

# Rheological Comparison of Silicone Rubber Crosslinking with Platinum Catalysts and Triethylamine, Methanol & Ethanolamine Solvents

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**Abstract:** The control of silicone rubber's viscoelastic properties such as loss factor, storage and loss moduli at crosslinking stage is crucial in their malleability. Hence, the objective in this study is to investigate the rheological behaviour of silicone rubber cured under different formulation using platinum catalysts and triethylamine, methanol & ethanolamine solvents. Measurements were conducted for the silicone rubber to cross-linker ratios of 2.5:7.5, 5:5, 7.5:2.5 and 10:1 at different temperatures, as well as for the silicone rubber with triethylamine, methanol and ethanolamine at different angular frequencies. The crossover of storage and modulus curve which signifies a gel point was not observed at higher ratios of platinum used across the temperature range of 25 – 100°C. However, the crossover was observed at 89 and 95°C with the formulation ratios of 10:1 and 7.5:2.5, respectively. On the other hand, the crossover point was observed for silicone rubber at 100 s<sup>-1</sup> for triethylamine, 3 s<sup>-1</sup> and 100 s<sup>-1</sup> for methanol, and 70 s<sup>-1</sup> alongside 290 s<sup>-1</sup> for ethanolamine. The presence of gel point indicates that crosslinking of silicone rubber and this study proves the possibility of controlling the crosslinking behaviour.

**Keywords:** Silicone rubber, Storage modulus, Loss modulus, Crosslink, Glass transition temperature, Rheological measurement

## 1. INTRODUCTION

Silicone rubber is a synthetic elastomer based on polyorganosiloxanes with excellent durability towards temperature and used as feedstock for high-performance materials. The molecular structure is made up of basic building block of silicone-oxygen (Si-O) bond as the backbone of the molecules and the organic group attached to the silicon atom through silicon-carbon (Si-C) bond [1- 2]. Silicone rubber has many excellent characteristics due to the presence of both organic groups attached to the inorganic Si-O backbone such as high thermal and oxidative resistance as well as a great resistance against electromagnetic and radiation compared to other organic plastics. It can maintain electrical and mechanical properties over an extensive range of temperature [3- 4]. Heat resistance of silicone rubber was far better than any other organic rubbers. No alteration of silicone rubber properties was recorded at 150°C and it can withstand over 10000 consecutive hours of usage even at 200°C for short term performance. It also can endure very low temperature as the embrittlement point

for silicone rubber was around -60 to -70°C compared to -20 to -30°C of other rubbers. Thus, silicone rubber retains its elasticity at temperature when organic rubber turns brittle.

Silicone rubber hardens when heated in air but softens when sealed as it deteriorates due to the degradation of the siloxane polymer [5]. Manipulation of silicone rubber formula can help to prevent the softening phenomenon. Ji et al. [6] reported that using methoxyl-capped MQ silicone resin (MMQ) as crosslinker in RTV silicone rubber produced an improvement in light transmission, hardness and tensile strength due to the dense crosslinking structures in the polymer structure. One of the mechanisms to crosslink silicone rubber is by addition curing or hydrosilylation, which involved a combination of polysiloxane containing hydrosilane (Si-H) and unsaturated organic compound containing catalyst such as platinum [7]. Throughout the crosslinking phase, changes in the molecular structure and properties are bound to occur. Rearrangement of molecules leads to nucleation and growth of polymer until they form a network of interconnected molecules through covalent

bond. The moment of appearance of the network is termed as gel point. Gel point marks the transition from the liquid phase to solid phase [8]. Prior to gel point, the molecules are limited in size, mobile and can flow out or dissolve in solvent. After gel point, the molecules form an interconnected network and no longer able to flow or dissolve [9]. In the meanwhile, the molecules continue to gradually bond by bridges until the complete network is formed. This process is represented by crosslinking degree [10]. Li et al. [11] investigated the properties of addition-cure liquid silicone rubber (ALSR) prepared through hydrosilylation process using platinum catalyst in concentration ranges from 5 to 100 ppm. It was reported that using platinum catalyst was able to increase the cure rate of ALSR through the hydrosilylation process. The erosion rate of the produced ALSR was also improved as higher concentration of platinum catalyst used. The optimum thermal stability and optimum mechanical properties was also reported to be at platinum catalyst concentration of 15 ppm [11]. Aside from that, Chen et al. [12] reported that by using different formulation of platinum catalyst and nitrogen-containing silane, the thermal stability of silicone rubber can also be improved due to the synergistic effect between platinum catalyst and nitrogen containing silane. This is because the nitrogen atom coordinated with platinum and enhance the catalytic efficiency of platinum.

In this work, the effect of different formulations of silicone rubber and crosslinker with and without the presence of solvent (i.e ethanolamine, methanol and triethylamine) on the crosslinking process was investigated in terms of rheological properties. Rheology behaviour is useful to measure the viscoelasticity changes on the gelation threshold at the condition when the three-dimensional network appears [13]. It is important to find the optimum ratio of silicone rubber to crosslinker in order to obtain a formulation ratio that can produce a stable product with an improved mechanical properties as different formulation ratio produces different properties of product which will have different application in real life scenario. It is also crucial to investigate how different solvent affects the cured silicone rubber due to the different functional group present in the solvent molecules.

## 2. EXPERIMENTAL PROCEDURE

### 2.1. Materials

The materials involved in this experiment were divided into two portions i.e Part A and Part B. Silicone rubber (Part A) was purchased from Shen Zhen Inno Silica Co. Ltd. while Part B consisted of the catalyst platinum solutions (containing platinum and polydimethylsiloxane (PDMS) as crosslinker). Ethanolamine, methanol and triethylamine was used as solvents.

### 2.2. Preparation of Samples

The sample was prepared by mixing 100mL of silicone rubber (Part A) with 10 mL of crosslinker solution (part B) for a 10:1 formulation ratio. The formulations of silicone rubber to crosslinker used were varied in 2.5:7.5, 5:5, 7.5:2.5 and 10:1 ratio where the reaction could occur in limiting and excess platinum solution. Various ratios were chosen to be investigated in order to find the optimum condition for the yield to have the most stable properties in order to predict the foaming behaviour in the future. Each material was used as received without any other treatment prior to the experiment. Another set of experiment was conducted to investigate the solvent effect to the crosslinking process, by adding different solvent i.e ethanolamine, methanol and triethylamine to the sample with 10:1 formulation ratio.

### 2.3. Rheology Measurements

Rheological instrument Physica MCR 301 (Anton Paar) was utilized to characterize and measure the storage and loss modulus of the sample. For different formulation experiment, the dynamic temperature sweeps were carried out at temperature ranging from 25 to 100°C, controlled by an environment controller with an accuracy of  $\pm 0.05^\circ\text{C}$ . The experiment was conducted at constant frequency and deformation with Couette geometry plate of 20 mm diameter. The temperature was kept constant at 25°C in the frequency sweeps experiment.

### 2.4. Fourier Transform Infrared Spectroscopy

Fourier Transform Infrared (FTIR) spectroscopy (Thermo Nicolet) with wave numbers ranging from 500 to 4000  $\text{cm}^{-1}$  was used to analyse the functional group of the samples.

## 2.5. Calculation

Gel point is considered as the point corresponding to  $\tan \delta = 1$  regardless of its temperature or frequency [14].  $\delta$  is the loss factor or sometimes called loss tangent, described in Equation 1.

$$\tan \delta = \frac{G''}{G'} = 1 \quad (1)$$

where  $G'$  and  $G''$  are the storage and loss moduli, respectively [15- 18]. Loss factor is the extent of energy lost and signifies the mechanical damping or internal friction in a viscoelastic system. It is a dimensionless number and a higher loss factor value represents highly nonelastic material and vice versa [17].

Storage modulus,  $G'$  describes the stiffness of a viscoelastic material. It is proportional to the energy stored during a loading cycle and is represented as Equation 2.

$$G' = \frac{\sigma_0}{\varepsilon_0} \cos \delta \quad (2)$$

where  $\sigma_0$  and  $\varepsilon_0$  are stress and strain, respectively [17]. The elastic property of rubber is close to those of metallic spring with energy absorbing properties like viscous liquid. It allows rubber to retain a constant form after deformation while at the same time absorbs the mechanical energy [19- 20].

The loss modulus,  $G''$  in Equation 3 [17] is proportional to the energy released during one loading cycle. It represents the energy lost as heat and is the extent of vibrational energy that has been transformed during vibration and cannot be recovered. The loss modulus is imperative to be studied due to the environmental concerns over the application of high damping material to a vibrating surface which converts energy to heat. The heat is dispersed within the material itself and not radiated as airborne noise. Hence, for structural application where sound or vibration absorption is needed, a high internal friction is required to reduce the effect of undesirable vibrations [21].

$$G'' = \frac{\sigma_0}{\varepsilon_0} \sin \delta \quad (3)$$

## 3. RESULTS & DISCUSSION

Figure 1 shows the plots of the storage ( $G'$ ) and loss ( $G''$ ) moduli at varied temperatures for multiple formulations of silicone rubbers. For 2.5:7.5 formulation of silicone rubber to crosslinker (Figure 1a), the storage modulus did not show a significant change in the curve while the loss modulus demonstrated slight increase as the temperature increased.

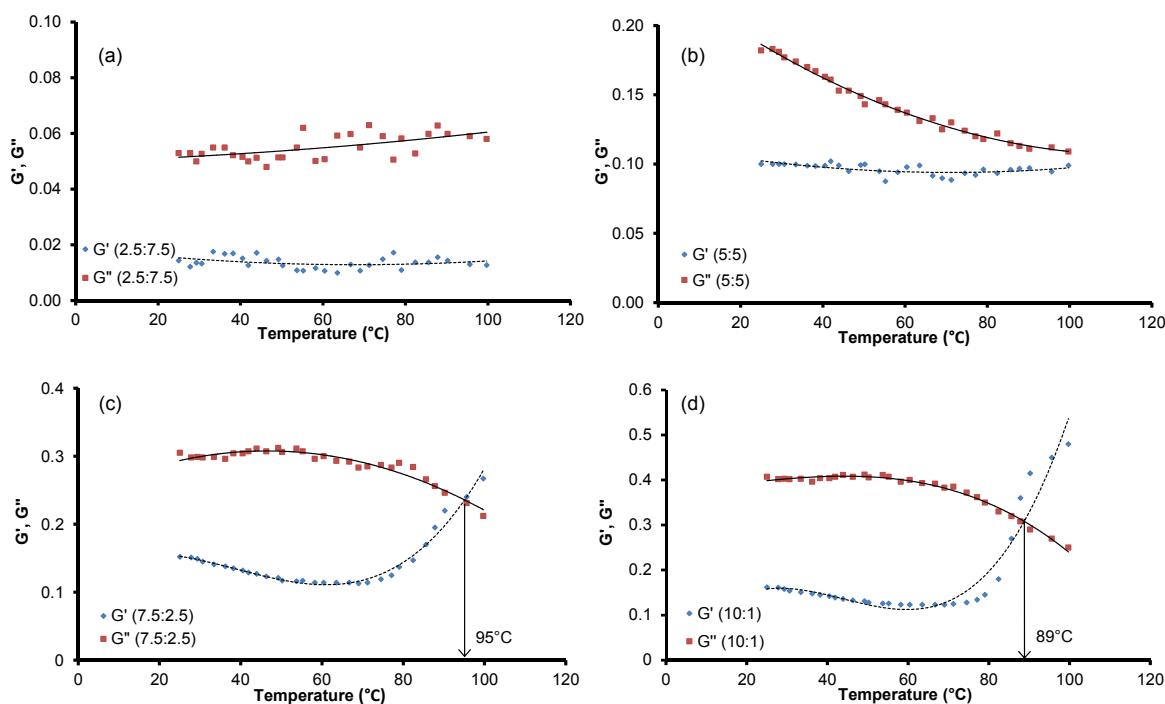


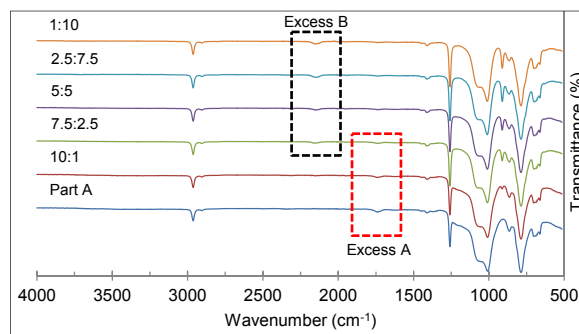
Fig. 1. Storage and loss moduli of silicone rubber system with different formulation at varying temperature.

For 5:5 ratio (Figure 1b), the storage modulus also did not exhibit a significant change in the curve while the loss modulus portrayed a decreasing curve as the temperature increased. The trend showed that the loss modulus was nearing the storage modulus value as the temperature increased. This suggests a possibility of crossover to occur above 100°C. Higher ratio of silicone rubber to crosslinker solutions such as in 7.5:2.5 (Figure 1c) improved the condition of the system since the crossover between storage and loss moduli was observed.

As the temperature rose,  $G''$  experienced significant decrease while  $G'$  observed a sharp surge. This means a transition of phase started to occur during the heating cycle [22]. Further hike in temperature produced a crossover at 95°C, indicating that gel point was achieved. A crossover between storage and loss modulus was considered as the transition point where the polymer transformed from linear polymer to crosslinked polymer [23]. The transition state was caused by the growth of linked structure over a large distance in a material. The long-range connectivity significantly affected the physical properties in general. Prior to gel point occurring, the material could flow and relax. At the gel point, the crosslinks were fully established, and the gel network produced had ceased to flow [24], or the stress/strain invariants had to exceed a yield value to be able to flow [25]. For 10:1 formulation of silicone rubber to crosslinker (Figure 1d), the trend of the curve was similar to the 7.5:2.5. However, the crossover of storage and loss modulus occurred at a lower temperature which was 89°C. At higher amount of crosslinker (platinum solution), the difference in the reaction was postulated to be predominantly attributed from the dilution effect due to the excess amount of platinum solution present. Hence the probability of a crosslink formation to occur was small.

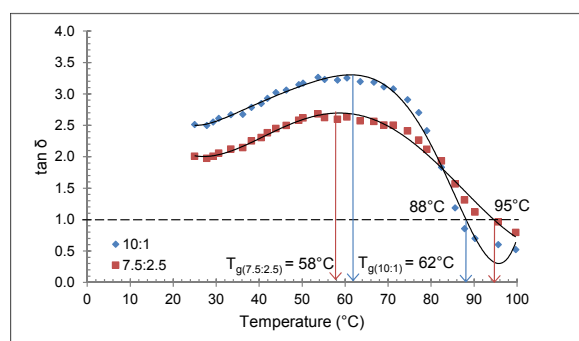
Figure 2 shows the FTIR spectra for the silicone rubber in different ratios of Part A and Part B. The crosslinked silicone rubber spectra at different ratios were compared with the spectrum of Part A. All tested combinations had a peak at 2962 cm<sup>-1</sup> showing the presence of CH<sub>3</sub> group. An excess of Part B was detected for 7.5:2.5 to 1:10 with the highest platinum solutions 1:10 having a more significant sharper peak. This means more unreacted species of Part B as its fraction got

higher. Meanwhile, only 10:1 ratio showed no absorption band around 2153-2161 cm<sup>-1</sup> for Si-H group in Part B, indicating that complete hydrosilylation process was accomplished [26]. In the meanwhile, excess silicone rubber (Part A) was observed for the 7.5:2.5 and 10:1 formulations.



**Fig. 2.** FTIR spectrum of product silicone rubbers

The glass transition temperature,  $T_g$  is usually the temperature at which the peak of loss factor ( $\tan \delta$ ) is maximum [27]. Figure 3 shows the temperature dependence of loss factor for silicone rubber/crosslinker formulation ratios at 7.5:2.5 and 10:1.



**Fig. 3.** Temperature dependence of  $\tan \delta$  (loss factor) of the silicone rubber/crosslinker system at 10:1 and 7.5:2.5 formulation ratios.

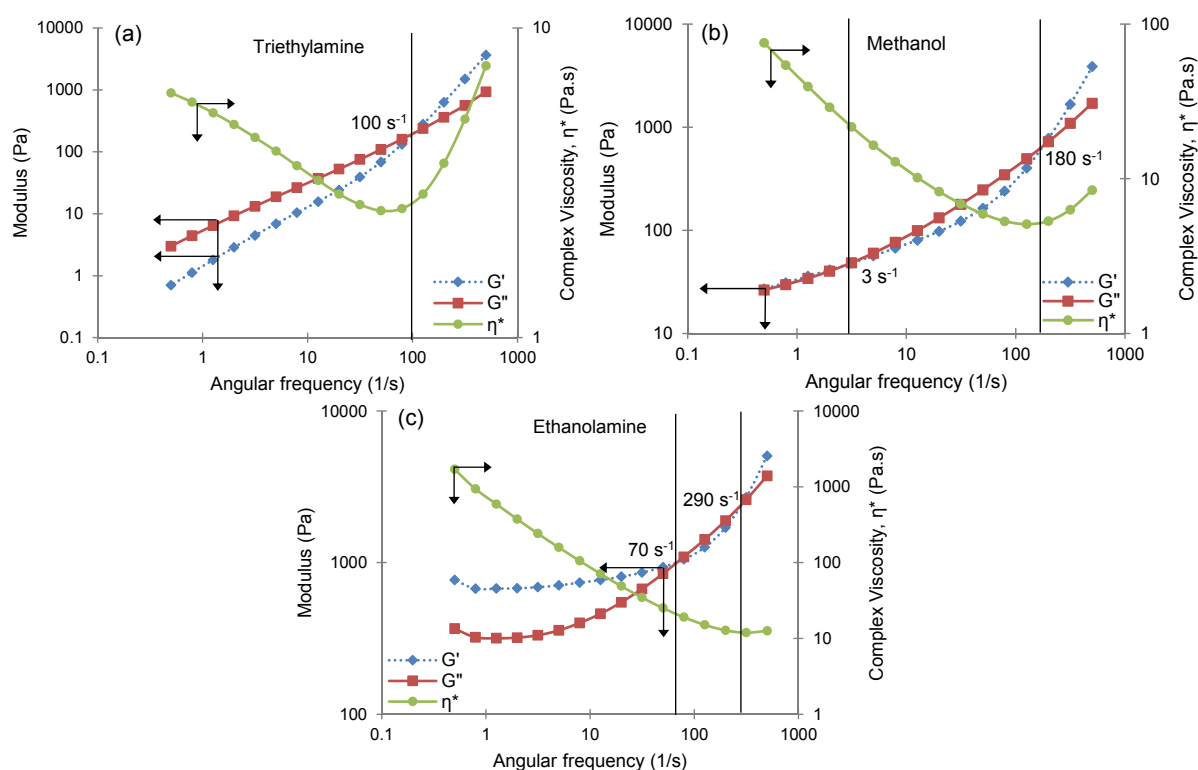
The  $T_g$  varied with different formulation ratio with both 7.5:2.5 and 10:1 showed a broad peak of  $T_g$  at 58°C and 62°C, respectively. The peak of  $\tan \delta$  and area under of the curve declined with the increase of silicone rubber monomer and decrease of platinum. The increase in the  $T_g$  could be explained by the higher presence of silicone rubber monomer which reduced its molecular mobility by establishing physical interaction with the neighbouring chains of silicone rubber matrix. The determination of gel point also could be measured graphically from the curve of  $\tan \delta$ , by taking the intersection value of  $\tan \delta$  and arbitrary

line at  $\tan \delta = 1$  as shown by the dashed line in Figure 3. By extrapolating the  $\tan \delta$  intersection to the x-axis, the gel points obtained were 95°C and 88°C for 7.5:2.5 and 10:1 ratios, respectively. These values showed good agreement with the gel point determined from the intersection of storage and loss modulus values (Figure 1) where the gel points obtained were 95°C and 89°C for 7.5:2.5 and 10:1 formulations, respectively.

Figure 4 illustrates the storage and loss moduli of silicone rubber in the presence of different chemical solutions together with the complex viscosity,  $\eta^*$  at different frequencies and at room temperature after curing. The magnitudes for the storage and loss moduli in triethylamine, methanol, and ethanolamine, were in increasing in that order. All systems showed that the viscoelasticity of silicone rubber increased when frequency grew. The frequency crossover point was also observed to occur for all systems. In Figure 4a, the frequency crossover point occurred at 100 s<sup>-1</sup> for triethylamine. Prior to that, the loss modulus,  $G''$  was higher than the storage modulus,  $G'$ .

In this region, the  $G''$  dominated and viscous behaviour triumphed. Above the crossover point,  $G'$  continued to rise, indicating a shorter relaxation time [28].  $G'$  was higher than  $G''$  after the crossover point and the elastic behaviour dominated, indicating good storage stability of the gel network [29].

Unlike triethylamine, the presence of methanol and ethanolamine affected the curing process of silicone rubber differently. In Figure 4b, the frequency crossover point occurred at 3 s<sup>-1</sup> and 180 s<sup>-1</sup> for methanol. At angular frequency below 3 s<sup>-1</sup>, the storage and loss moduli were similar in value. Then, the loss modulus dominated over the storage modulus (3 s<sup>-1</sup> < angular frequency < 180 s<sup>-1</sup>) until it reached the second crossover point at 180 s<sup>-1</sup>. It was clear that chemical solutions used affected the crossover point of the system. After the 180 s<sup>-1</sup>, storage modulus showed an elastic property. For the silicone rubber with ethanolamine (Figure 4c),  $G'$  predominated at the low angular frequency region, showing elastic behaviour.

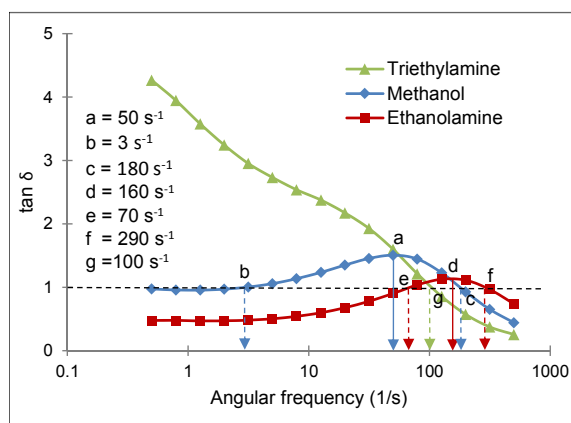


**Fig. 4.** Figure 4: Storage and loss moduli of silicone rubber in different chemical solutions and the complex viscosity for the same system at different angular frequencies recorded at room temperature.



The first crossover point was at  $70 \text{ s}^{-1}$ . As the frequency increased, both storage and loss moduli showed an increasing trend. Albeit being lower than  $G'$ ,  $G''$  curve showed a sharp increase compared to  $G'$  below  $70 \text{ s}^{-1}$ . After the first crossover point at  $70 \text{ s}^{-1}$ , both moduli increased where  $G''$  dominated over  $G'$  until the second crossover point was reached at  $290 \text{ s}^{-1}$ . At frequency higher than  $290 \text{ s}^{-1}$ , the elastic behaviour once again controlled the sample as the  $G'$  surpassed  $G''$ . The same occurrence was reported by Tian et al. [30] where multiple crossover points were observed in the viscoelastic investigation of silicone rubber and silicone oil where the critical shear strain was reached. The complex viscosity,  $\eta^*$  for all three silicone rubber systems having a similar trend across the frequency. The  $\eta^*$  reduced as the angular frequency increased until it reached a turning point around the frequency gel point, and then increased until the end of tested frequency.

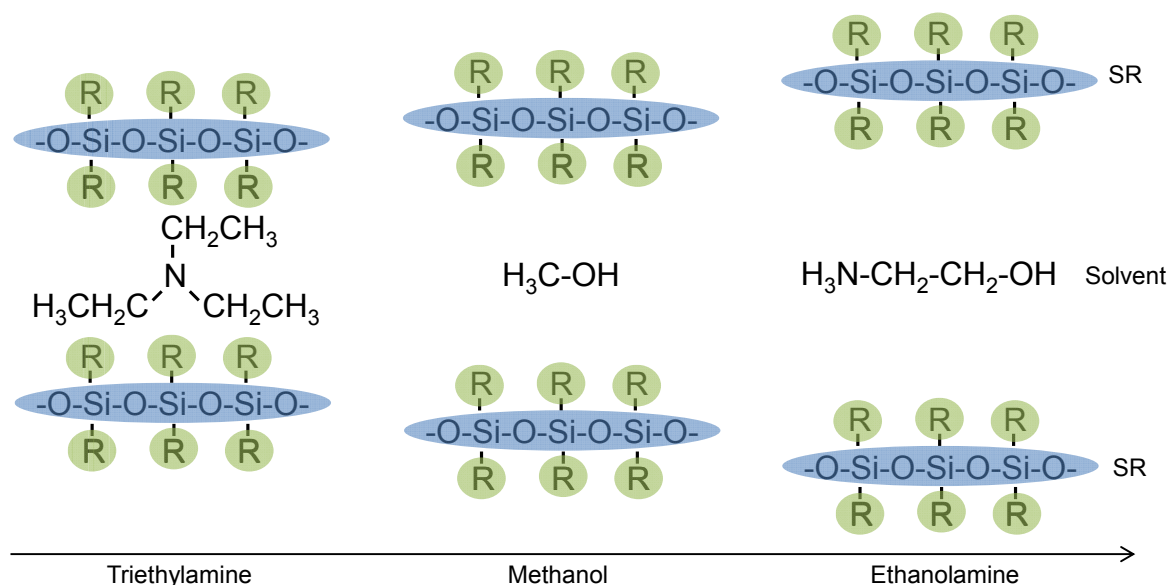
The crossover points at the lower angular frequency for the silicone rubbers in methanol and ethanolamine were due to the transformation of the silicone rubber forming network of crosslinking structure in the sample prior to gel point [31]. The gel points for silicone rubber in triethylamine, methanol and ethanolamine were expected to be at 100, 180 and  $290 \text{ s}^{-1}$  respectively, justified by the loss factor analysis in Figure 5. Hence, the magnitude for the frequency crossover point was also in the order of trimethylamine < methanol < ethanolamine. This behaviour was due to the polarity or dielectric constant where triethylamine, methanol and ethanolamine's dielectric constant values were 2.42, 33.1 and 37.7 respectively at  $25^\circ\text{C}$  [32- 33].



**Fig. 5.** Loss factor of silicone rubber in different catalysts

Polarized Si-O bond in the backbone of silicone rubber is shielded by the nonpolar methyl group (alkyl R) in the outer surface of the molecular structure (Figure 6). For highly polar ethanolamine solution having amine and hydroxyl group in its molecular structure, it tends to have a repulsive behaviour towards the nonpolar alkyl group. Hence penetration of the chemicals on the silicone rubber to assist in crosslinking process is more challenging. Thus, as the polarity of solution is higher, the crosslinking occurs at higher frequency.

From Figure 5, the system with methanol and ethanolamine solutions showed a similar trend with different peak magnitude of loss factor. However, a clear peak was not detected in silicone rubber with triethylamine solvent system. Nevertheless, different slope of loss factor curve was observed intersecting at frequency 3, 30 and  $200 \text{ s}^{-1}$ . This indicates that interactions happened at a different phase or rate during that time. The highest peaks for silicone rubber in methanol and ethanolamine solutions were at  $50$  and  $160 \text{ s}^{-1}$ , respectively. Since the temperature was kept constant at  $25^\circ\text{C}$  for solvent interaction with silicone rubber, this means that the glass transition temperature occurred at  $25^\circ\text{C}$  and at specific frequency of  $50$  and  $160 \text{ s}^{-1}$ . Gel point also could be determined from  $\tan \delta$  curve. Intersection at  $\tan \delta = 1$  yielded the same intersection frequency for all system as determined from the crossover point of modulus shown in Figure 4. Silicone rubber with triethylamine exhibited a solitary intersection at  $100 \text{ s}^{-1}$  while silicone rubber in methanol and ethanolamine demonstrated double intersection points at  $3, 180 \text{ s}^{-1}$  and  $70, 290 \text{ s}^{-1}$ , respectively. Since intersection at lower frequency for both methanol and ethanolamine occurred below the glass transition condition (highest peak of loss factor curve), it was unstable. The  $\tan \delta$  curve of silicone rubber in methanol and ethanolamine after the first intersection point also increased above 1 where the sample behaved like a fluid instead of solid/gel which discredited them as a gel point. Instead, the curve of  $\tan \delta$  of silicone rubber in methanol and ethanolamine after the second intersection point at higher frequency decreased below 1, indicating that the sample behaved in a gel-like behaviour. Hence, the second intersection point was taken as the gel point.



**Fig. 6.** Schematic representation of silicone rubber structure in the presence of chemical catalyst solutions. The higher the solution polarity, the greater its repulsion with silicone rubber.

#### 4. CONCLUSIONS

Rheological measurements provide useful information on the evolution of the physical properties such as shear modulus, viscosity and gel time. Manipulating the concentration of silicone rubber and the crosslinker (platinum solution) yielded a different gel point to the system. Higher ratio of silicone rubber to crosslinker reduced the gel point temperature, such that 7.5:2.5 and 10:1 ratios gave the gel point temperature at 95 and 89°C, respectively. Higher concentration of silicone rubber in the presence of catalyst made it easier for crosslinking and agglomeration. Different chemicals used also affected the crosslinking behaviour of silicon rubber due to the solvents' polarity. Multiple crossover points were also observed in the systems with methanol and ethanolamine solvent. At the end, controlling the crosslinking behaviour of the silicone rubber was achievable. More studies are needed to explore the viscoelasticity and crosslinking information to be able to tailor final product with specific properties

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#### 6. REFERENCES

- [1] Liu, P., Liu, D., Zou., H, Fan, P. and Xu, W., "Structure and Properties of Closed Cell Foam Prepared from Irradiation Crosslinked Silicone Rubber." J. of Appl. Polymer Science. 2009, 113, 3590-3595.
- [2] Liao, X., Xu, H., Zhaou, C., Li, G. and Park, C. B., "The Effects of Viscoelastic Properties on the Cellular Morphology of Silicone Rubber Foams Generated by Supercritical Carbon Dioxide." RSC Adv. 2015, 5, 106981-106988.
- [3] Lopez, L. M., Cosgrove, A. B., Hernandez-Ortiz, J. P. and Osswald, T. A. "Modeling the Vulcanization Reaction of Silicone Rubber." Polymer Eng. & Sci., 2007, 675-683.
- [4] Mahmood, S., Husin, H., Mat-Shayuti, M. and Hassan, Z. C. "A Review on the Cords & Plies Reinforcement of Elastomeric Polymer Matrix." IOP Conf. Series Earth and Env. Science, Kota Kinabalu, Malaysia, 2016, 36, 012034.
- [5] Shit, S. C. and Shah, P. "A Review on Silicone Rubber." National Academy Sci.

- Letters, 2013, 36, 355–365.
- [6] Ji, J., Pang, X., Liu, R., Wen, S., Sun, J., Liang, W., Ge, J. and Chen, X. “Synthesis and Characterization of Room Temperature Vulcanized Silicone Rubber using Methoxyl-Capped MQ Silicone Resin as Self-Reinforced Cross-Linker.” *Polymers*. 2019, 11(7), 1142.
  - [7] Harkous, A., Colomines, G., Leroy, E., Mousseau, P. and Deterre, R. “The Kinetic Behaviour of Liquid Silicone Rubber: A Comparison Between Thermal and Rheological Approaches Based on Gel Point Determination.” *Reactive and Functional Polym.*, 2016, 101, 20-27.
  - [8] Vallés, E. M. and Macosko, C. W. “Structure and Viscosity of Poly (dimethylsiloxanes) with Random Branches.” *Macromolecules*. 1979, 12, 521-526.
  - [9] Winter H. H. “The Critical Gel.” *NATO Sci Ser*. 2002, 439-470.
  - [10] Vallés, E. M., Carella, J. M., Winter, H. H. and Baumgaertel, M. “Gelation of a Radiation Crosslinked Model Polyethylene.” *Rheol Acta* 29. 1990, 535-542.
  - [11] Li, Y., Zeng, X., Lai, X., Li, H. and Fang, W. “Effect of the Platinum Catalyst Content on the Tracking and Erosion Resistance of Addition-Cure Liquid Silicone Rubber.” *Polymer Testing*. 2017, 63, 92-100.
  - [12] Chen, W., Zeng, X., Lai, X., Li, H., Fang, W. and Liu, T. “Synergistic Effect and Mechanism of Platinum Catalyst and Nitrogen-containing Silane on the Thermal Stability of Silicone Rubber.” *Thermochimica Acta*. 2016, 632, 1-9.
  - [13] Ponton, A., Barboux-Doeuff, S. and Sanchez, C. “Rheology of Titanium Oxide-based Gels: Determination of Gelation Time Versus Temperature.” *Colloids and Surfaces A: Physicochemical and Engineering Aspects*. 2000, 162, 177-192.
  - [14] Winter, H. H. “Can the Gel Point of a Crosslinking Polymer be Detected by the  $G'$ - $G''$  Crossover?” *Polymer Eng Sci*. 1987, 27, 1698-1702.
  - [15] Panwar, V. and Pal, K. “Dynamic Mechanical Analysis of Clay-Polymer Nanocomposites” *Clay-Polymer Nanocomposites*. 2017, 413–441.
  - [16] Gottfried, E., Gabriela, R. and Pia, T. “Dynamic Mechanical Analysis (DMA)”, *Thermal Analysis of Plastic*. 2004, 236-299
  - [17] Durand, D. and Nicolai, T. *Networks, Viscoelasticity of Encyclopedia of Materials: Science and Technology*, eds. K. H., Jurgen Buschow, R. W., Cahn, M. C., Flemings, B., Ilshner, E. J., Kramer, S. Mahajan and P., Veyssiere. 2001, 6116–6119.
  - [18] Kim, A. Y., Choi, D. G. and Yang, S. M. “Rheological of the Gelation Behaviour of Tetraethylorthosilane/vinyltriethoxysilane Hybrid Solutions.” *Korean J Chem Eng*. 2002, 19, 190-196.
  - [19] Schaefer, R. J. *Mechanical Properties of Rubber*. Harris’ Shock and Vibration Handbook, ed. A., Piersil and T., Paez, McGraw-Hill Companies Inc. 2010. 33.1-33.18.
  - [20] Ivanoska-Dacicj, A., Bogoeva-Gaceva, G., Buzarovska, A., Gjorgjiev, I. and Raka, L. “Preparation and Properties of Natural Rubber/Organo-Montmorillonite: From Lab Samples to Bulk Material.” *Macedonian Journal of Chemistry and Chemical Engineering*. 2014, 33, 249-265.
  - [21] Sewda, K. and Maiti, S. N. “Dynamic Mechanical Properties of High Density Polyethylene and Teak Wood Flour Composites.” *Polymer Bulletin*. 2013, 70, 2657-2674.
  - [22] Esmizadeh, E., Arjmandpour, M., Vahidifar, A., Naderi, G. and Dubois, C. “Preparation and Characterization of Silicone Rubber/Grapheme Nanosheets Nanocomposites by In-Situ Loading of the Coupling Agent.” *Journal of Composite Materials*. 2019, 53, 3459-3468.
  - [23] Nguyen, L. H., Koerner, H. and Lederer, K. “Gel Point Determination for the Copolymerization System of Cardanyl Acrylate and Styrene and its Critical Conversion.” *Journal of Applied Polymer Science*. 2002, 89, 2385-2390.
  - [24] Cassagnau, P. H. *Handbook of Advanced Materials Testing*, ed. N. P. Cheremisinoff. New York, 1995, 925
  - [25] Winter, H. H. *Encyclopedia of Polymer Science and Technology*. John and Wiley Sons. 2016.
  - [26] Ramli, M. R., Othman, M. B. H., Arifin, A.



- and Ahmad, Z. "Cross-link Network of Polydimethylsiloxane via Addition and Condensation (RTV) Mechanisms. Part I: Synthesis and Thermal Properties." *Polymer Degradation and Stability*. 2011, 96, 2064-2070.
- [27] Hu, X. L., Luo, W. B., Liu, X., Li, M., Huang, Y. J. and Bu, J. L. "Temperature and Frequency Dependent Rheological Behaviour of Carbon Black Filled Natural Rubber." *Plastics, Rubber and Composites*. 2013, 42, 416-420.
- [28] Cappelaere, E., Berret, J. F., Decruppe, J. P., Cressely, R. and Lindner, P. "Rheology, Birefringence, and Small-Angle Neutron Scattering in a Charged Micellar System: Evidence of a Shear-Induced Phase Transition." *Physical Review E*. 1997, 56, 1869-1878.
- [29] Chattopadhyay, H., Auddy, B., Sur, T., Sana, S. and Datta, S. "Accentuated Transdermal Application of Glucosamine Sulphate Attenuates Experimental Osteoarthritis Induced by Mosodium Iodoacetate." *Journal of Materials Chemistry B*. 2016, 4, 4470-4481.
- [30] Tian, T. F., Li, W. H., Ding, J., Alici, G. and Du, H. "Study of Shear-Stiffened Elastomers." *Smart Materials and Structures*. 2012, 21, 125009.
- [31] Zandrea, O., Jelinkova, L., Roy, N., Saha, N., Kitano, T. and Saha, P. "Viscoelastic Properties and Morphology of Mumio-Based Medicated Hydrogels." *Novel Trends in Rheology IV*. 2011, 1-11.
- [32] Shirke, R. M., Chaudhari, A., More, N. M., Patil, P. B. "Dielectric Measurements on Methyl Acetate + Alcohol Mixtures at (288, 298, 308 and 318) K using the Time Domain Technique." *J. Chem. Eng. Data*. 2000, 45, 917-919.
- [33] King, E. J. Acid-Base Behaviour. *Physical Chemistry of Organic Solvents System*. Eds . A. Covington and T. Dickinson, New York, USA, 1973, 331-403.