High-Temperature Elastomers: Glass Transition–Structure Correlations for Two Systematic Series of Linear Poly(Carborane–Siloxane)s. II. Incompatibility
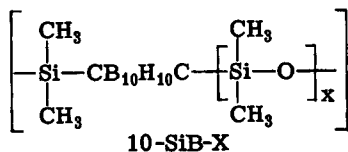
M. B. ROLLER* and J. K. GILLHAM, *Polymer Materials Program, Department of Chemical Engineering, Princeton University, Princeton, New Jersey 08540*
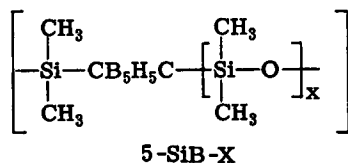
Synopsis

Previously reported results related glass transition temperature to structure in two systematic series of poly(carborane–siloxane)s using a well-known copolymer composition–glass transition relationship $1/T_g = W_1/T_{g1} + W_2/T_{g2}$. The relationship was originally proposed to apply not only to copolymers, but also to diluent systems. Accordingly, mixtures of polymers within each series were prepared and the thermomechanical spectra were determined by the technique of torsional braid analysis. The binary mixtures included poly(dimethylsiloxane) with polymers in both series and a mixture of two —$CB_{10}H_{10}C$— siloxane polymers. In all cases, the thermomechanical spectra revealed only those transition regions characteristic of the individual components. This type of behavior is indicative of phase separation of incompatible polymeric species.

INTRODUCTION

Previous results[1] related glass transition temperature (T_g) to structure in two systematic series of poly(carborane–siloxane)s using a copolymer composition–glass transition relationship (Fig. 1). The composition-glass transition relationship: $1/T_g = W_1/T_{g1} + W_2/T_{g2}$ was originally proposed to apply not only to copolymers, but also to diluent systems.[2] Therefore, mixtures of polymers in both series,

$$\left[\begin{array}{c} CH_3 \\ | \\ -Si-CB_{10}H_{10}C- \\ | \\ CH_3 \end{array} \left[\begin{array}{c} CH_3 \\ | \\ Si-O- \\ | \\ CH_3 \end{array}\right]_x \right]$$

10-SiB-X

and

$$\left[\begin{array}{c} CH_3 \\ | \\ -Si-CB_5H_5C- \\ | \\ CH_3 \end{array} \left[\begin{array}{c} CH_3 \\ | \\ Si-O- \\ | \\ CH_3 \end{array}\right]_x \right]$$

5-SiB-X

* Present address: Bell Laboratories, Whippany, New Jersey 07981.

COPOLYMER EQUATION FOR CARBORANESILOXANE POLYMERS

$$\frac{1}{T_g} = \frac{W_1}{T_{g_1}} + \frac{W_2}{T_{g_2}} = W_1\left(\frac{1}{T_{g_1}} - \frac{1}{T_{g_2}}\right) + \frac{1}{T_{g_2}}$$

x	T_g (°K)		W_1	
	10-SiB-x	5-SiB-x	10-SiB-x	5-SiB-x
1	298	213	0.730	0.655
2		185		0.488
2'	243 *		0.575	
2"	239 †		0.575	
3	205	177	0.475	0.400
4	198	171	0.404	0.346
5	185	165	0.351	0.281
∞	148	148	0.0	0.0

* 10-SEC. MODULUS } LITERATURE
† VOLUME-TEMP.

5-SiB-x OVERALL COMPOSITION RANDOM COPOLYMER. AT LEAST ONE $-Si(CH_3)_2O-$ BETWEEN $-CB_5H_5C-$ 'S

REGULARLY SPACED BY $x\{Si(CH_3)_2O\}$ GROUPS

W_1 = WEIGHT FRACTION $-Si(CH_3)_2-$

Fig. 1. Copolymer equation. Glass transition temperature–structure correlations for 10-SiB-X and 5-SiB-X polymers.

were prepared and thermomechanically characterized using torsional braid analysis[3-6] in order to check the applicability of the relationship to mixtures of those related polymers.

EXPERIMENTAL

Materials. The polymers used in this study were poly(dimethylsiloxane), $\{Si(CH_3)_2-O\}$ (commercial-grade SE-30) designated 10-SiB-∞ and 5-SiB-∞ (the limiting structures of each series[1]), and 10-SiB-3, 10-SiB-5, and 5-SiB-2. The structures and transitions of these polymers (and of 10-SiB-4) are given in Table I; 5-SiB-2 is a random copolymer, whereas the others have well defined structures.[7-10] The mixtures prepared are described in Table II.

Torsional Braid Analysis. The transition data of Table I were determined in dried nitrogen by the technique of torsional braid analysis[3-6] which involves a torsional pendulum experiment, operating at about 1 cps. The free-hanging specimen consists of a multifilamented (about 3600) glass braid impregnated with the sample polymer, allowing the study of semimicro quantities (<50 mg). The specimen is fabricated in situ to form a glass–polymer composite, by removing solvent from a braid that has been soaked in a polymer solution prior to mounting. The composite nature of the specimen has the advantage of allowing room-temperature handling of

TABLE I
Chemical Formulae and Transitions of Constituents of the Polymer Mixtures

DESIGNATION	STRUCTURE	T_m	T_{crys}	T_g	T_{sec}	T_m/T_g
10-SiB-3	$HO-[Si(CH_3)_2-O-Si(CH_3)_2-CB_{10}H_{10}C-Si(CH_3)_2-O-Si(CH_3)_2-O]_n-H$ $[\eta]_{KYLENE} = 0.15{-}0.20$ dl/g GPC PEAK MAX. ~10–12,000	40	10	−68	−140	1.54
10-SiB-4	$HO-[Si(CH_3)_2-O-Si(CH_3)_2-CB_{10}H_{10}C-Si(CH_3)_2-O-Si(CH_3)_2-O-Si(CH_3)_2-O-Si(CH_3)_2-O]_n-H$ GPC PEAK MAX. ~24,000	A	A	−75	−135	
10-SiB-5	$HO-[Si(CH_3)_2-O-Si(CH_3)_2-CB_{10}H_{10}C-Si(CH_3)_2-O-Si(CH_3)_2-O-Si(CH_3)_2-O-Si(CH_3)_2-O]_n-H$ GPC PEAK MAX. ~20,000	A	A	−88	−140	
5-SiB-2 RANDOM COPOLYMER	$HO-\{[Si(CH_3)_2-O-Si(CH_3)_2-CB_5H_5C-Si(CH_3)_2-O][Si(CH_3)_2-O]\}_n-H$ $\overline{M}_n = 6170 \pm 10\%$	A	A	−88	−145	
10-SiB-∞, 5-SiB-∞ SE-30	$CH_3-Si(CH_3)_2-O-[Si(CH_3)_2-O]_n-Si(CH_3)_2-CH_3$ MW >10^6	−40	−55	−125	A	1.58

A = ABSENT

materials that are gums or viscous fluids. The glass braid carries the tensile stress in the specimen. The transitions of the polymers are readily determined by monitoring changes in the dynamic rigidity modulus and mechanical damping of the specimen as a function of temperature.

Preparation of Mixtures. Known amounts of each of the two components were added to a weighing bottle. Chloroform was added to produce a 10% solution (g total polymer/ml solvent). The system was stirred with a magnetic stirrer at 25°C to produce a clear and uniform solution which was used for impregnating braids. Similar attempts with 10-SiB-3/10-SiB-∞ and with 10-SiB-5/10-SiB-∞ mixtures in benzene (a good solvent for each component of each mixture) gave cloudy solutions which separated into two phases on standing. The glass-braid impregnates

TABLE II
Composition of the Polymer Mixtures

Component 1	Component 2	Ratio of components	Comment
10-SiB-3	10-SiB-∞	1:2 (molar, repeat unit)	Prepared to approximate 10-SiB-5 composition
10-SiB-5	10-SiB-∞	1:1 (weight)	Prepared to give a $T_g \sim$ halfway between $-125°$ and $-88°C$
10-SiB-3	10-SiB-5	1:1 (molar, repeat unit)	Prepared to approximate 10-SiB-4 composition
5-SiB-2	5-SiB-∞	1:1 (weight)	Same component transitions as 10-SiB-5/ 10-SiB-∞; —CB₅H₅C— cage incorporated

were formed in situ by drying to 150°C in dried, flowing nitrogen. The specimens were stored overnight in dried, flowing nitrogen at 130°C (i.e., 90°C above the highest solid-to-fluid transition temperature, $T_m = 40°C$ for 10-SiB-3).

RESULTS AND DISCUSSION

The thermomechanical spectra (relative rigidity and mechanical damping versus temperature) of the individual component polymers are displayed in Figure 2. Corresponding mechanical spectra of the four mixtures are displayed in Figure 3. Two glass transition regions were in evidence for each mixture, the locations of which correspond to those of the separate constituents. Such behavior is characteristic of phase separation. The incompatibility was also manifested by the presence of the crystallinity of 10-SiB-3 and of 10-SiB-∞ (5-SiB-∞) in the mixtures, which points out the lack of disruption of the crystalline lattices by interpenetration of the species.
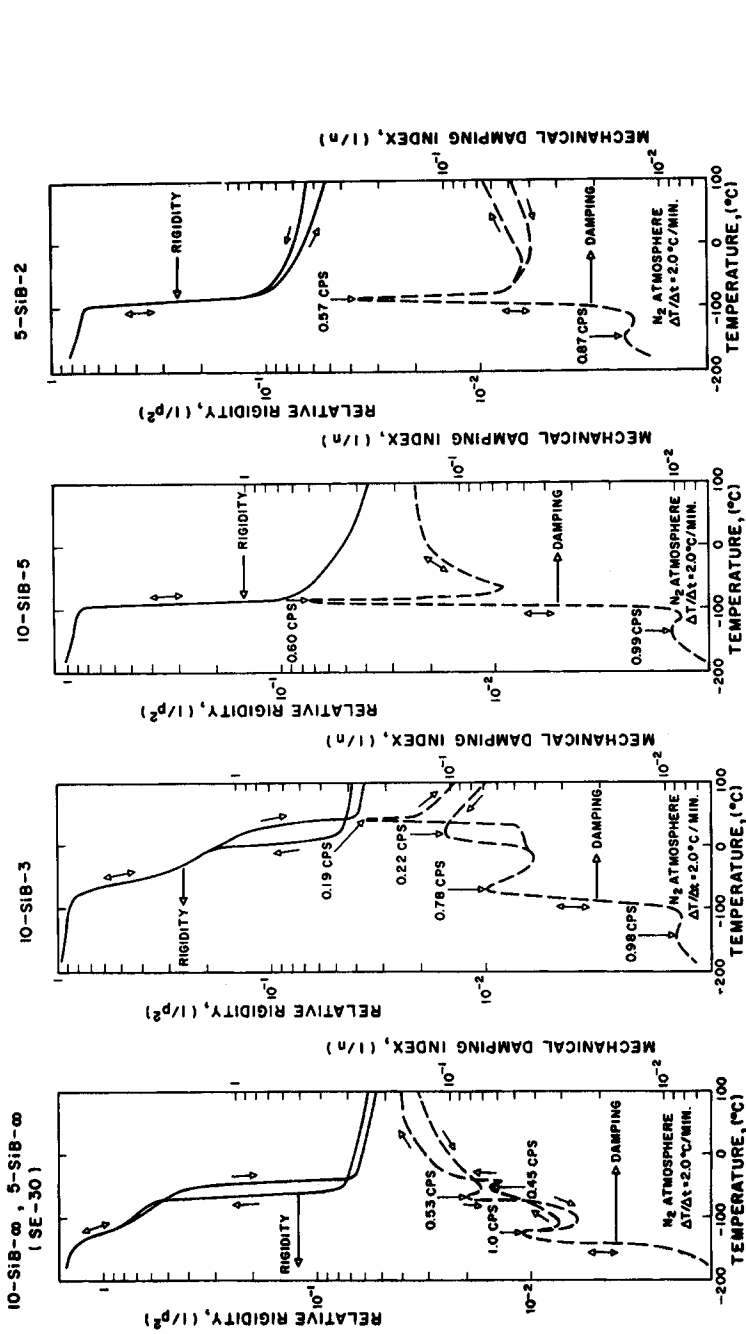
Fig. 2. Thermomechanical behavior in nitrogen of 10-SiB-∞ (5-SiB-∞), 10-SiB-3, 10-SiB-5, and 5-SiB-2 polymers. Cycle: 100° → −180° → 100°C at 2°C/min.
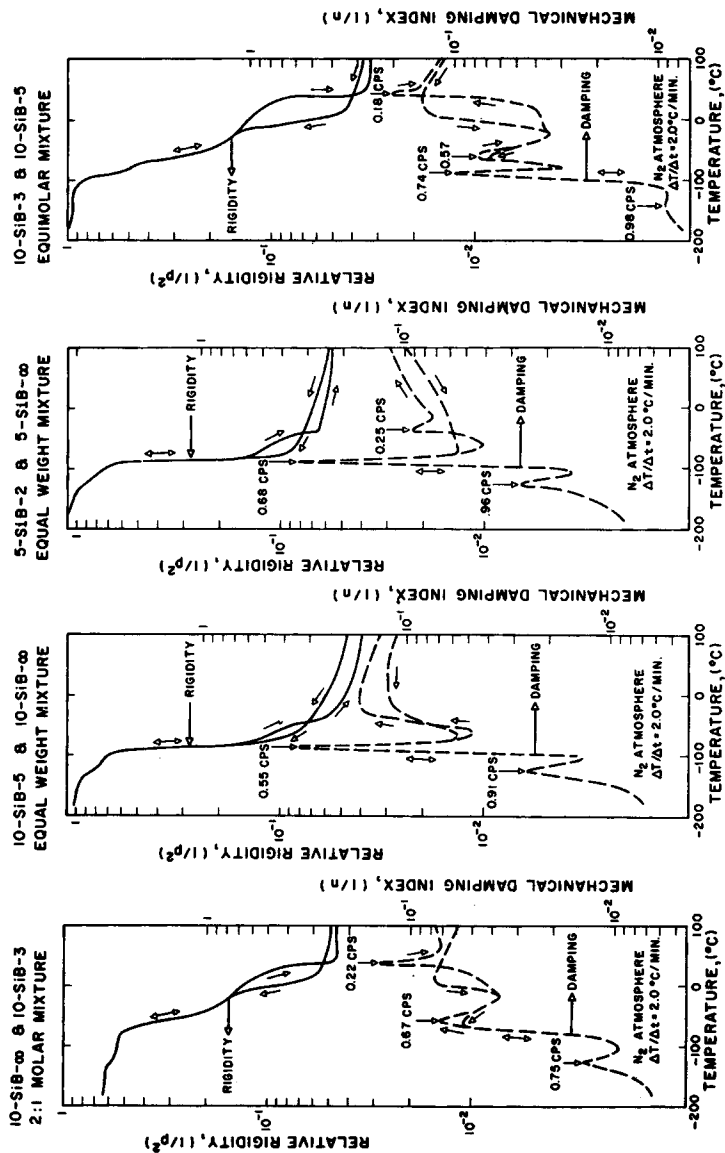
Fig. 3. Thermomechanical behavior in nitrogen of the following blends: 10-SiB-3/10-SiB- ∞ (1:2 molar ratio of repeat units), 10-SiB-5/10-SiB- ∞ (1:1 weight ratio), 5-SiB-2/5-SiB- ∞ (1:1 weight ratio), and 10-SiB-3/10-SiB-5 (1:1 molar ratio of repeat units). Cycle: 100° → −180° → 100°C at 2°C/min.

The mixture examined first, 10-SiB-3/10-SiB-∞, had the T_g of 10-SiB-3 and the T_m of 10-SiB-∞ overlapping. The 10-SiB-5/10-SiB-∞ mixture was made up to remove the complication of the overlap of T_g and T_m and to replace one crystalline component with an amorphous one. In this case, the T_g values are well defined and separated, but the degree of crystallinity of the 10-SiB-∞ mixture is lower relative to that of the pure 10-SiB-∞. The lower degree of crystallinity is revealed by the relatively small degree of thermohysteresis for the mixture. (Note: crystallization is more apparent in the reheating portion of the experiment.)

A mixture containing the smaller —CB_5H_5C— cage was also investigated. The 5-SiB-2/5-SiB-∞ mixture was prepared since the transitions of the constituents of this system were close to those of the 10-SiB-5/10-SiB-∞ system. The thermomechanical spectra were very similar to those of 10-SiB-5/10-SiB-∞, with excellent resolution of the transition regions of the components.

A mixture was prepared from two —$CB_{10}H_{10}C$— polymer components, 10-SiB-3 and 10-SiB-5; these were mixed in an equimolar ratio for the repeat units so as to approximate 10-SiB-4 in composition. Again, the transitions resolved excellently, even to the extent that the 10-SiB-3 T_m and T_{crys} transitions were unimpaired. In this case, the glassy state transition (T_{sec}) was resolved at $-140°C$. In each of the other systems, the low T_g ($-125°C$) of poly(dimethylsiloxane) resulted in a large rate of change of damping in the $-140°C$ region, which masked the T_{sec} of the other component.

CONCLUSIONS

The results discussed above indicate a basic incompatibility between the carborane-modified silicones and the parent poly(dimethylsiloxane). Indeed, there even is an incompatibility between two similar poly(carborane–siloxane)s, 10-SiB-3 and 10-SiB-5. ˇThis behavior tends to support the model proposed previously[1] to explain the deviation of the 10-SiB-1 polymer from the straight-line correlation shown in Figure 1. The model proposed that at some decreasing dimethylsiloxane chain length between carborane cages (approaching 10-SiB-1 from 10-SiB-∞), the cages themselves begin to associate. This could suggest that packing of the carborane cages is an important determinant of properties for the 10-SiB-1 polymer. The basic imcompatibility of the carborane–siloxane polymers for each other and for poly(dimethylsiloxane) as evidenced above would add some credibility to the idea of carborane cage aggregation.

References

1. M. B. Roller and J. K. Gillham, *J. Appl. Polym. Sci.*, **16**, 3095 (1972).
2. T. G. Fox, *Bull. Amer. Phys. Soc.*, **1**, 123 (1950).
3. A. F. Lewis, and J. K. Gillham, *J. Appl. Polym. Sci.*, **6**, 422 (1962).
4. J. K. Gillham, *Polym. Eng. Sci.*, **7**, 225 (1967).
5. J. K. Gillham, and M. B. Roller, *Polym. Eng. Sci.*, **11**, 295 (1971).
6. J. K. Gillham, *Torsional Braid Analysis*, in *Encyclopedia of Polymer Science and Technology*, Vol. 14, Interscience, New York, 1971, p. 76.
7. K. O. Knollmueller, R. N. Scott, H. Kwasnik, and J. F. Sieckhaus, *J. Polym. Sci. A-1*, **9**, 1071, (1971).
8. J. F. Sieckhaus, private communication.
9. R. E. Kesting, K. F. Jackson, and J. M. Newman, *J. Appl. Polym. Sci.*, **15**, 2645 (1971).
10. R. E. Kesting, letter to J. K. Gillham dated Sept. 15, 1971.