RHEOLOGICAL CHARACTERIZATION OF VARIOUS PERCENT WEIGHT OF SILICON RUBBER

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***Abstract*— Silicone rubbers are widely used for many industries purpose. There are two type of silicone rubbers which are liquid silicone rubbers and solid silicone rubber. However, liquid silicone rubber is uncured state or adhesive state which is required catalyst to be cured to form solid state. However the curing process is the result of the crosslink and curing agent. However, the right amount of percent weight between the liquid silicone rubber and curing is the key to determine the effectiveness of curing process take place. This report is to study the rheological properties and crosslink behavior on various percent weight of silicone rubber. The method that used in this experiment is mix and pour technique and the equipment involve is Electronic Rheometer. There are 5 sample of different ratio percent weight part A (liquid silicone rubber) and part B (platinum catalyst) which are 1:10, 2.5:7.5, 5:5, 7.5:2.5 and 10:1 As the end of the experiment, percent weight 10:1 give a better potential in term of curing process as it is highly crosslink, crosslink achieve and the sample shown a elastic behavior.**

I. Introduction

Silicone rubber (polysiloxane) is an inorganic synthetic elastomer and are commonly used in industry. It is a polymer that is composed from silicone, carbon, hydrogen, and oxygen that is form from the cross linked. A silicone based polymer. Silicone rubber is generally not reacted, stable properties, able to withstand extreme environment and temperature at -55C-300C. The silicone rubber mechanical properties such as tensile strength, elongation, tear strength and compression set are far superior to organic rubber. [1]

The silicone have become the commercial compound after great electrical insulation and thermal stability demonstrated by Hyde of Dow in 1940. [1] There are two type of silicone rubber. Liquid silicone rubber and Solid silicone rubber. These two type have many wide use in various industries such as medical, electrical chemical etc. In order to form a solid type silicone rubber, a curing process is required by mix the liquid silicone rubber with curing agent.[2]

In uncured state, silicone rubber is in form of liquid or adhesive state. To form a solid state silicone rubber, a curing process is required and this can be done by using platinium – catalysed cure system. Upon the completion of curing process, come of silicone rubber may be have the greater resistance of shear fracture, have stable properties and more elastic. This is result due to the the crosslink of silicone rubber and curing agent. [2] The right amount of ratio between silicone rubber and curing agent will determine the how much of curing process take place

In 1901, new compounds with the formula of R_2SiO was given a name "silicone" by Kipping. This name usually refer as linear polymers or polydimethylsiloxane (PDMS). The attachment of 'organic' and 'inorganic' groups provide the silicone with special characteristic to allow to use in many fields as it have high and low temperature, electronic insulation, great biocompatibility and excellent weathering resistance. [1]

There are several principal steps production of silicone. In 1824, Berzelius discovered Silicon from potassium fluorosilicate reduction with potassium

$$4K + K_2SiF_6 \rightarrow Si + 6\ KF$$

Tetrachlorosilane, SiCl4 is a volatile compound will later produced by the reaction of silicon and chlorine

$$Si + 2Cl_2 \rightarrow SiCl_4$$

In 1863, Friedel and Craft continue the next step and produce the first silicon organic compound known as tetraethylsilane

$$2Zn(C_2H_5)_2 + SiCl_4 \rightarrow Si(C_2H_5)_4 + 2\ ZnCl_2$$

The diluted acid (diethyldiethoxysilane) was observe by Ladenburg in 1871, notice that it will produce decomposed oil at a very high temperature.

The silicone begin to become the commercial compound in 1940 after the thermal stability and excellent resistance to electric of silicone resin was demonstrated by Hyde of Dow Coming. Furthermore, a direct method to produce silicone from Si and MeCl was discovered by Rochow of General Electric. [1]

Silicone rubber have an excellent compression set, odourless and tasteless. It possess a good mechanical properties, great flame resistance and non-toxic combustion product. It also has several of temperature range from -50°C to +300°C. The density of silicone rubber is between 1.05 to 1.60g/cm^3. [1]

Silicone rubber have many broad range of application. For example silicone rubber may use as sound-insulation panels for transportation, coffee machine tubing for household, Ignition technologies for automotive, heat and oil resistance for thermal resistance and many more of uses.

- Thermal aging resistance – There are many application of silicone that required high resistance temperature. For example, it use for heat transfer fluid, ovben seal, electrical cable insulation, etc. When fire occur, the silicone insulation will decompose to provide protection to electrical cable as combustion will start produced due to electrical conducting carbon.
- Chemical aging - At high temperature, the silicone can be degenerate due to depolymerisation catalyst. But, the nature of hydrophobic limit the contact with aqueous solutions and acknowledge many chemical material.

- Climate resistance – Silicone are easy to pigment. They have a low chain-yto-chain interaction and visible wavelght make it suitable to be used as sealant in building industry thus their outstanding weathering resistance.
- Release Properties – The silicone can be mould into any object like a sculpture. The perfect wetting occur due to properties of silicone that has a low surface tension. This low surface energy will help the process of demoulding.
- Biocompatibility – The low chemical reactivity, low surface energy and hydrophobicity of silicones explain the excellent biocompatibility, thus silicone is widely used in medical application.

Polymer is a long molecule chain that lie side by side. When the polymer are chemically chain to each other by covalent bond, it is known as cross linkage. The cross linkage molecule cannot slide over each other easily. This result make the material to become strong and less flexible, making it hard to stretch. [3]

According to Wacker, there are two type of silicone rubber that commonly manufacture which are solid silicon rubber and liquid silicone rubber. In uncured state, silicone rubber is in form of liquid or adhesive state. To form a solid state silicone rubber, a curing process is required and this can be done by using curing agent. The common curing agent that widely used is Platinum – Catalyzes Curing. This catalayze has short cycle time and the curing process is fast. Upon the completion of curing process, some of silicone rubber may have the greater resistance of shear fracture, have stable properties and more elastic. This is result due to the cross link of silicone rubber and curing process. Cross liked is required in order to form raw silicone rubber into stable pure product. [2]

Usually, before the cross link occur, the crosslinked polymer will be moulded. Once the cross linkage process happen, (at high temperature) the object can no longer be shaped due to the heat cause the cross linking to become permanent. This material is known as thermosets. The opposite of this material is known as thermoplastics, which is not cross link material and able to reshape when moulded

The common technique to study the viscoelasticity of material is Dynamic Mechanical Analysis. When a sample is inserted, stress and strain will be applied. This technique will analysing the response in order to obtain phase angel and deformation data. Thus, the damping or tan delta (δ) can be calculated. There are two type of approaches that is applied for DMA. (Smooth-On, 2016)

a) The signal is set at specific frequency, known as Forced Frequency
b) Free resonance

There are few parameter that need to be highlight during DMA. Damping factor or Tan delta is the dissipation of energy in a material under cyclic load. It is use calculate the energy of material release and reported as the tangent of the phase angle. This tell how well for a material absorbing energy. It varies with the state of the material, its temperature, and with the frequency. [2]. Storage modulus or also known as elastic modulus is a material's ability to store energy or energy to spring back while Loss modulus is an ability of a material to dissipate energy when applied to it.

Curing process heavily depend on percent weight of liquid silicone rubber and platinum catalyst. Thus, this study is conducted to study rheologcal properties and crosslink behaviour on various percent weight on silicone rubber.

II. METHODOLOGY

A. Materials

The sample is prepare by using double mix and pour technique. The silicon and curing agent are prepared in a beakers. The curing agent is pour into the silicone with the specific ratio and stirrer it. Next, prepared another new beaker, pour the mixture and stirrer it again. After that, the mixture will be pour into the original beaker and the mixing is completed. Each steps are repeated with a ratio of reactant A (Liquid Silicon Rubber) and Reactant B (Curing Agent) with 10:1, 7.5:2.5, 5:5, 2.5:7.5 and 1:10. [4]

B. Electronic Rheometer

The sample is then pour into measuring system with half the volume of the measuring system amount. The measuring system will be inserted in the Electronic Rheometer. After carefully insert the measuring system and lock it, set the Electronic Rheometer to lift down the measuring system to approximate 1mm. Next the machine will be set to polymer resin to carry out the test for the sample. In order to understand more theory about crosslink of silicone rubber, we need to set the Electronic Rheometer to carried out the tan delta versus temperature to while the plot of storage modulus and loss modulus.

III. RESULTS AND DISCUSSION

A. The effects of temperature on various percent weight of silicone rubber concentration

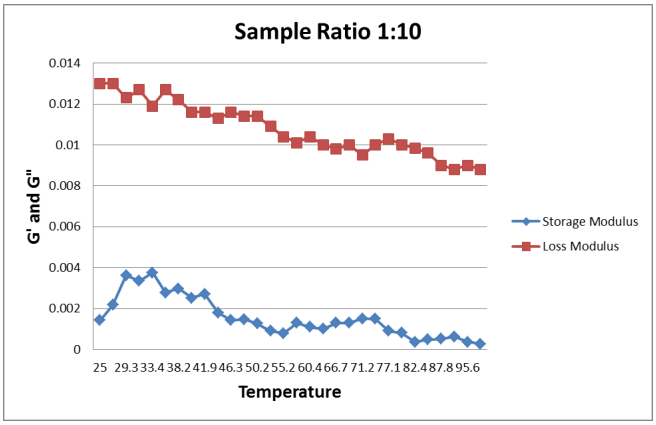
The temperature for every test, it will conducted with constant angular frequency of 0.1 (1/s) and varies in temperature starting from 25°C to 100°C**.**

Ratio 10:1

Table 1: The data of storage and loss modulus for ratio 1:10 percent weight

Measurement	Temperature	Angular Frrequency	Storage Modulus	Loss Modulus
1	25	0.1	0.00143	0.013
2	27.8	0.1	0.00217	0.013
3	29.3	0.1	0.00362	0.012
4	30.6	0.1	0.00335	0.013
5	33.4	0.1	0.00376	0.012
6	36.2	0.1	0.00278	0.013
7	38.2	0.1	0.00298	0.012
8	40.5	0.1	0.00252	0.012
9	41.9	0.1	0.00271	0.012
10	43.9	0.1	0.0018	0.011
11	46.3	0.1	0.00143	0.012
12	49.2	0.1	0.00147	0.011
13	50.2	0.1	0.00126	0.011
14	53.7	0.1	0.000898	0.011
15	55.2	0.1	0.000792	0.010
16	58.2	0.1	0.0013	0.010
17	60.4	0.1	0.0011	0.010
18	63.5	0.1	0.001	0.010
19	66.7	0.1	0.0013	0.010
20	69	0.1	0.0013	0.010
21	71.2	0.1	0.0015	0.010
22	74.5	0.1	0.00149	0.010
23	77.1	0.1	0.0009	0.010
24	79	0.1	0.0008	0.010
25	82.4	0.1	0.000373	0.010
26	85.6	0.1	0.000488	0.010
27	87.8	0.1	0.00052	0.009
28	90.2	0.1	0.00063	0.009
29	95.6	0.1	0.00037	0.009
30	99.7	0.1	0.00027	0.009

Figure 1: The trend of storage and loss modulus for ratio 1:10 percent weight



This test is conducted with ratio 1: 10 part A and Part B respectively at angular velocity 0.1 (1/s). For this test, the graph shown that the storage and loss modulus are fluctuate pattern starting from 25°C to 100°C. Part A has higher viscosity than part B. Since the sample has more ratio of part B than part A, the sample solution consider has a low viscosity. This explain why the measure signal become noisy and uncertainty.[5]

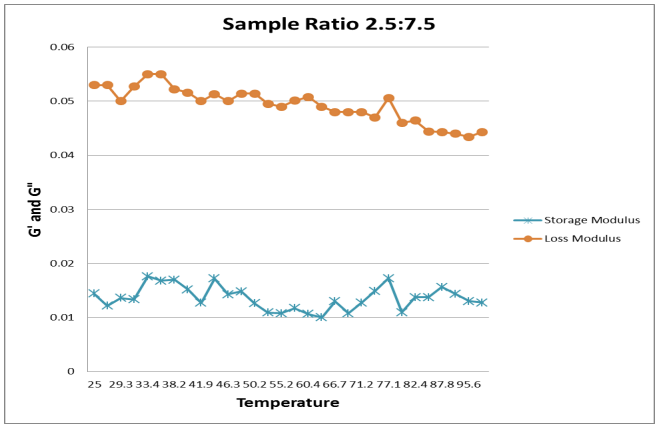
When the temperature increase, the catalyst start to aggregate and cause the storage modulus aggregate. But the cross link does not occur between storage modulus and loss modulus and the storage modulus remain lower than loss modulus. When loss modulus dominate and much more higher than storage modulus. The sample is consider as liquidity properties and indicate that curing process is not achieve. [6]

Ratio 2.5:7:5

Table2: The data of storage and loss modulus for ratio 2.5:7.5 percent weight

Measurement	Temperature	Angular Frrequency	Storage Modulus	Loss Modulus
1	25	0.1	0.01443	0.053
2	27.8	0.1	0.01217	0.053
3	29.3	0.1	0.01362	0.050
4	30.6	0.1	0.01335	0.053
5	33.4	0.1	0.0176	0.055
6	36.2	0.1	0.0168	0.055
7	38.2	0.1	0.01698	0.052
8	40.5	0.1	0.0152	0.052
9	41.9	0.1	0.01271	0.050
10	43.9	0.1	0.0172	0.051
11	46.3	0.1	0.0143	0.050
12	49.2	0.1	0.0148	0.051
13	50.2	0.1	0.0126	0.051
14	53.7	0.1	0.010898	0.050
15	55.2	0.1	0.010792	0.049
16	58.2	0.1	0.0117	0.050
17	60.4	0.1	0.01066	0.051
18	63.5	0.1	0.01	0.049
19	66.7	0.1	0.013	0.048
20	69	0.1	0.010776	0.048
21	71.2	0.1	0.01276	0.048
22	74.5	0.1	0.0149	0.047
23	77.1	0.1	0.01724	0.051
24	79	0.1	0.010976	0.046
25	82.4	0.1	0.01373	0.046
26	85.6	0.1	0.01373	0.044
27	87.8	0.1	0.01563	0.044
28	90.2	0.1	0.014373	0.044
29	95.6	0.1	0.01303	0.043
30	99.7	0.1	0.012773	0.044

Figure 2: The trend of storage and loss modulus for ratio 2.5:7.5 percent weight



On this test, the ratio is conducted with part A lower than part B, 2.5:7.5. The graph shown similar pattern for just like ratio 1: 10 which is uncertainty and fluctuated pattern. This main reason for this reason is because the test sample has low viscosity. [6] This will result the signal receive to be inconsistent.

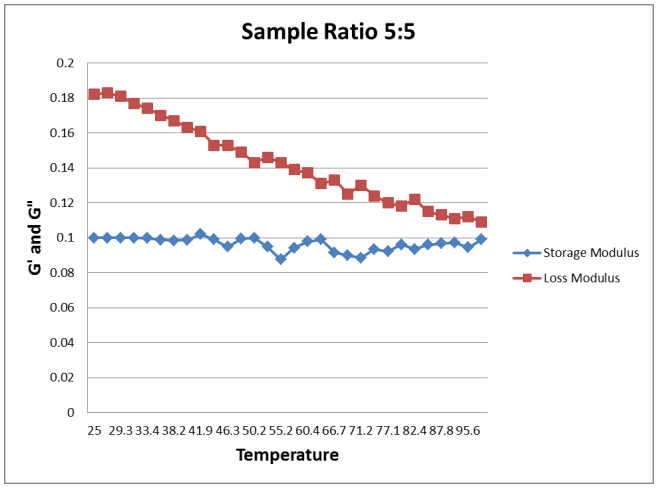
As the temperature increase, the storage modulus become uncertainty as the catalyst (part B) begin to react at desired temperature for the catalyst to become more active. Furthermore, the loss modulus dominate than storage modulus at the end of the test. This shown that the sample remain as liquidity properties.[5] Thus thre is no curing process happen as there is no cross link between two modulus.

Test 5:5

Table 3: The data of storage and loss modulus for ratio 5:5 percent weight

Measurement	Temperature	Angular Frrequency	Storage Modulus	Loss Modulus
1	25	0.1	0.1	0.182
2	27.8	0.1	0.1	0.183
3	29.3	0.1	0.1	0.181
4	30.6	0.1	0.1	0.177
5	33.4	0.1	0.0997	0.174
6	36.2	0.1	0.0988	0.17
7	38.2	0.1	0.0985	0.167
8	40.5	0.1	0.0988	0.163
9	41.9	0.1	0.102	0.161
10	43.9	0.1	0.099	0.153
11	46.3	0.1	0.0948	0.153
12	49.2	0.1	0.0993	0.149
13	50.2	0.1	0.0999	0.143
14	53.7	0.1	0.0948	0.146
15	55.2	0.1	0.0875	0.143
16	58.2	0.1	0.0942	0.139
17	60.4	0.1	0.0978	0.137
18	63.5	0.1	0.099	0.131
19	66.7	0.1	0.0915	0.133
20	69	0.1	0.0898	0.125
21	71.2	0.1	0.0886	0.13
22	74.5	0.1	0.0934	0.124
23	77.1	0.1	0.0921	0.12
24	79	0.1	0.0962	0.118
25	82.4	0.1	0.0934	0.122
26	85.6	0.1	0.096	0.115
27	87.8	0.1	0.0967	0.113
28	90.2	0.1	0.0972	0.111
29	95.6	0.1	0.0945	0.112
30	99.7	0.1	0.099	0.109

Figure 3: The trend of storage and loss modulus for ratio 5:5 percent weight



This test is conducted with same equal ratio 5:5 part A and part B respectively, the data show uniform points for storage modulus and loss modulus which is linear pattern. As temperature increase, the pattern for storage and loss modulus slowly come in contact with each other to form a crosslink.. The same amount of ratio will potentially undergoes a curing process but it take some time. Based on the graph, it is predicted that the process of cross link would happen more then 100°C for ratio 5 : 5

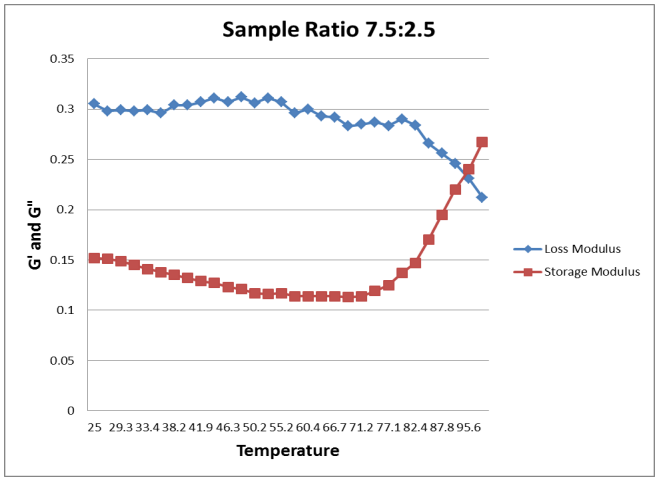
At the end of the test, the sample remain liquid as the loss modulus dominate storage modolus. The cross link happen for this sample in this is cannot be seen in this graph, thus specific point for this sample cannot be determined. However, it is safe to say that the curing process for 5:5 will likely to occur but with very slow rate and high temperature

Ratio 7.5:2.5

Table 4: The data of storage and loss modulus for ratio 7.5:2.5 percent weight

Measurement	Temperature	Angular Frequency	Storage Modulus	Loss Modulus
1	25	0.1	0.152	0.305
2	27.8	0.1	0.151	0.298
3	29.3	0.1	0.149	0.299
4	30.6	0.1	0.145	0.298
5	33.4	0.1	0.141	0.299
6	36.2	0.1	0.138	0.296
7	38.2	0.1	0.135	0.304
8	40.5	0.1	0.132	0.304
9	41.9	0.1	0.129	0.307
10	43.9	0.1	0.127	0.311
11	46.3	0.1	0.123	0.307
12	49.2	0.1	0.121	0.312
13	50.2	0.1	0.117	0.306
14	53.7	0.1	0.116	0.311
15	55.2	0.1	0.117	0.307
16	58.2	0.1	0.114	0.296
17	60.4	0.1	0.114	0.3
18	63.5	0.1	0.114	0.293
19	66.7	0.1	0.114	0.292
20	69	0.1	0.113	0.283
21	71.2	0.1	0.114	0.285
22	74.5	0.1	0.119	0.287
23	77.1	0.1	0.125	0.2832
24	79	0.1	0.137	0.29
25	82.4	0.1	0.147	0.284
26	85.6	0.1	0.17	0.266
27	87.8	0.1	0.195	0.256
28	90.2	0.1	0.22	0.246
29	95.6	0.1	0.24	0.231
30	99.7	0.1	0.267	0.212

Figure 4: The trend of storage and loss modulus for ratio 7.5:2.5 percent weight



This test is conducted for sample ratio 7.5:2.5 part A and part B respectively. When temperature reached at 71.2°C the storage modulus begin to shoot rapidly until the cross link happen between storage modulus and loss modulus. For this sample, it has high viscosity as part A is more than part B.Thus the signal is more steady.[8] The specific point or cross link occur at 94°C.

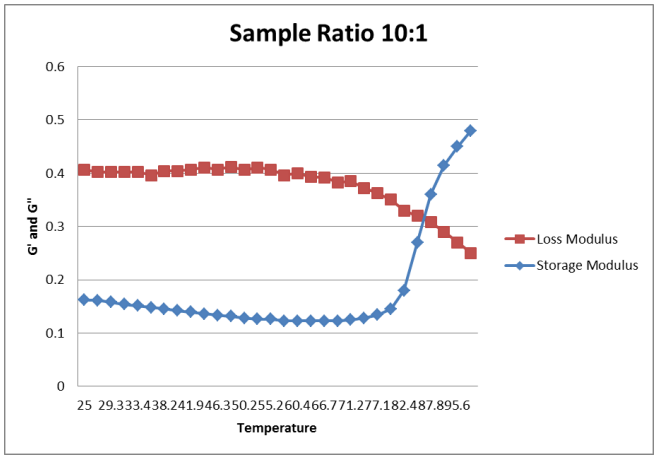
At the end of the test, the storage modulus dominate loss modulus,(G'>G") therefore it indicate that the sample have elastic behavior. [10] The gap between storage modulus and loss modulus after the curing point is close to each other and it consider as lightly cross-linked. [6]

Ratio 10: 1

Table 5: The data of storage and loss modulus for ratio 10:1 percent weight

Measurement	Temperature	Angular Frrequency	Storage Modulus	Loss Modulus
1	25	0.1	0.162	0.407
2	27.8	0.1	0.161	0.402
3	29.3	0.1	0.158	0.403
4	30.6	0.1	0.154	0.402
5	33.4	0.1	0.151	0.403
6	36.2	0.1	0.148	0.396
7	38.2	0.1	0.145	0.404
8	40.5	0.1	0.142	0.404
9	41.9	0.1	0.139	0.407
10	43.9	0.1	0.136	0.411
11	46.3	0.1	0.133	0.407
12	49.2	0.1	0.131	0.412
13	50.2	0.1	0.128	0.406
14	53.7	0.1	0.126	0.411
15	55.2	0.1	0.126	0.407
16	58.2	0.1	0.123	0.396
17	60.4	0.1	0.123	0.4
18	63.5	0.1	0.123	0.393
19	66.7	0.1	0.123	0.392
20	69	0.1	0.123	0.383
21	71.2	0.1	0.125	0.385
22	74.5	0.1	0.128	0.372
23	77.1	0.1	0.134	0.362
24	79	0.1	0.145	0.35
25	82.4	0.1	0.18	0.33
26	85.6	0.1	0.27	0.32
27	87.8	0.1	0.36	0.308
28	90.2	0.1	0.415	0.29
29	95.6	0.1	0.45	0.27
30	99.7	0.1	0.48	0.25

Figure 5: The trend of storage and loss modulus for ratio 10:1 percent weight



For this test, the For this test, the graph shown that the storage and loss modulus is in uniform pattern at lower temperature. As the temperature increase to 50 the storage modulus begin to increase tremendously. The crosslink occur for this sample. The specific point for this sample is at 86°C .Since the sample has more ratio of part A than part B, the sample solution consider has a high viscosity. This explain why the measure signal is much more steady compare to other sample ratio.

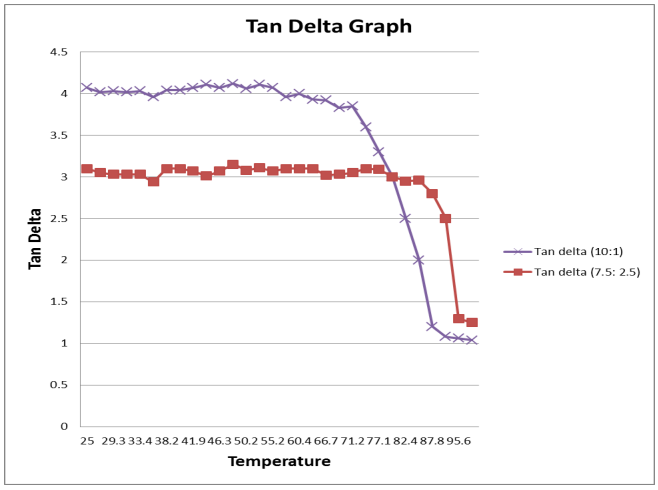
Based on the graph, the storage modulus dominate loss modulus(G'>G"); as temperature increase, thus making the sample to become elastic behavior According to R. Bruce Prime , the gap between storage and loss is for this graph is consider as highly crosslink, as the gap is bigger than ratio 7.5:2.5 thus indicating the tighter network structure and higher stiffness.[6]

B. The tan delta on cross link ratio percent weight of silicone rubber concentration

Table 6: The data tan delta (10:1) and tan delt (7.5:2.5)

Measurement	Temperature	Tan Delta (10: 1)	Tan delta (7 : 5)
1	25	4.07	3.1
2	27.8	4.02	3.05
3	29.3	4.03	3.03
4	30.6	4.02	3.03
5	33.4	4.03	3.03
6	36.2	3.96	2.94
7	38.2	4.04	3.1
8	40.5	4.04	3.1
9	41.9	4.07	3.07
10	43.9	4.11	3.01
11	46.3	4.07	3.07
12	49.2	4.12	3.15
13	50.2	4.06	3.08
14	53.7	4.11	3.11
15	55.2	4.07	3.07
16	58.2	3.96	3.1
17	60.4	4	3.1
18	63.5	3.93	3.1
19	66.7	3.92	3.02
20	69	3.83	3.03
21	71.2	3.85	3.05
22	74.5	3.6	3.1
23	77.1	3.3	3.09
24	79	3	3
25	82.4	2.5	2.95
26	85.6	2	2.96
27	87.8	1.2	2.8
28	90.2	1.08	2.5
29	95.6	1.062	1.3
30	99.7	1.04	1.25

Figure 6: The trend of tan delta (10:1) and tan delt (7.5:2.5)



According to R. Bruce Prime, the tan delta become frequency independent during curing process, where tan delta seem to be close but not necessarily equal to one.[6] There two sample test that achieve crosslink between two modulus which are 10:1 and 7.5:2.5. Both trend for tan delta drop drastically as the crosslink of both sample achieve.

For ratio 10:1, the tan delta is nearer to 1 compare sample ratio 7.5:2.5. The closer the tan delta equal to 1. Based on the the curing process occur when the storage modulus equal to loss modulus or tan delta equal to one. Thus ratio 10:1 is more effective in term curing process and gelification process

IV. Conclusion

Based on the test conducted on all sample ratio, it is conclude that ratio 10:1 is a better weight percent for effective curing process as the cross link occur at low temperature compare to other ratio weight percent. Besides that, it has achieve high crosslink after the gelification take place, which consider the silicone to be more stiffness and tighter network structure. Lastly the tan delta for this ratio is nearer to 1 which consider the best effective of curing process.

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