

Rheological Study on the Cure Kinetics of Two-component Addition Cured Silicone Rubber^{*}

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Abstract The cure kinetics for two-component silicone rubber formed by addition reaction was studied by the rheological method. The influence of reaction temperature (T) on the cure kinetics was explored in detail. It was observed that the data of gel time (t_{gel} , *i.e.* the time when the reaction reaches the gel point) or a specific reaction time (t_{nc}) (defined as the reaction time before which time the influence of confinement of network on the diffusion of reaction components can be neglected) versus T obey certain functional relationship, which was well explained by the cure kinetics model of thermoset network. The cure kinetics for the two-component silicone rubber can be well fitted by the Kamal-Sourour (autocatalyst) reaction model rather than Kissinger model. When the reaction time was before or equal to t_{nc} , the reaction order obtained by the Kamal-Sourour reaction model was 2, which was consistent with the reaction order inferred from the two components chemical reaction when the diffusion of reaction components was not influenced by the formed cross-linked polymer network. When the reaction time was larger than t_{nc} , such as to the end of reaction (t_{e}), the influence of confinement of network on the diffusion of reaction components cannot be neglected, and the reaction order obtained by the Kamal-Sourour reaction model was larger than 2. It was concluded that the confinement effect of network had a greater influence on the cure kinetics of the silicone rubber. The reaction rate constants (k_i) under different temperatures were also determined by Kamal-Sourour reaction model. The activation energy (E) for the two-component silicone rubber was also calculated from the results of $\ln t_{\text{gel}}$, $\ln t_{\text{nc}}$, and $\ln k_i$ versus $1/T$, respectively. The three values of E were close, which indicated that above analyses were self-consistent.

Keywords: Silicone Rubber; Cure kinetics; Rheology; Gel point; Reaction model.

INTRODUCTION

Silicone rubber consists of a poly(dimethyl siloxane) (PDMS) network, and the cure of silicone rubber arises from different chemical reactions, usually resulting from hydrosilylation, radical or condensation reactions, while silica particles and other fillers are often added^[1–4]. Silicone rubbers have attracted great industrial attention due to high thermal stability, ultralow temperature toughness, high extensibility, low dielectric constant, low surface energy, high gas permeability and excellent biocompatibility *etc*^[1–4]. Silicone rubbers are widely used as sealants, adhesives, high voltage insulation devices, electronics, automotive, and healthcare *etc*^[1].

^{*} This work was financially supported by the National Natural Science Foundation of China (No. 21274152) and the Science and Technology Development Project of Jilin Province, China (No. 20150301002GX).

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Received April 7, 2016; Revised April 27, 2016; Accepted May 8, 2016

doi: 10.1007/s10118-016-1847-8

The properties of silicone rubbers can be affected by the cure process. To control the properties of silicone rubber, the cure kinetics and cure mechanisms of silicone rubbers should be well understood. Most of the works reported the cure kinetics of silicone rubbers under a non-isothermal condition. Lopez *et al.* studied the influence of heating rate on the cure kinetics of a silicone rubber by dynamic differential scanning calorimeter (DSC) from 20 °C to 150 °C, and the cure kinetics was analyzed by the Kamal-Sourour (autocatalyst) reaction model^[5]. Hong *et al.* also conducted a similar research to study the influence of heating rate on the cure kinetics of a silicone rubber by DSC from 50 °C to 150 °C^[6]. Their work provided a valuable guide for the thermal processing of silicone rubber^[5, 6]. The cure kinetics of silicone rubber under an isothermal condition is also important for its production in industry. Zhang *et al.* studied the cure kinetics for two-component silicone rubber formed by addition reaction using rheological method under an isothermal condition, and the influence of reaction temperature on cure kinetics was explored, while the cure kinetics was not further analyzed by cure kinetics model in their work^[7]. To better understand the cure kinetics of silicone rubber under an isothermal condition, more work has to be done.

On the other hand, few works reported the influence of confinement effect of cross-linked polymer network on the cure kinetics of silicone rubber, while the diffusion rate of reaction components can be dramatically decreased because of the confinement effect of formed network^[8]. At later stage of cure reaction for silicone rubber, as a cross-linked network was already formed, it was expected that the confinement effect of cross-linked silicone rubber network should have a great influence on the further cure kinetics of the silicone rubber.

In this work, the cure kinetics of a commercial room temperature vulcanization two-component (abbreviated as RTV2) silicone rubber were studied by rheological method from 0 °C to 45 °C (under an isothermal condition), and further analyzed by cure kinetics model. At the same time, the influence of confinement of network on the cure kinetics of RTV2 silicone rubber was also explored.

EXPERIMENTAL

Materials

SILBIONE RT GEL 4317 A & B (Bluestar silicones) are two-component silicone elastomers that crosslink at room temperature by hydrosilylation addition reaction at 1:1 mixing ratio. Component A contains Pt catalyst and vinyl poly(dimethylsiloxane) while component B contains vinyl poly(dimethylsiloxane) and hydrosilyl poly(dimethylsiloxane) as reported by the manufacturer and the results of Nuclear Magnetic Resonance (NMR) performed by us^[7]. Both the components A and B are liquids.

For easier discussion below, the hydrosilylation addition reaction during the cure of the two-component silicone rubber in this work is explained first. The reaction rate of hydrosilylation addition reaction can be described by

$$d[-CH_2-CH_2-Si-]/dt = C [-CH=CH_2] [-Si-H] \quad (1)$$

where $[-CH_2-CH_2-Si-]$, $[-CH=CH_2]$, and $[-Si-H]$ represent the concentrations of product for hydrosilylation addition reaction, vinyl group, and hydrosilyl group at different reaction time (t), respectively. $d[-CH_2-CH_2-Si-]/dt$ is the reaction rate, and C is a constant. In Eq. (1), the influence of confinement of network on the diffusion of reaction groups ($[-CH=CH_2]$ and $[-Si-H]$) is not considered, and it is apparent that the reaction order is 2. The degree of reaction (α) can be expressed as^[5]

$$\alpha = \frac{[-CH_2-CH_2-Si-]_t}{[-CH_2-CH_2-Si-]_e} \quad (2)$$

where $[-CH_2-CH_2-Si-]_t$ and $[-CH_2-CH_2-Si-]_e$ represent the concentration of product for hydrosilylation addition reaction at different reaction time and at the end of reaction, respectively. The value of α is zero when there is no reaction and is equal to 1 when the reaction is complete.

Rotary Rheometer Measurements

A quantity of 4317 A (0.5 g) was mixed with 0.5 g of 4317 B by hand for about 2 min at room temperature, then the mixture was put in vacuum oven for about 3 min at room temperature to eliminate entrapped air bubbles. Then the mixture was used immediately for a rheological measurement.

Rheological experiments were performed on an AR-2000ex rheometer (TA Instruments) with 25 mm parallel plate geometry. The time sweep experiments under the multi-wave oscillatory frequency (1, 4 and 16 rad/s) were performed to determine the gel time (t_{gel}) of silicone rubber at different reaction temperatures (0, 5, 10, 15, 20, 25, 30, 35, 40 and 45 °C), while the strain was in the linear regime. Oscillatory frequency sweep was also performed from 1 rad/s to 100 rad/s with a strain in the linear regime to determine the viscoelastic properties of mixture at different reaction time regime under 40 °C.

Time sweep experiment under the single-frequency (10 rad/s) with a strain in the linear regime was used to analyze the cure kinetics of silicone rubber at above different reaction temperatures. From the value of storage moduli (G'), loss moduli (G''), the absolute value of complex moduli $|G^*|$, and the oscillatory torque (Torque) at different reaction time in above time sweep experiment under 10 rad/s, four different degree of reaction $\alpha_{G'}$, $\alpha_{G''}$, $\alpha_{|G^*|}$, and α_{Torque} were defined as follows^[9, 10]

$$\alpha_X = \frac{X(t) - X(t_0)}{X(t_e) - X(t_0)} \quad (3)$$

where X is G' , G'' , $|G^*|$, and Torque, respectively. $X(t_0)$ is the value of X at the beginning of reaction (t_0), $X(t)$ is the value of X at different reaction time (t), $X(t_e)$ is the value of X at the end of reaction (t_e).

RESULTS AND DISCUSSION

Determination of the Gel Time (t_{gel})

For the isothermal cure reaction of gel-like samples, the gel time (t_{gel}) is the time when the reaction reaches the gel point^[11]. From the results of linear dynamic-mechanical modulus for gel-like samples, Winter and Chambon proposed a criterion to determine the gel point, at which the storage (G') and loss moduli (G'') of the sample should show the same frequency scaling law, and all loss tangent $\tan\delta$ at different oscillatory frequencies (ω) coincide as follows^[11]:

$$G'(\omega) \sim G''(\omega) \sim \omega^n \quad (4)$$

$$\tan\delta = G''(\omega)/G'(\omega) = \tan(n\pi/2) \quad (5)$$

where n is relaxation exponent which depends on the molecular and structural details^[11]. So, t_{gel} can be identified as the time at which $\tan\delta$ at various frequency intersect^[11]. In this work, the gel time (t_{gel}) was determined from the results of time sweep experiments under multi-wave oscillation frequency (1, 4 and 16 rad/s).

In Fig. 1, time sweep experiment under the multi-wave oscillatory frequency (1, 4, 16 rad/s) for the mixture of 4317 A and 4317 B at 40 °C is shown as an example. The storage (G') and loss moduli (G'') versus time at three simultaneous frequencies (1, 4, and 16 rad/s) are shown in Fig. 1(a). Both G' and G'' increased with time in the experimental range, while G' was smaller than G'' at the beginning and G' became larger than G'' as the time further increased. As $\tan\delta$ is independent of frequency at the gel point, the curves passed through a single point and unambiguously defined the t_{gel} . In Fig. 1(b), for the mixture of 4317 A and 4317 B at 40 °C, the t_{gel} was determined to be 876 s. The t_{gel} for the mixture of 4317 A and 4317 B at other reaction temperatures were determined by above method, the detailed results are not shown in this work.

From Fig. 2, it is evident that for the frequency sweep beginning at 654 s (ended at 756 s) before the t_{gel} (876 s) of the mixture at 40 °C, the G' was smaller than G'' in the experimental range, inferring that the viscosity of the mixture dominates at this time^[11]. At 654 s, the powerlaw dependencies for G' and G'' versus frequency (ω) in the experimental range was $G' \sim \omega^{1.5}$ and $G'' \sim \omega^{1.0}$, respectively (the correlation coefficients of fitting was above 0.995), which had larger deviation to the criterion of Winter-Champon for the gel point ($G'(\omega) \sim G''(\omega) \sim$

ω^n). At 906 s which was just above the t_{gel} (876 s) of the sample at 40 °C, the G' was still smaller than G'' in the experimental range and the viscosity of the mixture also dominated at this time regime. At 906 s, there was $G' \sim \omega^{1.1}$ and $G'' \sim \omega^{0.9}$ (the correlation coefficients of fitting was above 0.998), the powerlaw dependencies for G' and G'' versus ω at this time was closer to the criterion of Winter-Champon for the gel point ($G'(\omega) \sim G''(\omega) \sim \omega^n$)^[11]. At 5604 s, the G' was much larger than G'' in the experimental range, which implies that a network structure was formed and the elasticity of the mixture dominated at this time^[11]. As the time was further increased to 98796 s, the value of G' and G'' increased slowly, thus indicating that the reaction rate was affected by the confinement of network structure.

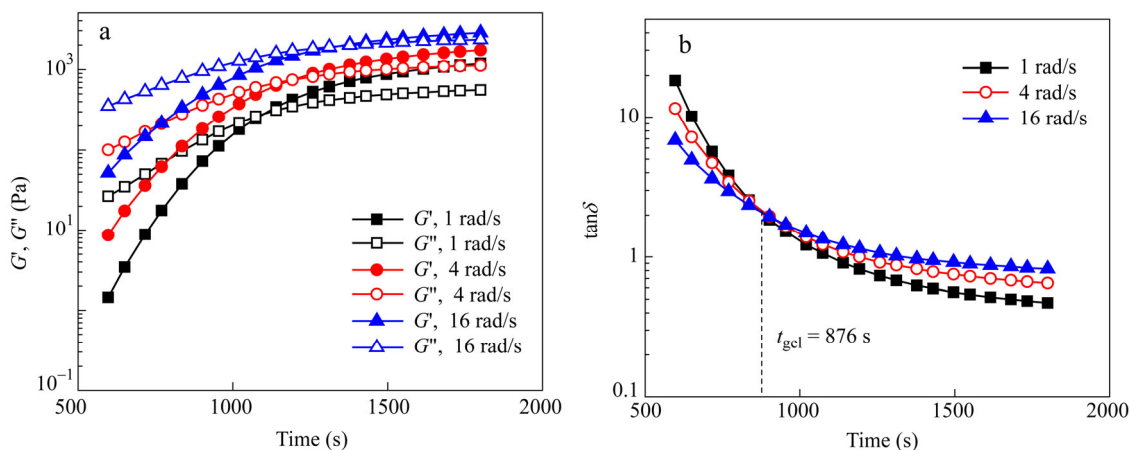


Fig. 1 Storage (G') and loss moduli (G'') (a), and loss tangent $\tan\delta$ (b) versus reaction time for the mixture of 4317 A and 4317 B under simultaneous frequencies (1, 4 and 16 rad/s) at 40 °C

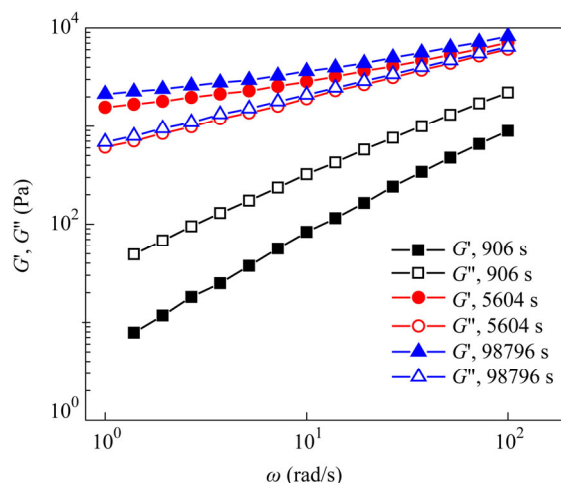


Fig. 2 Storage (G') and loss moduli (G'') versus angular frequency (ω) for the mixture of 4317 A and 4317 B at different reaction time regime under 40 °C

The different time started a frequency sweep is shown in the legend, while it needed 102 s to perform a frequency sweep from 1 rad/s to 100 rad/s.

Influence of Reaction Temperature on t_{gel}

The results of t_{gel} at different reaction temperatures are shown in Fig. 3(a). It can be observed that the t_{gel} was increased rapidly from 636 s to 78750 s, as the reaction temperature was decreased from 45 °C to 0 °C. Above results indicate that the reaction rate was decreased dramatically, as the reaction temperature was lowered.

An overall activation energy (E) for cross-linking can be obtained from gel times, assuming that the cure reaction can be described by differential equations containing one unique apparent activation energy, as

following^[12]

$$\frac{d\alpha}{dt} = A \exp\left(-\frac{E}{RT}\right) f(\alpha) \quad (6)$$

where α is the degree of reaction, A is a constant, E is the apparent activation energy for the overall reaction, R is the gas constant, T is the isothermal cure temperature, and $f(\alpha)$ is assumed to depend on α and to be independent of the cure temperature.

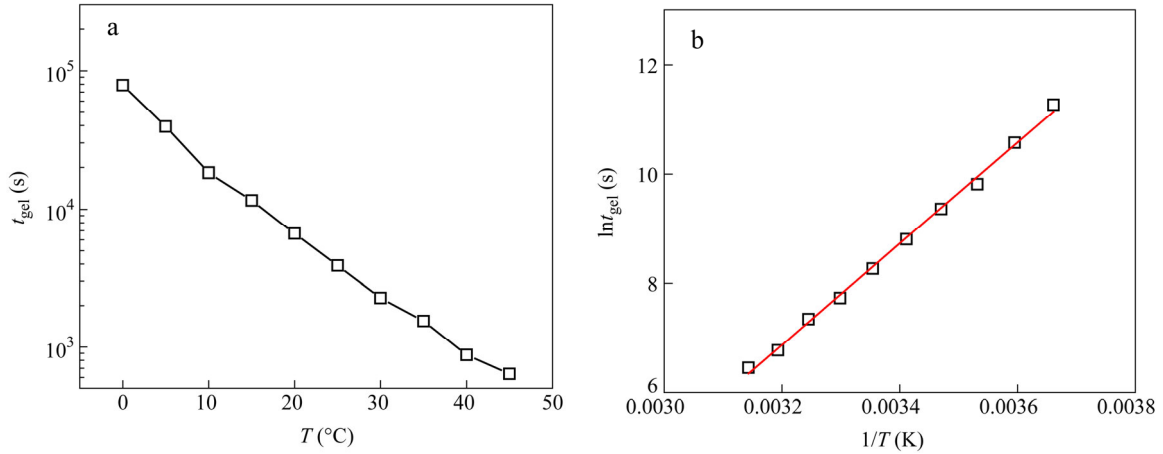


Fig. 3 (a) t_{gel} versus the reaction temperature (T , °C), (b) $\ln t_{gel}$ versus the reverse of reaction temperature ($1/T$) for the mixture of 4317 A and 4317 B under different reaction temperatures (0–45 °C) (The slope of the fitting line was 9274 with correlation coefficients of linear fitting about 0.997 in Fig. 3(b), while the intercept was –22.8.)

For the degree of reaction at the gel point α_{gel} , α_{gel} should be a constant for all the cure reaction at different reaction temperatures according to Flory's gel theory^[7, 12]. Integration Eq. (6) from the $\alpha = 0$ to $\alpha = \alpha_{gel}$ and taking the natural logarithms leads to^[9, 12]

$$\ln \int_0^{\alpha_{gel}} \frac{d\alpha}{f(\alpha)} = \ln A + \ln t_{gel} - \left(-\frac{E}{RT}\right) \quad (7)$$

The left-hand side of this equation is independent of reaction temperature T , so^[9, 12]

$$\ln t_{gel} = C + \frac{E}{RT} \quad (8)$$

The activation energy E can be calculated from the slope of the straight line of experimental valued of $\ln t_{gel}$ versus the reverse of reaction temperature ($1/T$), as shown in Fig. 3. From above method, the E for the cure of the silicone rubber was calculated to be 77.1 kJ/mol. The E for the cure of the silicone rubber will also be calculated by the kinetic model discussed below.

In this work, the t_{gel} at reaction temperature above 45 °C cannot be determined directly by rheometer, as t_{gel} is close or even smaller than the time of loading sample on rheometer. On the other side, to enhance the efficiency of production, higher reaction temperature above the room temperature is often used during the production of RTV2 silicone rubber in industry. From the slope and intercept of fitting results in Fig. 3(c), t_{gel} under different reaction temperatures can be estimated. For example, t_{gel} was estimated to be around 32 s when the reaction temperature was 80 °C.

Cure Kinetic Models

Phenomenological cure kinetic models are semiempirical and do not provide a clear description of the vulcanization process and the chemical mechanism. These models were widely used to describe the cross-linking process of different resin systems. They were based on the rate of reaction as a function of the amount of reacted resin and the rate constants^[5]. The Kissinger model was used as an n^{th} -order expression to model the kinetic reaction, defined as^[5]

$$\frac{d\alpha}{dt} = k(1-\alpha)^w \quad (9)$$

where k is the rate constant defined by the Arrhenius equation [$k = A \exp(-E/RT)$], and w is the order of the reaction^[5].

The Kamal-Sourour reaction (autocatalyst) model is one of the models used to accurately define autocatalytic cross-linking reactions; and is defined as^[5, 9]

$$\frac{d\alpha}{dt} = (k_1 + k_2\alpha^p)(1-\alpha)^m \quad (10)$$

where k_1 and k_2 are the rate constants described by the Arrhenius equation, and p and m are the reaction orders^[9]. Generally, the value of k_1 is much less than the value of $k_2\alpha^p$, so the Kamal-Sourour reaction model has another simple form as^[6, 10]

$$\frac{d\alpha}{dt} = k_t\alpha^q(1-\alpha)^s \quad (11)$$

where k_t is the rate constants described by the Arrhenius equation, and q and s are the reaction orders^[5].

The results of time sweep experiment for the mixture of 4317 A and 4317 B under 10 rad/s for 84894 s are shown in Fig. 4(a). From Fig. 4(a), it is evident that G' , G'' , the absolute value of complex moduli $|G^*|$, and the oscillatory torque (Torque) all increased slowly from beginning to about 300 s. This time regime can be called as induction regime. The degree of cross-linking is low in this time regime, and which does not have apparent influence on the rheological properties. Then, G' , G'' , $|G^*|$, and Torque increased fast from about 300 s to about 2000 s. In this time regime, the number of cross-linking increased quickly which has apparent influence on the rheological properties, and the value of G' was larger than that of G'' at the end of this time regime, indicating the formation of a network structure^[11]. Because of the confinement of network structure, the further reaction was restricted by the diffusion dynamic of two reaction components, so G' , G'' , $|G^*|$, and Torque increased slowly again from about 2000 s to about 68449 s. From about 68449 s to 84894 s, the value of G' , G'' , $|G^*|$, and Torque kept constant thus indicating the completion of cure reaction.

In Fig. 4(b), the different types of degree of reaction calculated from rheological results ($\alpha_{G'}$, $\alpha_{G''}$, $\alpha_{|G^*|}$, and α_{Torque}) are shown. As the value of G' , G'' , $|G^*|$, and Torque keep constant from about 68449 s to 84894 s (Fig. 4a), the value of $X(t_c)$ (Eq. 3) was taken as the mean value of X from 68449 s to 84894 s. From the results in Fig. 4(b), the differential value of cure rate $d\alpha/dt$ can be obtained. The results of $d\alpha/dt$ versus α are shown in Fig. 4(c). It can be observed that the Kissinger model (Eq. 9) cannot fit the results in Fig. 4(c), while both the full form (Eq. 10) and simple form (Eq. 11) of Kamal-Sourour reaction model can fit the results in Fig. 4(c) very well. When the full form (Eq. 10) of Kamal-Sourour reaction model was used for fitting, the value of k_1 was generally 3 orders smaller than that of k_2 , and the value of k_1 was even negative in some cases during the best fitting. So the full form (Eq. 10) of Kamal-Sourour reaction model was not good choice for the fitting and discussion. According to above discussion, the simple form (Eq. 11) of Kamal-Sourour reaction model was used for following fitting in this work.

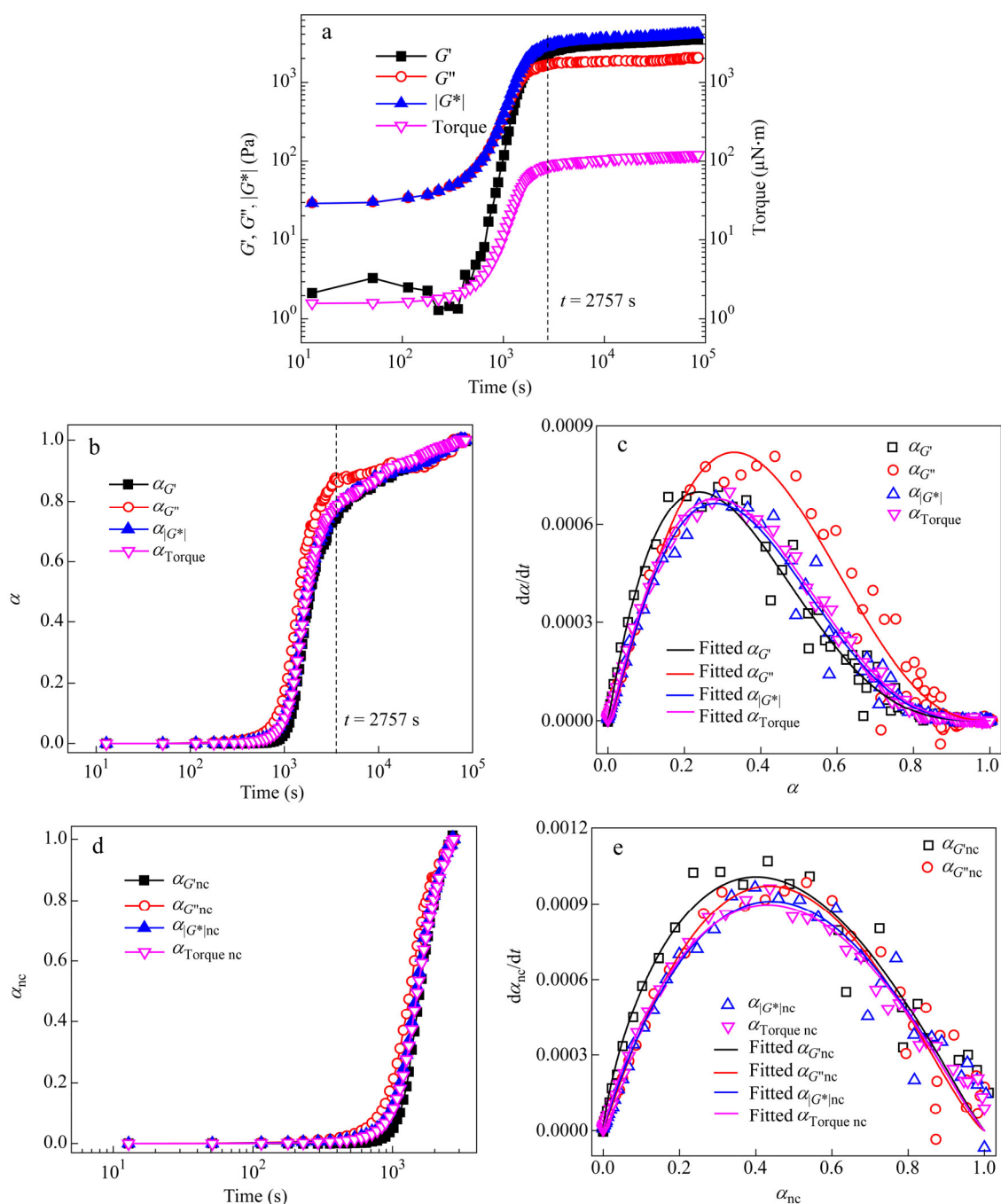


Fig. 4 (a) Storage (G') and loss moduli (G'') versus reaction time for the mixture of 4317 A and 4317 B under 10 rad/s for 84894 s at 40 °C, (b) degree of reaction (α) versus reaction time stopped at 84894 s, (c) $d\alpha/dt$ versus α for the reaction stopped at 84894 s, (d) degree of reaction (α_{nc}) versus reaction time stopped at 2757 s, which time was indicated in Fig. 4(b), (e) $d\alpha_{nc}/dt$ versus α_{nc} for the reaction stopped at 2757 s

In Fig. 4(c), the correlation coefficients of fitting were 0.97, 0.95, 0.97 and 0.99 for $\alpha_{G'}$, $\alpha_{G''}$, $\alpha_{|G^*|}$, and α_{Torque} , respectively. It seems that the cure kinetics for the mixture of 4317 A and 4317 B can be well fitted by the simple form (Eq. 11) of Kamal-Sourour reaction model. However, the reaction order s for $\alpha_{G'}$, $\alpha_{G''}$, $\alpha_{|G^*|}$, and

α_{Torque} was 3.27, 2.62, 3.17, and 3.05, respectively, while the reaction order q for α_G , $\alpha_{G''}$, $\alpha_{|G^*|}$, and α_{Torque} was 1.02, 1.29, 1.25, and 1.20, respectively. According to the expression in Eq. (1), if the influence of confinement of network on the diffusion of reaction group ($[-\text{CH}=\text{CH}_2]$ and $[-\text{Si}-\text{H}]$) is not considered, the reaction order (sum of q and s) should be 2. For the cure kinetics of two components silicone rubber studied by DSC or by rheometer in the literature, the sum of q and s was generally 2 for the cure kinetics of network while the higher level of reaction order was very rare^[5, 6]. Berlin *et al.* studied the influence of confinement effect of cross-linked polymer network on the chemical reaction kinetics^[8], and it was found that the diffusion rate of reaction components was decreased dramatically in the cross-linked polymer network. At later stage of cure reaction for the two component silicone rubber, as a cross-linked network was already formed, the confinement effect of cross-linked polymer network should also have a greater influence on the cure kinetics. However, for the cure kinetics of silicone rubber studied by DSC or by rheometer in the literatures, the cure kinetics of silicone rubber in a short rather than long reaction time (less than 30 min) were analyzed by the Kamal-Sourour (autocatalyst) reaction model in Lopez and Hong's work^[5, 6] and we suppose that the confinement effect of cross-linked polymer network on the diffusion rate of reaction components can be neglected in their work as the later stage of reaction was not considered in their work^[5, 6].

In this work, to exclude the influence of confinement of network on the diffusion rate of reaction components and the cure kinetics of silicone rubber, a shorter reaction time was used for analysis. And a specific reaction time (t_{nc}) was defined as the reaction time before which the influence of confinement of network on the diffusion rate of reaction components can be neglected. In this work, the t_{nc} was determined from the reaction time at which dramatic change of slope for degree of reaction (α) versus reaction time was observed. For example, for the time sweep of mixture of 4317 A and 4317 B under 10 rad/s at 40 °C, there was a dramatic change of slope for α versus time at 2757 s in Fig. 4(b). When the reaction time before t_{nc} was used for the analysis of cure kinetics of the silicone rubber, to be different with the definition in Eq. (2), the degree of reaction here (α_{nc}) is expressed as^[5]

$$\alpha_{\text{nc}} = \frac{[-\text{CH}_2-\text{CH}_2-\text{Si}-]_{\text{t}}}{[-\text{CH}_2-\text{CH}_2-\text{Si}-]_{\text{nc}}} \quad (12)$$

where $[-\text{CH}_2-\text{CH}_2-\text{Si}-]_{\text{t}}$ and $[-\text{CH}_2-\text{CH}_2-\text{Si}-]_{\text{nc}}$ represent the concentration of product for hydrosilylation addition reaction at different reaction time (before or equal to t_{nc}) and at t_{nc} , respectively. The corresponding cure rate was expressed as $d\alpha_{\text{nc}}/dt$ here. The degree of reaction calculated from rheological results is defined as following^[9, 10]

$$\alpha_{X_{\text{nc}}} = \frac{X(t) - X(t_0)}{X(t_{\text{nc}}) - X(t_0)} \quad (13)$$

where X is G' , G'' , $|G^*|$, and Torque, respectively. The parameters $\alpha_{G'_{\text{nc}}}$, $\alpha_{G''_{\text{nc}}}$, $\alpha_{|G^*|_{\text{nc}}}$, and $\alpha_{\text{Torque}_{\text{nc}}}$ are termed to be different with the definition in Eq. (3). Further $X(t_0)$ is the value of X at the beginning of reaction (t_0), $X(t)$ is the value of X at different reaction time (t) before or equal to t_{nc} , $X(t_{\text{nc}})$ is the value of X at time t_{nc} .

For the mixture of 4317 A and 4317 B at 40 °C, t_{nc} was determined to be 2757 s according to above discussion. From the results of time sweep experiment for the mixture of 4317 A and 4317 B under 10 rad/s before and equal to 2757 s in Fig. 4(a). The calculated results $\alpha_{G'_{\text{nc}}}$, $\alpha_{G''_{\text{nc}}}$, $\alpha_{|G^*|_{\text{nc}}}$, and $\alpha_{\text{Torque}_{\text{nc}}}$ were shown in Fig. 4(d), and corresponding cure rate $d\alpha_{\text{nc}}/dt$ versus α_{nc} were shown in Fig. 4(e). In Fig. 4(e), the correlation coefficients of fitting were 0.93, 0.91, 0.93 and 0.97 for $\alpha_{G'_{\text{nc}}}$, $\alpha_{G''_{\text{nc}}}$, $\alpha_{|G^*|_{\text{nc}}}$, and $\alpha_{\text{Torque}_{\text{nc}}}$, respectively. And the reaction order s for $\alpha_{G'_{\text{nc}}}$, $\alpha_{G''_{\text{nc}}}$, $\alpha_{|G^*|_{\text{nc}}}$, and $\alpha_{\text{Torque}_{\text{nc}}}$ was 1.13, 1.32, 1.19, and 1.16, respectively, while the reaction order q for $\alpha_{G'_{\text{nc}}}$, $\alpha_{G''_{\text{nc}}}$, $\alpha_{|G^*|_{\text{nc}}}$, and $\alpha_{\text{Torque}_{\text{nc}}}$ was 0.76, 1.02, 0.94, and 0.88, respectively. And the sum of q and s for $\alpha_{G'_{\text{nc}}}$, $\alpha_{G''_{\text{nc}}}$, $\alpha_{|G^*|_{\text{nc}}}$, and $\alpha_{\text{Torque}_{\text{nc}}}$ was 1.89, 2.34, 2.13 and 2.04, respectively. The reaction orders obtained here is consistent with the prediction of Eq. (1), when the influence of confinement of network on the diffusion dynamic of reaction group ($[-\text{CH}=\text{CH}_2]$ and $[-\text{Si}-\text{H}]$) was not considered. Comparing the results in Figs. 4(c) and 4(e), it can be observed that the formed network structure had great influence on the diffusion of

reaction components, and the cure kinetics of silicone rubber. For simplicity, the reaction time before or equal to t_{nc} was used for the analysis of cure kinetics in the following discussion.

For the cure kinetics of polymer network studied by rheometer in the literatures, $\alpha_G^{[9, 10]}$, $\alpha_{G'}^{[7]}$, $\alpha_{|G^*|}^{[10]}$, and $\alpha_{\text{Torque}}^{[10]}$ were all used for the analysis of cure kinetics. Domínguez *et al.* studied the cure kinetics of a phenolic-novolac resin by rheological method and DSC, and they concluded that torque was the most suitable rheological variable of the resin for evaluating changes in the degree of cure during the curing process of the novolac resin, while the results from α_G , $\alpha_{|G^*|}$ and α_{Torque} were all compared^[10]. As the value of G' was small and fluctuated at the beginning (Fig. 4a), the change of G'' was not directly related to the increase number of elastically active chain^[13], and there were larger correlation coefficients of fitting for α_{Torque} than other parameters (Figs. 4c and 4e), and so the results of torque versus time were used in this work for the following analysis of cure kinetics of silicone rubber^[10].

Influence of Reaction Temperature on the Cure Kinetics

The results of torque versus time for the mixture of 4317 A and 4317 B under 10 rad/s at different reaction temperatures are shown in Fig. 5. In Fig. 5(a), t_{nc} values from 0 °C to 45 °C were 173460, 89337, 49678, 28556, 17159, 9535, 6597, 4309, 2757 and 2039 s, respectively. The later stage of cure reaction after t_{nc} was not used for analysis in Fig. 5(a). In Fig. 5(b), the results of t_{nc} versus temperatures are shown. Obviously, it is clear that the cure time was longer as the temperature was lower (kinetic effect)^[14]. In Fig. 5(c), $\ln t_{nc}$ versus the reverse of

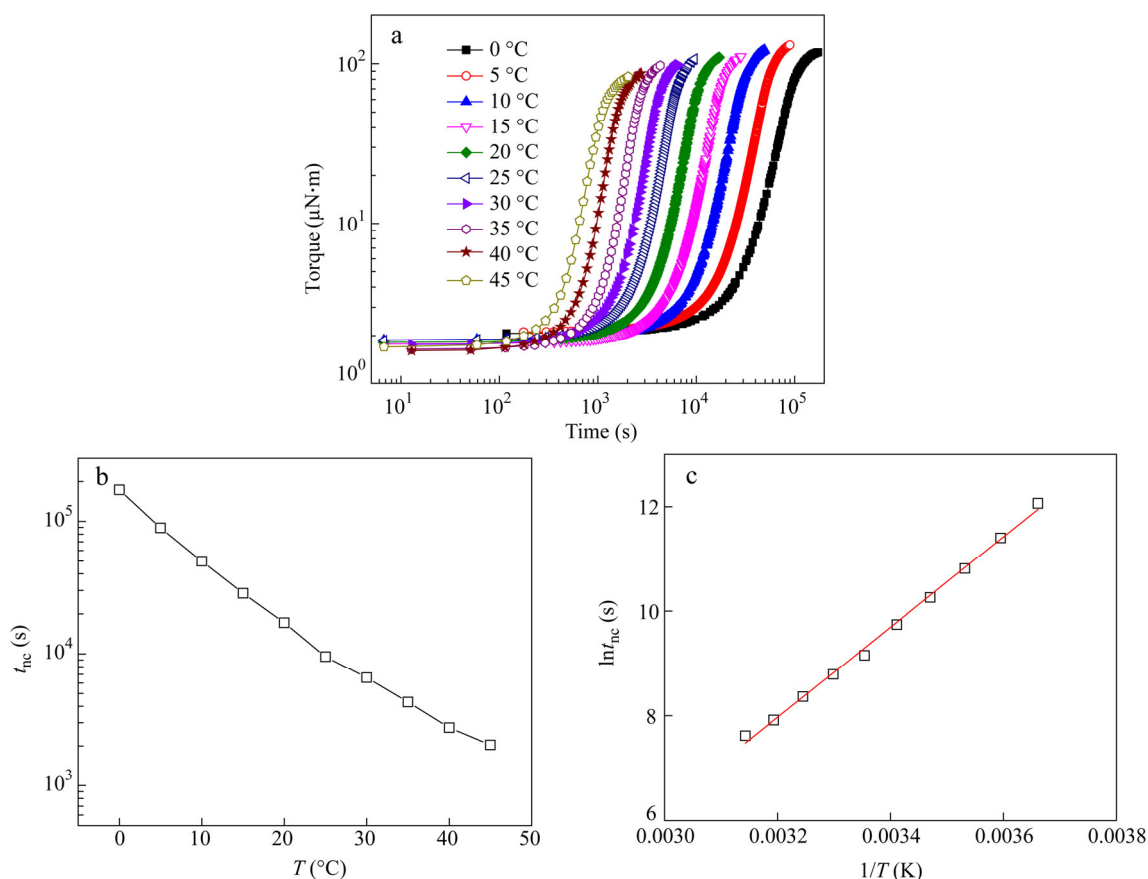


Fig. 5 (a) Torque versus time during the time sweep experiments for the mixture of 4317 A and 4317 B under different reaction temperature (0–45 °C), (b) t_{nc} versus the reaction temperature (T , °C) and (c) $\ln t_{nc}$ versus the reverse of reaction temperatures ($1/T$) for the mixture of 4317 A and 4317 B under different reaction temperatures (The slope of the fitting line was 8622 with correlation coefficients of linear fitting about 0.997 in Fig. 5c, while the intercept was −19.6.)

reaction temperature ($1/T$) can be well fitted by line fitting. According to previous discussion in Eqs. (6)–(8), if $\alpha_{\text{Torque nc}}$ was almost constant at t_{nc} (consistent with the experimental results in Fig. 5a), following equation can be obtained as^[9, 12]

$$\ln t_{\text{nc}} = D + \frac{E}{RT} \quad (14)$$

where D is a constant. The activation energy E can be calculated from the slope of the straight line in Fig. 6(c), which was about 71.7 kJ/mol that was close to the value of E (77.1 kJ/mol) calculated from Fig. 3(b). The consistence for the experimental results in Fig. 5(c) and theoretical model in Eq. (14) illustrate that above rule used to determine the t_{nc} was reasonable.

The t_{nc} at reaction temperature above 45 °C was also hard to be determined directly by rheometer, as the time used to load the sample on rheometer was short. From the slope and intercept of fitting results in Fig. 5(c), the t_{nc} under different reaction temperatures can be estimated. For example, t_{nc} was estimated to be around 121 s when the reaction temperature was 80 °C.

In Fig. 6, the value of Torque (t_{nc}) was taken as the value of torque at t_{nc} from the results in Fig. 5, and the results of differential value $d\alpha_{\text{nc}}/dt$ versus α_{nc} were well fitted by the simple form (Eq. 11) of Kamal-Sourour reaction model. In Fig. 6(a), the correlation coefficients of fitting were above 0.97 and the sum of q and s ranged from 1.98 to 2.04 which was close to the value of reaction order in other work for the cure kinetics of silicone rubber^[5, 9, 10], and which was consistent with the reaction order inferred from the two component chemical reaction (Eq. 1) when the diffusion of reaction components was not influenced by the formed cross-linked

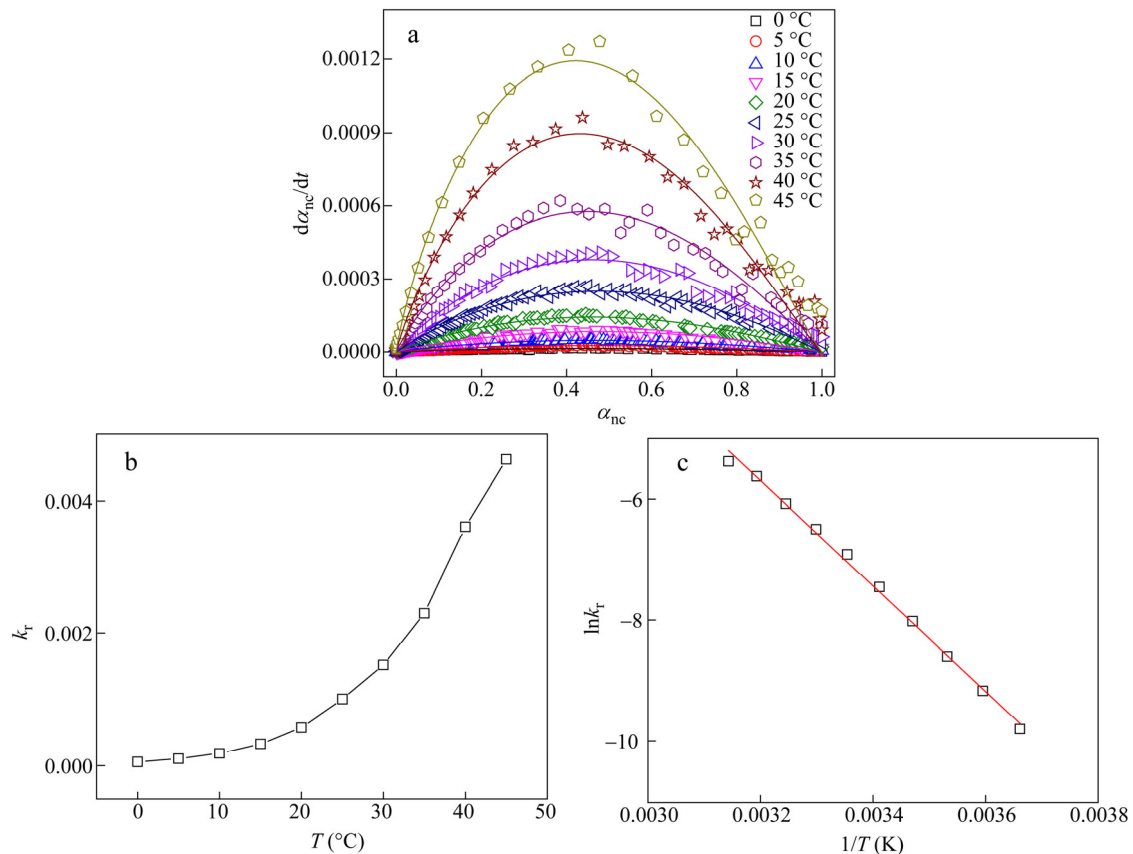


Fig. 6 (a) $d\alpha_{\text{nc}}/dt$ versus α_{nc} from the data in Fig. 5(a) (the fitting results by Eq. (11) were also shown), (b) value of k_r versus the reaction temperature (T , °C) from the data in Fig. 6(a) and (c) $\ln k_r$ versus $1/T$ from the data in Fig. 6(b) (The slope of the fitting line was 8704 with correlation coefficients of linear fitting about 0.996 in Fig. 6c)

polymer network. From above fitting results, the rate constants k_r under different reaction temperatures were obtained (Fig. 6b). The rate constants k_r increased slowly at low temperature and increased fast at higher experimental temperatures. The results of $\ln k_r$ versus the reverse of reaction temperature ($1/T$) are shown in Fig. 6(c), and the activation energy E calculated from the slope was about 72.4 kJ/mol, which was close to the value of E (77.1 kJ/mol) calculated from Fig. 3(b), indicating that above analysis of cure kinetics based on the simple form (Eq. 11) of Kamal-Sourour reaction mode was reasonable.

CONCLUSIONS

The cure kinetics for two-component silicone rubber formed by addition reaction was studied by the rheological method. The gel time (t_{gel}) of the silicone rubber under different temperatures was determined by the Chambon-Winter criterion from the time sweep experiments under multi-wave oscillatory frequency. As the reaction temperature was increased, the t_{gel} decreased, and it was observed that t_{gel} versus reaction temperature obey certain functional relationship. According to the theoretical cure kinetics model of thermoset network, the above functional relationship between t_{gel} and reaction temperature was explained as the reaction degree at the gel point (α_{gel}) remained constant under different reaction temperatures. It was also observed that the influence of reaction temperatures on a specific reaction time (t_{nc}) (defined as the reaction time before which time the influence of confinement of network on the diffusion of reaction components can be neglected) was similar as that of t_{gel} versus reaction temperature. The time sweep results of samples under single frequency was analyzed by different cure kinetics models, it was observed that the cure kinetic for two-component silicone rubber can be well fitted by the Kamal-Sourour (autocatalyst) reaction model rather than Kissinger model. When the reaction time was before or equal to t_{nc} , the reaction order obtained by the Kamal-Sourour reaction model was 2, which was consistent with the reaction order inferred from the two components chemical reaction when the diffusion of reaction components was not influenced by the formed cross-linked polymer network. When the reaction time was larger than t_{nc} , such as to the end of reaction (t_e), the influence of confinement of network on the diffusion of reaction components cannot be neglected, the reaction order obtained by the Kamal-Sourour reaction model was larger than 2. It was concluded that the confinement effect of network had a great influence on the cure kinetics of the silicone rubber. The cure rate constant (k_r) under different temperatures was also determined by the above Kamal-Sourour reaction model. The activation energy E for two-component silicone rubber was calculated from the results of $\ln t_{\text{gel}}$, $\ln t_{\text{nc}}$, and $\ln k_r$ versus $1/T$, respectively, while the three values of E were close, which indicated that above analyses were self-consistent. It is believed that the rheological study about cure kinetics of silicone rubber is helpful for its production in industry.

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