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Mechanistic interpretation of the curing kinetics of tetra-functional cyclosiloxanes

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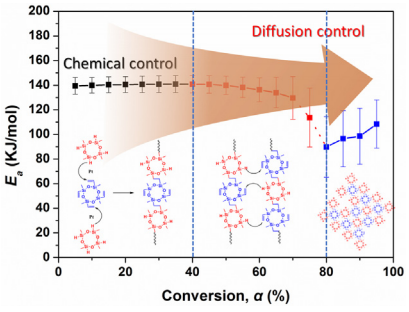
HIGHLIGHTS

- Curing kinetics for hydrosilylation of tetra-functional cyclosiloxanes was analyzed.
- The conversion dependency of E_a reveals the complexity of the curing process.
- The complex kinetic behavior is analyzed by model fitting and model free method.
- Friedman method shows the shift of reaction from chemical to diffusion control.
- Structural formation and arrangement during hydrosilylation were identified.

GRAPHICAL ABSTRACT



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ABSTRACT

Investigation of the curing kinetics of a resin is one of the prerequisites for designing and optimization of the process parameters for the curing process which will help to control and predict the curing cycle of the materials. Non-isothermal curing kinetics for hydrosilylation of tetra-functional cyclosiloxanes was analyzed through both model-fitting and model-free methods for the first time. The conversion dependency of the activation energy (E_a) reveals the complexity of the curing process which leads to a complex kinetic behavior. The Friedman method shows the shift of a chemical control reaction to a diffusion control reaction due to the change of viscosity during the curing process. Detailed analysis of the curing kinetics at the molecular level shows that E_a dependency on conversion is a combined effect of diffusion of monomers and reaction intermedia, solidification of the reaction medium, "clicking" of chain-like structures, and steric hindrance pose by the hyper-branched molecules. We tentatively attribute the presence of shoulders on the non-isothermal curves to the delay in curing reaction due to diffusion process and high steric hindrance.

1. Introduction

Polysiloxane is a family of materials composes of inorganic silicone-oxygen (Si-O) backbones with organic groups covalently attached to each Si atoms [1]. It is also called silicone and is one of the most widely used organic-inorganic hybrid polymeric materials [2]. Owing to its high backbone flexibility, UV resistance,

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moisture resistance, flame retardancy, chemical resistance and thermal stability, polysiloxane and its derivatives have been found or realized its applications in the fields of aerospace, cosmetics, sealants, medical devices, electronic devices and so on [3–10].

Recently, the novel hybrid resin fabricated from tetra-functional monomers has been attracting much attention since the highly crosslinked hybrid network was molecularly smooth, thermally stable, hard but elastic at the same time [11,12]. Among all the synthesis methods used for polysiloxane, hydrosilylation, one of the addition-crosslinking methods, is preferred since it is able to minimize the volume shrinkage problem encountered during polycondensation. The absence of by-products eliminated processing conditions such as vacuum and high temperature which are typically needed for polycondensation [8,13]. The excellent properties and green preparation method made it an environmentally friendly and 'unusual material that has multiple uses' [11,12]. In general, the molecular structures of monomers, the curing process, and conditions have significant effects on both chemical and physical properties of the final thermosetting materials. The ability to monitor and control the curing process proves to be highly relevant in preventing under-curing or over-curing of a polymeric material during manufacturing. Understanding the fundamental science of the curing kinetics allows optimization of the curing cycle to improve the properties and the performances of the final products. Many different analytical methods have been employed to characterize curing reaction and monitor curing process of polymers, such as differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA) [14–16]. Curing kinetics and modeling of hydrosilylation for commercially available silicone were studied using DSC by various research groups [17–19]. However, the bifunctional monomers or linear oligomers used for these studies were unable to give an accurate indication for systems with branched monomers, such as the tetra-functional monomers used in this study, due to the certainly more complex curing process. Additives being added to the commercial silicones as reinforcement might participate in the curing process and lead to deviation in kinetics parameters calculation. It is essential to perform kinetics study on an additive free hybrid silicone resin of tetra-functional cyclosiloxanes to gain insights on the curing kinetics of hydrosilylation. The mechanistic interpretation of the curing process can be served as a guidance to control and optimize the production processes and understand how they influence the properties of the final products.

In this paper, we reported the curing kinetics of an additive free hybrid silicone resin prepared by hydrosilylation of tetra-functional cyclosiloxanes and correlate the findings to the molecular structure formations for the first time. The present study focused on non-isothermal DSC kinetics. The curing behavior observed was examined by both model-fitting and model-free methods. Mechanistic interoperation of the curing kinetics was done to access the intrinsic kinetic parameters, and, ultimately, gather information about the complex curing mechanisms of tetra-functional cyclosiloxanes, i.e., the perspective of molecular structure formation and the subsequent structural growth.

2. Experimental section

2.1. Materials

1,3,5,7-tetravynyl-1,3,5,7-tetramethylcyclotetrasiloxane (D_4V, 99%), 2,4,6,8- tetramethylcyclotetrasiloxane (D_4H, 97%), and platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex (Karstedt's catalyst, 3.2 wt% Pt) were purchased from Alfa Aesar and used as received.

2.2. DSC sample preparation

0.1 wt% (to the total mass of D_4H and D_4V, molar ratio of Pt:Si-vinyl = $1:3.55 \times 10^4$) of Karstedt's catalyst was dissolved in D_4V, followed by the addition of D_4H. In this study, the mass ratio of D_4H:D_4V was 1:1 (molar ratio 1.43:1). The solution was mixed using magnetic stirrer and stored at −10 °C before DSC test.

2.3. DSC measurement

Isothermal heating was carried out at 90 °C according to a pre-run non-isothermal DSC curve with a heating rate of 5 °C/min by a TA Instruments (Q10). A series of non-isothermal scans were conducted from 25 to 250 °C at heating rates of 1, 5, 10, 15 and 20 °C/min, respectively. The instrument was calibrated by Indium prior the actual test. To minimize the effect of sample size, the mass of the samples was kept between 4 and 5 mg. Hermetic aluminum pans were used as sample holders. All the DSC measurements were carried out in high-purity nitrogen with the flow rate of 60 mL/min. The DSC curves were analyzed without any smoothing to avoid possible systematic errors in the calculation of kinetic parameters [20].

3. Theory of curing kinetics

Kinetics deals with parameterization of process. For curing process, the reaction rate can be expressed by the following equation:

$$d/dt = k(T)f(\alpha)h(P) \tag{1}$$

where α is the extent of conversion, t is the time, $k(T)$ is the rate constant which depends on the temperature T, $f(\alpha)$ is the reaction model which depends on α, and $h(P)$ is pressure P dependent. Usually $h(P)$ is ignored in most of the thermal analysis [20]. Since there are no gaseous reactants or products during the hydrosilylation of tetra-functional cyclosiloxanes, $h(P)$ was ignored. Hence, Eq. (1) can be simplified as follow:

$$d\alpha/dt = k(T)f(\alpha) \tag{2}$$

$k(T)$ is usually assumed to follow the Arrhenius equation:

$$k(T) = A\ exp\left(-\frac{E_a}{RT}\right) \tag{3}$$

where A is the pre-exponential factor or Arrhenius frequency factor, E_a is the activation energy, R is the gas constant, and T is the absolute temperature of the sample.

In DSC test, the data can be correlated with fractional conversion and reaction rate. They are assumed to follow the following equation:

$$\alpha = \frac{\int_0^t (dH/dt)dt}{\Delta H_0} \tag{4}$$

where H is the heat flow, t is the reaction time, and ΔH_0 is the total reaction exothermic heat. Based on Eqs. (2)–(4), the reaction rate can be described as follows:

$$\frac{d\alpha}{dt} = \frac{dH/dt}{\Delta H_0} = k(T)f(\alpha) = A\ exp\left(-\frac{E_a}{RT}\right)f(\alpha) \tag{5}$$

4. Results and discussion

Fig. 1 gives a schematic illustration for the hydrolysation of D_4H and D_4V under the presence of Karstedt's catalyst. The cured D_4H/D_4V hybrid silicone resin is optically transparent as shown by the digital image. Non-isothermal DSC measurement was conducted in an attempt to study the curing behavior of tetra-functional