

## Polymer Composition Versus Low-Temperature Characteristics of Polysiloxane Elastomers

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### I. INTRODUCTION

The subject of low-temperature stiffening of elastomers has received a great deal of attention because of its practical significance. Rubbery polysiloxanes stand out among all other elastomers because of their excellent low-temperature properties. Several papers<sup>3-7</sup> on the subject of low-temperature properties of silicone rubber have been published, but none has correlated polymer composition with low-temperature behavior. It will be the purpose of this paper to correlate polymer make-up with the effect on stiffening at low temperatures. Three experimental methods were used in this work to study the unique low-temperature behavior of polysiloxane elastomers. These methods were Gehman cold flex, dilatometer, and stress-temperature at zero extension.

The factors which cause an elastomer to become stiff at some particular temperature are crystallization, second-order transition, or a superposition of the two phenomena. Both of these phenomena can be affected by changing the architecture of the polymer. For example, it is well known in organic polymer chemistry that the crystallization temperature,  $T_1$ , of a polymer can be lowered by disrupting the regular structure of a homopolymer through the addition of bulky groups. This is also true in polysiloxane chemistry. In addition, the temperature,  $T_2$ , of the second-order transition will be increased if the intermolecular forces are increased or, conversely, the temperature will be decreased if the intermolecular forces are decreased. Since the phenyl group is bulky compared with the methyl group and also has a larger intermolecular force constant than the methyl group, it serves as an interesting group to substitute for methyl groups attached to silicon. Pendant groups other than phenyl can be substituted for methyl to disrupt the regularity of the polymer chain, but this paper will limit the discussion to the effect of substituting varying amounts of phenylmethylsiloxane,  $\text{PhMeSiO}$ , units for dimethyl siloxane,  $\text{Me}_2\text{SiO}$ , units.

### II. EXPERIMENTAL

The elastomers used in this investigation were prepared from copolymers varying in phenyl methyl siloxane content from 0.0 to 99.858 mole-%. Each polymer contained an equal amount (0.142 mole-%) of methyl vinyl siloxane. The remaining 100 mole-% composition was made up of dimethyl siloxane units. The desired molar ratios of the cyclic tetramers of the aforementioned siloxanes were mixed and catalyzed with potassium hydroxide as recommended by Hyde (2). The phenyl methyl siloxane molar concentrations were: 0, 1.0, 3.5, 5, 7.5, 10, 12.5, 15, 30, 60, and 99.858%.

The formulation used with the copolymers was 100 parts polymer, 40 parts silica, 1 part ferric oxide, 0.2 parts *tert*-butyl perbenzoate (TBPB) (except for the 60 and 99.858 mole-%  $\text{PhMeSiO}$ -containing copolymers which had 0.5 and 1 part TBPB, respectively). The compounds were vulcanized at 150°C. for 10 minutes, followed by an oven cure of 24 hours at 250°C.

The Gehman cold-flex apparatus described in ASTM D 1053-54 T was modified to include an automatic temperature-control system with liquid nitrogen as the coolant. Studies with the Gehman apparatus employed two different temperature-history methods. One method was used to determine the stiffening temperature. This was accomplished by first measuring the Gehman twist value at room temperature, followed by testing at successively lower temperatures. Each temperature was maintained for at least one hour or longer, if necessary, until an equilibrium twist value was obtained. The time necessary to give the equilibrium twist value varied from 5 minutes to 3 hours. The data obtained by this method are identified as Gehman twist data obtained at decreasing temperatures (see Table I).

The other temperature-history technique allowed the observation of supercooling tendencies as well as measuring the relaxation temperature or the melting temperature in the case of those elastomers that crystallized. The history used for these tests was rigorously followed. Only one specimen

TABLE I  
 Gehman Twist Data Obtained at Decreasing Temperatures<sup>a</sup>

Mole-% PhMeSiO:											
Test temp., °C.	0	1	3.5	5	7.5	10	12.5	15	30	60	99.858
	Degree twist										
25	153	150	147	153	148	151	153	153	147	167	166
-20	148	142	138	149	140	141	152	144	140	162	119
-30	146	139	135	149	137	136	151	143	136	159	12
-40	14	137	132	148	133	127	149	139	132	149	6
-50	8	12	131	144	133	127	149	139	129	81	6
-60	5	7	19	144	130	127	148	135	121	3	6
-70	5	7	13	23	124	125	142	130	108	—	—
-80	4	4	9	12	120	118	141	126	12	—	—
-90	—	—	—	—	107	109	128	109	—	—	—
-100	—	—	—	—	103	101	116	82	—	—	—
-110	—	—	—	—	39	6	3	3	—	—	—
-120	—	—	—	—	2	—	—	—	—	—	—

<sup>a</sup> These data were obtained on a Gehman Cold Flex Tester. All samples were maintained for at least one hour at each progressively lower test temperature until an equilibrium twist value was obtained. Low twist values indicate stiffness of the elastomer.

 TABLE II  
 Gehman Twist Data Obtained at Increasing Temperatures<sup>a</sup>

Mole-% PhMeSiO:											
Test temp., °C.	0	1	3.5	5	7.5	10	12.5	15	30	60	99.858
	Degree twist										
+25	136	142	135	136	134	143	153	147	133	164	160
-130	1	1	1.5	1	2	2	2	1	2	2	0
-110	3	38	78	6	77	16	75	2	2	2	0
-100	4	8	66	88	93	88	123	34	2	2	0
-90	5	7	41	103	101	107	137	101	3	2	0
-80	5	9	20	86	108	114	145	115	72	3	2
-70	6	11	27	55	113	118	148	119	95	3	2
-65	7	12	36	71	115	122	148	123	102	3	2
-60	8	14	50	92	117	123	149	124	106	3	2
-55	10	20	88	118	118	126	149	126	110	4	2
-50	14	43	119	131	120	128	149	129	111	12	3
-40	54	103	130	133	—	—	—	—	—	129	4
-30	126	134	133	134	127	136	150	134	122	148	12
-20	—	—	—	—	—	—	—	—	—	—	108
0	—	—	—	—	—	—	—	—	—	—	146

<sup>a</sup> These tests were obtained on a Gehman Cold Flex Tester. The 25°C. test was obtained first. The sample was then cooled rapidly (approximately 5 minutes) to -130°C. The sample was held for 5 minutes at each progressively higher temperature before testing. It requires from 1 to 3 minutes to change temperature. Only one sample was run at a time. Low twist values indicate stiffness of the elastomer.

was run at a time. First the room-temperature twist value was obtained, then the temperature was rapidly decreased (approximately 5 minutes) to -130°C. The sample was held for 5 minutes at each progressively higher temperature before testing. These temperatures were: -130, -110, -100, -90, -80, -70, -65, -60, -55, -50, -40, -30, and -20°C. The time required to change temperature varied from one to three minutes over the range of temperatures, but was consistent for a given temperature change (i.e., from -90° to -80°C.). The data obtained by

this method are identified as Gehman twist data obtained at increasing temperatures (see Table II).

The dilatometric measurements of volume changes were made in a special dilatometer consisting of a calibrated, precision-bore, 36-in. length capillary attached to a 10-cc.-volume base by a 29/42 ground glass joint. Carefully weighed silicone rubber samples (approximately 2 cc.) were placed in the base, and *n*-propyl alcohol was added as the immersant liquid to a level about midway on the ground glass joint. Air bubbles were easily dislodged before putting the capillary in place.

The male part of the ground glass joint was coated with a thin film of silicone stopcock grease. As the capillary was put in place, the immersant liquid was forced up the capillary. Steel springs were used to hold the glass joint together during the volume-temperature experiment. Methyl cyclopentane was used as the low-temperature bath medium. Both dry ice and liquid nitrogen were used as coolants for the bath. The temperature was decreased at a rate of 0.25 to 0.33°C./minute. Capillary readings were taken at desirable temperature intervals during the experiment. The capillary readings were converted to relative volume changes by correcting for volume changes of the normal propyl alcohol and Pyrex glass. Relative volume in this case refers to a volume of 1 cubic centimeter at +25°C.

The immersant liquid did affect the exact value of the coefficient of volume expansion but did not alter either the  $T_1$  or  $T_2$  temperatures. They compared well with  $T_1$  and  $T_2$  temperatures determined by a stress-temperature method reported in this paper. Crystallization temperature,  $T_1$ , reported by Ohlberg et al.<sup>4</sup> Warrick,<sup>6</sup> and Weir et al.<sup>7</sup> for a polydimethyl siloxane agrees well with the value on the 99.858 mole-% polydimethyl siloxane-based elastomer. The  $T_2$  value also agrees with the value determined by Weir et al. (7). The elastomer prepared from the zero phenyl methyl siloxane-content polymer had a volume expansion over the temperature range of 25° to -20°C of  $8.12 \times 10^{-4}$  when mercury was used as the immersant fluid compared with a value of  $9.44 \times 10^{-4}$  when normal propyl alcohol was used. Thus it was concluded that the dilatometric measurements made when normal propyl alcohol was used as the immersant liquid gave valid  $T_1$  and  $T_2$  temperatures, but slightly high values for the coefficient of expansion. Although corrections could probably be applied to the expansion coefficients, this was not done in this work.

Stress-temperature measurements were made on a stress-strain apparatus constructed by Castor Laboratory Equipment Company, Pittsburgh, Pa., and described in a previous publication by Warrick.<sup>6</sup> The sample jaws were modified to use ring specimens to eliminate the possibility of slippage during test. Ring specimens approximately 1 inch in diameter with cross-section dimensions of  $0.060 \times 0.060$  inches were placed over 0.125-inch diameter mandrel-type holders. The jaws were separated until the ring took on an oval shape without stretching the ring as measured by bench marks previously placed on the ring. Some stress was necessary to bend the rings to an

oval shape, however. Thus, since samples were below the thermoelastic inversion point, a decrease in temperature should cause an increase in stress due to volume change. Indeed, this was the finding, and both the crystallization temperature,  $T_1$ , and second-order transition temperature,  $T_2$ , were defined by this type of experiment. The temperature was lowered at a rate of about 0.4°C./min.

### III. RESULTS

#### Gehman Cold Flex Studies

The Gehman cold-flex tester was used to determine at what temperature the various copolymer elastomers became stiff when allowed up to 3 hours to reach equilibrium stiffness values at each progressively lower temperature. The steady-state twist values given in Table I were plotted as a function of temperature. A smooth curve was then drawn through the points. The resulting curves were similar in the respect that, at some temperature range characteristic of each particular elastomer, the twist values rapidly decreased down to a low value and then leveled off with further decrease in temperature. This formed a sharp bend or inverse knee in the curve. The stiffening temperature was taken as the point of intersection of two straight-line projections of the curve on either side of the inverse knee of the stiffening curve. Figure 1 shows a plot of these stiffening temperatures as a function of the phenyl methyl siloxane content of the copolymers. It may be seen that the stiffening temperature is drastically lowered with relatively small increases in phenylmethylsiloxane content. The minimum stiffening temperature of -112.7°C. was obtained at a 7.5 mole-% PhMeSiO content. The 10, 12.5, and 15

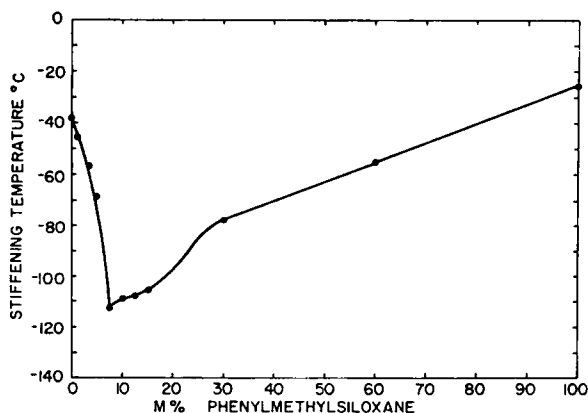


Fig. 1. Stiffening temperature as a function of phenylmethylsiloxane molar content.

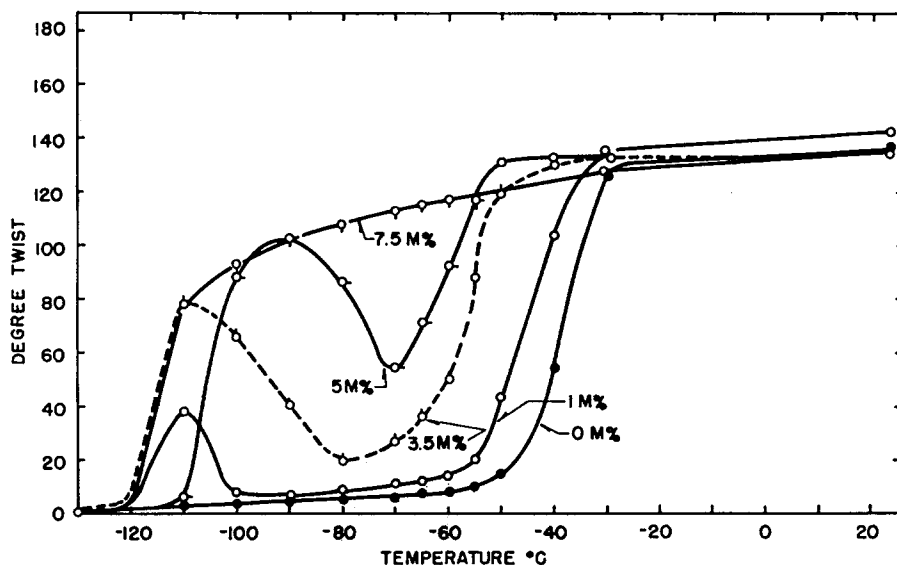


Fig. 2. Gehman twist versus temperature for different phenylmethylsiloxane-containing elastomers.

mole-% phenyl methylsiloxane copolymers also showed excellent low-temperature-stiffening values, but their stiffening-temperature values increased slightly with increase in molar concentration.

An investigation was carried out to determine if another minimum low-temperature stiffening point occurred in the phenyl methyl siloxane-rich region, but another minimum was not found. Thus it may be concluded that only one minimum stiffening temperature exists in the dimethyl-phenylmethyl siloxane copolymer system.

The results from volume-temperature and stress-temperature measurements will be used to aid in explaining the reasons for stiffening temperatures found in the above data. This will be brought out in the discussion section of this paper.

Data were also obtained at increasing temperatures (see Table II). The purpose of this experimental technique was to observe several possible phenomena. These were: (a) supercooling effects, (b) the restoration of flexibility as the second-order transition temperature was exceeded, (c) the formation and the melting of crystallites. To demonstrate these phenomena the data of elastomers compounded from copolymers containing 0, 1, 3.5, 5, and 7.5 mole-% PhMeSiO were plotted on Figure 2. It should be pointed out that the data in Table II and Figure 2 are not equilibrium values like the data given in Table I. The difference in data demonstrates the effect of changing the temperature history of the samples. The data given in Table II are enlightening, in that they demonstrate clearly the unusual low-temperature characteristics of polysiloxane-containing elastomers.

Weir, Leser, and Wood<sup>7</sup> reported that the second-order transition temperature for polysiloxanes was  $-123 \pm 5^\circ\text{C}$ . On the basis of their findings, the temperature of  $-130^\circ\text{C}$ . was used as the lowest temperature to ensure that all samples were below their second-order transition temperature. In other words, at this temperature all samples would be in the glass region. Indeed, the data plotted in Figure 2 clearly show that all of the polysiloxane elastomers studied were very stiff at  $-130^\circ\text{C}$ . as shown by the very low Gehman twist values. As the temperature was increased from  $-130^\circ\text{C}$ ., the elastomers behaved differently, depending upon the copolymer composition. For example, the 0 mole-% PhMeSiO copolymer remained stiff until essentially complete flexibility was regained between the temperatures of  $-50$  and  $-30^\circ\text{C}$ . No supercooling effects were noted for this elastomer. Instead, crystallization occurred rapidly during the time (about 5 minutes) of reducing the temperature down to  $-130^\circ\text{C}$ .

The introduction of 1 mole-% PhMeSiO into the copolymer enables the elastomer to be supercooled. This is shown in Figure 2 by the increase in degree twist as the temperature is increased above  $-130^\circ\text{C}$ ., followed by the rapid stiffening due to the onset of crystallization. The 3.5 and 5 mole-% PhMeSiO-containing elastomers also exhibited supercooling and subsequent rapid crystallization when favorable temperature conditions were reached. As the phenyl methyl siloxane content was increased from 0 to 5 mole-%, the ease and extent of crystallization was reduced. This is apparent from examination of the width and height of the minima of

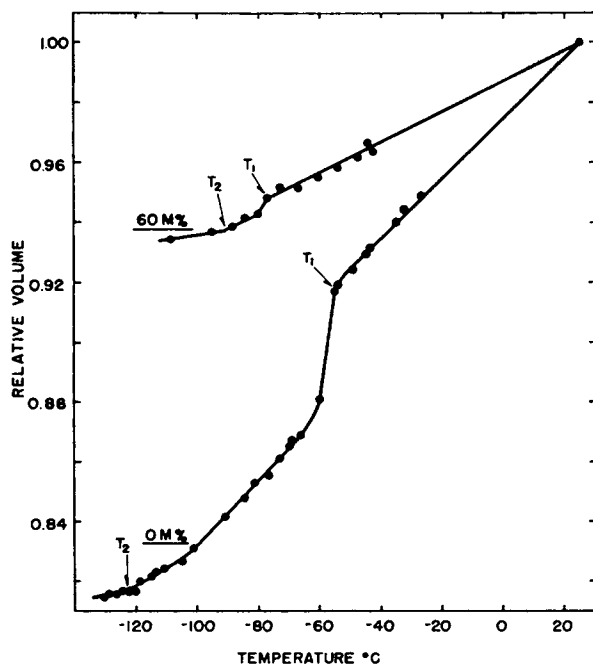


Fig. 3. Relative volume versus temperature for different phenylmethylsiloxane-containing elastomers.

the curves following the onset of crystallization. The width of the minima indicate the ease of crystallization and the range of temperatures at which crystallites are present. The height of the minima are inversely related to the extent of crystallization as measured by relative degree of stiffening due to the presence of crystallites. Also, it may be noted that the melting temperature range was lowered with increase in phenyl-methyl siloxane content.

The elastomers containing 7.5 mole-% and above phenyl methyl siloxane did not exhibit supercooling. No crystallization was found for copolymers containing 7.5 to 15 mole-% PhMeSiO. More will be said later about crystallization effects. The 7.5 mole-% PhMeSiO data plotted in Figure 2 represent the best elastomer studied in this copolymer series with respect to extreme low-temperature flexibility.

### Dilatometer Studies

Dilatometric measurements were carried out on the 0, 3.5, 7.5, 30, 60, and 99.858 mole-% phenyl methyl siloxane-containing elastomers. The crystallization temperatures,  $T_1$ , and the second-order transition temperatures,  $T_2$ , found in these studies are summarized in Table III. Figure 3 shows a plot of the data for the 0 and 60 mole-% PhMeSiO-containing elastomers as an example of the curves obtained. Out of the series of elastomers studied for volume change, only the 7.5 mole-% PhMeSiO-

TABLE III  
Summary of Low Temperature Data

Mole-% PhMeSiO	Stiffening Tempera- ture, °C. <sup>a</sup>	$T_1$ , <sup>(b)</sup> °C.	$T_2$ , <sup>(b)</sup> °C.	$T_1$ , <sup>(c)</sup> °C.	$T_2$ , <sup>(c)</sup> °C.
0	-38	-54	-123	-54	-122
1	-45.3	—	-121.5 <sup>(d)</sup>	—	—
3.5	-56.7	-70	-120	—	—
5	-68.3	—	-116.5 <sup>(d)</sup>	—	—
7.5	-112.7	None	-114	None	-115
10	-108.7	—	-111.7 <sup>(d)</sup>	—	—
12.5	-108	—	-109.7 <sup>(d)</sup>	—	—
15	-106	—	-108 <sup>(d)</sup>	—	—
30	-78	-77	-100	—	—
60	-55.5	-77	-91	-77.5	-92
99.858	-26.7	-35	-86	—	—

(<sup>a</sup>) Determined from Gehman twist equilibrium data.

(<sup>b</sup>) Determined from volume-temperature data.

(<sup>c</sup>) Determined from stress-temperature data.

(<sup>d</sup>) Values not measured but read from Figure 4.

containing sample did not exhibit crystallization observable as a discontinuity in the volume-temperature plot. The data for this elastomer did show a second-order transition at  $-114^\circ\text{C}$ ., typified by a sharp change in slope of the volume-temperature curve. This finding was also substantiated by the stress-temperature data to be discussed below.

Although volume-temperature data were not obtained for the 10, 12.5, and 15 mole-% PhMeSiO-containing elastomers, stiffening temperatures obtained from Gehman flex data indicate that these elastomers, like the 7.5 mole-% PhMeSiO-containing elastomer, did not crystallize. Stiffening was due in these cases to nearness to their respective second-order transition temperatures. In other words,  $T_1$  was lowered to some temperature below  $T_2$  for the 7.5 to 15 mole-% PhMeSiO-containing elastomers. The effect of increasing the molar content of phenyl methyl siloxane on the second-order transition temperature is clearly seen in Figure 4. The value for  $T_2$  is increased from  $-123^\circ\text{C}$ . for the 0 mole-% PhMeSiO-containing sample to  $-86^\circ\text{C}$ .

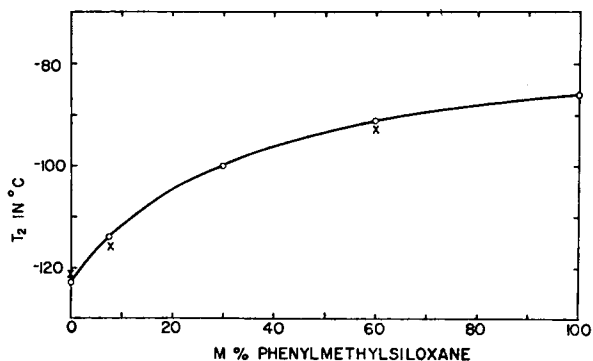


Fig. 4. Effect of phenylmethylsiloxane content on second order transition temperature.

for the elastomer which had complete substitution of PhMeSiO groups for Me<sub>2</sub>SiO units.

The coefficients of expansion measured as described in the experimental part of this paper showed a decrease with increase in phenyl methyl siloxane molar content from  $9.44 \times 10^{-4}$  for 0 mole-% to  $4.69 \times 10^{-4}$  for 99.858 mole-% over the temperature interval of 25° to -20°C.

### Stress-Temperature Studies

The stress-temperature properties (from zero extension at 25°C.) of three elastomers containing 0, 7.5, and 60 mole-% PhMeSiO, respectively, were studied by the procedure described in the experimental part of this paper. The main interest in using this particular technique was to ascertain whether a simple experimental method could be used to identify both the first- and second-order transitions. The results were indeed gratifying, as both first- and second-order transitions were identifiable by this method. Further, the transition temperatures duplicated those determined by the volume-temperature method. The experimental results are plotted in Figure 5. The transition temperatures found are given in Table III.

As found from volume-temperature measurements, no crystallization was observed for the 7.5 mole-% PhMeSiO-containing elastomer. Slight curvature occurred in the stress temperature plot as  $T_2$  was approached, and, just at  $T_2$ , a sharp change in slope was followed by a linear change in stress with temperature.

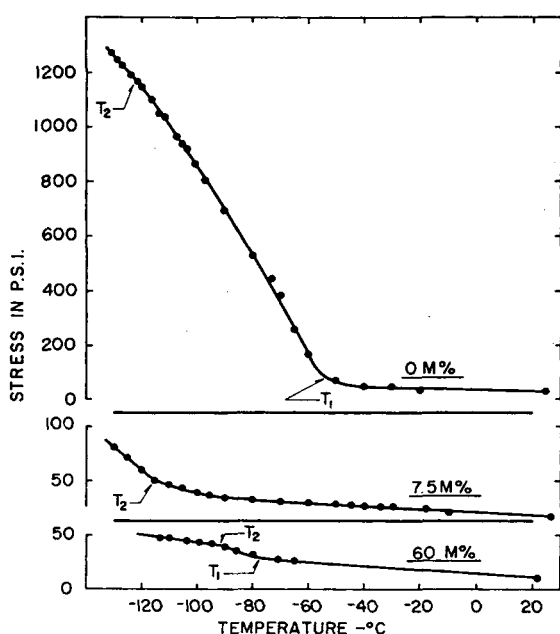


Fig. 5. Stress versus temperature for phenylmethylsiloxane-containing elastomers at  $\alpha = 1$ .

It is interesting to note the large increase in stress of the 0 mole-% PhMeSiO-containing sample upon crystallization compared with the relatively small increase in stress of the 60 mole-% PhMeSiO-containing sample. This is indicative of a difference in the number of crystallites in each elastomer. However, it should be pointed out that the coefficient of expansion of the PhMeSiO-containing sample was smaller by a factor of 2. This would also result in a smaller increase of stress with a decrease in temperature.

### IV. DISCUSSION

Table III gives a summary of the relationship of phenyl methyl siloxane molar content of the elastomers with stiffening temperatures obtained by Gehman equilibrium-twist data and  $T_1$  and  $T_2$  values obtained by volume-temperature and stress-temperature data. It may be noted that the stiffening temperatures for the crystallizable elastomers (0, 1, 3.5, 5, 30, 60, 99.858 mole-% PhMeSiO), with the one exception of the 30 mole-% PhMeSiO sample, were higher than the incipient crystallization temperatures measured. The reason for this lies in the important point of temperature history. In general low-temperature rubber work this fact has been known for a long time. The reason for stiffening at temperatures higher than the  $T_1$  values observed by both dilatometric and stress-temperature measurements stems from differences between "equilibrium" and "incipient" crystallization temperatures. Incipient crystallization temperature is observed on the first cooling, or rapid cooling in the absence of previous nuclei; equilibrium crystallization temperature is observed on slow cooling or with rapid cooling in the presence of nuclei. For example, data have been obtained for shorter induction times with the Gehman cold flex tester at a series of decreasing temperatures which showed stiffening at temperatures corresponding to the incipient crystallization temperatures,  $T_1$ . Thus, in the case of the above-listed elastomers, stiffening was caused by crystallization. In addition, these crystallization temperatures were well above the second-order transition temperatures,  $T_2$ .

Elastomers studied in this work containing 7.5 to 15 mole-% PhMeSiO all stiffened because of nearness to their respective second-order transition temperatures and, therefore, represent a copolymer composition range in which  $T_1$  has been lowered below  $T_2$ . This is apparent by comparing the results given in Table III.

It may be seen from this work with polysiloxane elastomers that the substitution of a bulky group,

such as phenyl, for methyl has two very important effects on the low-temperature behavior of the elastomer. First, by small additions up to 5 mole-% PhMeSiO, the crystallization temperature and degree of crystallization can be lowered. When 7.5 to at least 15 mole-% quantities of PhMeSiO units are substituted, crystallization can be completely eliminated. At higher additions, crystallization can again occur. Secondly, the addition of phenyl in place of methyl in the polysiloxane copolymer has the concomitant effect of raising the second-order transition temperature, i.e., from  $-123$  to  $-86^{\circ}\text{C}$ . for the 0 and 99.858 mole-% PhMeSiO-containing copolymers. It is indeed fortunate that crystallization can be completely eliminated with only a relatively small sacrifice of  $9^{\circ}\text{C}$ . increase in  $T_2$ .

Both the crystallization and second-order effects of elastomers prepared from polysiloxanes follow the theories set forth in the literature. They are unique, however, in the details of how these phenomena occur. The biggest difference between polysiloxanes and other polymers lies in the time necessary for crystallization to occur. For those polysiloxanes that exhibit crystallization, the formation of nuclei and subsequent crystal growth occur in a matter of minutes rather than the hours or days required in hydrocarbon elastomer systems. The second difference is the lower second-order transition temperature exhibited by polysiloxanes.

The reason for the unique low-temperature properties of polysiloxane elastomers is the molecular make-up of these polymers. The silicon-oxygen-silicon backbone of these polymers gives a flexible chain whose segments move readily and require only a small energy input to do so. In addition, the ease of rotation of the organic groups attached to the silicon atoms plays an integral part in the low-temperature characteristics. The energy barrier hindering internal rotation of methyl groups attached to the silicon atom in tetramethylsilane was shown by Aston<sup>1</sup> to be 1300 calories, as compared to 4540 calories for analogous rotation in neopentane. For polysiloxanes, the inter- and intramolecular attraction forces are low compared with hydrocarbon polymers. This is especially true for all-methyl-substituted polysiloxanes. These factors all contribute to a low-temperature coefficient of viscosity over a broad temperature range. Here we are interested in the relative mobility or perhaps the viscosity of the molecular segments between the crosslinks of the vulcanized elastomer. Referring first to the all-methyl polymer, the rapid crystallization of the vulcanizate suggests that the well-ordered polymer may consist of many like kinetic units, most of which require about the same free-

energy change associated with the formation of nuclei. This effectively limits any extensive nucleation to a relatively narrow temperature range. When the proper conditions are reached, nucleation takes place on a relatively large scale. From there the growth of the crystallites progresses rapidly because of the high mobility of both the chain segments and the organic groups attached to silicon. However, this rapid growth is soon stopped by the strains or interference imposed by the neighboring crystallites. As has been shown, crystallization can be completely eliminated by the introduction of the proper amount of a bulky group such as phenyl.

The above reasons given for the flexible polysiloxane chains possessing low intermolecular attraction forces also explain the low  $T_2$  values. Increasing the intermolecular attraction forces through the introduction of the phenyl group raises  $T_2$  in the manner expected.

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### Synopsis

Gehman cold-flex, volume-temperature, and stress-temperature studies were used to investigate the low-temperature characteristics of polysiloxane copolymers with respect to copolymer composition. A complete range of phenyl methyl-dimethyl siloxane copolymers were examined as elastomeric compounds. Like other copolymers, the stiffening temperature was dependent upon the composition of the copolymer. Stiffening of the elastomers was due to crystallization in some cases and second-order transition in others. Copolymers having either low or high amounts of PhMeSO stiffened because of crystallization, while copolymers of intermediate composition (7.5 to 15 mole-% PhMeSiO) stiffened because of nearness to their respective second-order transition temperatures. Second-order transition temperature increased with the PhMeSiO content. For those siloxane polymers and copolymers that crystallized, the process was rapid when compared with crystallization behavior of other polymer systems. Only one minimum low-temperature stiffening point was found in the phenyl methyl-dimethyl siloxane copolymer system. The unique low-temperature characteristics of polysiloxane elastomers are explainable on the basis of three factors. These are: (a) very flexible molecules, (b) low temperature coefficient of viscosity over a broad temperature range including low temperatures, and (c) copolymerizability of dimethyl

siloxane with other siloxanes containing bulky pendant groups which lower the stiffening temperature.

### Résumé

On a déterminé les caractéristiques des copolymères de polysiloxane aux basses températures en fonction de leur composition; à cet effet on a utilisé des études tension-température, volume température et de flexibilité à froid suivant Gehman. On a examiné une série complète de copolymères du phénylméthyl-diméthylsiloxane en tant que composés élastomères. Comme les autres copolymères, la température de durcissement dépend de la composition du copolymère. Le durcissement de ces élastomères serait dû à la cristallisation dans certains cas, et à des points de transition de second ordre dans d'autres. Les copolymères ayant soit de basses, soit de grandes quantités de PhMeSiO durcissent par cristallisation, tandis que les copolymères de composition intermédiaire (7,5 à 15 mole-% de PhMeSiO) durcissent à cause de la proximité de leurs températures respectives de transition de second ordre. La température de transition de second ordre augmente avec la quantité de PhMeSiO. Quant aux polymères et copolymères de siloxanes qui cristallisent, le processus est rapide quand on le compare au pouvoir cristallisant d'autres systèmes polymériques. Lors de l'étude du système copolymérique du phénylméthyl-diméthylsiloxane, on a trouvé seulement un seul point de durcissement minimum à basse température. On peut expliquer sur la base de trois facteurs l'existence d'une seule basse température des élastomères de polysiloxane. Ils sont les suivants: (a) des molécules très flexibles, (b) un faible coefficient de température de viscosité s'étendant à un vaste domaine de température y compris les basses températures, et (c) la copolymérisabilité du méthylsiloxane avec d'autres siloxanes contenant des groupes encombrants latéraux ce qui abaisse la température de durcissement.

### Zusammenfassung

Bestimmung der Kaltbiegung nach Gehmann, der Volum-Temperatur- und der Spannungs-Temperaturabhängigkeit wurden zur Untersuchung der Tieftemperaturcharakteristik von Polysiloxanocopolymeren in Abhängigkeit von der Copolymerzusammensetzung herangezogen. Eine vollständige Reihe von Phenylmethyl-Dimethylsiloxanocopolymeren wurde als elastische Verbindungen untersucht. Wie bei anderen Copolymeren, war hier die Einfriertemperatur von der Zusammensetzung des Copolymeren abhängig. Die Versteifung des Elastomeren wurde in einigen Fällen durch Kristallisation, in anderen durch eine Umwandlung zweiter Ordnung verursacht. Copolymeren, die entweder niedrige oder aber hohe Mengen von PhMeSiO enthielten, zeigten Versteifung durch Kristallisation, während bei Copolymeren von mittlerer Zusammensetzung (7,5 bis 15 Mol % PhMeSiO) diese Versteifung in Folge der Nähe der entsprechenden Umwandlungstemperaturen zweiter Ordnung erfolgte. Die Umwandlungstemperatur zweiter Ordnung nahm mit dem PhMeSiO-Gehalt zu. Bei denjenigen Siloxanpolymeren und -copolymeren, die kristallisierten, verlief dieser Vorgang rasch im Vergleich zum Kristallisationsverhalten anderer polymerer Systeme. Beim Phenylmethyldimethylsiloxanocopolymerensystem wurde nur ein Minimeinfrierpunkt bei tiefer Temperatur gefunden. Die einzigartige Tieftemperaturcharakteristik von Polysiloxanelastomeren ist auf Grund von drei Faktoren verständlich. Diese sind: (a) Moleküle von grosser Biegsamkeit, (b) niedriger Temperaturkoeffizient der Viskosität über einen breiten Temperaturbereich, einschliesslich tiefer Temperaturen und (c) Copolymerisationsfähigkeit von Dimethylsiloxan mit anderen Siloxanen mit grossen, anhängenden Gruppen, die die Einfriertemperatur herabsetzen.

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