

VULCANIZATION KINETICS OF SILICONE RUBBER

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ABSTRACT

Vulcanization rate of silicone rubber with the aid of organic peroxide or hydrosilylation agent was studied by using oscillation disk rheometer. It was found that the process of network formation would take place through one, two or three steps depending on the structure of the reactants. The effect of phenyl group, vinyl terminals on polysiloxane chain and the functionality of silylation agent was also studied.

Vulcanization is an important step in the fabrication of rubber. Better understanding on the mechanism and controlling the rate of the reaction are desirable for manufacturing good products. Silicone rubbers can be vulcanized with organic peroxide or hydrosilylation agent. Many papers on the methods of compounding, technology of crosslinking and their effect on properties of the products have been published. However, only a few works can be found about the kinetic study of vulcanization. Andrianov studied the crosslinking rate of dimethyl-vinylmethyl silicone rubber with a series of hydrosilylation agents by tracing SiH band absorption at 2180 cm^{-1} [1]. Barrell determined the energy of activation of crosslinking of low molecular silicone with polyhydrosiloxane by DSC [2]. The structure-reactivity relationship of these components was discussed.

Oscillation disk rheometer (ODR) can display the change of torque of the compounds during vulcanization which is shown to be linearly related to the change of crosslink density of the vulcanizates [3]. It has been applied successfully in the study of natural and some synthetic rubbers but no data is available for silicone rubber.

By using ODR method, the vulcanization kinetics of silicone rubber with organic peroxide and hydrosilylation reagent as crosslinking agent was studied. The reactivity of the components as well as the mechanism of reaction was discussed.

EXPERIMENTAL

1. Apparatus

Oscillation disk rheometer — a product of Beijing Chemical Machine Works, oscillation angle $\pm 3^\circ$, frequency of oscillation, 3 cycles per min, disk cavity, 30 mm in diameter, temperature control $\pm 0.1^\circ\text{C}$, recorder span 1 mv.

2. Material

a. Silicone gum: (1) Dimethyl, mol. wt. 4.8×10^5 , (2) dimethyldiphenyl, containing diphenyl linkage, 4.0%, 10.5% and 32.4% with mol. wt. 4.8×10^5 , 6×10^5 and 9.5×10^5 respectively are industrial products having vinyl linkage 0.15–0.20%. (3) vinyl terminated poly-dimethylsiloxane

containing 0.1% pendent vinyl group was synthesized in laboratory with dispersity index of 11 and a maximum molecular weight 1.2×10^5 . Vinyl content of all the samples was determined by indirect coulometry^[4].

b. Crosslinking agent: For one set of samples, 1% of di-tert. butyl peroxide was used. For another set, low molecular hydrosilane such as $\text{Ph}_2\text{Si}(\text{OSiMe}_2\text{H})_2$, $\text{PhSi}(\text{OSiMe}_2\text{H})_3$, medium molecular hydrosilicone oil with 8% and 50% mole hydrosiloxy group were used. The ratio of vinyl to hydrosilyl group was kept at 1:1.2 for all the hydrosilylations. A complex of chloroplatinic acid with tert. butyl hydroperoxide was used as catalyst. The amount of platinum used is about 10 ppm of the silicone used.

c. Operation: Silicone gum was mixed with crosslinking agent (organic peroxide or hydrosilylation agent) and catalyst. 10 g of the mixture was placed rapidly into the disk of the rheometer preheated to the test temperature. The torques E_0 at minimum, E_∞ at maximum and the values E_t at time t were taken from the cure curve. At the beginning stage of vulcanization, data were taken in 1 min interval. They were recorded up to constancy of torque value.

RESULTS AND DISCUSSION

The kinetic interpretation of the cure curve is different as the composition of sample and test temperature differ. For instance, Coran^[5] reported, the crosslinking of natural rubber by sulfur and additives can be described by the first order kinetics after induction period, eq.1.

$$\frac{E_t - E_0}{E_t} = e^{-k(t-t_0)} \quad (1)$$

where t_0 is the time of induction. Nakashima^[3] showed the cure curve can be divided into two parts in the presence of carbon black. The first was attributed to the interaction of filler with rubber matrix and the latter to the crosslinking of polymer themselves. Scheele^[6] and Yukovskii^[7] reported that when degradation of polymer takes place during vulcanization at higher temperature, the kinetics can be expressed in the form of consecutive first order reaction, eq.2

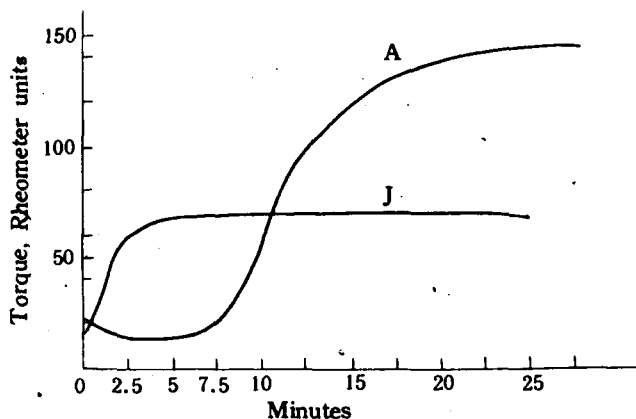


Fig.1. Cure curves of sample A at 150°C and sample J at 110°C, permitting to derive only one rate constant.

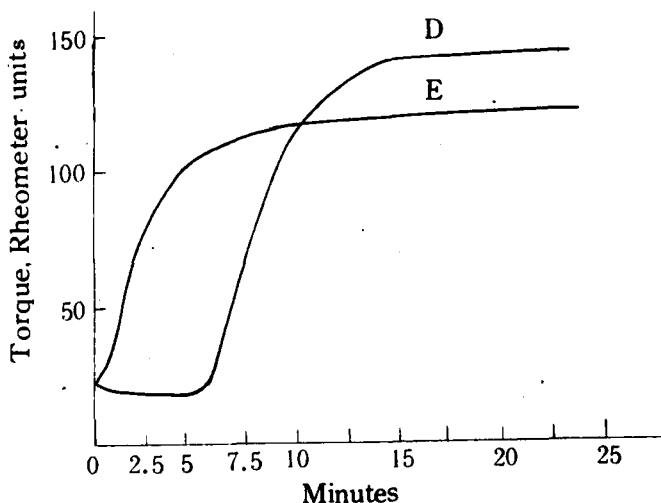


Fig.2 Cure curves of sample D at 160°C and sample E at 120°C, permitting to derive two rate constants.

$$\frac{E_t - E_0}{E_\infty - E_0} = \frac{k_1}{k_1 - k_2} (e^{-k_1 t} - e^{-k_2 t}) \quad (2)$$

Deriving from a theoretical model Furukawa^[8] divided the cure curve of SBR into three parts: for the first, the plot of reciprocal torque against time gave a straight line; for the second, a first order kinetics was observed; for the third, a plot of $\log E_t$ against $\log t$ gave a line with a slope 1/4.

It was found that in the vulcanization with organic peroxide induction periods were observed in the ODR diagrams, as shown in the initial parts of curves A and D in Figs.1 and 2 respectively. They were interpreted as the result of peroxide decomposition. On the other hand, the induction period was hardly observed when silicone gum was cross-linked with hydrosilylation agent, as shown on curves E and J in the same figures. A, J and E, D represent two types of reactions. If the induction period is eliminated from the former, both types can be treated similarly in kinetics study.

Furukawa's hypothesis is helpful for interpreting our data although some modification has to be made. Three steps may be involved in the vulcanization of silicone gum but each step is not bound to occur in the network formation. Three different cases were observed.

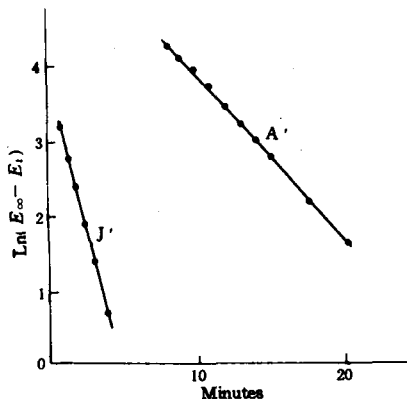


Fig.3 Derivation of k_1 from cure curves A and J

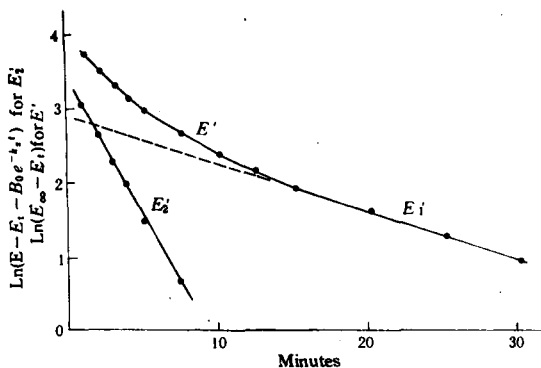


Fig.4 Derivation of k_2 and k_1 from cure curve E

(1) When dimethylsilicone gum was crosslinked with organic peroxide or difunctional silylation agent such as $\text{Ph}_2\text{Si}(\text{OSiMe}_2\text{H})_2$, curves A and J were observed (Fig.1). They can be described by a first order kinetic equation since the plot of $\ln$ torque values against time results in straight lines A' and J' in Fig.3. Only one rate constant can be derived from each curve. The author's opinion, it is the unusual flexibility of organosiloxane chain that allows the functional groups including the pendent ones on the network chains to be able to react with the same rate up to completion.

(2) When the gum containing phenyl group was vulcanized with peroxide, or when the dimethyl gum was vulcanized by hydrosilylation agent with more than two SiH groups, cure curves like D and E were observed respectively in Fig.2. The plot of $\ln (E_\infty - E_t)$ versus t for the curve E gives curve E' in Fig.4. The second part of the curve is a straight line, E'_1 which can be expressed by $B = B_0 e^{-k_2 t}$, where k_2 is the slope of this straight line and B_0 the intercept on the ordinate. The first part of this curve can be transformed to another straight line, E'_2, with the expression $A = A_0 e^{-k_1 t}$, where A is derived from $E_\infty - E_t - B_0 e^{-k_2 t}$ and k_1 is its slope. The overall vulcanization can be described by the equation

$$\frac{E_\infty - E_t}{E_\infty - E_0} = A_0 e^{-k_1 t} + B_0 e^{-k_2 t} \quad (3)$$

Similar treatment of curve D also gives two rate constants.

The vulcanization of all samples except A, J and L can be described by this expression. Furukawa's concept of stepwise network formation is applicable here. k_1 is assumed to represent the crosslinking rate forming the basic network, whereas k_2 the rate of the pendent functional groups on the network chains, as illustrated in Fig.5. Since introduction of phenyl group or polyfunctional hydrosiloxane makes the basic siloxane network less flexible, they will retard the interaction of functional groups on them. Two rate constants were observed.

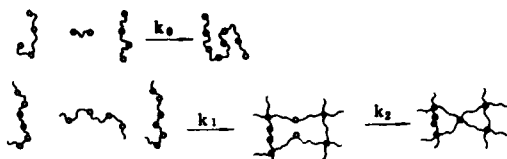


Fig.5 Mode of chain extension and crosslinking after Furukawa

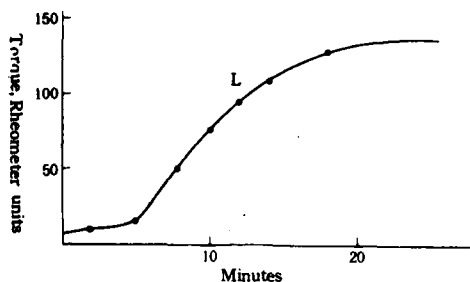


Fig.6 Cure curve of sample L at 120°C, permitting to derive three rate constants

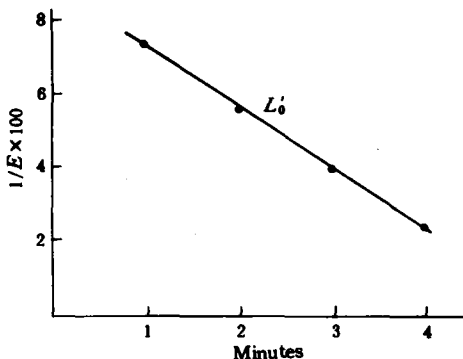


Fig.7 Derivation of chain extension constant k_0 from initial part of curve L

Table 1 Vulcanization rate constants of silicone gum crosslinked by di-tert-butyl peroxide

No.	Composition Silicone gum	Constant (min ⁻¹)	413	Temperature (K)			<i>E</i> (kJ/mol)
				423	433	443	
A	dimethyl	<i>k</i> ₁	0.09	0.23	0.49	0.67	85
		<i>k</i> ₂	—	—	—	—	—
B	dimethyl contg.	<i>k</i> ₁		0.21	0.34	0.75	60.7
	15.6% diphenyl	<i>k</i> ₂		0.02	0.05	0.11	115.7
C	dimethyl contg.	<i>k</i> ₁		0.29	0.58	1.31	116.9
	7.8% phenylmethyl	<i>k</i> ₂		0.08	0.16	0.41	124.9
				Temperature (K)			<i>E</i>
				443	453	463	(kJ/mol)
D	dimethyl contg.	<i>k</i> ₁		0.35	0.56	1.12	98.3
	32.4% diphenyl	<i>k</i> ₂		0.06	0.10	0.23	126.3

Table 2 Vulcanization rate constants of silicone gum crosslinked by hydrosilylation agent

No.	Composition gum + hydrosilane	Constant (min ⁻¹)	Temperature (K)					E (kJ/mol)
			353	373	393	413	433	
E	dimethyl HSO* contg. 50% SiH	k_1		0.11	0.30	0.58	0.96	42.8
		k_2		0.04	0.06	0.11	0.28	41.8
F	dimethyl contg. 4% diphenyl HSO contg. 50% SiH	k_1		0.25	0.54	0.76		41.6
		k_2		0.05	0.06	0.12		45.6
G	dimethyl contg. 10% diphenyl HSO contg. 50% SiH	k_1		0.20	0.23	0.43		50.6
		k_2		0.02	0.05	0.08		58.3
H	dimethyl contg. 15.6% diphenyl HSO contg. 50% SiH	k_1		0.13	0.26	0.36		40.6
		k_2		0.03	0.06	0.12		45.8
I	dimethyl HSO contg. 8% SiH	k_1		0.26	0.61	0.95		41.5
		k_2		0.05	0.14	0.19		41.9
J	dimethyl Ph ₂ Si(OSiMe ₂ H) ₂	k_1	0.15	0.88	1.36			45.7
		k_2	—	—	—			—
K	dimethyl PhSi(OSiMe ₂) ₃	k_1	0.35	0.85	1.00			44.4
		k_2	0.08	0.27	0.38			45.7
L	dimethyl Vi terminal	$k_0 \times 10^3$	0.91	5.1	7.5**	26.0***		80.0
	Ph ₂ Si(OSiMe ₂ H) ₂	k_1	0.23	0.22	0.67	1.05		35.9
	HSO contg. 50% SiH	k_2	0.03	0.06	0.08	0.10		32.0

* HSO = hydrosilicone oil, ** The reaction was carried out at 383 K.

*** The reaction was carried out at 403 K.

(3) When the vinyl dimethyl terminated gum of medium molecular weight was combined with α,ω -dihydrosiloxane and polyhydrosilicone oil, as in the sample L, three rate constants could be derived from curve L (Fig.6). The treatment of latter part of this curve by the above procedure gives two straight lines L_1 and L_2 with slopes k_1 and k_2 like that shown in Fig.4. The remaining initial part of the curve could be transformed to a straight line L_0 (Fig.7) with a slope k_0 too, when $1/(E_t - E_0)$ was plotted against t . Since k_0 could be derived only from the sample pertinent to chain extension it should represent this kind of reaction.

The vulcanization rate constants of a series of silicone gum with di-tert. butyl peroxide and hydrosilylation agent as crosslinking agent are listed in Table 1 and Table 2 respectively.

The rate constants thus determined can be used to compare the reactivity of the gums and the vulcanization agents. A few comments can be made as follows.

(1) The presence of phenyl group up to a certain amount, 4%, will retard the crosslinking. The more the phenyl content the smaller the rate constant will be.

(2) The vulcanization rate with hydrosilicone oil having scattered (8%) SiH groups is higher than that of those having concentrated (50%) ones, as seen from sample E and I.

(3) Vulcanization with difunctional hydrosilane, $\text{Ph}_2\text{Si}(\text{OSiMe}_2\text{H})_2$, proceeds faster than that with trifunctional hydrosilane, $\text{PhSi}(\text{OSiMe}_2\text{H})_3$. The data of samples J and K show this clearly.

(4) The apparent energy of activation for the vulcanization with peroxide is much higher than that with hydrosilylation agent.

Keywords:

Silicone rubber; Vulcanization; Kinetics; Hydrosilylation.

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