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The kinetic behavior of Liquid Silicone Rubber: A comparison between thermal and rheological approaches based on gel point determination

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ABSTRACT

Liquid Silicone Rubber (LSR) belongs to the category of High Temperature Vulcanization rubbers (HTVs). Due to its implementation facility, its mechanical and thermal properties and its convenience for the medical and food industries, LSR is used in a wide range of applications.

In order to examine LSR kinetic performances, thermal and rheometric experimental investigations are conducted to characterize the material and discuss the kinetic model describing crosslinking behavior.

The Gel Point is investigated at different temperatures to improve our understanding of the different crosslinking steps and determine which characterization method (thermal or rheological) best represents the reaction. The results show that the LSR network undergoes specific development during crosslinking. Gel point occurs before the mechanical reaction starts. Gelation behavior resembles that of a thermosetting material despite the elastomer properties confirmed by the thermal study.

Finally, the thermal method seems more reliable to describe the crosslinking kinetics of LSR.

1. Introduction

Developed during the 70s, the popularity of Liquid Silicone Rubber (LSR) elastomers has rapidly increased thanks to interesting viscoelastic and thermal properties, medical and food compatibilities, and the ability to compete with traditional silicones and other elastomers [1,2]. These advantages explain its success in various applications of everyday life (e.g., appliances, kitchen tools…) [3]. LSR is also popular due to its characteristics of implementation such as short cycle time and long pot life at room temperature. These qualities promote its use by the industrials (e.g., automotive, aerospace, dental, etc. industries) [4,5].

A two-component LSR is prepared by mixing two components “A” and “B” [6]. These two components are not reactive alone. However, once mixed, they produce a crosslinking reaction.

There are three mechanisms by which the silicone can be crosslinked: the peroxide curing, the condensation curing and the addition curing (known under the name of hydrosilylation) [7]. The LSR crosslinks by hydrosilylation method only [8] (Scheme 1). The hydrosilylation is the combination of a hydrosilane (Si-H) with an unsaturated organic compound [9].

The platinum catalyst contained in component “A” accelerates the reaction between the polysiloxane and the vinyl contained in component “B”. Polysiloxane has silane (Si-H) functions used as crosslinking agents.

In this study, thermal and rheometric measurements carried out using temperature ramps are used to calculate the kinetic model, which describes the crosslinking reaction. Many models describing crosslinking kinetics have been developed. Some describe crosslinking chemical mechanisms (e.g., Coran law [10,11]). Other authors have preferred phenomenological models, which, despite no real physical sense, offer numerical benefits (simplicity and adjustable parameters). Among these so-called empirical models, Isayev [12] and Kamal [13] laws are particularly notable. For confidentiality reasons, we cannot give the detailed LSR formulation here. We, therefore, have chosen the empirical model of Kamal whose advantages have been discussed previously [14,15].

In this paper, crosslinking kinetics, measured using both thermal and rheological methods are compared. The thermo-kinetic model is calculated first. Then, before calculating the rheo-kinetic model, we determine the gel point [16] of LSR at given temperatures. The gel time analysis reveals that the rheological characterization does not show the chemical evolution of the network. Its development appears to be related to the mechanical behavior. Therefore, the thermal method is finally chosen as the best suitable method to measure the crosslinking.

2. Experimental

Symbols and units of the parameters occurring in the measurements/calculations were collected in Table 1.

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Table 1
Nomenclature and symbols.

Symbols	Parameters	Units
C_p	Specific heat at constant pressure	$J \cdot kg^{-1}\ K^{-1}$
E, E_a	Activation energy	$J \cdot mol^{-1}$
f	Frequency	Hz
G	Shear modulus	Pa
G'	Storage modulus	Pa
G''	Loss modulus	Pa
H	Enthalpy	$J \cdot g^{-1}$
k, K_1, K_2	Temperature dependent parameters according to Arrhenius law	s^{-1}
m	Mass	mg
Q_T	Total released heat flow	mW
$dQ(t)/dt$	Released heat flow at time t	$mW \cdot s^{-1}$
R	Universal gas constant	$J \cdot mol^{-1}.K^{-1}$
T	Temperature	°C; K
t	Time	s
t_0, m, n, A_1, A_2	Temperature independent constants	s^{-1}
t_{gel}	Gel time	s
t_i, t_z	Induction time	s
$\tilde{t}$	Non-isothermal induction time	s
α	Crosslinking degree	
$d\alpha/dt$	Crosslinking rate	s^{-1}
γ	Deformation	%
$tan\delta$	Loss tangent	
η	Viscosity	$Pa \cdot s$
Φ	Heat flow	$W \cdot g^{-1}$
ω	Pulsation	$rad \cdot s^{-1}$

2.1. Material

A commercially available two-component “SILBIONE LSR 4350 HC A + B” manufactured by “Bluestar Silicones™” company is used. It consists of a polymethylvinylsiloxane and silica-based “A” component containing platinum ($m < 1\%$), and a polymethylvinylsiloxane and polymethylhydrosiloxane-based “B” component containing silane-hydrogen bonds (Si-H). Both components are mixed with a 50:50 weight ratio (i.e., same proportion in volume) [17].

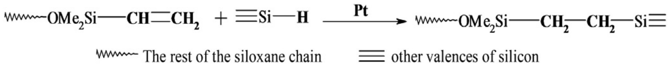
The crosslinked LSR density is $1114.6 \pm 0.9\ kg \cdot m^{-3}$ (Archimedes principle method), which is equivalent to uncured material [17]. Conductivity and thermal diffusivity measurements are carried out using the “Transient Plane Source (TPS)” technique. The average thermal conductivity is $0.218\ W \cdot m^{-1} \cdot K^{-1}$ with a standard deviation equal to 2.4×10^{-3}.

2.2. Differential scanning calorimetry (DSC)

The Differential Scanning Calorimetry (DSC) analyses are conducted under nitrogen on a “Mettler Toledo DSC 1” device calibrated with indium. *40* µl aluminum alloy crucibles are used. The sample mass ranges from 15 mg to 40 mg. They are weighed using a “Mettler Toledo analytical balance”.

For all the measurements detailed below, the sample temperature is stabilized at −20 °C during 5 min, and then, brought up to 220 °C at different heating rates. Two measurement cycles are performed for each sample to make sure that the material is stable and to check the influence of crosslinking on the material properties at the final set.

The crosslinking reaction is detected using the thermo-kinetic measurements carried out at different heating rates within the range $1\ K \cdot min^{-1}$–$20\ K \cdot min^{-1}$. Crosslinking, indeed, being an exothermic reaction, crosslinking rates may be related to the released heat [18].



Scheme 1. Hydrosilylation reaction.

The progress of the crosslinking reaction, here, is referred to the “crosslinking degree, α”. α is not directly determined from the evolution of the amount of reactive species during the chemical reaction but is deduced from the measurement of the physicochemical [19], thermal [20] or mechanical [21] changes.

On the DSC, $dQ(t)/dt$ is the released heat flow at time t. The assumption made for the kinetic analysis is that heat flow is proportional to the crosslinking rate [22] (Eq. (1)).

$$\frac{d\alpha}{dt} = \frac{1}{Q_T}\frac{dQ(t)}{dt} \tag{1}$$

Q_T is the total heat released during the reaction. Its value is obtained by integrating the exothermic peak on the total reaction time and represent $\alpha = 1$. At time t, the evolution of the conversion as a function of time is obtained by integrating the heat curve at each time step (Eq. (2)) and by normalizing it in relation to the total heat, with t_1: start of the reaction, t_2: end of the reaction and the instant t in question between t_1 and t_2 [23].

$$\alpha(t) = \frac{\int_{t_1}^{t}\left(\frac{dQ(t)}{dt}\right)dt}{\int_{t_1}^{t_2}\left(\frac{dQ(t)}{dt}\right)dt} = \frac{Q(t)}{Q_T} \tag{2}$$

2.3. Rheometry

The “HAAKE™ MARS™ III” rheometer used, is manufactured by “Thermo Sientific™”, operates in parallel-plate mode. The trays have a diameter of 20 mm and a thickness of 2 mm. A force of 5 N is imposed when the measurement starts, while the resulting gap is maintained. The temperature of the trays is controlled using a “Peltier” effect oven and a cooling pump. Each measurement is carried out twice to guarantee the repeatability of the obtained values.

The rheometric measurements are imposed with constant deformation (0.5%) and frequency (1 Hz). The objective is to examine how curing affects the mechanical behavior of the material and to measure crosslinking progress.

The gel point is determined with some isothermal measurements performed at 70 °C, 80 °C, 90 °C and 100 °C at different pulses (1 to 88 $rad \cdot s^{-1}$) and with constant deformation (0.5%).

2.4. Kinetic models

Among the available kinetic models, two analytical models are selected for the study: the Isayev [12] and the Kamal [13] models. Isayev and Deng [12] propose a kinetic law based on a discontinuous but simple mathematical formula: Three variables establish the relationship between the degree of crosslinking, time and temperature (Eq. (3)). The induction and reaction phases are treated separately.

$$\alpha = \frac{kt^n}{1 + kt^n} \tag{3}$$

k is a rate constant according to Arrhenius law [24].

During the induction phase t_i, conversion and crosslinking rate are considered null. In the isothermal mode, t_i is given by Eq. (4):

$$t_i = t_0 e^{\frac{E}{RT}} \tag{4}$$

In the non-isothermal case, the isothermal induction time is replaced by a reduced dimensionless time $\tilde{t}$ (Eq. (5)) [12]. Isayev considers