

Modeling the Vulcanization Process of High Consistency Rubber and Liquid Silicone Rubber

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Abstract

A kinetic model of the vulcanization process of high consistency rubber (HCR) and liquid silicone rubber (LSR) was developed. The exothermal vulcanization process was measured with a differential scanning calorimeter. Viscosity was measured with a cone and plate rheometer. A computer program fit coefficients to the experimental data. Values for activation energy and fitted rate coefficient were found using both n th order polynomial and autocatalytic models. A kinetic model of vulcanization will help manufacturers understand and optimize their production processes.

Introduction

Silicone rubber has many applications. It is widely used in electronics, aerospace, consumer goods, and the medical industries. It maintains its mechanical properties over a range of temperatures, has good electrical conductivity, is easy to color, and comes in medical quality grades. Silicone rubber is a thermoset elastomer with a backbone of alternating silicone and oxygen atoms and methyl or vinyl side groups, as seen in Fig. 1. There are two types of silicone rubber, solid and liquid. The basic structure of the two types of silicone rubber is the same, but the cure and processing are radically different.

High Consistency Rubber (HCR) is produced in large batches. The components are mixed at high temperature, and a peroxide catalyst is added. Some cross-linking occurs, but the process is interrupted before vulcanization is complete. The lightly cross-linked silicone rubber is formed into sheets for shipping and storage. When the HCR is ready to be used, it is mixed with rollers and transfer molded. After

the part is molded, it is transferred to an oven where post-vulcanization occurs.

Liquid Silicone Rubber (LSR) is a two-component system. Component A contains a platinum catalyst and component B contains methylhydrogensiloxane as a cross-linker and an alcohol inhibitor. The two components are stored separately and mixed during processing. LSR is processed with cold runner injection molding equipment.

During vulcanization, the long chains of the elastomer chemically cross-link. Each cross-linking releases a quantum of energy, making it an exothermic reaction. During this process, the catalyst creates bonds between the long chains, creating a three dimensional matrix. This network greatly improves the mechanical properties of the rubber. It is important to understand how silicone rubber vulcanizes in order to optimize the processing conditions and choose the correct material for each application.

DSC Measurement of Vulcanization

Vulcanization can be studied with a Differential Scanning Calorimeter (DSC). To take a measurement with a DSC, two small pans are placed in the DSC's heating chamber. One pan contains the material to be measured. An empty pan serves as a reference. Thermocouples underneath the pans measure the temperature. During a thermal sweep, the sample pan and the reference pan are maintained at the same temperature. The sample with the higher heat capacity will absorb a larger amount of heat, which is proportional to the difference between the heat capacity of the measured sample and the reference sample (1).

The energy released in the exothermal reaction is proportional to the cross-linked bonds formed and it is assumed that each bond releases the same amount of energy. The vulcanization of the sample is found by measuring the energy released as the sample is heated from below room temperature to well above the vulcanization temperature.

The heat released during vulcanization can be calculated by,

$$Q = \int_0^{\tau} \dot{Q} dt \quad (1)$$

where Q is the heat released up to time τ and \dot{Q} is the change in heat of the sample. The total heat of reaction, Q_T , is therefore equal to,

$$Q_T = \int_0^{\tau-final} \dot{Q} dt \quad (2)$$

where τ -final is the time at which the reaction is complete. The reaction rate, dc/dt , is then calculated as,

$$\frac{dc}{dt} = \frac{\dot{Q}}{Q_T} \quad (3)$$

The measured data is then fit to the theoretical model. The silicone vulcanization reaction can be described by an autocatalytic model. For an autocatalytic curing reaction, the Kamal-Sourour reaction model (2, 3) as shown in equation 4 is used.

$$\frac{dc}{dt} = (k_1 + k_2 c^m)(1 - c)^n \quad (4)$$

In equation 4, m and n are the reaction orders, c is the extent of the vulcanization reaction, defined by $c = Q/Q_T$, and k_1 and k_2 are the Arrhenius overall constants defined by,

$$k_1 = a_1 \exp\left(\frac{-E_1}{RT}\right) \quad (5)$$

$$k_2 = a_2 \exp\left(\frac{-E_2}{RT}\right) \quad (6)$$

where a_i is the fitted rate coefficient, E_i is the activation energy, R is the universal gas law constant, and T is the vulcanization temperature.

It is not necessary to modify the constants of the reaction due to diffusion, because the materials vulcanize above their glass transition temperatures. For materials that vulcanize below the vitrification point, the model accurately predicts the total process. This is due to the fact that while performing the test above the glass transition temperature there is sufficient free volume between the molecules to allow for freedom of movement during the molecular cross-linking process, and therefore diffusion does not play a large role.

The six parameters from the Kamal-Sourour model that need to be fitted to the experimental data can be represented as an unknown vector quantity, via a least-squares estimation algorithm developed by Marquardt (4).

$$X = \{m \ n \ a_1 \ E_1 \ a_2 \ E_2\} \quad (7)$$

The parameters then are expanded into a power series with temperature (T) as the independent variable (5)

$$x_i = a_{i1} + a_{i2}T + a_{i3}T^2 + O(T^3) \quad (8)$$

where $i=1, \dots, 6$ and a_{ij} are the new goal of the fitting.

Experimental Procedures

Differential scanning calorimeter equipment manufactured by Netzsch (DSC 200 PC) was used to measure the heat of reaction for the samples. Sealed aluminum pans were used to contain all reactions. The mass of the samples used ranged from 10 mg to 30 mg. An empty pan was used as a reference. The total heat of reaction was measured by a dynamic scan using heating rates of 1, 2.5, 5, and 10 K/min. Multiple scanning rates were used to gain insight into the effect of time and temperature on the vulcanization reaction. Repeatability was obtained for each heating rate. All scans were performed under nitrogen purge. The A and B components of the liquid silicone rubber were mixed with a Mixpac (DMA 50) 1:1 static mixer using a Kenics mixing chamber. A 1:10 ratio of Sylgard 184 curing agent to elastomer was used for the PDMS.

Results

Repeatability was obtained for the DSC data. The model fitting was performed for the LSR and HCR at each vulcanization rate. As can be seen in Figs.2 through 5, the DSC data corresponds well with theory. The total heat of reaction and the peak temperatures for each material are included in Table 1. Experimental data and fitted models are graphed together for LSR and HCR in Figs. 6 and 7. The relationship between the LSR and PDMS can be seen in Fig. 5.

The corresponding values of m , n , a_1 , E_1 , a_2 , and E_2 for LSR and HCR are summarized in Tables 1 and 2, respectively. The peak temperature for the three materials at all scan rates can be seen in Table 3.

Conclusion

The vulcanization reactions of LSR and HCR, as well as PDMS were measured using the DSC. The modified Kamal-Sourour model was utilized to identify the vulcanization reaction of liquid and solid silicone rubber from dynamic DSC experimental data. A set of vulcanization

kinetics parameters was obtained using a non-linear least squares Levenberg-Marquardt algorithm. The developed model resulted in good agreement between the experimental data and the predictions. Further work is being done to fit other models to the vulcanization reaction of silicone rubber materials.

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Table 1. LSR. Fitted values using a 5 K/min scan.

Parameter	O(1)	O(T)	O(T ²)
m	7.4140E+01	-7.0540E-02	-3.5051E-04
n	-1.5130E+00	-3.3828E-03	2.7015E-05
a_1	7.8546E+01	-4.6229E-01	6.8078E-04
E_1	5.3011E+04	6.3376E+00	-2.8889E-01
a_2	3.4989E+01	2.7318E-01	2.2352E-04
E_2	-1.3530E+05	1.1428E+02	8.7977E-01

Table 2. HCR. Fitted values using a 5 K/min scan.

Parameter	O(1)	O(T)	O(T ²)
m	8.4455E+01	-5.5926E-01	9.0122E-04
n	2.0456E+01	-1.0317E-01	1.2983E-04
a_1	1.6682E-22	-7.1679E-21	1.8524E-23
E_1	1.1447E+05	-6.5515E+02	2.1787E-01
a_2	-1.5320E+03	6.6209E+00	-7.1566E-03
E_2	-2.2411E+05	1.4717E+01	1.0666E+00

Table 3. Total Heat of Reaction and Peak Temperature

Material	Heating Rate (K/min)	Peak Temperature (°C)
HCR	1	157.7
	2.5	170.6
	5	177.6
	10	183.3
LSR	1	73.4
	2.5	81.7
	5	91.2
	10	95.9
PDMS	2.5	82.0
	5	90.5
	10	100.8

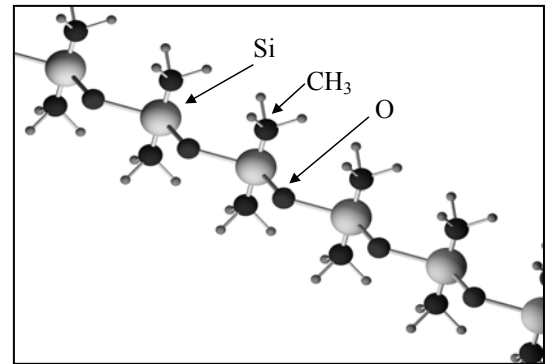


Figure 1. Molecular Structure of Silicone Rubber

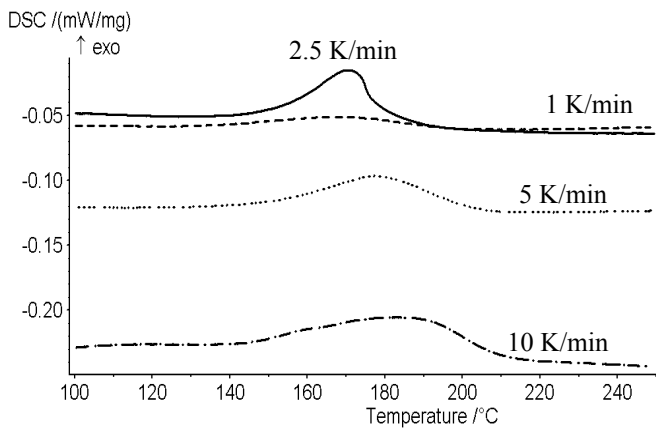


Figure 2. Dynamic Scans of HCR

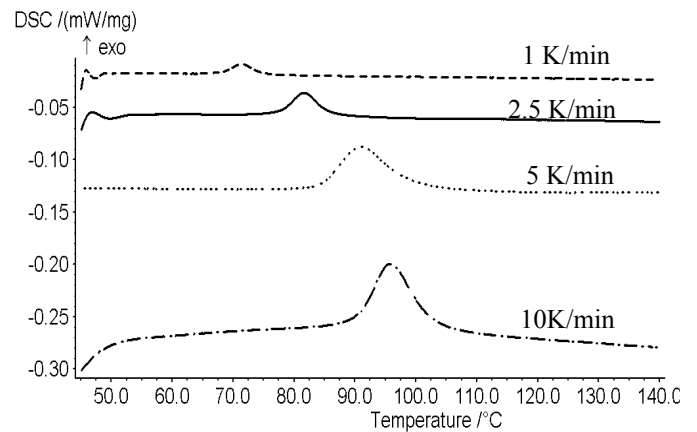


Figure 3. Dynamic Scans of LSR

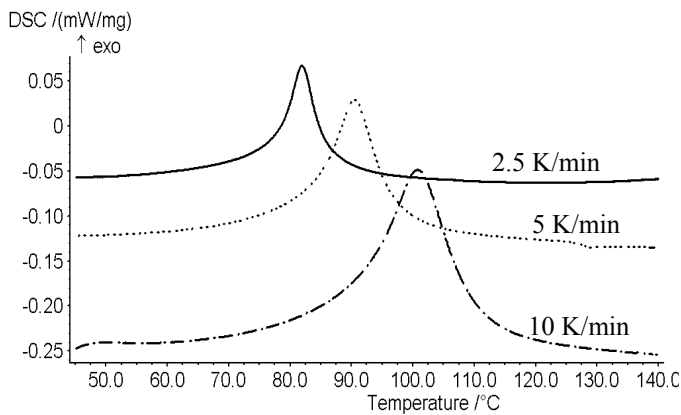


Figure 4. Dynamic Scans of PDMS

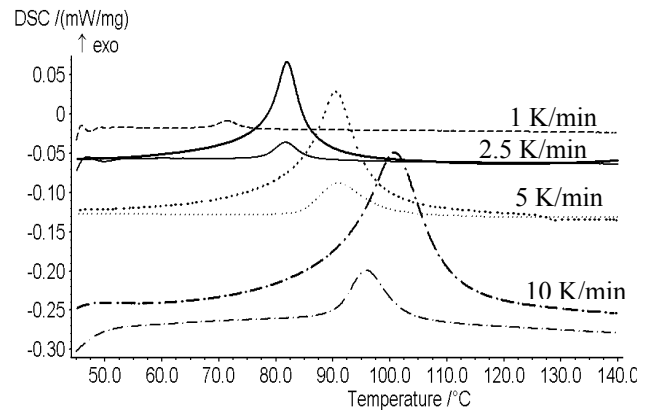


Figure 5. Comparison of Dynamic Scans of LSR and PDMS

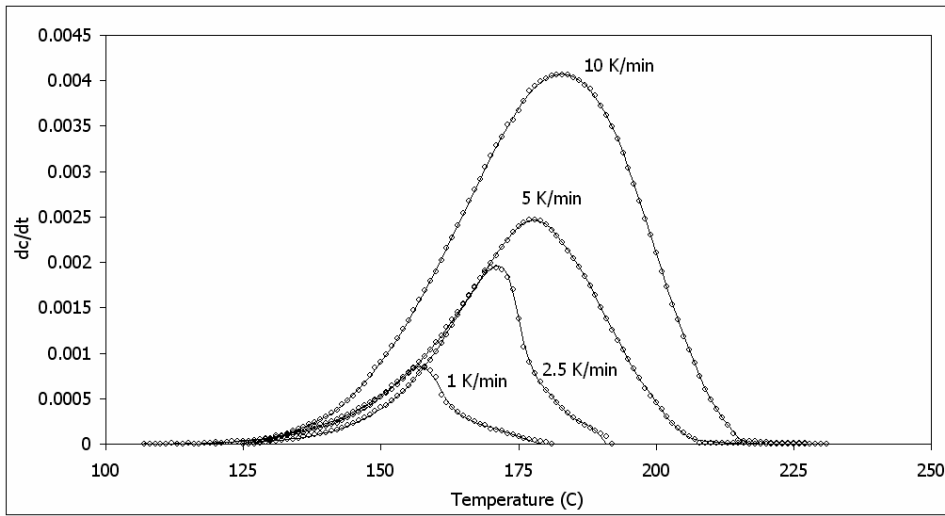


Figure 6. Fitted Model and Experimental Data for HCR

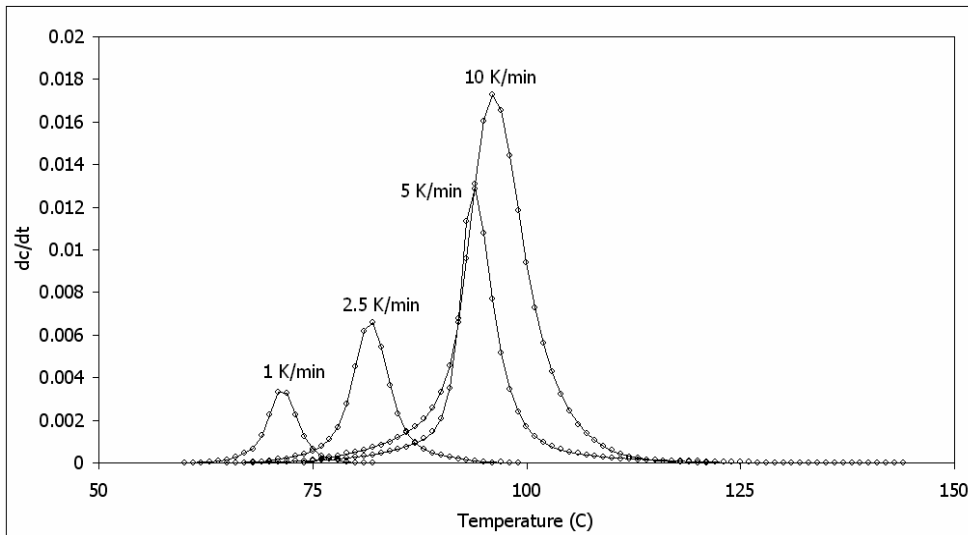


Figure 7. Fitted Model and Experimental Data for LSR