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Rheological, extractive and thermal studies of the room temperature vulcanized polydimethylsiloxane

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Abstract

The rheological behavior of the room temperature vulcanized polydimethylsiloxane (precursor) with tetraethylorthosilicate (crosslinker) was studied. Data collected from a constant stress rheometer showed that, during the vulcanization, the phase angle increased until reaching the gel point where the elasticity predominated over the viscosity causing a drastic decrease. At a higher ratio of crosslinker to precursor, the vulcanization accelerated and the gel point was reached sooner, thus resulting in a shorter gel time. However, data collected from our extraction experiments indicated that the degree of completion for vulcanization was actually lowered because of an increased amount of sol species, thus necessitating a longer cycle time for a complete cure. The validity of this observation was corroborated by comparing the data collected from the extraction method against those collected from two independent thermal analytical methods, namely the heat capacity method and the cold crystallization method. The degree of completion for vulcanization at each reaction instant determined using these three methods were in excellent agreement with each other. In addition, the presence of residue sol species in the vulcanized products caused a slight decrease in the thermal stability. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Silicone; Elastomer; Rubber

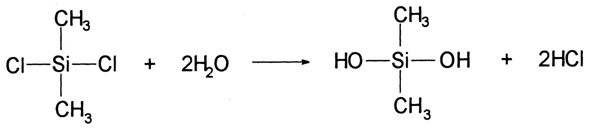
1. Introduction

Silicone elastomers have good thermal characteristics, chemical resistance, and environmental stability over a vast temperature range, and offer excellent hydrophobicity and gap filling capabilities between surfaces [1–4]. They are made by a vulcanization (cure) process converting low-molecular weight linear polydimethylsiloxanes (precursor fluid) to a polymer network which is elastomeric in character. The vulcanization can be conducted using various processes, such as capacitively coupled plasma [5], radiation [6], rhodium complexes [7], photoinduced radical [8], and platinum-catalyzed addition reaction [9]. Among all the cure processes, the room temperature vulcanizing (RTV) silicone systems do not require external heating whilst providing as good thermal stability, electric properties, and water repellency as other systems [1,10,11]. The cure occurs at room temperature through complicated multistage reactions involving the precursor fluid, a crosslinker, a catalyst, and air-borne water moisture. During the vulcanization, the morphology changes from a low viscosity precursor fluid to a high modulus silicone elastomer, and the rate of change increases with an increase in the amount of crosslinker or catalyst. While the chemistry of RTV processes and the properties of such formed silicone elastomers were extensively studied [11–28], little information about the change in rheological and thermal behaviors during the vulcanization are known. In addition, how the degree of completion for vulcanization varies with the cure time has never been studied. Therefore, it is our purpose in this work to conduct thermal and rheological analyses for better understanding such facets of the RTV process. Of particular interest are the use of tetraethylorthosilicate as the crosslinker owing to its high reaction reactivity and the noncorrosive nature of the reaction byproduct.

2. Experimental

2.1. Chemistry and materials

RTV silicone elastomers are generally formed in the following multistage reactions. First, dimethyldichlorosilane is hydrolyzed to form dimethylsilanol,



$$Cl-\overset{CH_3}{\underset{CH_3}{Si}}-Cl + 2H_2O \longrightarrow HO-\overset{CH_3}{\underset{CH_3}{Si}}-OH + 2HCl$$

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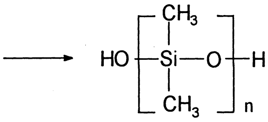
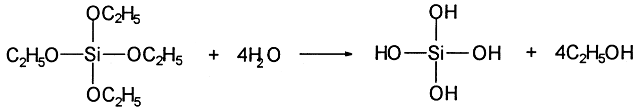
The formed dimethylsilanol is unstable and tends to oligomerize forming a silanol-functional silicone fluid with a byproduct, H_2O,

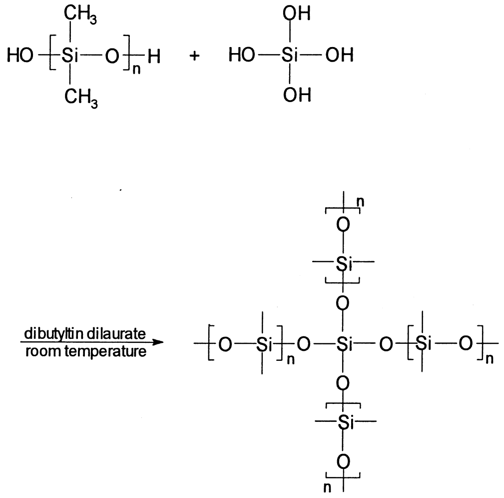


$$\longrightarrow HO\left[\begin{array}{c}CH_3\\ |\\ -Si-O-\\ |\\ CH_3\end{array}\right]_n H$$

Finally, this silicone fluid undergoes a vulcanization process, in the presence of moisture at room temperature, to form the vulcanized polydimethylsiloxanes having a three-dimensional network structure. The vulcanization mechanism liberates a byproduct of which the type varies with the crosslinker used. Tetraethylorthosilicate (TEOS, from Aldrich) was used as the crosslinker in our work because of its multiple functionalities and the noncorrosive ethyl alcohol it evolved. Dibutyltin dilaurate (DBTDL, from Merck) was chosen as the curing catalyst, and was added in an amount of 0.5 wt.% of the combined weights of silicone fluid and the crosslinker.



$$C_2H_5O-\overset{OC_2H_5}{\underset{OC_2H_5}{Si}}-OC_2H_5 + 4H_2O \longrightarrow HO-\overset{OH}{\underset{OH}{Si}}-OH + 4C_2H_5OH$$



As our studies were aimed at the vulcanizing reaction, the terminal-functional silicone fluid, Q1-3563, readily available from Dow Corning Company was used as the starting material (precursor) in our work. This precursor fluid is an oligomeric polydimethylsiloxane with terminal silanol reactivity, and has a room temperature viscosity of 100 cSt and a low molecular weight of 3400.

2.2. Instruments and procedures

A rheometer system (model CVO, Bohlin Instruments, Germany) was used to study the rheological behavior of the silicone system during the RTV process. Following ASTM D4473 method, a low frequency was used in the viscoelasticity measurements. Measurements in an oscillation mode were conducted using a cone-and-plate measuring head. The gap size was 150 mm, and the stress was set at 0.1 Pa. A low frequency of 0.1 Hz was used throughout our work in order to minimize the inertia effect incurred onto the spindle by the rotating electromagnetic field. In addition, testing at a low frequency alleviates the gap loading effect caused by the uneven shear rate distribution across the measuring gap. The thermal experiments including the measurements of specific heat (C_p) were conducted using a modulated differential scanning calorimeter (model MDSC 2910/TA 4000 controller, TA Instruments) equipped with a gas washing bottle for entraining the moisture. Compared to the regular DSC, the MDSC combines a sinusoidal heating rate with the underlying constant heating rate to render both a better resolution and a higher sensitivity. In addition, the MDSC makes the C_p determination simpler and more accurate. The ramping rate of the temperature was 5°C/min, and the rate of modulation was ±0.4°C every 50 s. The thermal stability was observed using a thermogravimetric analyzer (model TGA 2950, TA Instruments). The temperature was ramped from room temperature to 800°C at a rate of 10°C/min.

3. Results and discussion

3.1. Viscoelastic behavior

The change in the viscoelasticity during the vulcanization of precursor was studied from oscillatory experiments using a constant stress rheometer (CVO, Bohlin Instruments, Inc.). The technique used was to apply a stress whose value was changing continuously according to a sine wave equation, resulting in an induced response also following a sine wave. Thus, the sample could be excited continuously but never exceed a certain limit, and its structure would not be destroyed. The measurement was conducted under low shear so as to ensure that the material was tested in its linear viscoelasticity region. In our oscillatory experiments, the frequency and the shear stress were set at 0.1 Hz and 0.1 Pa, respectively. The assurance of linear viscoelasticity under such conditions could be best seen from a stress scan of the material prior to the vulcanizing. As the starting materials (both our thickest sample and our thinnest sample) were fluid, the linear viscoelasticity assumption required the stress scan show a phase lag greater than 45°, i.e., $\tan\delta = G''/G' > 1$, indicating a G'' dominance over G'. As shown in Fig. 1, this requirement was met within the range of 0.08 Pa ∽ 3.6 Pa.

Our dynamic viscoelasticity test was conducted at 25°C on a sample having a formulation of 2 : 1 precursor to crosslinker ratio, plus 0.5 wt.% of catalyst. The results are shown in Fig. 2. The ongoing cure reactions manifested themselves as the gradual increases of the storage modulus (G') and loss modulus (G''). The gradual increase in the G'' (and the resulting phase angle) also indicated an increase in the

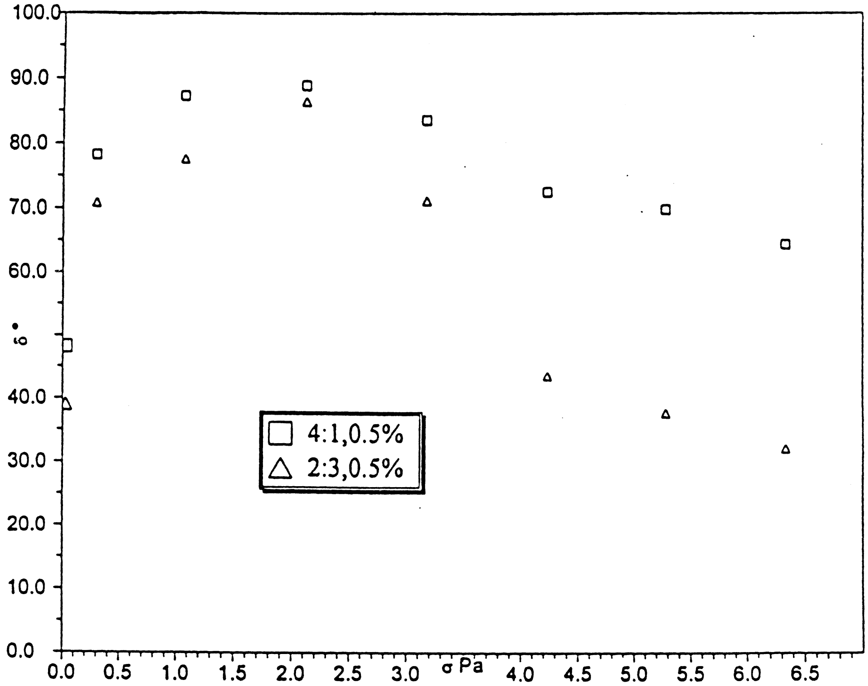


Fig. 1. Stress scan of samples having the thickest formulation (□, 4 : 1 precursor to crosslinker ratio) and the thinnest formulation (Δ, 2 : 3 precursor to crosslinker ratio).

viscous behavior caused by the branching or partial crosslinking of the precursor. The gel point was reached when the G'' curve intersected the G' curve after 9970 s (~3 h), indicating the start of elasticity dominance over viscosity. The phase lag δ dropped at this gel point concurrently. The gelled precursor hardened in approximate 20 min, resulting in a zero degree phase angle.

As the ratio of crosslinker to precursor increased, the

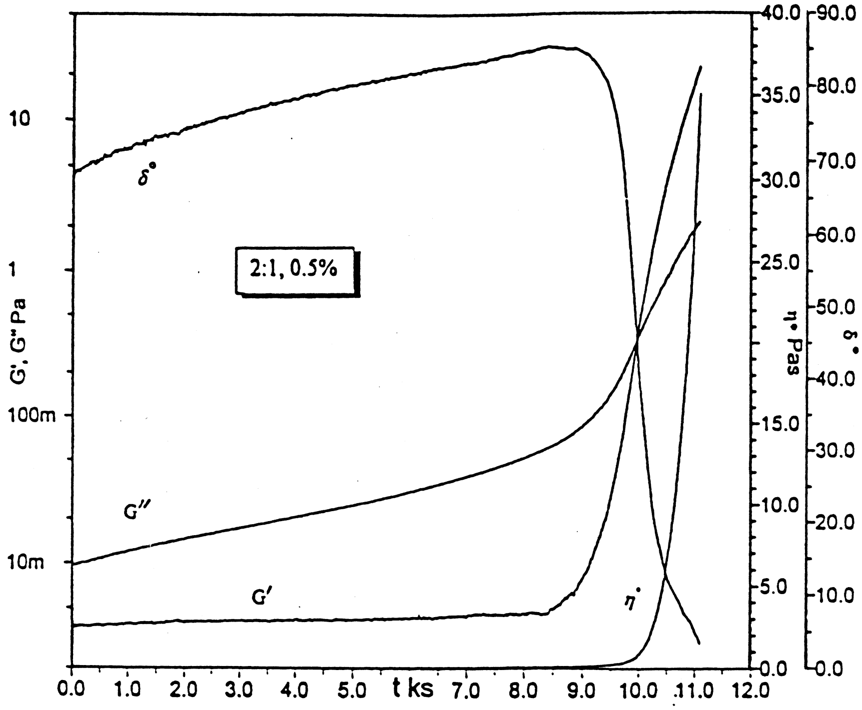


Fig. 2. Dynamic viscoelasticity measurements at 25°C on the sample having a formulation of 2 : 1 precursor to crosslinker ratio, plus 0.5% DBTDL catalyst.

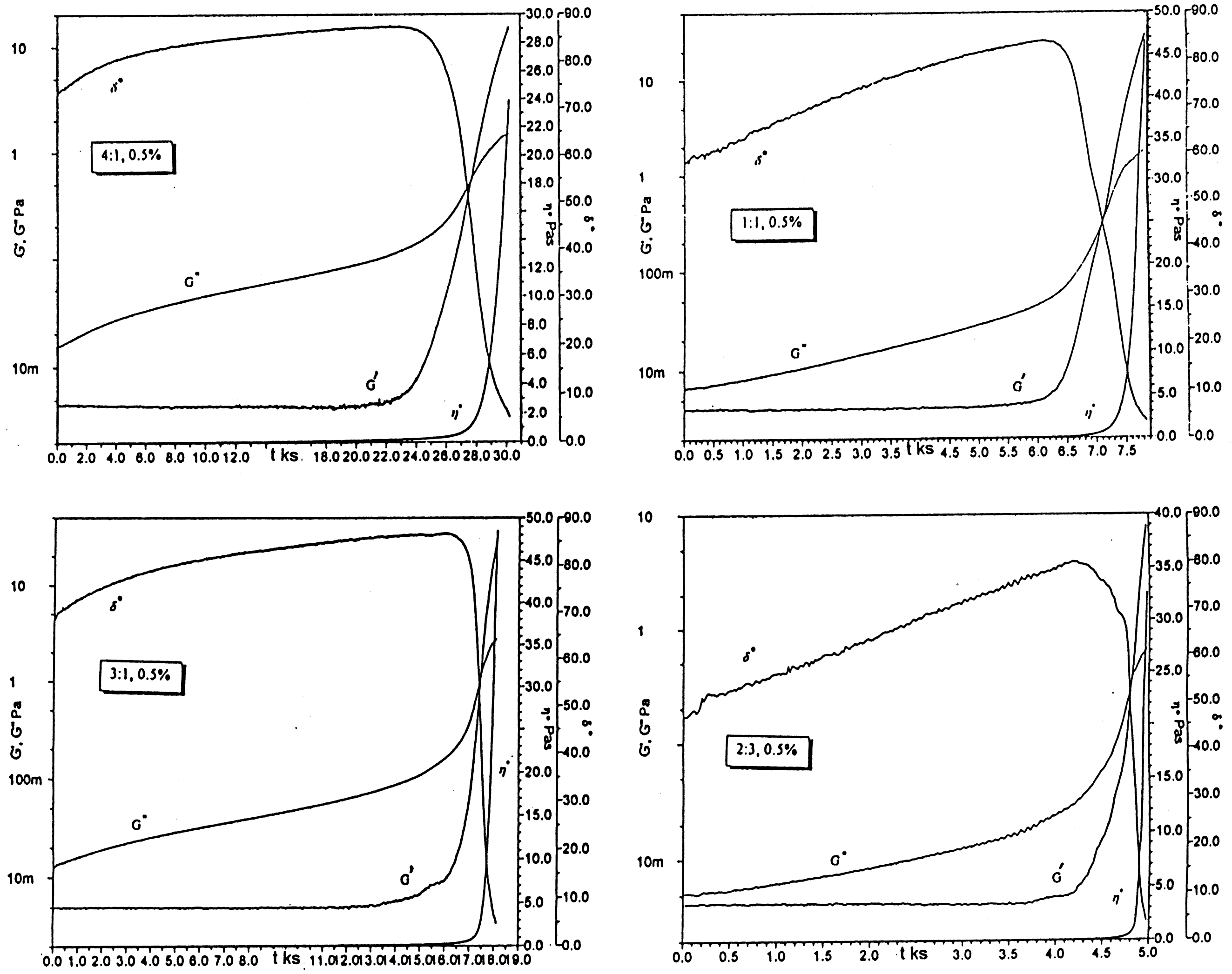


Fig. 3. Dynamic viscoelasticity measurements at 25°C on samples having formulations of different ratios of precursor to crosslinker.

starting G'' (and the resulting phase angle) was lowered as shown in Fig. 3, indicating a decrease in the viscosity owing to the dilution. However, with the extent of branching or partial crosslinking, the G'' (and the resulting phase angle) gradually increased to approximately the same maximum value before gelling. In contrast, a higher ratio of crosslinker to precursor accelerated the vulcanization and markedly shortened the time span over the phase angle drop. This was unsurprising because the increased amount of functional groups (i.e., linking group –OR) on the crosslinker facilitated the crosslinking reaction whereas those on the precursor only enabled polymeric chain extension.

3.2. *Measurement of the degree of completion for vulcanization*

3.2.1. *By extraction experiments*

The degree of completion for vulcanization was directly determined by performing an extraction experiment with a Soxhlet extractor using *n*-hexane as the solvent. As the vulcanizing reaction proceeded, the insoluble gel portion increased while the soluble sol portion decreased. The degree of completion for vulcanization was defined as the fraction of total weight that remains after the *n*-hexane extraction.

Table 1
Degree of completion for vulcanization determined from the change in the heat capacity of the reaction mixture

Reaction time (h)	Degree of completion for vulcanization (%)
2.8	30.0
5.5	52.2
8.5	71.2
12.5	86.0
18	93.5
25.5	95.8
35.5	97.1
53.5	98.3

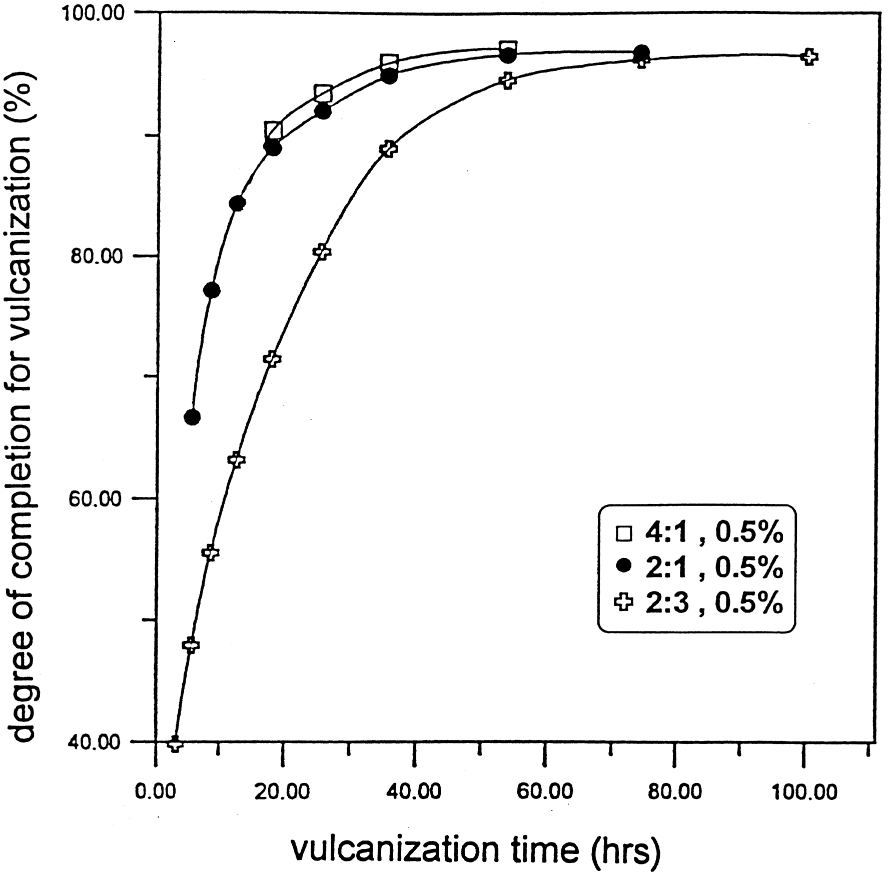


Fig. 4. Degree of completion for vulcanization determined from an extraction method for three samples having different ratios of precursor to crosslinker.

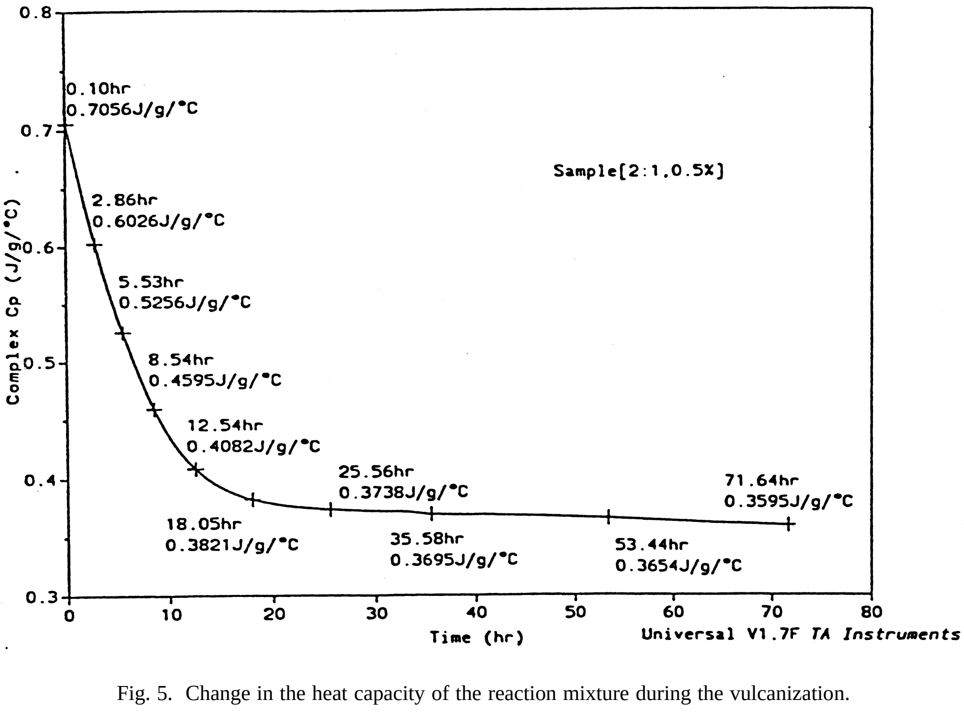


Fig. 5. Change in the heat capacity of the reaction mixture during the vulcanization.

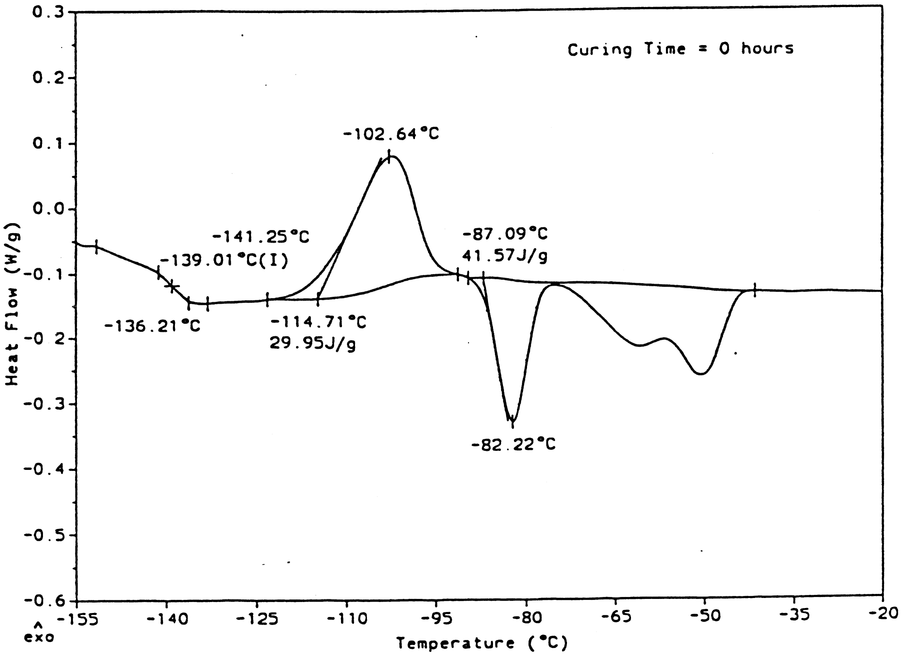


Fig. 6. MDSC curve on the sample having a 2 : 1 ratio of precursor to crosslinker prior to the vulcanization at 25°C.

The extraction experiments were conducted for several reaction mixtures of which each had a different crosslinker to precursor ratio. The degree of completion for vulcanization was measured at various time instants, and data collected from these experiments are shown in Fig. 4. While our aforementioned rheological study showed that an increased amount of crosslinker accelerated the rate of gelling, our extraction data clearly indicated the incorporation of the sol portion into the network was slower however. This was quite contrary to the general belief that adding more crosslinker would shorten the cycle time for a complete cure. In fact, adding more crosslinker increased the possibility of branching, thus shortening the gel time needed for forming insoluble network molecules. Nevertheless, the cycle time of a complete cure became longer because

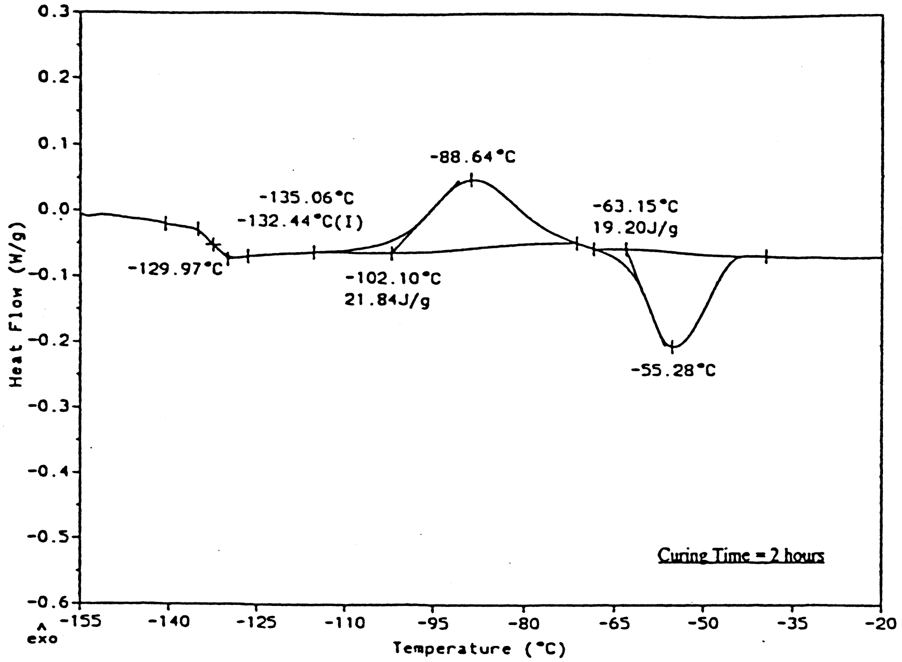


Fig. 7. MDSC curve on the sample having a 2 : 1 ratio of precursor to crosslinker after 2 h of vulcanization at 25°C.

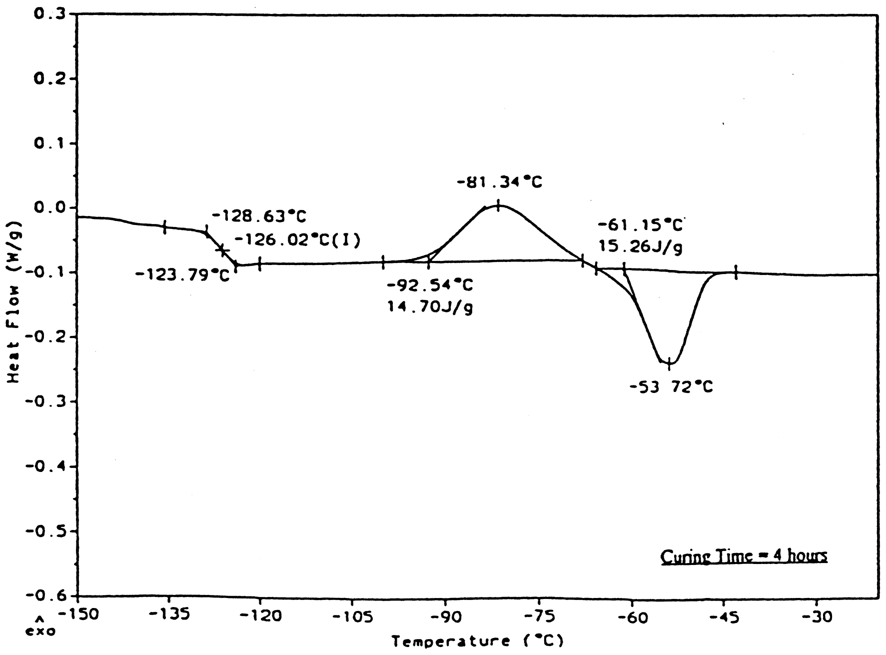


Fig. 8. MDSC curve on the sample having a 2 : 1 ratio of precursor to crosslinker after 4 h of vulcanization at 25°C.

the excessive amount of crosslinker enhanced the possibility of self-reacting with each other leading to an increased amount of sol species.

To corroborate the validity of our observation, the degree of completion for vulcanization was determined independently using two other thermal analytical methods, as given now.

3.2.2. By heat capacity (C_p) measurements using MDSC

One method of determining the degree of completion for vulcanization was through the change of heat capacity of the reaction mixture during the vulcanization reaction. The heat capacity of the reaction mixture decreased with the reaction time, and leveled off as the vulcanization was near completion as shown in Fig. 5. At the completion, the structure of

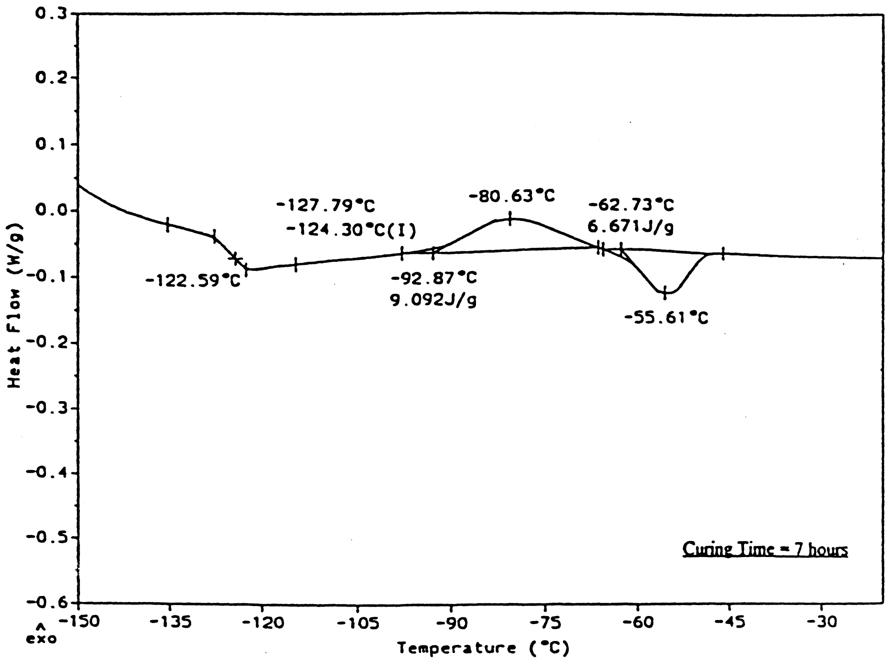


Fig. 9. MDSC curve on the sample having a 2 : 1 ratio of precursor to crosslinker after 7 h of vulcanization at 25°C.

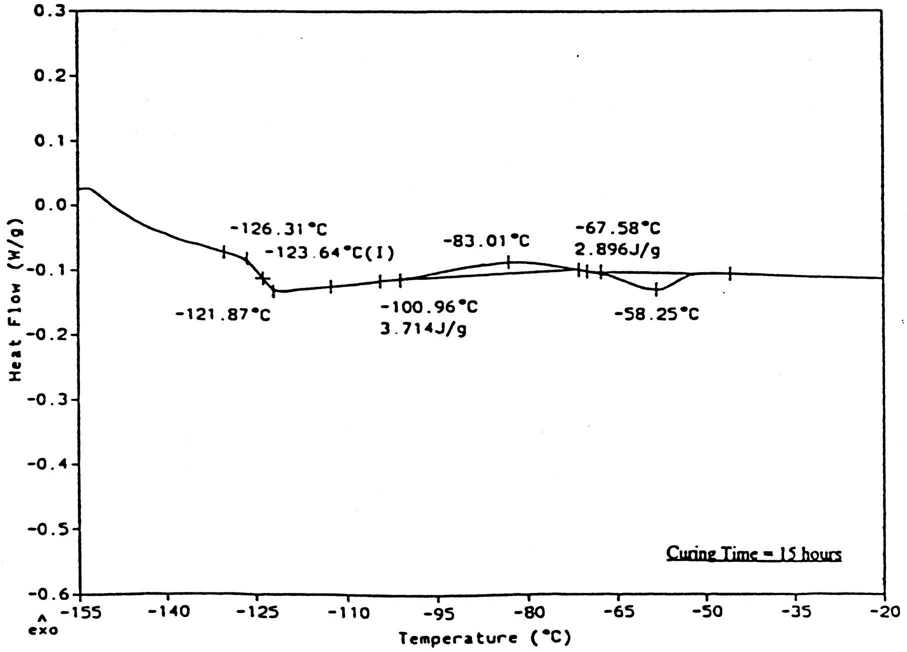


Fig. 10. MDSC curve on the sample having a 2 : 1 ratio of precursor to crosslinker after 15 h of vulcanization at 25°C.

the vulcanized elastomer no longer changed and the heat capacity remained constant. The degree of completion for vulcanization was thus calculated as follows:

$$\text{Degree of completion for vulcanization} = \frac{C_{p_0} - C_{p_t}}{C_{p_0} - C_{p_\infty}}$$

where C_{p0} and $C_{p\infty}$ were the heat capacity at the beginning and end of the vulcanization, respectively. At a 2 : 1 ratio of precursor to crosslinker, the degree of completion for vulcanization determined from the change in the heat capacity of the reaction mixture is shown in Table 1.

3.2.3. By heat flow measurement of cold crystallization using MDSC

The degree of completion for vulcanization has also been studied by examining the heat flow of cold crystallization of

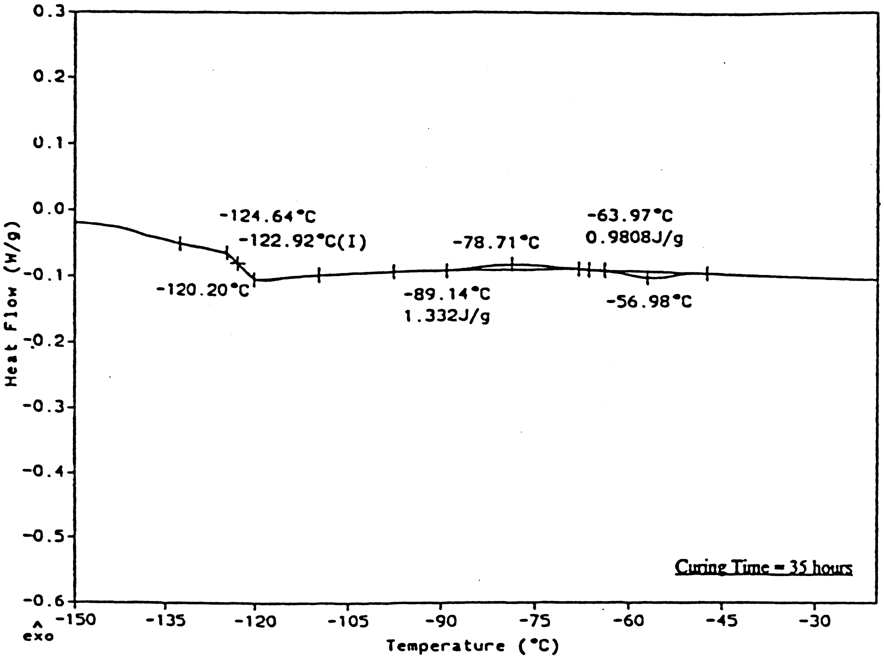


Fig. 11. MDSC curve on the sample having a 2 : 1 ratio of precursor to crosslinker after 35 h of vulcanization at 25°C.

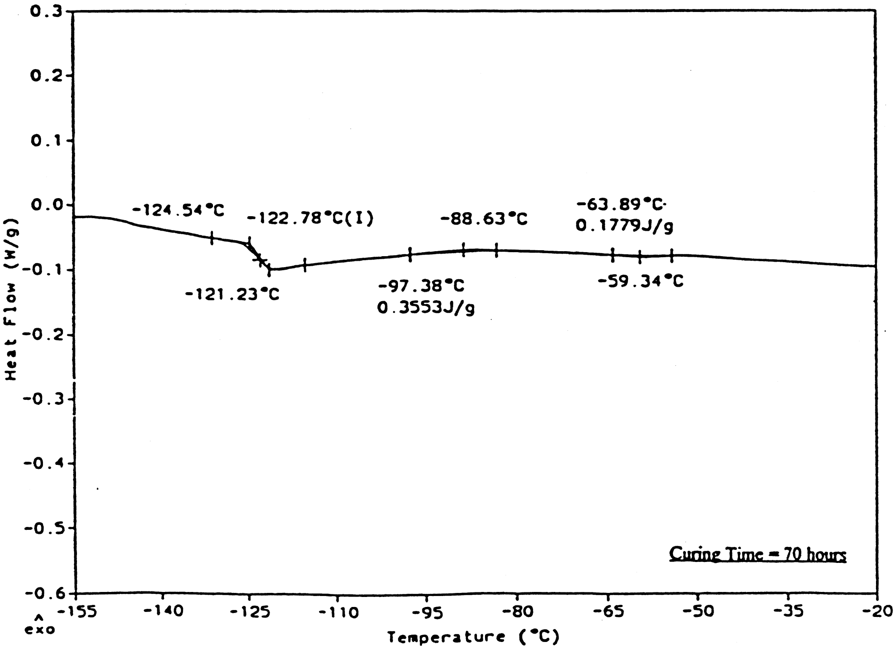


Fig. 12. MDSC curve on the sample having a 2 : 1 ratio of precursor to crosslinker after 70 h of vulcanization at 25°C.

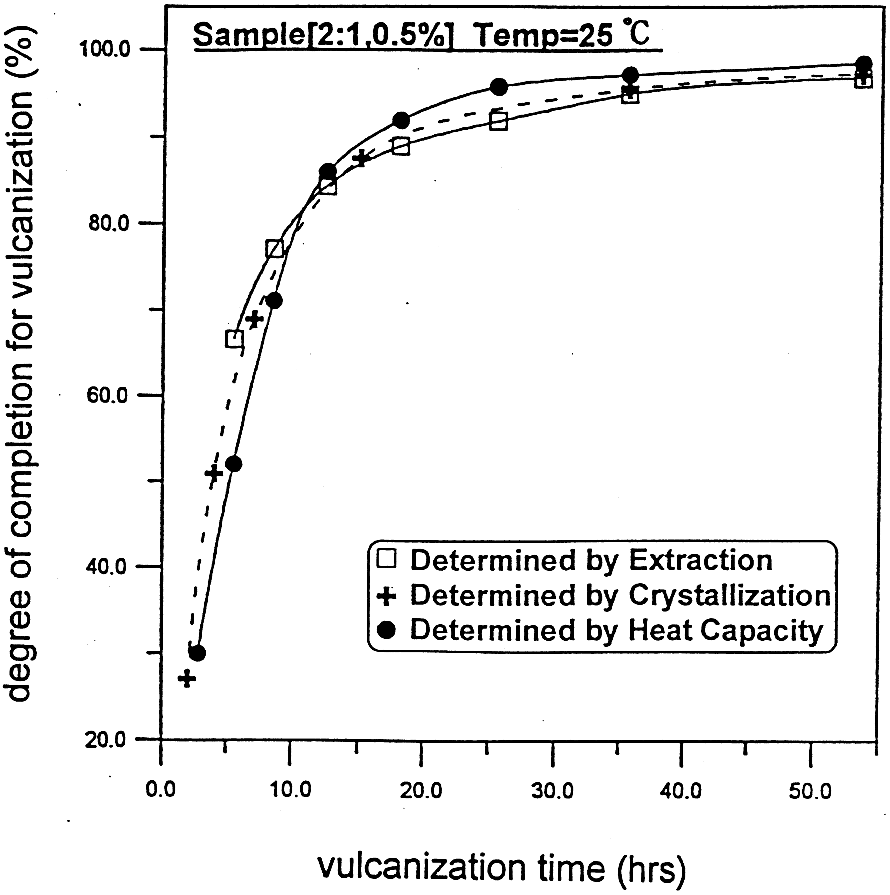


Fig. 13. Degree of completion for vulcanization determined from three different methods.

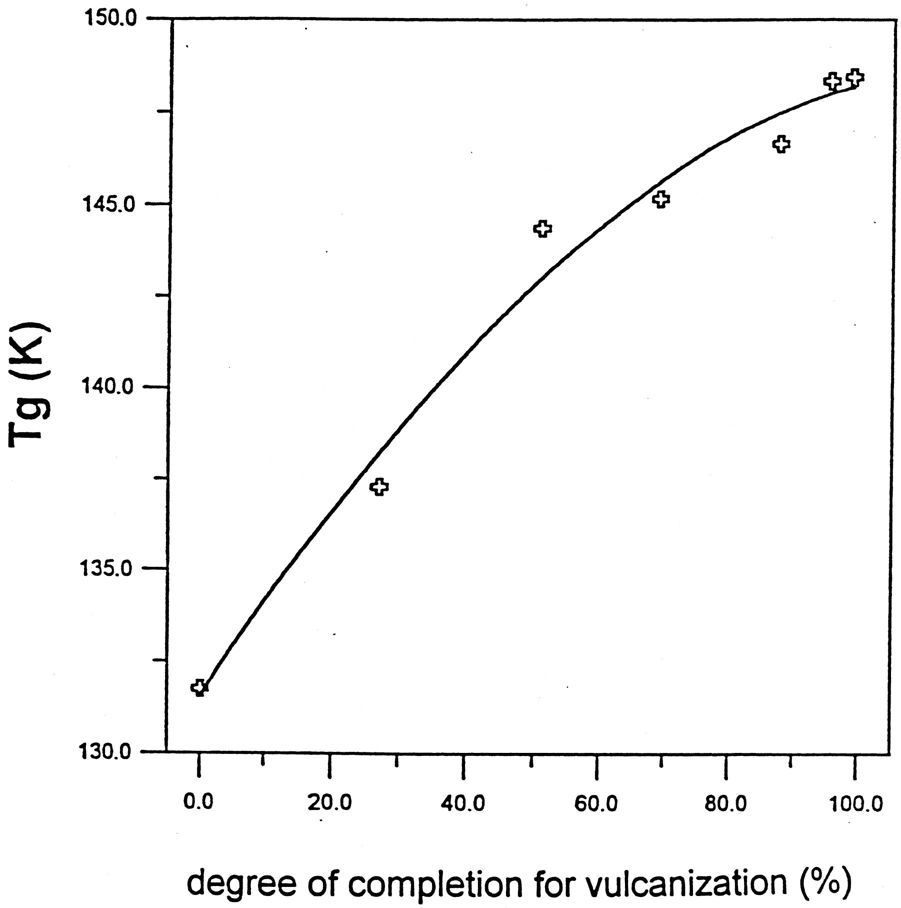


Fig. 14. Effect of the degree of completion for vulcanization on T_g of the reaction mixture.

the reaction mixture. At each sampling instant, the reaction mixture was put into the MDSC cell and quenched rapidly down to −162°C using liquid nitrogen. The temperature of the MDSC cell was then ramped up at a linear rate of 5°C/min superimposed with a modulated sinusoidal heating rate of ±0.4°C every 50 s. The slow linear heating rate provided a high resolution while the fast sinusoidal heating modulation afforded a better sensitivity. As shown in Fig. 6 the glass transition temperature was detected as −139°C for the reaction mixture prior to the vulcanization. As the temperature was continuously increased the cold crystallization of precursor fluid occurred with a heat release. When the temperature was further raised up, three endothermic peaks were observed. These three endotherm peaks arose from the crystal melting of the precursor. TEOS, and DBTDL in the reaction mixture. As depicted in Figs. 7–12, the observed T_g increased with an increase in the reaction time, and had a value of −122°C at the end of 70 h vulcanizing. In addition, both exothermic and endothermic peaks diminished with reaction time because of the cross-linking, and eventually the completely vulcanized silicone system became totally amorphous.

The diminishing of the heat flow of cold crystallization prompted us to relate quantitatively the degree of completion for vulcanization as follows:

$$\text{Degree of completion for vulcanization} = \frac{H_0 - H_t}{H_0}$$

where H_0 was the heat flow at the beginning of the vulcanization. The degree of completion for vulcanization determined from the heat flow of cold crystallization is shown in Table 2.

Data collected from all three methods are shown simultaneously in Fig. 13. They are in excellent agreement with

Table 2
Degree of completion for vulcanization determined from the heat flow of cold crystallization

Reaction time (h)	Heat flow (W/g)	Degree of completion for vulcanization (%)
0	29.95	0
2	21.84	27
4	14.70	51
7	9.092	69
15	3.714	87.6
35	1.332	95.5
70	0.355	98.8

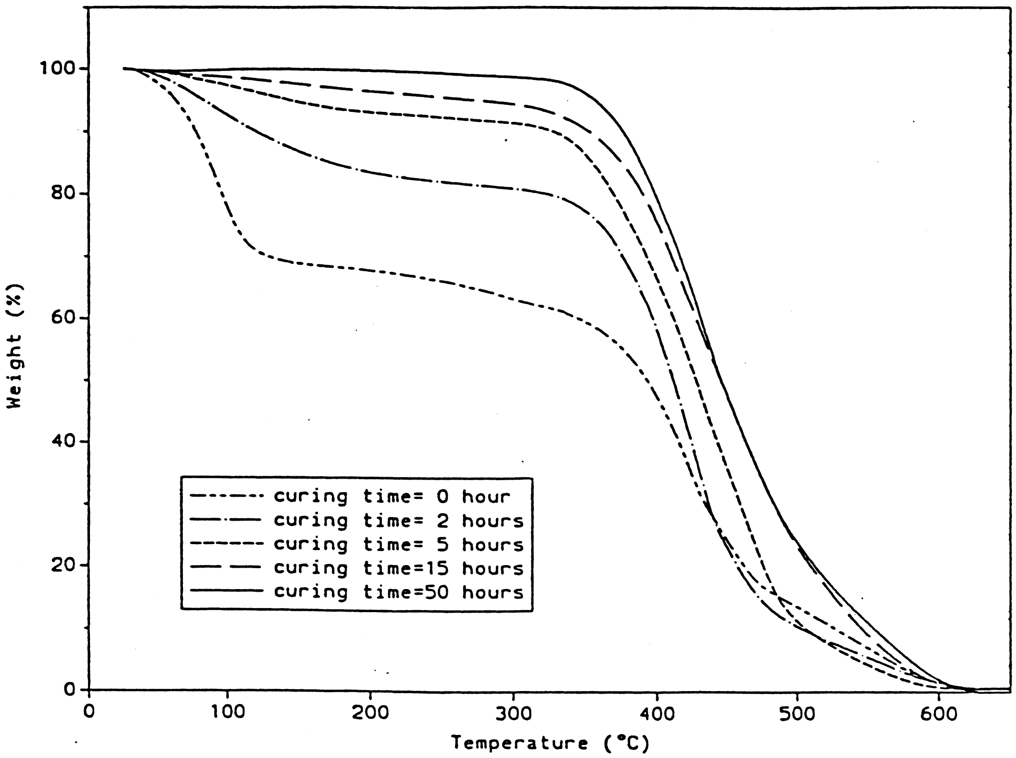


Fig. 15. Effect of vulcanization time on the thermal stability of the reaction mixture.

each other, and have thus corroborated the validity of our observations. Based on the data determined from the heat flow of cold crystallization, the effect of degree of completion for vulcanization on the increase in T_g was also shown in Fig. 14. T_g increased with a decrease in the molecule mobility caused by the crosslinking.

3.3. Thermal stability of silicone elastomers

Apart from the MDSC studies, TGA analyses were also conducted on samples taken at various reaction times. Fig. 15 clearly indicates that the thermal stability of the reaction mixture increased with an increase in the degree of

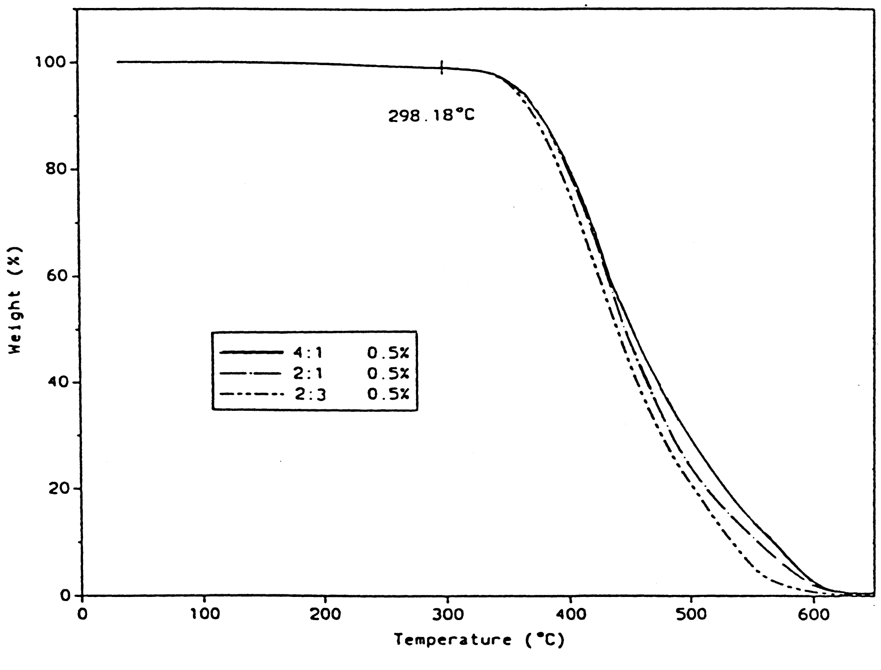


Fig. 16. Thermal gravimetric analysis on samples having formulations of various ratios of precursor to crosslinker.

completion for vulcanization. However, formulations with various precursors to crosslinker ratios would lead to final vulcanized products with slightly different thermal stabilities as shown in Fig. 16. As described in our extraction experiments, an excessive amount of crosslinker slowed down the rate of incorporation of sol portion into the network thus increasing the cycle time for a complete cure. The slight decrease in the thermal stability of the final vulcanized product made with higher crosslinker to precursor ratio could therefore be ascribed to the presence of residue sol species.

4. Conclusions

The rheological behavior of the room temperature vulcanized polydimethylsiloxane with tetraethylorthosilicate at a 2 : 1 ratio was studied in the presence of 0.5 wt.% dibutyltin dilaurate as the catalyst. An increase in the viscosity as a result of branching or partial crosslinking caused a gradual increase in the loss modulus prior to reaching the gel point. The elasticity predominated over the viscosity at the gel point leading to a drastic decrease in the phase angle. At a higher ratio of crosslinker to precursor, the starting loss modulus was lowered and the vulcanization accelerated. Although the gel time was shortened, our extraction experiment indicated that the degree of completion for vulcanization was lowered because of an increased amount of sol species, thus necessitating a longer cycle time for a complete cure. The degree of completion for vulcanization determined from the extraction method at each reaction instant was checked against those determined from two independent thermal analytical methods, namely, the heat capacity method and the cold crystallization method. Data collected from these three methods were in excellent agreement with each other. In addition, the presence of residue sol species in the formed silicone products caused a slight decrease in the thermal stability.

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