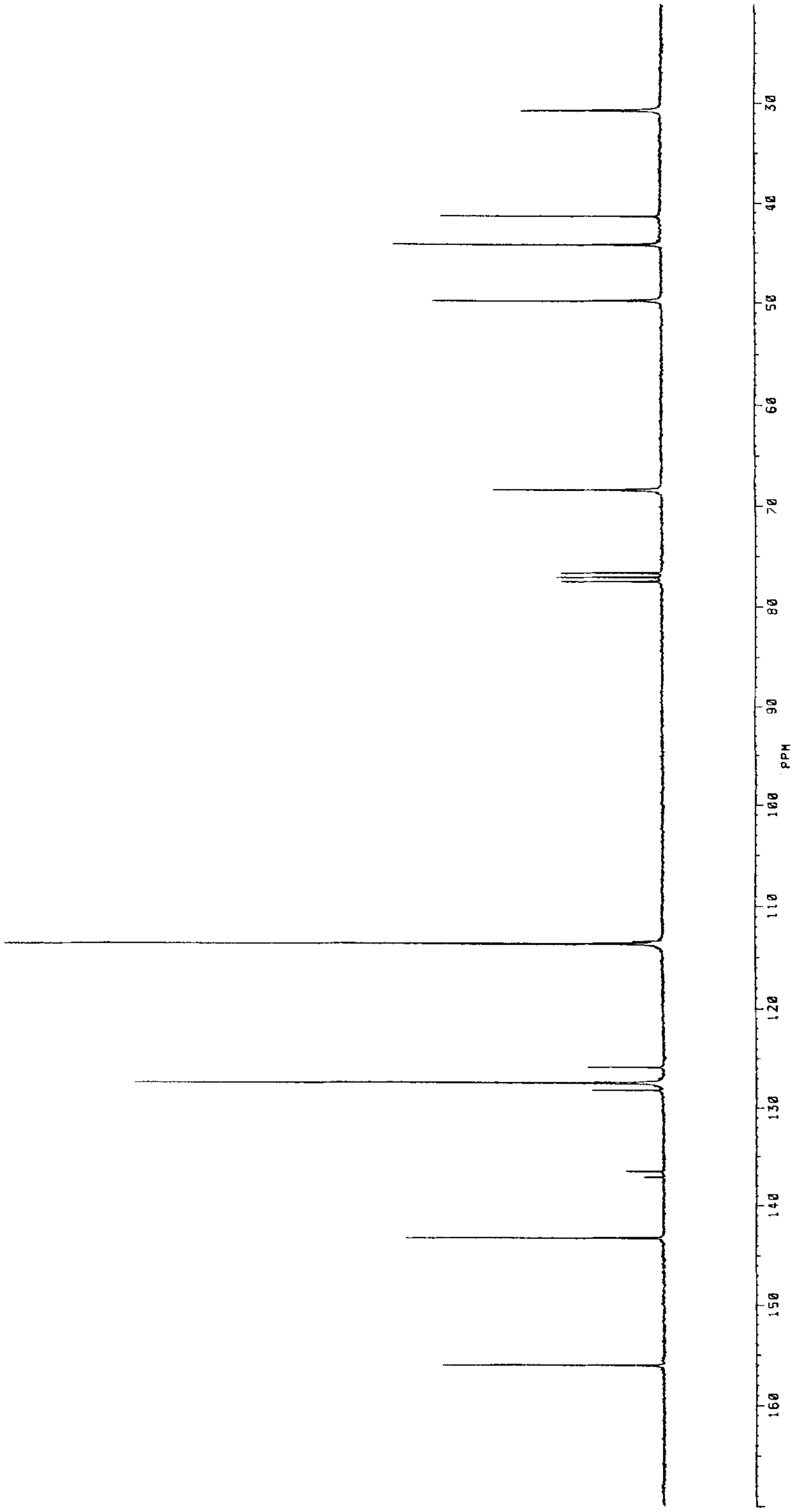

FIG. 3. ^{13}C-NMR spectrum of YD-128–styrene formulation (100/7 by weight).

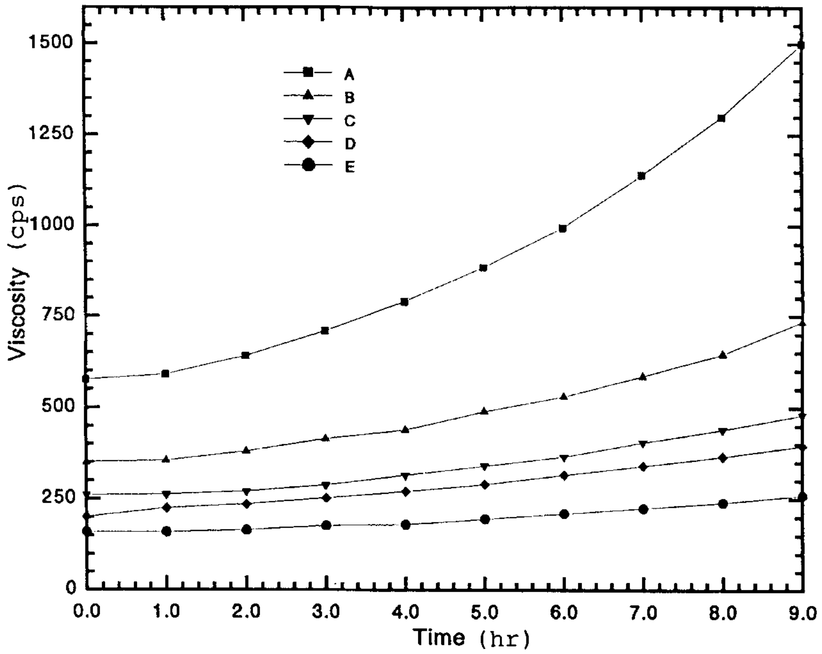

FIG. 4. Viscosity profiles of five YD-128-styrene/KH-100 resin formulations at 40°C.

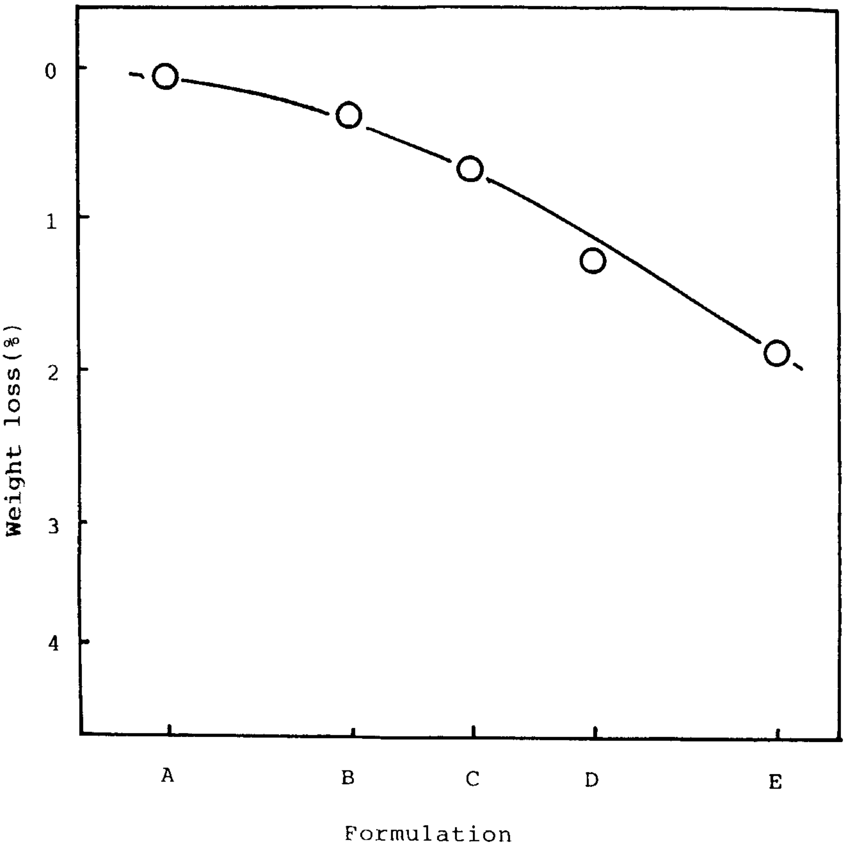

FIG. 5. Weight loss of neat resins during cure (200 g scale).

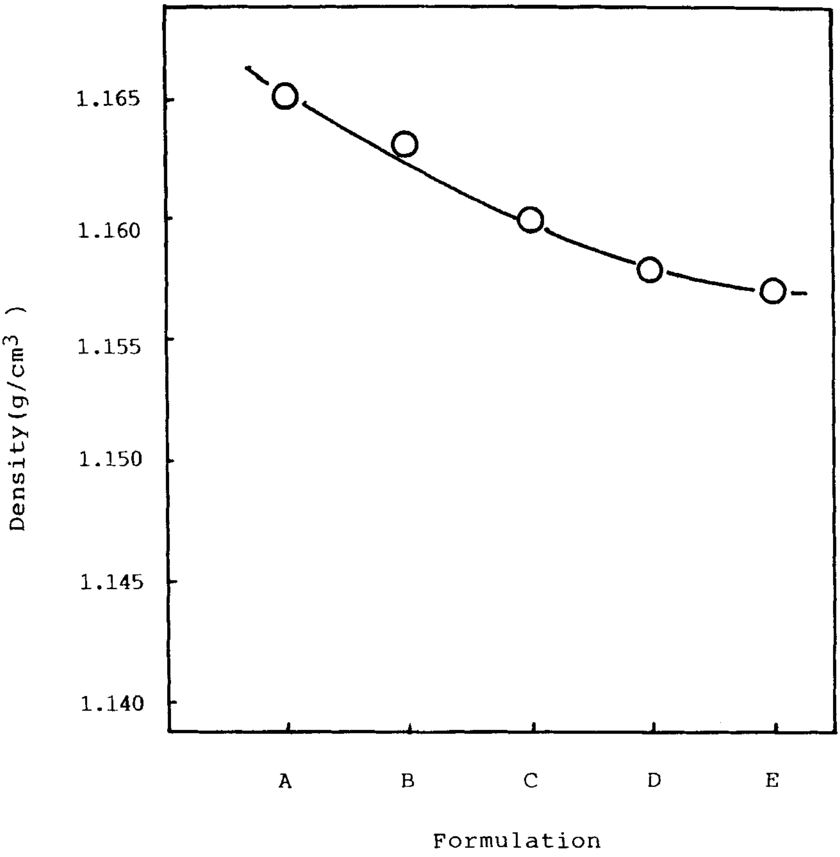

FIG. 6. Density changes of cured matrices according to the styrene content.

E, the major portion of styrene (about 75%) participates in the curing process as a reactive diluent.

Figure 6 shows the density change of epoxy-styrene thermoset blends based on the styrene content in the formulations. As the styrene content in the formulations increases, the density decreases gradually from 1.165 g/cm^3 for Formulation A to 1.157 g/cm^3 for Formulation E.

Mechanical Properties

Results related to tensile and compressive tests are shown in Figs. 7-10. Figure 7 shows the tensile strengths of epoxy-styrene thermoset blends according to styrene content. The original tensile strength of the cured epoxy specimen with no styrene moiety was 9100 psi. The tensile strengths of the present cured matrices were found to be similar, although a slight increase was observed as the styrene content in the formulations increased. Figure 8 shows the tensile modulus of the same specimens. The tensile modulus was similar regardless of the styrene content. The failure strain increased from 3.7% for Formulation A to 5.8% for Formulation E as the styrene content increased.

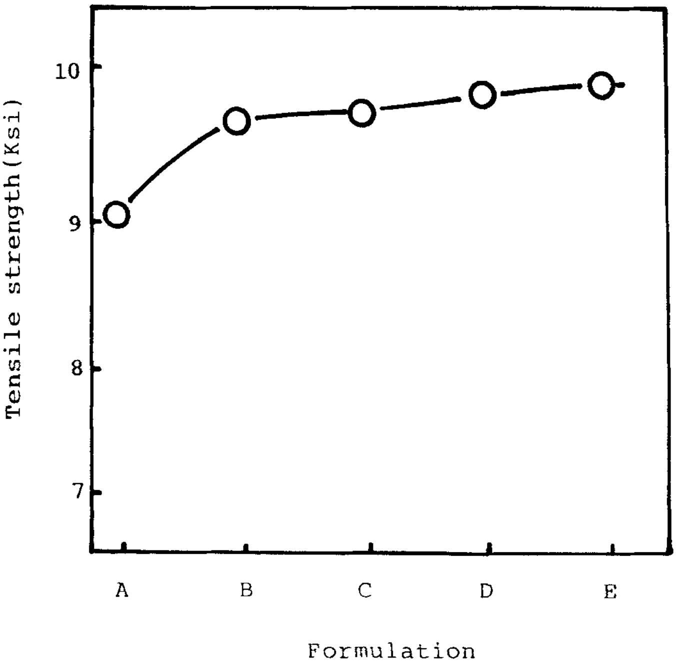

FIG. 7. Tensile strength of cured matrices according to styrene content.

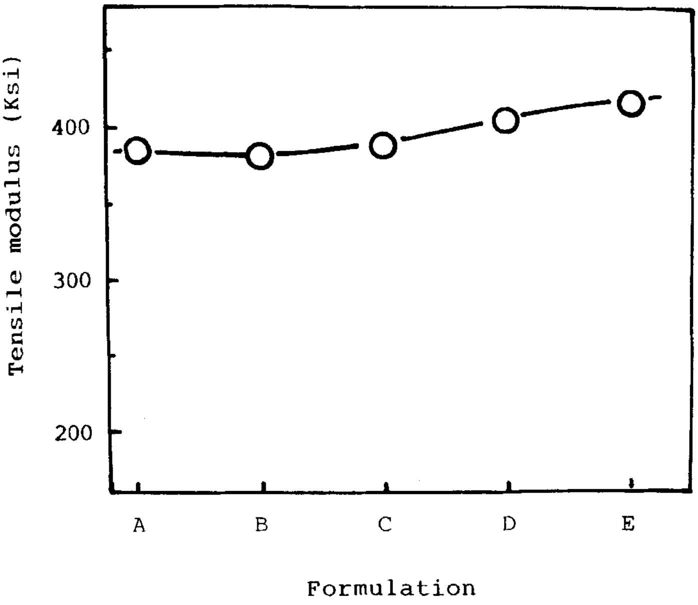

FIG. 8. Tensile modulus of cured matrices according to styrene content.

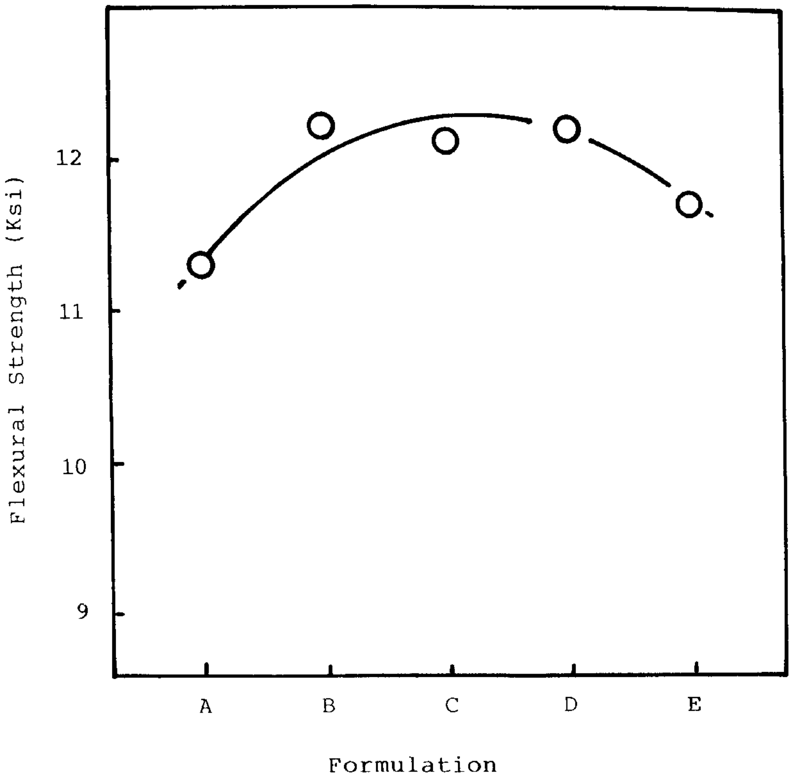

FIG. 9. Flexural strength of cured matrices according to styrene content.

Figure 9 shows the flexural strengths of epoxy-styrene thermoset blends according to the styrene content. The flexural strengths were similar and in the 11,300 to 12,200 psi range. The flexural moduli (Fig. 10) of the same specimens decreased slightly as the styrene content in the formulations increased. This indicates that the styrene moiety in the cured matrix acts as a chain softener, though the exact mechanism is not fully understood.

Thermal Properties

Figure 11 shows the heat-deflection temperature (HDT) of epoxy-styrene thermoset blends according to the styrene content. As expected, the HDT of the matrices gradually decreased from 166°C for Formulation A to 131°C for Formulation E.

DMA and DSC data for the five epoxy-styrene thermoset blends are given in Figs. 12–15 for the flexural storage modulus, flexural loss modulus, glass transition temperature, and tan δ traces, respectively.

Figure 12 shows the elastic modulus E' over the 20 to 250°C temperature range for five cured epoxy blends with a styrene moiety. The elastic moduli E' in the glassy state decrease monotonically and show similar values up to 155, 146, 140, and 137°C for our thermoset blends A, B, C, D, and E, respectively. Above these

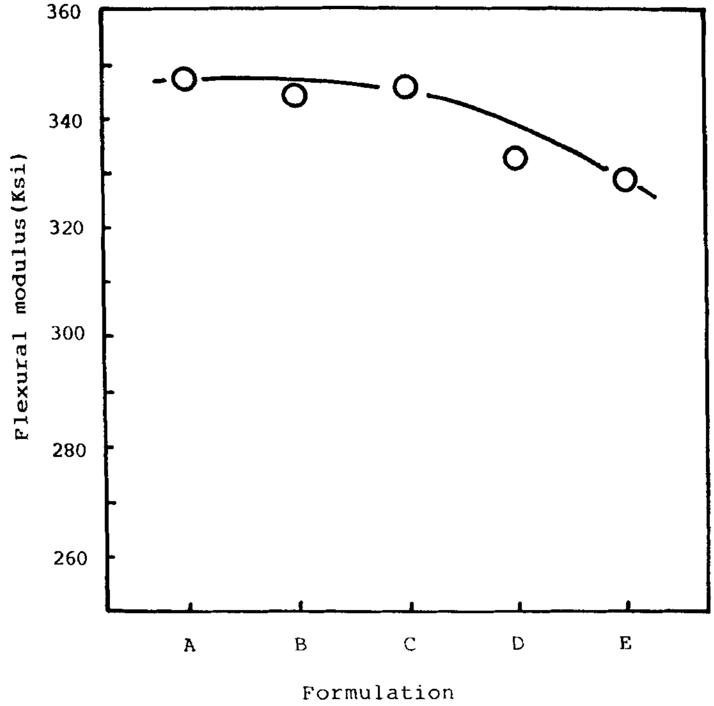

FIG. 10. Flexural modulus of cured matrices according to styrene content.

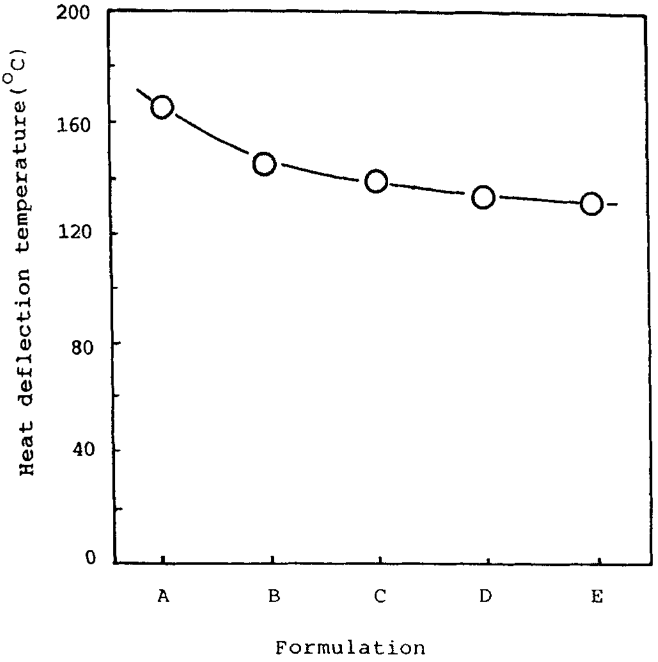

FIG. 11. Heat deflection temperature of cured matrices according to styrene content.

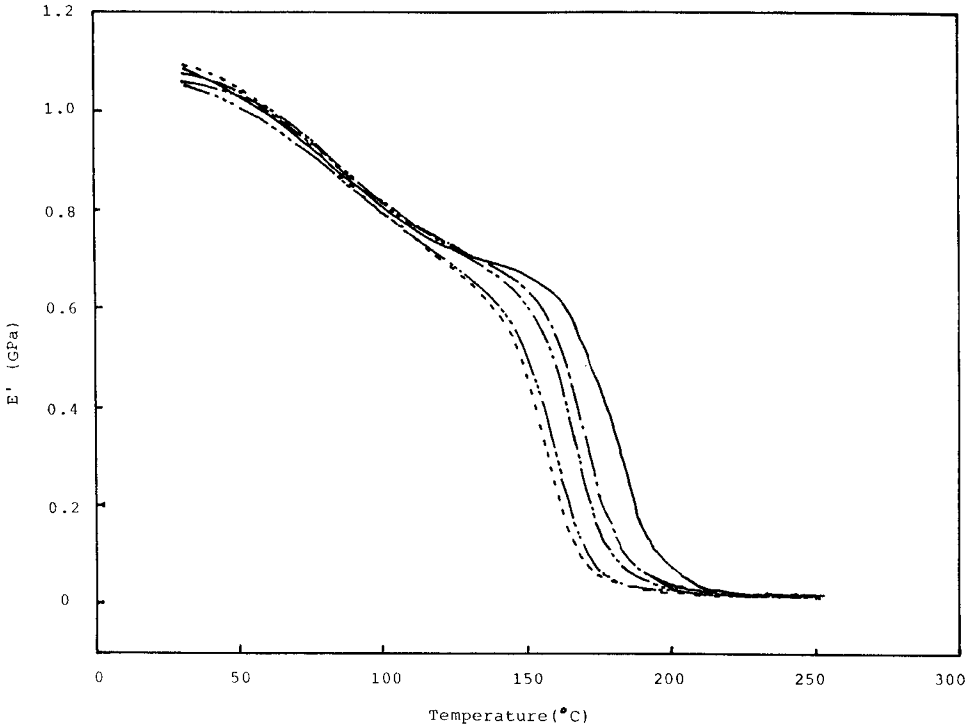

FIG. 12. Elastic modulus (E') of the cured matrices: A (——), B (-‧-), C (-‧‧-), D (-‧‧‧-), and E (‧‧‧).

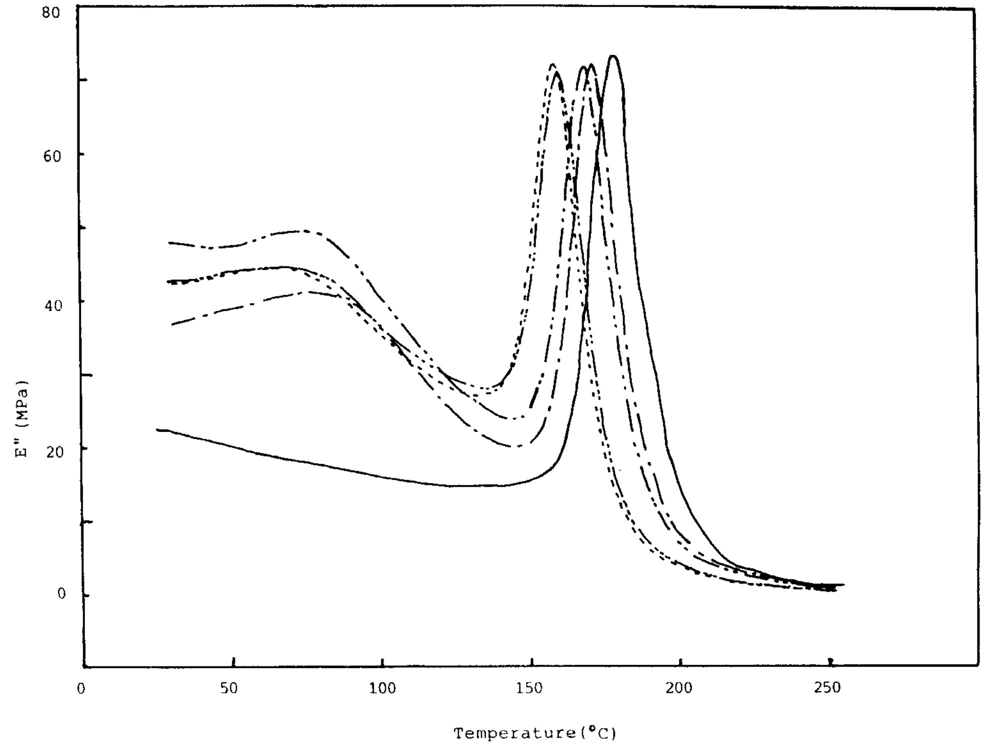

FIG. 13. Flexural loss modulus (E'') of cured matrices: A (——), B (-‧-), C (-‧‧-), D (-‧‧‧-), and E (‧‧‧).

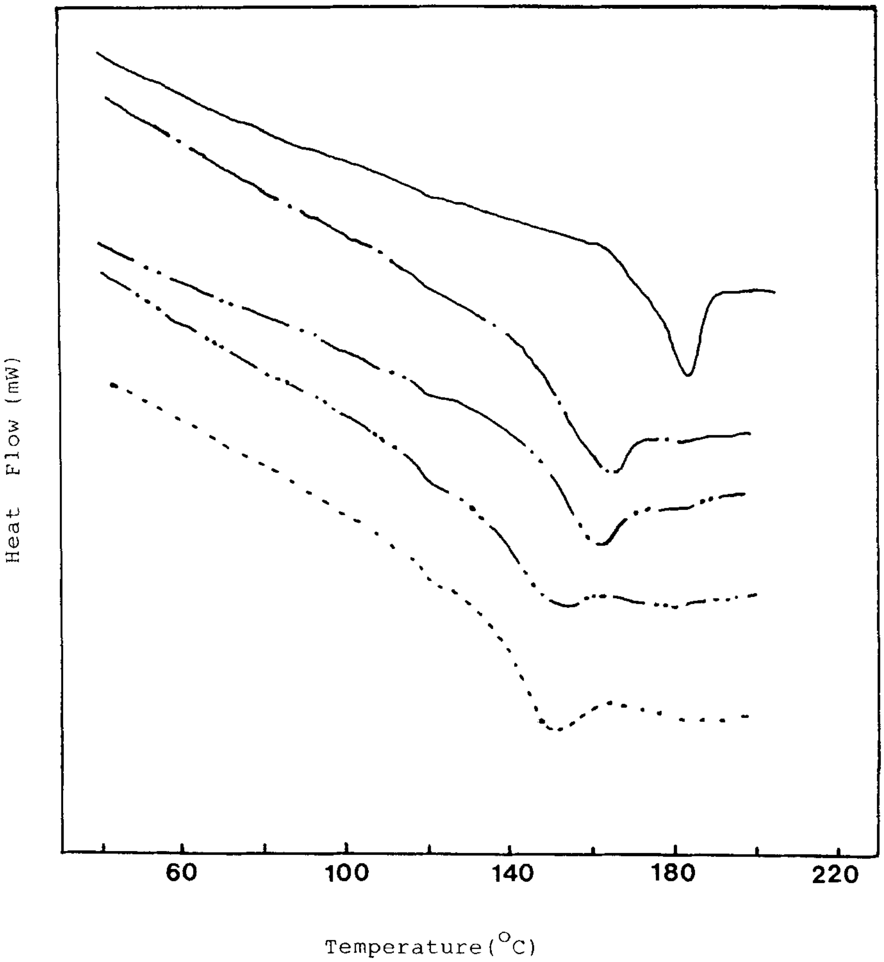

FIG. 14. DSC thermograms of cured matrices: A (—), B (-··-), C (-···-), D (-····-), and E (···).

temperatures, the elastic modulus rapidly decreased. From these results it was concluded that the more styrene moiety a thermoset blend contains, the lower will be the transition temperature observed.

Figure 13 shows the flexural loss moduli E'' for the five cured epoxy blends over the 20 to 250°C temperature range. The temperature of maximum flexural loss modulus E'' gradually decreases as the styrene moiety is increased from A (0 parts) to E (10 parts). The phenomenon that the T_g of cured epoxy blends decreases when the amount of styrene moiety increases is evident from DSC thermograms of the same blends, as shown in Fig. 14. The T_gs obtained by DSC thermograms of the five cured epoxy blends decreased from 166 to 136°C as the styrene moiety increased from 0 to 10 parts. The decrease of the transition temperature of the present blends with higher amounts of the styrene moiety is believed to be due to the chain softening effect of the styrene moiety and/or the decrease of crosslinking density.

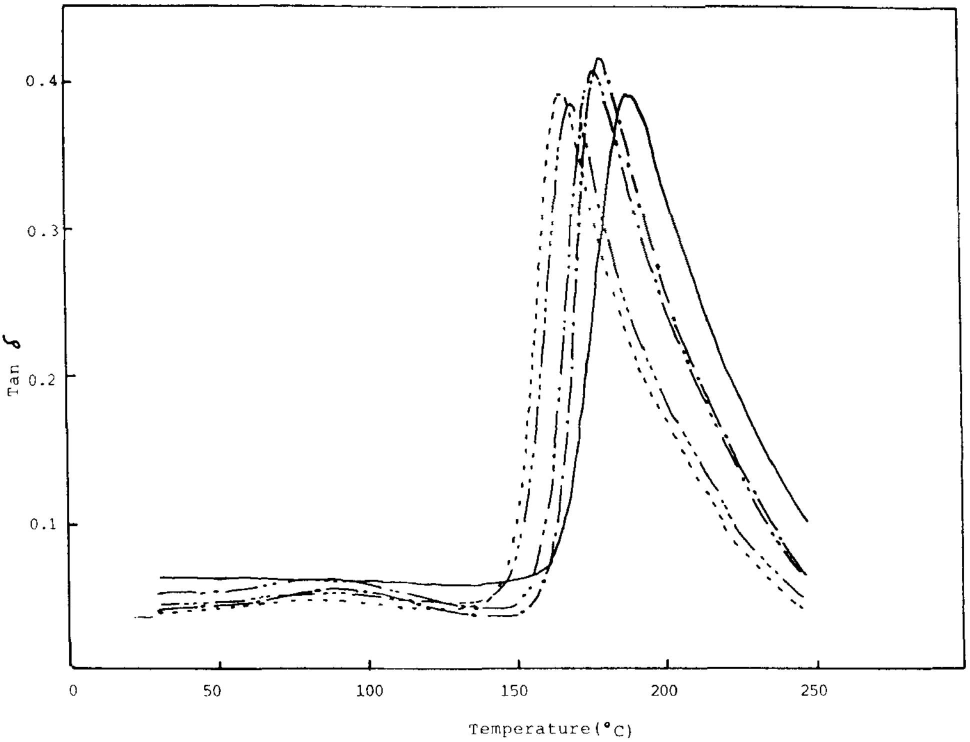

FIG. 15. Tan δ curves of cured matrices: A (——), B (---), C (-·-·-), D (-··-··-), and E (···).

Figure 15 shows the tan δ curves of the five cured epoxy blends. The transition centered at about 90°C has been identified as the ω-transition [27] and can be attributed to unreacted molecular segments and/or inhomogeneities in the epoxy blends arising from regions of dissimilar crosslinking densities. The transition at higher temperature, in which the maximum peak temperature decreases as the styrene moiety increases, was identified as the α-transition and can be clearly attributed to the glass transition of the blends.

Figure 16 shows the TGA thermogram of the cured matrix (Formulation D). It shows rapid decomposition at temperatures between 370 and 410°C. The residual weight after heating up to 640°C was 14.2%. The TGA thermograms of the other four formulations were similar to that of Formulation D. The midpoint temperature of the transition was in the 393 to 402°C range.

CONCLUSIONS

In this article an epoxy resin system containing a styrene moiety as the reactive diluent for filament winding was formulated. The chemical and physical properties were studied. It was found that a small amount of styrene lowers the resin viscosity considerably, which results in increases of the wetting of fiber reinforcement with

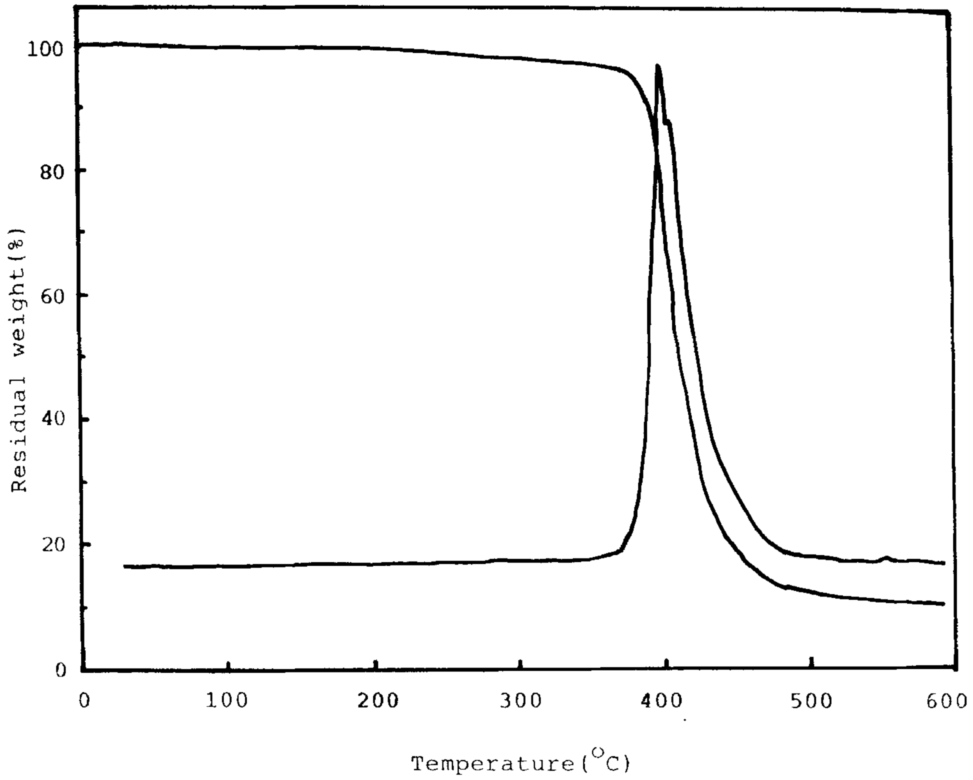

FIG. 16. TGA thermograms of cured matrix (Formulation D).

resin and the pot life. The major part of styrene in the epoxy resin participates in the curing process as the reactive diluent. There was no notable decrease of mechanical properties although some decrease of thermal properties (HDT, T_g, etc.) was observed. It is concluded that these epoxy-styrene thermoset blends are adequate for the filament winding fabrication of high performance composite structures based on viscosity, pot life, and mechanical and thermal properties.

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