The Effect of Heat Energy on Gelation Point of Silicone Rubber

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Abstract— **The study conducted was on the effect of heat energy on gelation point of silicone rubber. The test conducted will be mainly on the gelation point of silicone rubber. The objectives of this study is to determine the effect of heat energy and to determine the critical gel point. Gel point is a temperature at which substance freezes solid or no longer flow by gravity or usually act as liquid such as liquid silicone rubber. It occurs before mechanical reaction starts for example the strength, ductility, hardness, fracture or toughness. Critical gel point tc which is the time to reach gel point or the liquid-solid transition will be monitor and evaluated throughout the experiment. Gel point can only be reach by tested with different temperature. The experiment will be tested on the thermo kinetics study method by using DSC. The study had been compared with the Kamal's model for the validity of the experiment. The crosslinking process was been observed throughout the experiment.**

Keywords— Differential Scanning Calorimeter(DSC), Gel Point, Crosslink, Liquid Silicone rubber, Crystallization temperature (tc), Melting temperature (tm), Heat Flux

I. INTRODUCTION

Liquid Silicone Rubber (LSR) has existed since the late 1970s, and has become the material of choice for manufacturing rubber parts and products. For nearly 40 years, many companies in the major industries have chosen liquid silicone rubber to manufacture their rubber parts because of the manufacturability of the raw material. Various applications of silicone rubber produce a consistent part quality and improved productivity of manufacturing. Liquid Silicone Rubbers (LSR) is also called as heat curable liquid materials. Materials are processed on specially designed injection moulding and extrusion production equipment. Liquid silicone rubber has become the ideal material for very demanding applications because of its unique properties, which include durable, chemical and temperature resistance, and biocompatibility. It has higher heat resistance and chemical stability and provide better electrical insulation. Silicone molecules are helical in shape and intermolecular force is low which result in high elasticity, high compressibility and good resistance to cold temperatures. Other than that, silicone rubber is an electrical insulation. Its insulating properties are stable over a wide range of temperatures and in high voltage applications. These qualities promote its use by the industrials for example, automotive, aerospace, and dental.[7]

This study focus on the effect of heat energy on silicone rubber during gelation point. Gel point is the time at when the crosslinking or curing is occurred. Gel point is a temperature at which the substances freezes solid, and no longer flow by gravity. It happened before mechanical reaction such as the ductility, hardness, fracture, toughness starts to change. Gel point can be achieving by using different temperature. Before gel point, the polymer molecules are limited in size. After gelation, the network is insoluble and no longer flows. Gel point is where a network of covalent bond is form. Time at which the viscosity abruptly increases. Gel point usually occurs at low temperature between 40-100℃. [2]

The critical gel point is the time at which the silicone rubber reach gel point t_c which is the liquid-solid transition. Gel time can be affected by the temperature and catalyst concentration. Gel point can be determine by two methods either by using thermal methods or rheological methods. Rheological method or rheo-kinetic is a method which need to monitor the evolution of network structure during gelation. The second method is a thermo kinetic study by using Differential scanning calorimetry (DSC) at different heating rates. According to [2], thermal method is the best suitable method to measure crosslinking. In the paper stated that the gel time analysis revealed that the rheological characterization does not show the chemical evolution of the network. Its development appears yo be related to the mechanical behavior. Therefore, the thermal method is finally chosem.

This study was done to form crosslinks between the polymer chain to another to form covalent bond and ionic bond. Crosslinks can increase hardness and melting point but reducing the flexibility. Based on this study, it has been focus on the thermo kinetic study by crosslinking kinetics liquid silicone rubber. Crosslink will be control to make it well connected and stable. The effect of heat energy between crosslinks will be identified. The cure kinetics is a complex phenomena and includes several steps. During the process, macromolecules are linked with chemical bonds and a cross-linked network is obtained. These reactions are exothermic and irreversible. Numerous experimental techniques have been used to analyze the cure kinetics, but Differential Scanning Calorimetry (DSC) is the most popular.

Most silicone rubbers are two-component systems. In the case of liquid silicone rubber, component A consists of polysiloxane, polymethylvinylsiloxane and polymethylhydrosiloxane while Part B contains a platinum catalyst in the reaction. The equipment used in the study is the Differential scanning calorimetry (DSC) by manipulating the temperature. Five different ratios of 10:1, 7:5, 2:5, 5:5, and 1:10 were used in the experiment to manipulate the catalyst concentration.

Gel point is the time when curing process occurs. The curing process begins by the formation of short polymer chain, and then chains were branched and subsequently cross-link to form three dimensional (3D) network. During isothermal curing, the reactant mixture changes via gelation which depend on the curing temperature and time. The experiment had been conducted by using DSC. The results will show which ratio and temperature will achieved gel point. The data has been analysed and comparisons has been made. Silicone rubber curing at room temperature had been the reference for the experiment. By leaving the rubber about 18 hours in room temperature, then monitor the changes. By using DSC, gel point can be achieved just by heating up to 2 minutes. In order to observe the crosslinking structure change during isothermal curing, low curing temperature was desired to keep the silicone rubber within the rheological fixture during heating. In hypothesis, LSR quick crosslink at low temperature. The results are compared further to understand the whole process of curing reaction. [3]

II. METHODOLOGY

A. Materials

A commercially available two-components of silicone rubber is used. The experiment was conducted by reacting Part A which consists polysiloxane, polymethylvinylsiloxane and polymethylhydrosiloxane with Part B consists of of platinum catalyst, polymethylvinylsiloxane, and silica-based in the reaction. Using the silicone rubber which part B contains liquid silicone rubber and part A contains platinum-catalyzed. The double mix and pour technique was used to mix the part A and B. Inadequate mixing is the number one reason for material not curing. The double mix-and pour technique can solve the problem. Part A and B will be measured into different container. The mixing process was conducted by using the ratio of A:B for five samples which were, 10:1, 7:5, 2:5, 5:5, and 1:10.

Combine both part into one container. Thoroughly, the materials were mixed while scrapping the sides and bottom of the container several times. Then, all material has been transfer to a new and clean mixing container. Thoroughly, the materials were mixed again with a clean mixing stick while scraping the sides and bottom of the container. Material was ready to be poured over original model.

B. Differential Scanning Calorimeter (DSC)

The DSC technique measures the instantaneous heat, Q, from a reactive sample as a function of temperature. It can be used directly, accurately and quickly to study the rate of curing from the reaction heat.It is used for the themo-kinetic study of the gel point. The test will be done by manipulated the temperature. The silicone rubber will cure at room temperature will act as reference to the others. By using DSC, lowered the temperature to monitor the polymer degradation which the visualised properties of silicone rubber. Different in amount of heat is required to increase temperature of sample. Polymer degradation will be done by lowering the melting point.

Study on the isothermal curing will be carried out using differential scanning calorimeter (DSC). A Netzsch DSC-204 instrument operated in nitrogen atmosphere using aluminium pans. The silicone rubber was cured at room temperature. It has been act as the reference and standard for calorimeter calibration. The curing was carried out at isothermal temperature at 60,70,80,90℃ with a constant heating rates of 10K/min.

C. Thermal Method

Themal method is another method to determine gel point by crosslinking kinetics LSR. It also called as thermo-kinetic study by using differentials scanning calorimeter (DSC). This study was done at different temperature. It will be compared with Kamal's model which used the reaction rates. By using isothermal measurements about 60,70,80,90℃ to determine gel point. Silicone rubber cured at room temperature will be the reference [2] Curing is a formation of short polymer chains that the chains will branched and cross-linked to form 3D network and it is the time for a gel formation. During isothermal curing, reactant mixture will change via gelation depend on curing temperature and time [3]

D. Kinetics Model

For the kinetics model, Kamal model was selected. Kamal propose a kinetic law based on discontinuous but simple mathematical formula. The degree of crosslinking, time and temperature, were established by the three variables.[6]

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

K is a rate constant according to Arrhenius law.

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

$$t_i = t_o e^{\frac{E}{RT}}$$

In the non-isothermal case, the isothermal induction time is replaced by a reduced dimensionless time $\tilde{t}$ that the end of the induction period is reached when the value of reduced time $\tilde{t}$ reached to 1.

$$\tilde{t} = \int_0^t \frac{dt}{t_i(T)}$$

In contrast, Kamal's autocatalytic model, based on differential equation, simulates progress of the reaction rate $d\alpha/dt$ and the crosslinking degree α at a time, t. by applying the initial conditions $(\alpha = 0\ at\ t = 0)$, the induction time will be included in the model. The reactive part can also described alone by assuming $\alpha = 0\ at\ t = t_2$ where t_2 is the induction time.

$$\frac{d\alpha}{dt} = (K_1 + K_2\alpha^m)(1 - \alpha)^n$$

K_1 and K_2 vary with the temperature according to Arrhenius law as equation.

$$K_1 = A_1 e^{\left(\frac{E_1}{T}\right)} \qquad K_2 = A_2 e^{\left(\frac{E_2}{T}\right)}$$

$$t_2 = B_1 exp\left(\frac{B_2}{T}\right)$$

$B_1(s)\ and\ B_2(K)$ were constants related to the induction time. Kamal autocatalytic model presents an advantage over other laws from the integration of the induction time. This integration, indeed, describes kinetics with short induction time. Kamal's model includes six parameters $(A_1,\ A_2, E_1, E_2, m\ and\ n)$. It has been obtained by smoothing the experimental points using a numerical optimization method. [7]

E. Theoretical Background

Curing kinetics study basic equation of conversion, $d\alpha/dt$ is a concentration of reactants through a temperature-dependent reaction rate constant k(T). By ignoring the reaction details, the curing kinetics can be represented by the variety of phenomenological models of rate equation. The conversion rate is as below

$$\frac{d\alpha}{dt} = k(T)f(\alpha)$$

Where α is the curing conversion,t is the reaction time, $f(\alpha)$ is a kinetic model-dependent function. k(T) is expressed by the Arrhenius equation

$$k(T) = e^{\left(\frac{-Ea}{RT}\right)}$$

A is the pre-exponential factor, E_a is the apparent activation energy, R is the gas constant, T is absolute temperature.

An assumption for the application of DSC technique to curing kinetics has been made. The assumption is that the conversion rate $d\alpha/dt$ is proportional to the heat flow rate dH/dt as

$$\frac{d\alpha}{dt} = \frac{(dH/dt)}{\Delta H}$$

ΔH is the total heat of curing reaction, which was determined from the integration of the non-isothermal DSC curve.

For isothermal DSC measurements, the Kamal model has been described from the curing kinetics of epoxy resins.

$$\frac{d\alpha}{dt} = (K_1 + K_2\alpha^m)(1-\alpha)^n$$

Same as the kinetics model, where m and n are the reaction order, K_1 and K_2 are the non-catalytic and autocatalytic reaction rate constant, respectively. This equation was successfully applied to many curing systems, where there was a maximum in the isothermal reaction rate. Therefore, Kamal’s model has been used for the reaction for DSC. (Hu et al., 2016)

F. Thermo-kinetic Study

The reliability of the model to represent the reaction of the material was affected by the reliability of the measurements used to determine a kinetic model and their ability to cover all the crosslinking steps. At the starting of the network creation by crosslinking, it brings out the mechanical behaviour such as shape, elasticity and the thermal behaviour. The best calculation method of kinetic model can describe the crosslinking reaction. Thus, a DSC study has been done at different temperature to achieve crosslinking. The exothermic signal of the reaction can be detected by the temperature.

The identification of Kamal’s model parameter using the numerical optimizations were as below. The crosslinking degrees are compared with experimental.

$$E = E_1 = E_2 = 73.6 kJ/mol$$
$$A_1 = 2.11 \times 10^7 s^{-1}$$
$$A_2 = 6.97 \times 10^8 s^{-1}$$
$$m = 1.31 \text{ and } n = 1.$$

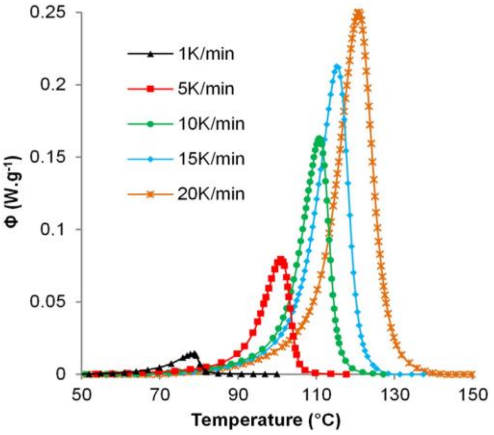


Figure 1 : Heat flow measured using DSC at different heating rates

A good consistency has been reveal for the comparison at different heating rates.based on figure 1, the higher the hearing rates is the more the heat flow which is consistent to literature [8] Experimental and calculated crosslinking rates $d\alpha/dt$ are compared. The reaction rates depend on the thermal diffusion rates within the material.

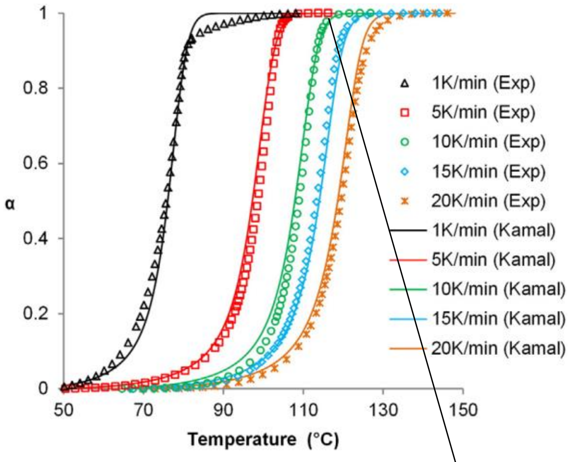


Figure 2: Comparison between experimental and calculated crosslinking degree using Kamal’s model

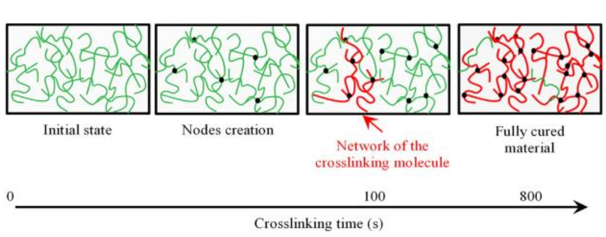


Figure 3: The process of crosslinking

Then the comparison between experimental and calculated crosslinking rate using Kamal's model was done in figure 2. The position and height of the peaks present light deviation. The experimental peak is higher than the calculated for many heating rates. Kamal's model also presents an accurate description of LSR crosslinking. According to [9], the curing process occurred when the gel point was reach at the peak of the graph which is the gel point time shown in figure 3.

The study of polymer liquid gel transition was done by a considerable amount of effort due to the impact of the phenomenon on the development of high tech materials, including adsorbents, membranes, thin optical layers and electronics devices, available for different application. The critical gel point during liquid gel-transition can be describe by the investigation relevance for this phenomenon which related to tests and methods.

During crosslinking phase, the molecular structure and properties was affected by the quick changes. The polymer molecules increase in size and in branching until they form a 3D network of sample size. The moment of apparition of network is called "Gel Point". It marks the change from liquid to solid state.

Moreover, the tests has been be carried out at low temperature (60-90℃). At these temperatures, the average time required for setting up the sample and for starting the collection, is in a small comparison with gel time. The determination of gel time is more accurate and the test are more reproducible at low temperature.

III. RESULTS AND DISCUSSION

A. The Theory of DSC Data

The results obtained are the graph of heat flux against temperature or time. Heating rate used was constant at $10^{\circ}\mathrm{C}/min$ by using the ratio of 1:10, 2:5, 5:5, 7:5 and 10:1. Part A contains liquid silicone rubber and part B contains platinum catalysed. The sample were prepared by using the double mix-and pour technique. Based on our experiment which is to research the effect of heat energy on gelation point, thus first the graph has been analysed on the effect of heat flux on gelation point based on temperature and different ratio.

The graph obtained show that all of the sample undergoes exothermic reaction which also can be defined as crystallization process. For exothermic process, less heat is required to raise sample temperature. At the point where the temperature increase, the heat flux increase with time. According to [2], heat flow is proportional to the crosslinking rate. The heat energy is needed to undergo liquid-solid transition. When temperature increases, liquid become less viscous. It has enough freedom of motion to spontaneously arrange themselves into crystallization, Tc. The glass transition temperature can be determining from the DSC test. When the polymer was heat, the plot will shift upward suddenly after a certain temperature. [15]

Above the glass transition, the polymers have a lot mobility. When they reach the right temperature, they gained enough energy to move into very ordered arrangements which called crystals. When polymers fall into these crystalline arrangements, they give off heat. The temperature at the lowest point of the dip is usually considered to be the polymer's crystallization temperature, or Tc. measure, and that shows the latent energy of crystallization for the polymer. Moreover, the crystallization is an an exothermic transition because the polymer gives off heat when it crystallizes [14]

Next, melting point can be obtain in DSC test. Heat may allow crystals to form in a polymer, but too much of it can be their undoing.

Continued heating may reach to another thermal transition, one called melting. When reach the polymer's melting temperature, or Tm, those polymer crystals begin to fall apart, that is they melt. The chains come out of their ordered arrangements, and begin to move around freely. Well when we reach the Tm, it's payback time. There is a latent heat of melting as well as a latent heat of crystallization. When the polymer crystals melt, they must absorb heat in order to do so. Melting is a first order transition. The temperature of polymer do not rise when reach the melting temperature until all crystals has melted.

Based on figure 4, a step in the plot when the polymer was heated past its glass transition temperature. Then a big dip when the polymer reached its crystallization temperature. Then finally a big peak when the polymer reached its melting temperature. Not everything shown here will be on every DSC plot. The crystallization dip and the melting peak will only show up for polymers that can form crystals. Completely amorphous polymers do not show any crystallization, or any melting either. But polymers with both crystalline and amorphous domains, will show all the features you see above. [15] Furthermore, the peak also show the crosslinking occur. For our sample, it can form crystals as it results in melting and crystallization temperature.

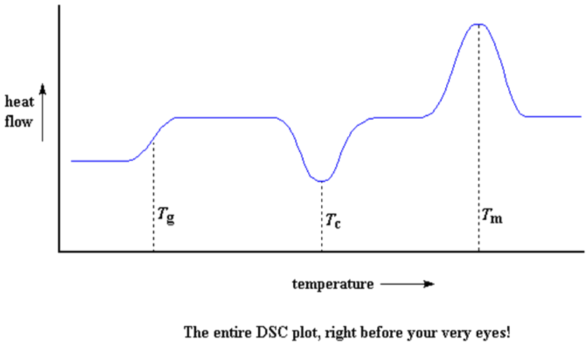
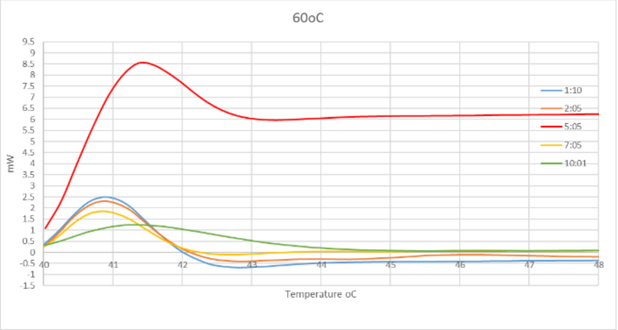


Figure 4: The process of Thermo-Kinetic using DSC

B. Different Temperature with Different Ratio

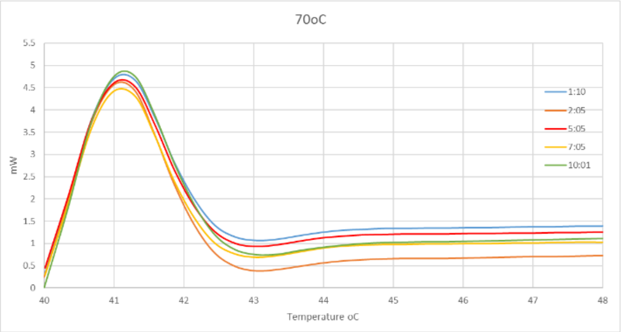
The results shown were varies from the temperature of 60℃,70℃,80℃ and 90℃. The sample was heated from 40℃ to each various temperature. Based on graph 1, the first temperature is 60℃.



Graph 1: Temperature 60℃

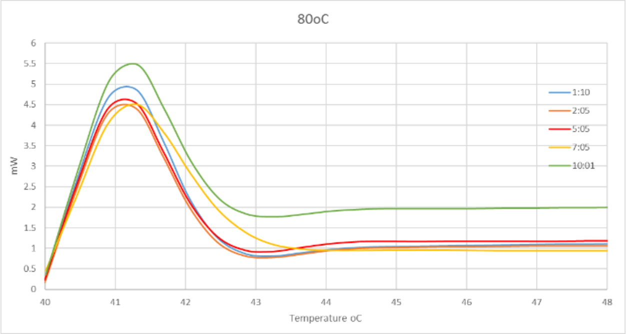
Ratio 5:5 need a higher heat than others which is 8.5mW. While for others were in average from 1 to 2.5mW. Seems like it need so many energy to crystallize. The peak shows the Tm which the latent heat of melting will start to occur after peak. While the temperature needed for the peak is at 41.5℃ for ratio 5:5 and 10:1, while for others is at temperature 41℃. The fastest ratio to begin crystallize is ratio 7:5 at 40.8℃ where the part A is higher than catalyst. The sample become stable at temperature above 48℃. For this test, the heat flux is lower than other test with other temperature.

From graph 2, all of the samples were having quite a same value for the temperature at 70℃, All of the sample shows the heat flux needed at average from 4.3mW to 4.8mW. Seems like it need same heat energy to become crystallization. While the temperature needed for crystallization is at 41℃. The sample become stable at temperature above 48℃. For temperature 70℃, it shows that all of the sample are quite stable and do not have much different between samples.



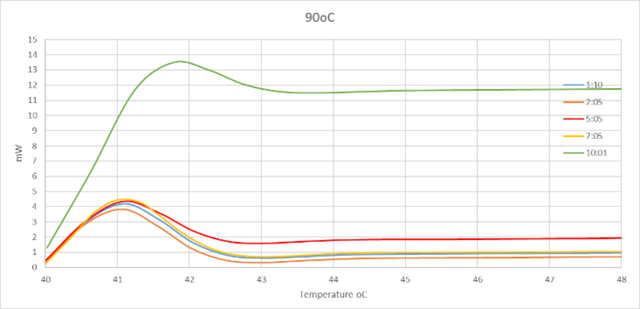
Graph 2: Temperature 70℃

For temperature at 80℃ in graph 3, the heat flux required is higher a little from the previous temperature 70℃. The heat energy is from 4.5 to 5.5mW and the temperature for the peak is at 41℃. It differs in the point of where melting stops for sample 10:1 due to its high heat flux than others. The samples stable at 48℃, but for sample 7:5 it can be seems that the samples were denatured because the graphs shown unstability of the sample until heated to 80℃. Others sample has become stable with constants heat flux. For sample 10:1 it seems that low catalyst would results in higher heat flux needed than others.



Graph 3: Temperature 80℃

Lastly, by referring to graph 4 for sample 90℃, all of the samples results in the same value of heat flux except for ratio 10:1. The heat flux is higher up to 13.5mW to raise the peak where crystallization occur. Tm occur after the heat flux going down. Other samples raise to the peak at 41℃. For sample 10:1 it seems that less catalysts resuls in higher heat flux needed than others. Later on we will discuss on Kamal’s model compared with the results based on others experiment involving differential scanning calorimeter on liquid silicone rubber.

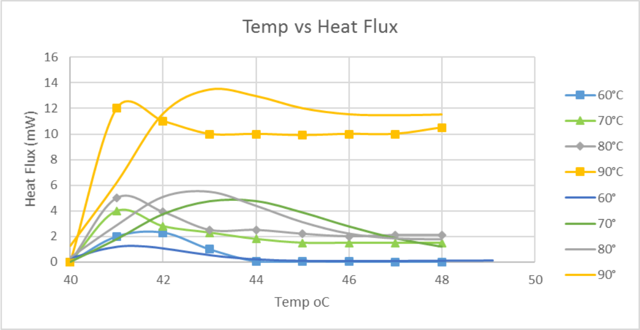


Graph 4: Temperature 90℃

From experimental data, it can be concluded that curing happened at low temperature which is 42℃. Peak point of every graph shows that fully cured materials occurred. Referring to figure 3, the network of crosslink occurs at time 100s, while for this experiment network of crosslink happened at 0.1-0.2s. This experiment shows that silicone rubber that we are using needs low temperature and shorter time for the crosslink to occur. Based on the ratio 10:1, the higher the temperature thus the higher the heat energy required.

C. Comparisons with Kamal’s Theory

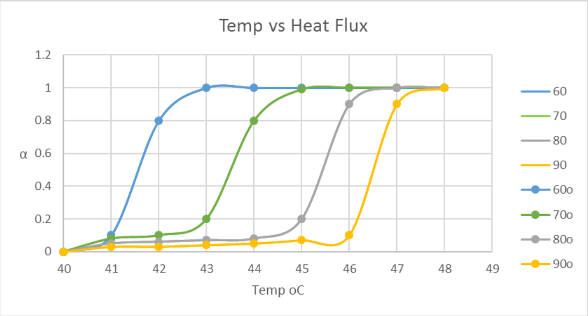
For the comparisons with Kamal’s Theory, the ratio of 10:1 is used. This is due to the different chemical behavior in the ratio than others.



Graph 5: Comparison of heat flux from experimental data (line) and Kamal’s Model (dotted line)

Based on the above graph, it shows the comparison between experimental and calculated crosslinking rates. Kamal’s theory were using the different of heating rates in the experiment. While this study were using different temperature. According to [13], the heat flow is proportional to the crosslinking rates. Thus, the results obtained was according to the literature. The comparison reveals a good consistency at different temperature. Based on the Kamal’s model, the heat flux is lower using Kamal’s model rather than experiment. The graphs shows the similarities with the shape of graph where the crystallization occurs in both experimented and calculated graphs. Both graphs shows there is the latent heat of crystallization and stops at the Tm where the crosslinking happened. Crosslinking occurs at the peak of graph.

Both graphs shows that the latent heat of melting occurs and the sample will be stable at the end of experiment. For the higher temperature, it needs higher heat flux to raise to the peak. Moreover, the Kamal’s model can be used in this experiment as they both shows the same results. The experiments has been carried out in low temperatures. The tests are more reproducible and the determination of gel time or crystal is more accurate. Consequently, the thermal measurements are used to describe the LSR crosslinking by Kamal's model that seems an appropriate kinetic model.



Graph 6: Comparison of heat flux from experimental data (line) and Kamal'sModel (dotted line)

Based on graph 6, the crosslinking rate graph vs temperature shows that both experimental and Kamal's theory data is the same. The crosslinking rate $\alpha = 1$ shows the sample is fully cured. Therefore, the Kamal's theory was valid for the experiments. Lower temperature reach crosslinking fastest than higher temperature. The position and height of the peak present light deviation. The experimental peaks are higher than the calculated one. Kamal's model presents an accurate description of LSR crosslinking.

IV. CONCLUSION

This study demonstrates the reliability of the experimental method applied to characterize LSR materials with the aim of improving our understanding of the material behavior during molding process. Similarly, the kinetic results presented here confirm that Kamal's kinetic model describe well the LSR crosslinking kinetics. Its shape suits the description of crosslinking degrees and their derivatives. The kinetic model and the parameters related to the LSR properties are used to validate the development of an experimental device using a numerical simulation. The experimental setup will be thermally controlled to optimize LSR processing and improve productivity. The liquid silicone rubber crosslink at lower temperature. High temperature is not necessary as the reaction has completely reacted. In conclusion, heat energy increases when using higher temperature and gel point occur at crystallization point where the crosslinking happened and the sampleis fully cured.

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