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# The effect of pre-curing UV-irradiation on the crosslinking of Silicone rubber

Marta Gallo<sup>a</sup>, Renaud G. Rinaldi<sup>b</sup>,

<sup>a</sup> Department of Applied Science and Technology, Politecnico di Torino, Corso Duca degli  
Abruzzi 24, 10129, Torino, Italy

<sup>b</sup> Univ Lyon, INSA-Lyon, CNRS UMR5521, Mateis, Villeurbanne F-69621, France

## Abstract

A recent work made use of selective pre-curing UV-irradiation and its effect on the kinetics of reaction of heat-cure silicone elastomers to spatially tune its viscoelastic properties and design architected solid membranes. The present study adds to the possibility of controlling the local properties of spatially graded materials by exploring the effect of key processing parameters such as the UV dose and the silicone mix thickness on the vulcanization kinetics. Dynamic Differential Scanning Calorimetry measurements have been performed showing that the higher the UV dose, the slower the kinetics reaction. Additionally, complete crosslinking was always reached. Companion modelling effort using the Kissinger reaction model is attempted and the effects of processing parameters on the apparent activation energy are discussed. This work is a crucial first step towards the control of the processing settings needed to design architected silicone rubber membranes with spatially controlled mechanical property gradients obtained from a unique macromolecular network.

**Key words:** Silicone rubber, curing, UV irradiation, DSC, Architected membrane.

## Introduction

Materials-by-design qualifies the strategy of developing material solutions when considering the final use of the part [1]. To that end, architected materials, e.g. the family of complex material solutions with mesoscopic interplay of materials and/or space, are often designed to achieve special, often multifunctional, properties that could not be attained otherwise [2]. For

instance, open-cells truss structures are often listed as strong and light materials [3,4], dense long fiber composites combine stiffness and anisotropy [5], and sandwich materials can combine enhanced bending stiffness and damping [6, 7]. Those are a few examples of architected materials and the booming of additive manufacturing techniques, in addition to the conventional efficient processing methods, promise to broaden the possible topological patterns. Focusing on additive manufacturing, the limitations are, to date, often associated with the cost / time and dimensions of the final parts (omitting the parts weakening resulting from the layer-by-layer in some processing techniques). Focusing on “planar” geometries, alternative techniques for the rapid design of architected parts exist, yet minimizing the aforementioned limitations. Jacobsen *et.al.* developed a rapid method for processing interconnected cellular truss lattices using photo-curable thiolene materials and selective irradiation [8, 9]. Whereas various geometries could be made, through-thickness heterogeneities, resulting from the imperfect self-propagation and associated attenuation of the UV-light, still remain [10, 11].

Stricher *et.al.* also employed selective irradiation to design anisotropic dense Liquid Silicone Rubber (LSR) membranes by spatially controlling the in-plane large strain mechanical properties of the elastomer at the mesoscale [12]. Recently Gallo *et.al.* adapted this straightforward method to design hybrid aluminum - Room Temperature Vulcanization (RTV) silicone sandwich structure, with 2D tuning of the viscoelastic properties of the silicone rubber thin core, offering enhanced structural capabilities [13]. In the last two aforementioned works, the silicone mix, referring to the silicone in its liquid state prior to curing, was UV-irradiated (in presence of an aromatic solvent) prior to heat cure. The UV-light / matter interaction was proven to degrade the platinum Karstedt’s catalyst [14], thus slowing the kinetics of the thermally activated crosslinking of silicone rubber [12]. The spatial patterning was achieved when inserting a mask between the UV source and the polymer to locally control the UV doses. Consequently, a given isothermal treatment (fixed temperature and duration) applied to a partially irradiated material can ascertain to reach different crosslinking states in different locations. The additional cooling and/or end-capping of the remaining

reactive groups is then applied to stabilize the solid elastomer with heterogeneous mechanical properties at the macroscale [12]. Ultimately, the final properties of the architected membrane requires a careful control of the vulcanization reaction kinetics, and thus necessitates the investigation of the underlying relations between pre-curing UV-irradiation and heat-curing.

Silicone rubber materials describe thermoset elastomers commonly resulting from the platinum-catalyzed hydrosilylation reaction involving vinyl and Si-H reactive groups, which does not generate by-products [15-17]. The vulcanization process is manifested by an exothermic and irreversible chemical reaction so that Differential Scanning Calorimetry (DSC) experiments are widely used for its characterization [18-22]. Dynamic tests are often preferred to isothermal tests for obvious experimental convenience, such as measurement precision and the fact that the targeted temperature in isothermal tests cannot be reached instantaneously [19].

The modeling of the reaction of silicone rubber, relating the crosslinking reaction rate to the temperature and the degree of reaction, is largely attempted with both mechanistic and phenomenological approaches [18, 19]. Yet, no such work can be found on the silicone systems that have been previously submitted to UV-irradiation. Thus, the present work investigates the effect of pre-curing UV-irradiation on the vulcanization of RTV silicone elastomers with use of dynamic DSC experiments. The characteristics of the exothermic event associated to the curing reaction are monitored for various UV doses and silicone mix thicknesses, corresponding to key processing parameters. Companion modeling using the Kissinger model is then pursued to provide some insights towards the development of a predictive tool that turns to be crucial for controlling the realization of complex architected solid silicone rubber membranes.

## **Materials and methods**

The experiments were carried out on commercial bi-parts silicone rubber Bluesil™ RTV141 (RHODORSIL Bluestar, France) in which the platinum Karstedt's catalyst and 1-ethynyl-1-

cyclohexanol are used as the catalyst and inhibitor respectively. The two base components were mixed in a weight ratio of 9:1 and with the addition of 10 wt.% xylenes solvent purchased from Sigma-Aldrich and used as received (ACS reagent,  $\geq 98.5\%$ , mixture of isomers). The mixture was bar coated onto an aluminum mold with isolated compartments of varying depth as illustrated in Figure 1a and irradiated in a UV Crosslinker CL-1000 (UVP, USA) (Figure 1b). The distance between the UV lamps and the top surface of the mold remains constant throughout the study and equal to 105 mm. All irradiations were performed at the wavelength  $\lambda$  equal to 254 nm (UVc) and the exposure time was varied to modify the applied dose. UV doses ( $D$ ) of 1 kJ/cm<sup>2</sup> and 3 kJ/cm<sup>2</sup> were tested. The correspondence between the duration of the UV irradiation and the doses, along with its spatial uniformity between the different compartments (reaming) were verified with a UV radiometer Power Puck II EIT<sup>®</sup>. With the mold being centered within the crosslinker, less than 10% variation between the nine reaming compartments was found.

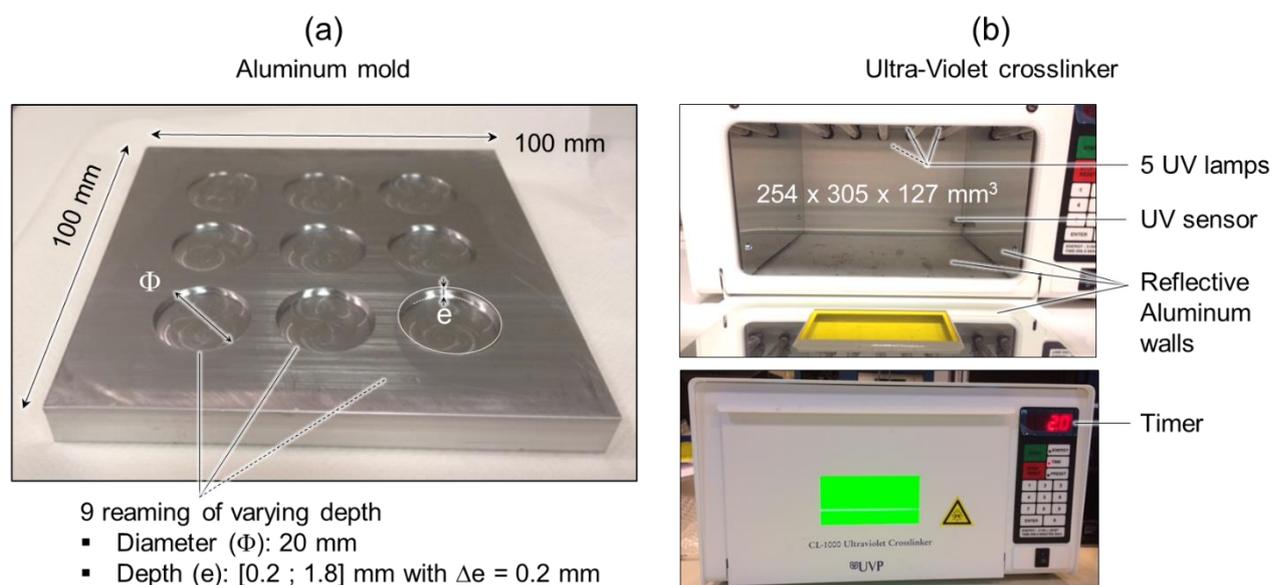


Figure 1: UV-irradiation set-up. (a) Aluminum mold. (b) UV-crosslinker (top image: irradiation chamber / bottom image: during irradiation).

A thermocouple was used to monitor the temperature during the UV-irradiation to ascertain that no significant temperature increase occurred, which could potentially trigger the onset of

curing. Hence, the irradiation was set in order to limit the temperature rise within the chamber to 3 °C or less. Finally, after UV-irradiation and prior to thermal curing, the silicone mix was degassed for an hour at room temperature to remove the solvent, yet limiting the formation of bubbles in the final membranes.

Differential Scanning Calorimetry tests were carried out on a Q20 equipment (TA Instruments, USA) according to the following thermal treatment: stabilization at 20 °C, ramp from 20 up to 220 °C (with little variation of the maximum temperature depending on the UV irradiation imposed to ascertain the monitoring of the entire exothermic event) at controlled heating rate (denoted  $\beta$  and varying from 1 to 20 °C/min) in flowing nitrogen gas. A cooling step from the maximum temperature down to 20 °C (at 10 °C/min) was punctually performed to confirm that the curing was completed (no deviation from the baseline was observed upon cooling). The Universal Analysis© software was used to plot the heat flow per unit mass with respect to temperature profiles and conduct companion post-processing studies.

Four physical quantities were determined from the curing exothermic event as illustrated in Figure 2a: the onset temperature  $T_{\text{onset}}$ , the peak temperature  $T_{\text{peak}}$  corresponding to the temperature at maximum heat flow, the end temperature  $T_{\text{end}}$  and the total heat per unit mass  $Q_{\text{tot}}$ . The comparison of these physical quantities allows studying the influence of irradiation parameters on curing, such as the sample thickness as illustrated in Figure 2b and discussed in the following section.

For sake of clarity, in the following, a pre-exponent corresponding to the UV dose in kJ/cm<sup>2</sup> will be added to physical quantities of interest to distinguish between the different UV treatments experienced by the silicone mix. Hence,  ${}^0T_{\text{peak}}$  defines the peak temperature of the pristine (no irradiation) silicone rubber.

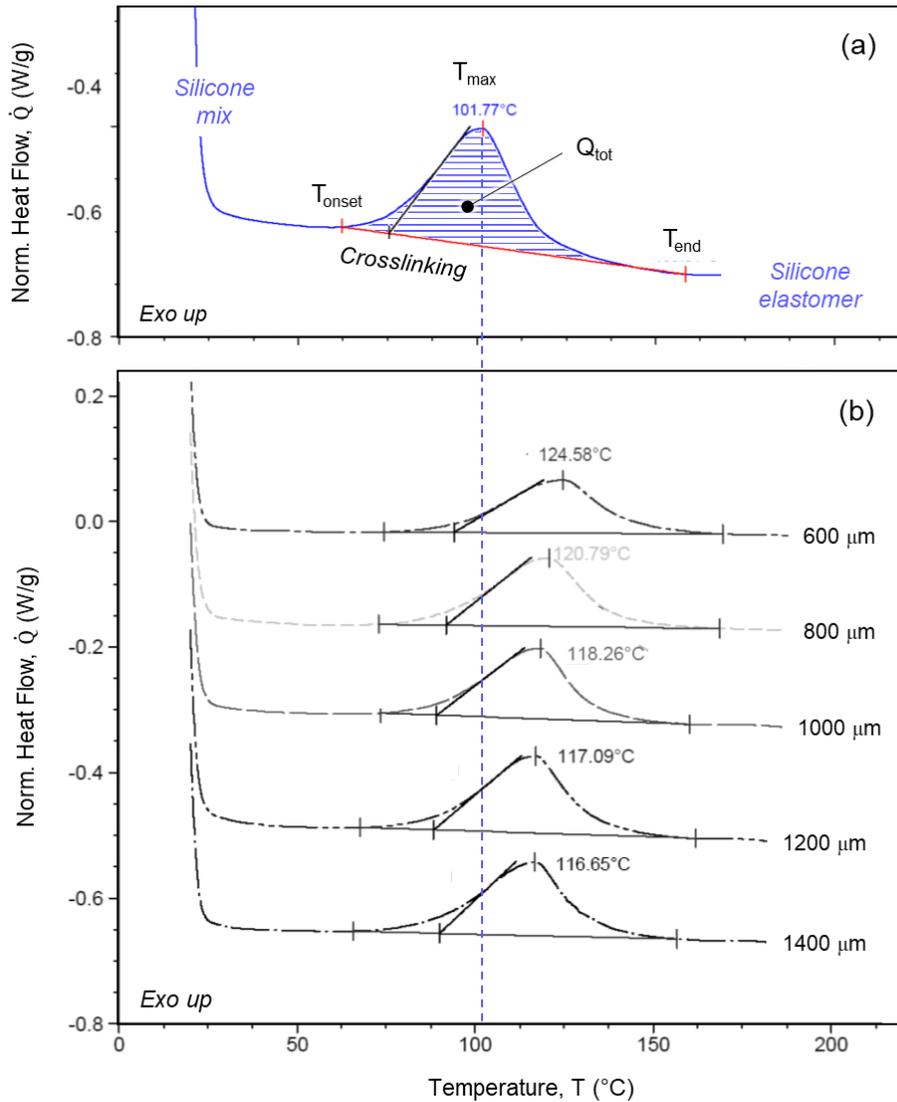


Figure 2: Typical DSC thermograms of the exothermic curing reaction of RTV silicone mix heated at 10 °C/min; (a) associated physical quantities monitored (pristine sample). (b) Effect of the silicone mix depth on the curing of irradiated samples ( $D=3 \text{ kJ/cm}^2$ ). *N.B. the thermograms have been shifted for reading comfort.*

## Results

### *Curing of pristine silicone rubber*

Figure 2a displays the DSC thermogram associated with the crosslinking of pristine RTV silicone heated from 20 °C to 160 °C at 10 °C/min. A well-defined exothermic event is observed in the vicinity of 100 °C. Eight identical tests have been performed on different batch mixtures and the average and standard deviation of the peak temperature  $^0T_{\text{peak}}$  were

found equal to 102.1 °C and 2.0 °C respectively. Similar statistical data reduction of the total heat per unit volume  ${}^0Q_{\text{tot}}$  led to 19.2 J/g and 1.8 J/g respectively.

#### *Curing of UV-irradiated silicone rubber*

Figure 2b presents the heat flow as a function of temperature for UV-irradiated silicone mixtures of varying depths heated from 20 °C to 180 °C at 10 °C/min. The specimens were all submitted to a pre-curing UV dose  $D$  of 3 kJ/cm<sup>2</sup>. The exothermic events associated to the silicone crosslinking are here again clearly observed but are found to be shifted towards higher temperature compared to the non-irradiated sample (figure 2a). Also, the thinner the silicone mixture, the greater the temperature shift. A shift of the peak temperature greater than 20 °C is found between the 600 μm-thick irradiated silicone rubber and the pristine one. A similar study has been performed on mixtures initially submitted to 1 kJ/cm<sup>2</sup> UV irradiation and the results are hereafter compared with the pristine and 3 kJ/cm<sup>2</sup> specimens. Figure 3 displays the evolution of the peak temperatures  $T_{\text{peak}}$  as a function of the mixtures depth and pre-curing irradiation UV dose. Since the mixture's depth has no effect on the curing of the pristine silicone rubber, a bounded depth-independent region is plotted (in grey), with its upper and lower bounding values corresponding to the average value of the peak temperature  $\langle T_{\text{peak}} \rangle$  plus or minus the standard deviation respectively.

The graph in figure 3 evidences that the higher the UV-dose the higher the peak temperature, whatever the mixture's thickness. For the thinner 400 μm specimen, the relative increase in the peak temperature is greater than 30% compared to the pristine sample. Also, for a given UV-dose, not only does the peak temperature decrease with increasing the mixture's depth as previously stated, but the sensitivity to depth's variation is seen to decrease as the depth increases, seemingly disappearing for values greater than 1 mm as the peak temperatures tend to reach a plateau value.

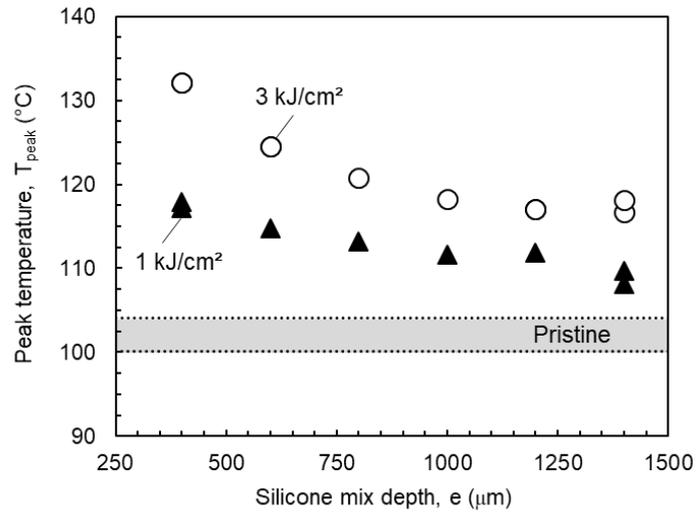


Figure 3: Curing peak temperatures of RTV silicone rubber heated at 10 °C/min as a function of the silicone mixture's depth and pre-curing irradiation UV dose.

Similar plots are made regarding the onset and end temperatures. The results, along with the peak temperature for the samples receiving 3 kJ/cm<sup>2</sup> pre-curing UV dose, are displayed in Figure 4 and compared to the pristine statistical values.

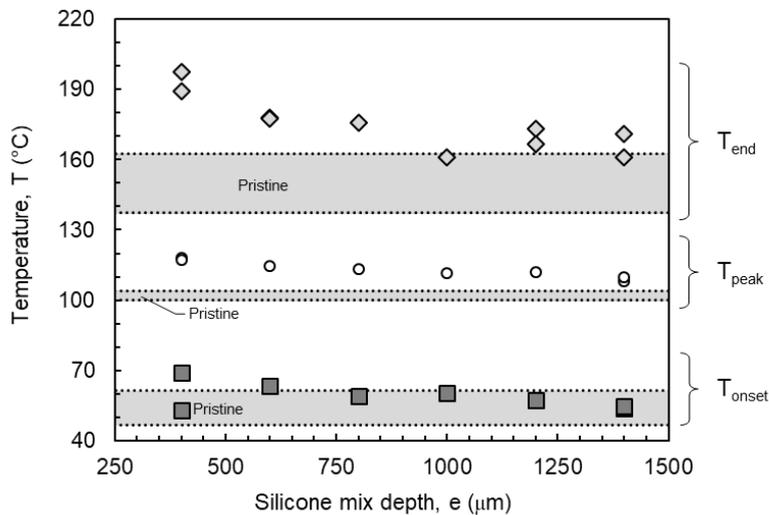


Figure 4: Curing onset, peak and end temperatures of RTV silicone rubber heated at 10 °C/min as a function of the silicone mixture's depth. The results for pristine (thick greyed regions) and UV-irradiated ( $D = 3 \text{ kJ/cm}^2$ ) samples are displayed.

The onset ( ${}^3T_{\text{onset}}$ ) and end ( ${}^3T_{\text{end}}$ ) temperatures, both their absolute values and evolutions, are seen to decrease as the depth increases. Noticeably, whereas the irradiated peak temperature remains always higher than the pristine one, both onset and end temperatures fall closer to the pristine ones (above all for thicknesses greater than 1 mm). Yet, these observations must be discussed cautiously as the dispersions of the onset and end temperatures of the pristine samples (8.3 and 13.5 % respectively) are higher than that of the peak temperature (1.9 %), which could be explained by the fact that the peak temperature remains the relevant metric to be unequivocally determined on the DSC profiles, whereas the onset and end temperatures highly depend on the quality of the DSC baseline.

Finally, the effect of UV dose and mixtures depth on the total heat energy released throughout curing  ${}^iQ_{\text{tot}}$  are presented in Figure 5. No significant effect of UV-dose nor mixture's depth can be found as the total heat for the irradiated samples fall close to the pristine values. The latter are here again figured as a bounded depth-independent greyed region with upper and lower values equal to the average value  $\langle {}^0Q_{\text{tot}} \rangle$  plus or minus the standard deviation respectively.

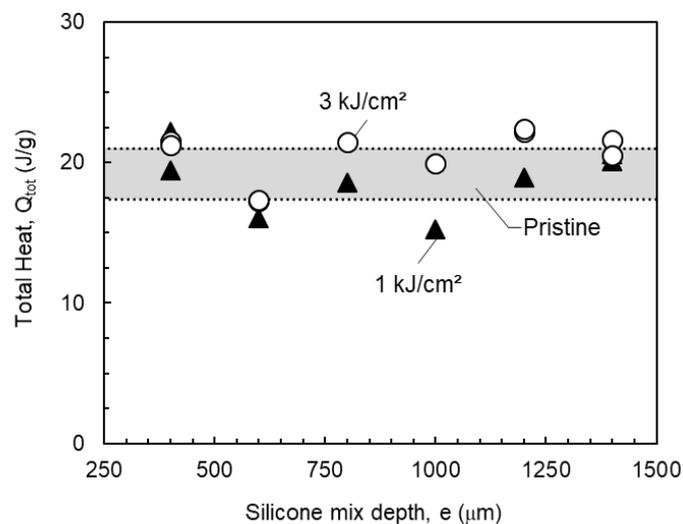


Figure 5: Total heat released during the dynamic heat-cure of RTV silicone rubber heated at 10 °C/min as a function of the silicone mixture's depth and pre-curing irradiation UV dose.

## Discussion

The use of DSC measurements to investigate the degree of vulcanization of polymer resins [23-27], and silicone rubber in particular [18, 19, 21], has been widely reported. For silicone elastomer such as the RTV under study, the crosslinking results from the exothermic platinum-catalyzed hydrosilylation reaction, where the Si-H sites of the chain extender reacts with the reactive vinyl double group of the PDMS chains and does not generate by-products [18]. Consequently, each crosslink is assumed to release the same amount of energy so that the macroscopic energy released ( $Q$ ) at any given time  $t$ , compared to the total energy released for the complete thermal curing ( $Q_{tot}$ ), is directly related to the degree of reaction  $c$  (indiscriminately described as the degree of vulcanization or the degree of conversion). At any given time,  $c(t)$  can then be determined as follow:

$$c(t) = \frac{Q(t)}{Q_{tot}} \quad (1)$$

$c$  is a positive strictly growing variable ranging from 0 (onset) to 1 (end) and both  $Q(t)$  and  $Q_{tot}$  are determined from the time integration of the instantaneous rate of heat released by the sample and measured during DSC curing experiments.

Since the total heat was found to be independent of the UV dose and mixture depth but also equal to the pristine value (Figure 5), complete crosslinking is always achieved. Therefore, the pre-curing UV-irradiation steps applied seem to alter only the kinetics of the reaction, with, qualitatively speaking, the higher the UV-dose the slower the kinetics (Figure 3). Since the UV light is responsible for the neutralization of the platinum catalyst [12, 14], this implies that enough catalyst remains at all time to complete the curing of the silicone elastomer. It has yet to be established if the neutralization is potentially reversible (completely or partially) and/or if a larger UV dose would lead to an incomplete curing of the RTV membrane.

The depth sensitivity highlights the limitation in transmission of the UV light throughout the silicone material. The onset temperature tends to be of the order of the pristine one for thick silicone mixture (mixture deeper than 1 mm) suggesting that the UV-light does not reach the bottom part of the mixture (Figure 4). Locally, in the deep part of the silicone mixture, the

curing behavior should be equivalent to non-irradiated silicone systems. Further investigations are required to fully characterize the transmission properties of UV light and thick silicone materials (as it cures!) which is out of the scope of the current paper. Indeed, focusing on the targeted application, *i.e.* the planar tuning of the silicone elastomeric membrane mechanical properties, through-thickness heterogeneity has to be avoided. Furthermore, since thin viscoelastic core layer within a sandwich structure for instance remains of interest [7, 13, 28], the present work focuses on thin membrane (<1 mm) for which through-thickness homogeneity is assumed.

The general equation describing the curing kinetic relates the isothermal reaction rate  $\left. \frac{dc}{dt} \right|_T$  to the conversion function  $f(c)$ . Under isothermal condition, the two are linearly related and an Arrhenius description of the reaction constant is used, leading to the expression below:

$$\left. \frac{dc}{dt} \right|_T = \left( A e^{-\frac{E}{RT}} \right) f(c) \quad (2)$$

With A a pre-exponential factor ( $\text{min}^{-1}$ ), E the apparent activation energy (J/mol), R the universal gas constant (J/mol/K) and T the absolute temperature (K). Numerous more or less complex phenomenological expressions have been proposed for the conversion function  $f(c)$  so that accurate simulation of the curing kinetics of various reactions can be achieved. A substantial list of models ( $N^{\text{th}}$  order, free kinetics, autocatalytic) can be found in table 4 in [23], table 1 in [24], and references herein. Among the many models, the Kissinger model uses a  $n^{\text{th}}$ -order expression for the conversion function and has been widely employed since it leads to a straightforward graphical evaluation of the apparent activation energy without precise knowledge of the reaction mechanism involved [29]. The Kissinger model writes as follow:

$$\left. \frac{dc}{dt} \right|_T = \left( A e^{-\frac{E}{RT}} \right) (1 - c)^n \quad (3)$$

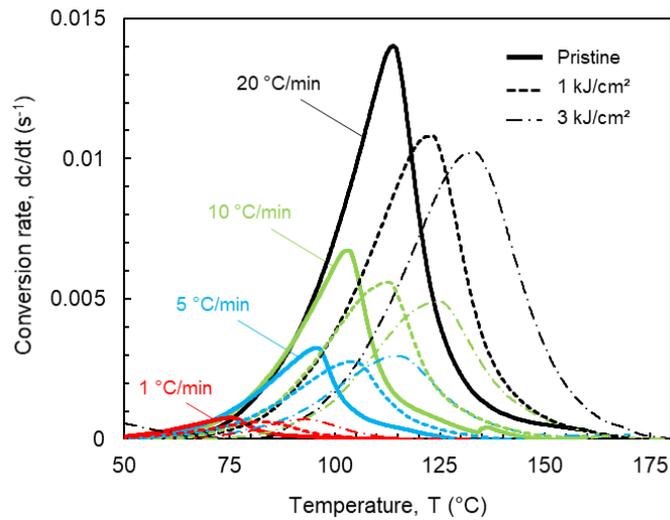
Considering the material curing at constant heating rate  $\beta$  ( $dT/dt$ ), which describes the dynamic DSC experiments performed, the Kissinger method links the peak temperature to the heating rate (a detailed derivation of the following equation can be found in [19]):

$$-\ln\left(\frac{\beta}{T_{\text{peak}}^2}\right) = -\ln\left(\frac{AR}{E}\right) + \frac{E}{RT_{\text{peak}}} \quad (4)$$

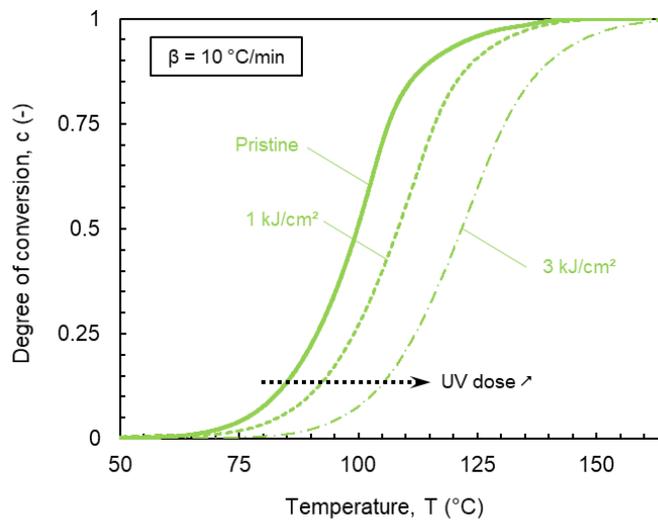
By performing a series of dynamics curing experiments with varying constant heating rates, the apparent activation energy can be identified by plotting  $-\ln\left(\frac{\beta}{T_{\text{peak}}^2}\right)$  as a function of  $\frac{1}{T_{\text{peak}}}$ .

The Kissinger method is a robust single point method, which it is not significantly affected by the baseline shift. Aside from being valid for many types of reactions (since, as evoked, the method does not depend on the detailed knowledge of the reaction mechanism), it is also proven to be relatively insensitive to the effect of solvent and potential secondary reactions [30]. In the current study, the solvent is removed from the mixture prior to curing and the chemical reaction of RTV silicone rubber is widely acknowledged to be “simple” with no byproducts [18, 19]. Therefore, the use of the simplistic single point method for the calculation of a single apparent activation energy tends to suffice. Furthermore, it has been applied along with other models (Ozawa, Flynn-Wall-Ozawa and Friedman) by Hong and Lee onto several Liquid Silicone elastomers and the differences between the apparent activation energies obtained from the various models did not exceed 5% [18]. Also, it is worth noting that the Kissinger method is used (as a first step) to determine the only parameter with a physical meaning in the modeling suggested by Hernandez-Ortiz and coworkers and based on the Kamal-Sourour reaction model [20].

Finally, dynamic DSC experiments at various heating rates (1, 5, 10, 20 °C/min) in flowing nitrogen gas were performed on pristine and UV-irradiated (1 and 3 kJ/cm<sup>2</sup>) silicone mix of 600 μm thickness. The DSC heat flow rate was converted into the reaction rate and the obtained profiles are presented in figure 6a as a function of temperature.



(a)



(b)

Figure 6: Effect of UV-irradiation on the silicone rubber curing using dynamic DSC experiments (UV-irradiated mixtures are 600  $\mu\text{m}$  thick). (a) Conversion rate at different heating rates. (b) Degree of conversion at constant heating rate of 10  $^{\circ}\text{C}/\text{min}$ .

Focusing on a given irradiation, as expected, the profiles are shifted towards higher temperatures as the heating ramp increases. Also, whatever the heating ramp, increasing the UV-dose delays and slows down the conversion since the profiles are shifted towards higher temperature (time and temperature being proportional) and the maximum rates (and its average) decrease. This is further evidenced in figure 6b where the degree of conversion is plotted for the samples heated at 10  $^{\circ}\text{C}/\text{min}$ ; the well-established sigmoidal profiles are not only shifted but also flatten as the irradiation increases.

The corresponding Kissinger plots and the associated linear regressions are presented in Figure 7 for the pristine material and the 600 μm thick irradiated samples (filled symbols). Data for 1 mm thick mixture submitted to 1 kJ/cm<sup>2</sup> UV dose have been added onto the plot (unfilled triangles △).

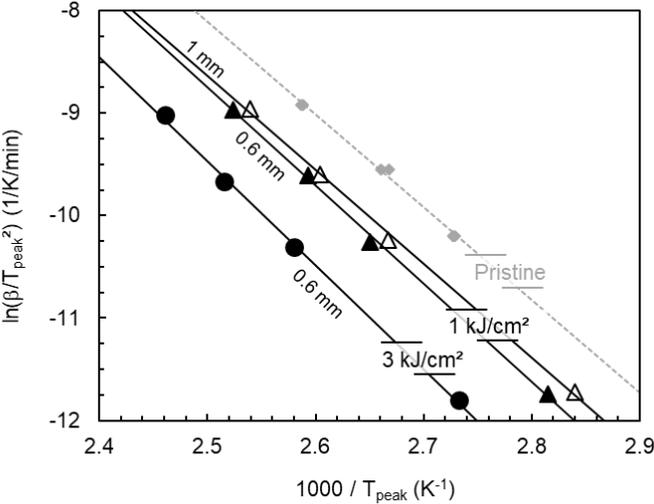


Figure 7: Kissinger plot for RTV silicone rubbers (the UV doses and silicone mixture thicknesses are specified next to the data points).

The obtained values for the apparent activation energies and the corresponding correlation coefficients ( $R^2$ ) are listed in Table 1. A noticeable increase of the activation energy is observed with increasing UV-dose.

At constant UV-dose of 1 kJ/cm<sup>2</sup>, the thicker system (1 mm) exhibits a smaller activation energy compared to the thinner one (0.6 mm). If the volume of material was considered rather than the exposed surface, meaning that the dose was expressed in terms of energy per unit volume instead of per unit surface, it would be explicit that the thicker sample would have been submitted to a smaller dose, justifying that the apparent activation energy, in average, is found to be closer to the pristine material.

Table1: Activation energies and regression factors derived from the Kissinger model.

UV irradiation dose D (kJ/cm <sup>2</sup> )	Silicone mix depth e (μm)	Activation Energy Kissinger, E (kJ/mol)	Correlation coefficient, R <sup>2</sup> (-)
Pristine (0)	n.a.	75.3	0.995
1	600	79.7	0.999
	1000	76.2	0.998
3	600	84.4	0.998

The hypothesis (reported elsewhere [14]) that the UV-light / silicone mixture interaction is responsible for converting the platinum catalysis into inert complex is in accordance with the measured apparent energy determined. Indeed, the higher the dose, the less concentrated the catalyst, resulting in an increased activation energy. It is worth noting that the observation should not be extrapolated. Indeed and as already evoked, the effect of larger doses and the potential unwanted side effects (such as chain scission for instance) have to be explored. Yet, the quantification of the varying apparent activation energy is of key importance towards the controlled design of graded silicone elastomeric membrane. This is symbolically illustrated in Figure 8 where the degree of conversion is displayed for 2 heating rates (1 °C and 10 °C) and two UV states (0 and 3 kJ/cm<sup>2</sup>).

If we were to make a thin two-phase membrane, as depicted on the scheme on the right of figure 8, with the stiffer phase, not irradiated, targeting a degree of conversion of 0.75 (the horizontal dashed black line), the final state of the softer irradiated phase (the stars) would depend on the heating rate, reaching about 0.1 with a heating rate of 1 °C/min and 0.2 with a heating rate of 10 °C/min. For obvious experimental reasons, isothermal curing is preferred to the dynamic curing so that the aforementioned scenario is symbolic (this also applies to the value of the degree of conversion). Nevertheless, the exercise insists on the need for

fully describing the curing kinetics of the silicone elastomer and the interplay with UV irradiation.

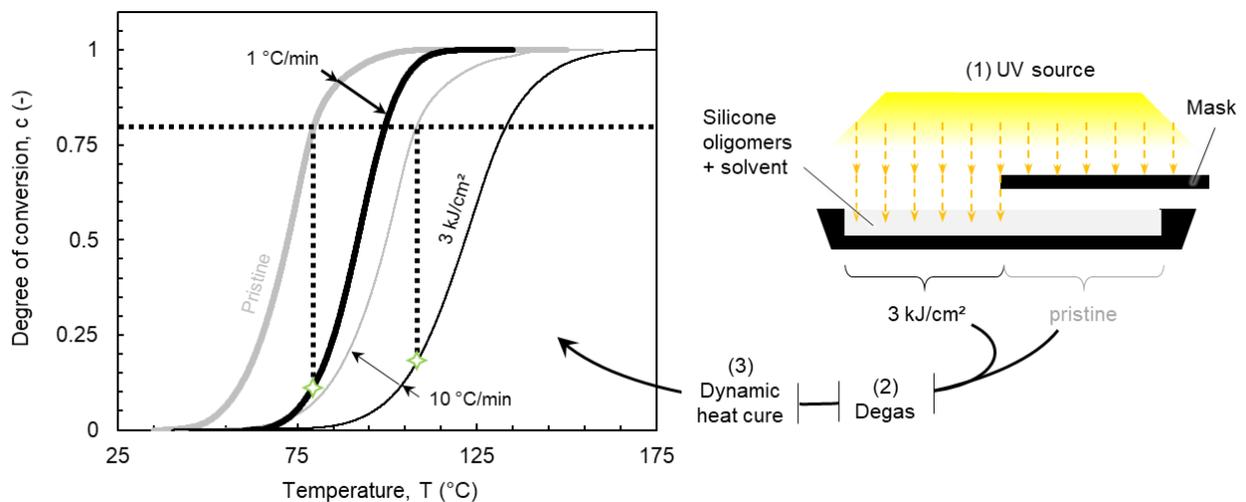


Figure 8: Evolution of the degree of conversion with temperature at 1 and 10 °C/min for the pristine and irradiated (0.6 mm & 3 kJ/cm<sup>2</sup>) silicone elastomers.

## Conclusion

The effect of pre-cure UVc-irradiation on the curing of a commercial RTV silicone elastomer was studied by dynamic DSC. The UV-dose, in presence of aromatic solvent, affects the catalysis performance of the platinum catalyst, resulting in the slowing of the kinetics of the crosslinking reaction. In addition, the higher the dose, the slower the kinetics. Within the range of UV-dose explored, the Kissinger reduction of the DSC data, with its use being justified by the simple crosslinking hydrosilylation curing reaction, permitted to evidence an increase of the apparent activation energy with increasing the UV-dose. Also, with the UV-dose being applied on the free surface of the silicone mixture, a careful study of the impact of the mixture's depth was conducted. For systems of 1 mm and above, the characteristics of the dynamic exothermic events corresponding to the curing of the liquid silicone rubber were seen to plateau so that through-thickness homogeneity cannot be further guaranteed. Ultimately, the understanding and the quantification of the effect of UV-curing on the kinetics of silicone membrane is key to the pursued objective that is the design of planar graded architected silicone elastomers, obtained through selective pre-curing irradiation of the

silicone viscoelastic membrane. Ongoing efforts now aim at accurately modeling the curing reaction so that the processing-time–temperature curves for a large set of UV condition can be obtained (see figure 10 in [18]).

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## **References**

1. Ashby, M.F. and K. Johnson, *Materials and design: the art and science of material selection in product design*, 2013: Butterworth-Heinemann.
2. Ashby, M., *Designing architected materials*. *Scripta Materialia*, 2013. 68(1): p. 4-7.
3. Fleck, N., V. Deshpande, and M. Ashby, *Micro-architected materials: past, present and future*. *Proceedings of the Royal Society A: Mathematical, Physical and Engineering Sciences*, 2010. 466(2121): p. 2495-2516.
4. Zok, F.W., R.M. Latture, and M.R. Begley, *Periodic truss structures*. *Journal of the Mechanics and Physics of Solids*, 2016. 96: p. 184-203.
5. Berthelot, J.-M. and F.F. Ling, *Composite materials: mechanical behavior and structural analysis*, 1999: Springer.
6. Berthelot, J.-M., et al., *Damping analysis of composite materials and structures*. *Composite Structures*, 2008. 85(3): p. 189-204.
7. Ege, K., et al., *Assessment of the apparent bending stiffness and damping of multilayer plates; modelling and experiment*. *Journal of Sound and Vibration*, 2018. 426: p. 129-149.

8. Jacobsen, A.J., W. Barvosa-Carter, and S. Nutt, Micro-scale truss structures with three-fold and six-fold symmetry formed from self-propagating polymer waveguides. *Acta Materialia*, 2008. 56(11): p. 2540-2548.
9. Jacobsen, A.J., W. Barvosa-Carter, and S. Nutt, Micro-scale truss structures formed from self-propagating photopolymer waveguides. *Advanced Materials*, 2007. 19(22): p. 3892-3896.
10. Rinaldi, R.G., et al., Effects of material heterogeneities on the compressive response of thiol-ene pyramidal lattices. *Journal of Materials Science*, 2012. 47(18): p. 6621-6632.
11. Rinaldi, R.G., C. Hammett, and F. Zok, Ameliorating property gradients in photocured polymer lattices via thermal curing. *Materials Letters*, 2013. 105: p. 155-158.
12. Stricher, A., et al., Light-Induced Bulk Architecturation of PDMS Membranes. *Macromolecular Materials and Engineering*, 2016. 301(10): p. 1151-1157.
13. Gallo, M., et al., Spatial Patterning of the Viscoelastic Core Layer of a Hybrid Sandwich Composite Material to Trigger Its Vibro-Acoustic Performances. 2018, SAE International.
14. Fischer, H.R., et al., Degradation mechanism of silicone glues under UV irradiation and options for designing materials with increased stability. *Polymer degradation and stability*, 2013. 98(3): p. 720-726.
15. Lynch, W., *Handbook of silicone rubber fabrication*. Vol. 221. 1978: Van Nostrand Reinhold New York.
16. Lyon, R.E., An integral method of nonisothermal kinetic analysis. *Thermochimica Acta*, 1997. 297(1-2): p. 117-124.
17. Stricher, A., et al., How I met your elastomers: from network topology to mechanical behaviours of conventional silicone materials. *RSC Advances*, 2015. 5(66): p. 53713-53725.
18. Hong, I.-K. and S. Lee, Cure kinetics and modeling the reaction of silicone rubber. *Journal of Industrial and Engineering Chemistry*, 2013. 19(1): p. 42-47.
19. Lopez, L., et al., Modeling the vulcanization reaction of silicone rubber. *Polymer Engineering & Science*, 2007. 47(5): p. 675-683.
20. Hernandez-Ortiz, J. P., & T.A. Osswald, A novel cure reaction model fitting technique based on DSC scans. *Journal of polymer engineering*, 2005. 25(1), 23-38.
21. Hernández-Ortiz, J. P., & T.A. Osswald, Modeling processing of silicone rubber: Liquid versus hard silicone rubbers. *Journal of Applied Polymer Science*, 2011. 119(3): p. 1864-1871.

22. Haberstroh, E., Michaeli, W., & E. Henze, Simulation of the filling and curing phase in injection molding of liquid silicone rubber (LSR). *Journal of reinforced plastics and composites*, 2002. 21(5): p. 461-471.
23. Haddadi, S.A., et al., Effects of nano-silica and boron carbide on the curing kinetics of resole resin. *Journal of Thermal Analysis and Calorimetry*, 2017. 128(2): p. 1217-1226.
24. Vyazovkin, S., & C. A. Wight, Model-free and model-fitting approaches to kinetic analysis of isothermal and nonisothermal data. *Thermochimica acta*, 1999. 340: p. 53-68.
25. Mazali, C.A.I. and M.I. Felisberti, Vinyl ester resin modified with silicone-based additives: III. Curing kinetics. *European Polymer Journal*, 2009. 45(8): p. 2222-2233.
26. Vyazovkin, S. V., & Lesnikovich, A. I., An approach to the solution of the inverse kinetic problem in the case of complex processes: Part 1. Methods employing a series of thermoanalytical curves. *Thermochimica Acta*, 1990. 165(2): p. 273-280.
27. Guo, J., K. Lin, and Z. Xu, Curing kinetic analysis of phenolic resin filled with nonmetallic materials reclaimed from waste printed circuit boards. *Thermochimica Acta*, 2013. 556: p. 13-17.
28. Irazu, L. and M.J. Elejabarrieta, The effect of the viscoelastic film and metallic skin on the dynamic properties of thin sandwich structures. *Composite Structures*, 2017. 176: p. 407-419.
29. He, K., Reaction kinetics in different thermal analysis. *Analytical chemistry*, 1957. 29(11): p. 1702-1707.
30. Duswalt, A., The practice of obtaining kinetic data by differential scanning calorimetry. *Thermochimica Acta*, 1974. 8(1-2): p. 57-68.