



Effect of Incremental Curing Agent Additions on Thermal Degradation of Polydimethylsiloxane in Air: A Kinetic Study

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Polydimethylsiloxane samples produced *via* several curing agent: Elastomer base ratios (5, 10, 15 and 20 w/w %) have been thermally degraded under air atmosphere. Thermogravimetric analysis shows that for all polydimethylsiloxane samples, the onset of significant oxidative degradation is at 290 °C and subsequently two distinct degradation stages (290-400 and 400-600 °C) can be observed. At temperatures higher than 600 °C, polydimethylsiloxane samples produced using 5, 10, 15 and 20 wt % curing agent experience weight reductions by 60, 53, 47 and 42 %, respectively. Linear regression analysis using *LINEST* function in Microsoft Excel indicates that data within the 290-400 °C range fit the Arrhenius model far better than the data within the 400-600 °C range. Increments in wt % curing agent from 5 to 15 % enhance the thermal stability of polydimethylsiloxane samples within the temperature range 290-400 °C.

Keywords: Polymer, Polydimethylsiloxane, Thermal analysis, Arrhenius model.

INTRODUCTION

Polydimethylsiloxane is a highly important silicone rubber (siloxane polymer) with wide industrial applications. Examples include applications as sealants and adhesives¹, biomedical materials² and microfluidic devices³. Polydimethyl-siloxane rubber is usually synthesized by crosslinking silicone elastomer base by means of a curing agent. By virtue of its molecular structure, polydimethylsiloxane rubber has excellent low- and high-temperature retention of mechanical properties as well as excellent ageing and dielectric properties⁴. Many researchers have reported that polydimethylsiloxane is 'thermally stable'^{4,5} and has 'good thermal resistance'^{6,7}, but we feel that this statement is generalized since the onset temperature of polydimethylsiloxane degradation varies with different polydimethylsiloxane production methods and applications. It has been reported that polydimethylsiloxane is thermally unstable at temperatures higher than 300 °C under vacuum⁸. Also, it is well-established that polydimethyl-siloxane materials crosslinked/cured at different conditions yield a silicone rubber with dissimilar chemical and/or mechanical properties. For example, Nguyen *et al.*⁶ synthesized polydimethylsiloxane of different crosslinking degrees by varying the ratio of crosslinker-to-vinyl-type polydimethyl-siloxane

and found that the swelling degrees of the polymer in pure water and ethyl acetate decrease when the aforesaid ratio increases. Few researchers, however, focus on thermal degradation kinetics of polydimethylsiloxane at different curing agent concentrations even though the kinetics of thermal degradation and depolymerization of end-blocked with (CH₃)₃Si-groups polydimethylsiloxane have been widely studied for a period of over 50 years^{9,10}.

The main objectives of the study are to analyze and compare thermal degradation kinetics data of polydimethylsiloxane produced *via* several curing agent-to-elastomer base (w/w %) ratios under air atmosphere. For this purpose, kinetic reaction parameters have been determined by using the well-known Arrhenius model. Findings from our study can assist in improving the thermal stability of polydimethylsiloxane-based materials for various applications.

EXPERIMENTAL

The method used in this study is a conventional method used to produce polydimethylsiloxane for microfluidic applications³. Polydimethylsiloxane was produced via mixture of Sylgard® 184 silicone elastomer base (specific gravity = 1.03) and curing agent (Dow Corning) at curing agent-to-elastomer base (w/w %) ratios of 0.5:9.5 (5 wt. %), 1.0:9.0 (10 wt %),

1.5:8.5 (15 wt. %) and 2.0:8.0 (20 wt. %). The mixture was thoroughly centrifuged for 30 sec and defoamed for another 30 sec using a high-speed mixer to ensure homogeneity. The mixture was subsequently degassed using vacuum chamber to remove trapped bubbles. It was then heated in an oven at 65 °C for an hour to complete the hardening process of the polydimethylsiloxane.

Thermogravimetric (TG) analyses were conducted using the Mettler-Toledo TGA/SDTA851 thermogravimetric analyzer. The instrument was set to increase temperature at a rate of 10 °C/min (temperature range: 25 to 1000 °C) under air atmosphere with a flow rate of 50 mL/min. The TG and derivative TG (DTG) curves were recorded concurrently with temperature increase.

RESULTS AND DISCUSSION

Fig. 1 shows the TG and DTG curves of polydimethylsiloxane samples (5 to 20 wt. % curing agent) in air flow. From room temperature to 290 °C, there are negligible weight changes for all samples. It appears that the onset of significant degradation is at 290 °C and subsequently, two distinct degradation stages can be observed. These two stages occur within approximate temperature ranges 290-400 °C (A₁) and 400-600 °C (A₂). For stage A₁, polydimethylsiloxane samples produced using 5 and 10 wt. % curing agent experience weight reductions by 4 % while polydimethylsiloxane produced using 15 and 20 wt. % curing agent experience slightly higher weight reductions (6 %). It is well-known that siloxane undergoes stepwise degradation of the backbone of polymer and oxidation of methyl groups (-CH₃) above 200 °C¹¹. At temperatures higher than stage A₂, polydimethylsiloxane samples produced

using 5, 10, 15 and 20 wt. % curing agent experience weight reductions by approximately 60, 53, 47 and 42 %, respectively. This two-stage oxidative degradation process has been reported by Camino *et al.*¹⁰ where they suggest that oxygen catalyzes the depolymerization reaction of polydimethylsiloxane to volatile cyclic oligomers, leading to a lower temperature for beginning of weight loss, which, interestingly, also commences at 290 °C.

It is apparent that there is a correlation between the quantity of curing agent used and thermal stability of polydimethylsiloxane in oxidative environment at elevated temperatures (> 600 °C). It is suggested that the lower degree of decomposition for the higher wt. % of curing agent is due to higher oxidative crosslinking which renders the polymer thermally more stable at temperatures higher than 600 °C. However, the major weight loss at this higher temperature is due to the loss of carbon, oxygen and hydrogen at the expense of the combustion of organic compounds since silicon based residues are robust in nature which could stand a higher temperature than 600 °C. At the end of the degradation process (1,000 °C), the clear and robust polydimethylsiloxane rubber turns into white ash (silicon-based residues) indicating removal of volatile materials that originate from methyl groups present in polydimethylsiloxane.

Kinetic reaction parameters are determined by using the established Arrhenius equation¹²⁻¹⁵ expressed as:

$$k = Ae^{-E/RT} \quad (1)$$

where k = rate constant, A = frequency factor, R = universal gas constant, T = absolute temperature and E = activation energy of the reaction. According to IUPAC, the frequency factor, A expresses the empirical temperature dependence of the rate coefficient on temperature. The global kinetics of the revitalization reaction can be expressed as¹⁴:

$$\frac{-1}{w_o - w_f} \frac{dw}{dt} = k \left(\frac{w - w_f}{w_o - w_f} \right)^n \quad (2)$$

where w_o = initial mass at the start of thermal degradation, w_f = final mass at the end of thermal degradation, w = mass at time t , $\frac{dw}{dt}$ = ratio of change in mass with respect to time and n = order of reaction. By combining equations (1) and (2), the following expression can be obtained:

$$\ln \left[\frac{-1}{w_o - w_f} \frac{dw}{dt} \right] = \ln(A) - \left(\frac{E}{RT} \right) + n \ln \left(\frac{w - w_f}{w_o - w_f} \right) \quad (3)$$

eqn. (3) can be expressed in the following form:

$$y = B + Cx + Dz \quad (4)$$

where $y = \ln \left[\frac{-1}{w_o - w_f} \frac{dw}{dt} \right]$; $x = \frac{1}{T}$; $z = \ln \left(\frac{w - w_f}{w_o - w_f} \right)$;

$$B = \ln(A); C = -\frac{E}{R}; D = n \quad (5)$$

Constants B , C and D are determined using linear regression analysis for stages A₁ and A₂. We use *LINEST* function in Microsoft Excel, B , C and D to quantify and subsequently determine A , E and n values. This *LINEST* function essentially provides statistical information that describe a linear trend

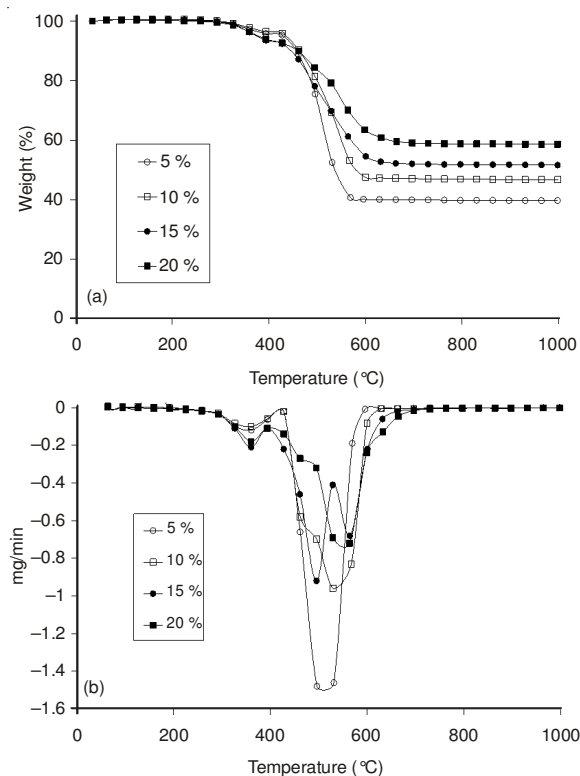


Fig. 1. TG (a) and DTG (b) curves of polydimethylsiloxane samples (5 to 20 wt. % curing agent) in air flow

TABLE-1
KINETIC AND STATISTICAL PARAMETERS OF THERMAL DEGRADATION OF POLYDIMETHYLSILOXANE SAMPLES

Degradation stage	Temperature range (°C)	Curing agent (wt. %)	A (min ⁻¹)	E (kJ/mol)	n	R ²	Standard deviation of residuals, σ_{res}
A1	290- 400	5	1.69×10^4	60.75	0.1002	0.9084	0.2915
		10	1.91×10^5	72.21	0.4270	0.9496	0.2005
		15	1.70×10^6	84.71	0.1147	0.9878	0.1456
		20	2.56×10^5	75.11	0.0963	0.9897	0.1195
A2	400- 600	5	3.21×10^9	157.90	0.4716	0.7848	1.3335
		10	5.32×10^9	161.51	0.6065	0.7779	0.9562
		15	90.5	46.02	0.2245	0.6364	0.4528
		20	5.54×10^3	72.59	0.2411	0.9630	0.1582

matching known data points by fitting a straight line using the least squares method. We specify the sets of dependent variable (y) and independent variables (x and z) from our thermogravimetric data^{15,16}. We set the third and fourth arguments in the *LINEST* function to be 'TRUE' so that the constant B is not equal to nil and the statistical parameters used to evaluate the 'goodness of fit' of our data to the Arrhenius model can be shown.

Table-1 shows the kinetic and statistical parameters of thermal degradation of polydimethylsiloxane produced at different wt. % curing agent. Our determined E values (46 to 162 kJ/mol) can be compared to previous E values of polydimethylsiloxane subjected to thermal degradation under inert atmosphere (54 to 250 kJ/mol) reported by Camino *et al.*¹⁰. The result clearly indicates that stage A1 data fit the Arrhenius model far better than stage A2 data since the former has correlation of determination, R² values higher than 0.9. This is further supported by the generally lower sres values of A2 data compared to A1 data. This strongly implies that the stage A1 values predicted using the Arrhenius equation are more consistent with the experimental data points compared to stage A2 data. At this juncture, we concede the fact that stage A2 data probably require a model-free approach represented by the isoconversional method (multiple-heating rate method) recommended by Vyazovkin and Wight¹⁷ as opposed to the single-heating rate method used in our study. Nonetheless, we feel that our non-isothermal approach may afford fast estimation of kinetics parameters for thermal degradation of polydimethylsiloxane.

The orders of reaction values are all less than 1 and do not seem to exhibit any clear trend with the increase of wt. % curing agent. For A1, increments in wt. % curing agent from 5 to 15 % increase the A and E values, indicating higher amount of energy needed to degrade the polydimethylsiloxane. This implies that the added curing agent enhances thermal stability of the polydimethylsiloxane within the temperature range 290-400 °C. For polydimethylsiloxane produced using 20 wt. % curing agent, there are slight decreases in A and E values from the preceding data (15 wt. % curing agent), though these values are still higher the 10 wt. % curing agent data. It is possible that the amount of 20 wt. % curing agent is approaching the maximum limit for which oxidative crosslinking can occur (*i.e.*, saturation of crosslinking networks). To further support our claims, we have conducted a repeat of the experiment for polydimethylsiloxane produced using 25 wt. % curing agent (curve not shown) and found that the amount degraded after the end of the run is more than polydimethylsiloxane produced using 20 % wt. curing agent.

Conclusion

The thermogravimetric and kinetic data of thermal degradation of polydimethylsiloxane produced using 5 to 20 wt. % curing agent under air atmospheres have been analyzed. The onset of significant oxidative degradation is at 290 °C and subsequently two distinct degradation stages (290-400 and 400-600 °C) can be observed. At temperatures higher than 600 °C, the polydimethylsiloxane samples produced using 5, 10, 15 and 20 wt. % curing agent experience weight reductions by 60, 53, 47 and 42 %, respectively. Linear regression analysis using *LINEST* function in Microsoft Excel indicates that data within the 290-400 °C range fit the Arrhenius model far better than the data within 400-600 °C range. Increments in wt. % curing agent from 5 to 15 % enhance the thermal stability of the polydimethylsiloxane within the temperature range 290-400 °C. Findings from our study can assist in improving the thermal stability of polydimethylsiloxane-based materials for various applications.

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