SCHOOL OF MATERIALS AND MINERAL RESOURCES ENGINEERING

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EVALUATION OF SILICONE SEALANT CURE CHARACTERISTICS USING A FABRICATED PARALLEL PLATE RHEOMETER

By

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DECLARATION

I hereby declare that I have conducted, completed the research work and written the dissertation entitled **"Evaluation of Silicone Sealant Cure Characteristics Using a Fabricated Parallel Plate Rheometer".** I also declare that it has not been previously submitted for the award of any degree or diploma or other similar title for any other examining body or university.

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ABSTRAK

Ciri-ciri pematangan pengedap silikon adalah penting bagi pengguna dalam industri pembinaan kerana ia mengandungi maklumat yang berguna untuk memastikan pengedap tidak akan gagal semasa aplikasi perkhidmatannya. Dalam kajian ini, tiga jenis Pematangan Suhu Bilik (RTV) digunakan untuk mengkaji ciri-ciri pematangan menggunakan rheometer piring selari yang direka dan rheometer komersial Anton Paar. Kesan sistem pematangan, suhu, kekerapan ayunan, dan ketinggian jurang telah disiasat. Data pengukuran yang diperoleh dari rheometer piring selari yang direka iaitu arus elektrik dan sudut kekerapan dinilai untuk menghasilkan corak pematangan yang terdiri daripada induksi, pematangan dan pematangan berlebihan. Corak pematangan adalah hasil daripada plot tork melawan waktu pada suhu malar untuk menunjukkan perkembangan proses penyambung-silang dengan masa. Berdasarkan analisis ciri-ciri pematangan, masa pelembutan dan waktu bebas melekit diperolehi. Masa pelembutan adalah masa di mana pengedap mempunyai sifat aliran yang bagus yang boleh digunakan dengan baik oleh mana-mana cara. Sementara itu, masa bebas melekit adalah jarak masa sebelum pengedap menahan kerosakan dengan menyentuh. Berdasarkan hasil yang diperolehi, rheometer piring selari yang direka dapat menggambarkan parameter ciri-ciri pematangan yang dikaji dengan memuaskan. Ia menunjukkan bahawa analisis ciri-ciri pematangan boleh memberikan platform yang baik untuk menyiasat masa pelembutan dan bebas likat daripada bahan pengedap silikon.

EVALUATION OF SILICONE SEALANT CURE CHARACTERISTICS USING A FABRICATED PARALLEL PLATE RHEOMETER

ABSTRACT

The cure characteristics of a silicone sealant are important to the consumers in the construction industry as it contains useful information to ensure the sealants will not fail during its service applications. In this study, three types of Room Temperature Vulcanization (RTV) silicone sealants were used to study its cure characteristics using a fabricated parallel plate rheometer and commercial Anton Paar rheometer. The effects of curing system, temperature, oscillation frequency, and gap height were investigated. The measurement data obtained from the fabricated parallel plate rheometer, which are electrical current and angular speed were evaluated to yield the cure characteristics curve which consists of induction, curing and over cure regions. The curve was a plot of torque versus time at a constant temperature to show the progression of a crosslinking process with time. Based on the cure characteristics analysis, softening time and tack-free time were obtained. Softening time was the time where the sealant had the good flow properties that can be best applied by any mechanical means. Meanwhile, the tack-free time was the time taken before the sealant resisted damage by any contacts. Based on the results obtained, fabricated parallel plate rheometer was able to describe the curing characteristics of the studied parameters satisfactorily. It showed that the curing characteristics analysis could provide a good platform to investigate the softening and tack-free time of the silicone sealants

1.0 INTRODUCTION

1.1 OVERVIEW

Sealant is a material that is able to isolate assemblies and joints. According to Petrie, 1999, a sealant basically has three general functions:

- It fills a gap between two or more substrates
- It forms a barrier by the physical properties of the sealant itself and by its adhesion to the substrate
- It maintains its sealing property for the expected lifetime, service conditions, and environments.

Sealants are largely used in construction industry thus the sealants must full-fill the important material requirements such as elasticity, movement capability, weather resistance and strength. According to Ramachandran *et al.*, 2002, most sealants are used in exterior applications, hence, they must be deformable, have good recovery properties, and should have good overall elastic properties. Many sealants used in the construction industry are required to maintain functional performance characteristics over many years. While in service, sealants are exposed to environmental factors such as UV radiation, water, oxygen, and thermal cycling. Depending on which face of the building sealants are placed, type of substrate, and geographic region, they may be exposed to extreme environmental conditions, stress, and strain gradients.

Silicone is widely used as raw materials in sealant formulations due to its superior properties such as high flexibility, high resistance to extreme temperatures, water and chemical resistance, high durability, good thermal and electrical conductivity and good transparency. These superior properties can be explained by its chemical structure. Silicone is one of the polymeric materials which is identified as Polydimethylsiloxane (PDMS). It consists of methylated linear siloxane polymers having imitating units of the formula $(CH_3)_2SiO$ as their backup with trimethylsiloxy end-blocking units of the formula $(CH_3)_3SiO$. According to Francois, 2001 the silicone polymers are easily transformed into a three dimensional networks and an elastomer via a crosslinking reaction, which allows the formation of chemical bonds between adjacent chains. This is achieved according to one of the following reactions: crosslinking by condensation, addition or radical reaction.

Properties of silicone sealant is directly related to state of cure. High level of cure indicates high degree of vulcanization of a silicone compound. According to Allen, Hutchinson and Pagliuca, 1994, curing is a very important aspect of sealant technology because the polymeric chains extend crosslink and the level of these interactions determines the characteristics properties of strength, elasticity and movement capability of the materials. Different generic types of sealant cure via different processes, and variations also exist within given generic types.

One of the method that is able to study the cure characteristics of a sealant is rheometer. Rheometer is a measurement device used to measure flow and deformation of materials under force or in the other words, to measure the rheological properties of material. It is essential to characterize the rheological behaviour due to its direct effects on the product handling and flow characteristics especially in manufacturing process practice. In construction industry, information such as softening time, tack free time and sagging time are essential, thus by performing rheometer test, those information can be obtained directly. However, performing rheometer test of sealant sometimes will produce error results due to the misinterpretation of software that will be discussed further in chapter 2.

Softening time is the time where the sealant has the good flow properties that can be best applied by any mechanical means before it starts to cure and become tacky thus will have poor flow properties (Petrie, 1999). This information is important to overcome the difficulties in handling sealant paste with very high viscosity.

According to ASTM C679, the tack-free time is a measure of the surface cure time and may generally be correlated to a variety of useful parameters such as the time interval before the sealant resists damage by touch or light surface contact, resists job-site or airborne dirt pick-up and resists impinging rainfall (ASTM C679, 2015).

Meanwhile, sealant can be classified as either self-levelling or non-sagging. To justify this, ASTM C 639 describes test methods to determine whether a sealant can be considered self-levelling or non-sagging and the degree of sag-resistance (ASTM C639, 2015). Sagging time is directly related to the thixotropic behaviour of the sealant as will be discussed further in chapter 2.

Vulcanization curve is valuable data to the manufacturers of elastomeric products. Meanwhile for the sealant industry, it is a valuable data for the consumers. Vulcanization curve of sealant also can explain the behaviour of materials during curing. Vulcanization curve of elastomer can be yielded by performing curemeter test. However, for the sealant it is not possible due to its liquid nature. In order to justify the curing behaviour of silicone sealant, further understanding of vulcanization curve of elastomer is appropriate.

According to Khimi and Pickering, 2014, generally there are three stages can be represented by a vulcanization curve. The first stage is the induction period which is characterized by slow chemical reaction between rubber and the additives. The second stage is where the vulcanization of rubber molecular chains take place to form three dimensional networks structures. The last stage can involve over curing reactions depending on the rubber type, vulcanization agent and temperature.

Information such as minimum viscosity (M_L) and maximum viscosity (M_H) are important in determining the scorch and cure time. Scorch time is the time taken from initial exposure on the compound to a particular temperature, to the time of onset of cure where rapid increase in torque is experienced by the rotor at that temperature. Scorch time, t_{s2} is reported at the two degrees arc setting as the time required for the torque to rise two torque units (either in dN-m or in-lb) above the minimum elastic torque M_L.

Meanwhile cure time is the time taken for the curve to reach a height expressed as the value of M_L plus a percentage of the difference between M_H and M_L. It indicates the time taken for the silicone sealant to become fully cured. It is defined as the time required to reach the elastic torque value of $(M_L + 0.9(M_H - M_L))$ where M_H represents the maximum elastic torque and M_L represents the minimum elastic torque.

Considering the fact that the fundamentals of curemeter application involve monitoring the torque value to assess the cure characteristics, suggest that the parallel plate geometry of fabricated parallel plate rheometer could also be used for evaluating the cure characteristics of a silicone sealant. Fabricated parallel plate rheometer can be simply described as monitoring torque changes with respect to the stiffness changes of the sample whilst analysing the material's response to that deformation. From this, a variety of fundamental material parameters can be determined such as vulcanizing behaviour, softening time, and tack free time.

The aim of this project is to evaluate the cure characteristics of silicone sealant samples using a fabricated parallel plate. This information is crucial for manufacturers and consumers in studying the behaviour of silicone in sealant applications.

1.2 PROBLEM STATEMENT

In sealant industry, thermosetting polymeric material with different formulations will give different cure characteristics. Currently available measurement instruments such as rheometer are very expensive and not affordable to most practitioners and researchers in the related field of study. In addition, determining the cure characteristic of a sealant requires modest calculation and technology thus a sophisticated rheometer is not recommended due to the low utilization of rheometer capabilities used by the practitioners. There are not many studies regarding to the cure characteristic of silicone sealant that have been done. Most of the studies done by researchers are focusing on the cure characteristics of the solid rubber compound. Previous studies on sealants cure characteristics by other researchers will be discussed comprehensively in Chapter 2.

Moreover, the measurement of the cure characteristics of a sealant is not as straightforward as for other polymer systems, such as vulcanized rubber compounds. Room Temperature Vulcanizing (RTV) sealants cure in a slower, more time consuming than conventional rubbers. Allen, Hutchinson and Pagliuca, 1994 reported that conventional techniques such as hardness tests is not ideal in determining sealant cure characteristics. Hardness tests are specially limited for one-component sealants which tend to form a cured skin layer comparatively fast meanwhile the overall bulk remains unvulcanised.

Despite suggested method to determine cure characteristic of sealant, rheometry has been introduced, some challenges have been addressed by the previous researchers. Rheometer tests are accomplished on very small specimens of sealant thus in determining the optimum cure time can be performed quite well. In this case, parallel plate was the best geometry to suit the behaviour of the silicone sealant during their application. However, the parallel plate rheometer test is time consuming. Some researchers suggest that the test is conducted at least 24 hours in order to yield meaningful results (Allen et al., 1994). Moreover, the small quantity of specimen preparation typically used in these tests is not comparable with the geometry and size of sealant beads used during actual applications, which means that the rheometer results are not relatively relevant and comparable. In order to overcome this challenge, corrections must be done on potential testing errors during conducting the rheometer test (Lynch, 1996).

Misinterpretation of results analysis by available software in determining the correct location of important values sometimes may lead to erroneous results. There are many factors that contribute to this error, mostly due to the viscoelastic behaviour of the silicone sealant. These fault numbers will further deteriorate and result in invalid testing. This is happened in the rheometry test of the sealant. The fundamentals calculations of the results will be discussed comprehensively in Chapter 2.

To overcome this, the study of silicone sealants cure characteristic using a fabricated parallel plate rheometer is introduced. In this work, silicone sealant is used to determine its induction, curing and overcure regions whilst derives the softening time and tack free time based on the vulcanization curve.

1.3 RESEARCH OBJECTIVES

1. Evaluate silicone sealant cure characteristics based on the measurement data obtained from fabricated parallel plate into rheological data.
2. To obtain softening time, tack free time, induction, curing and overcure stages of silicone sealants.
3. To study the effect of curing system, oscillation frequency, temperature and gap height towards the cure characteristics of silicone sealants.

1.4 SCOPE OF STUDY

This study only focused on determination of silicone sealant cure characteristics by using a fabricated parallel plate rheometer. Silicone has been chosen because it is widely used in the sealant industry. It is also represented the general behaviour of thermoset polymer. Thus, the vulcanization curve, softening and tack free time can be obtained from this study.

1.5 SIGNIFICANCE OF STUDY

This finding of this study will benefit other researchers and rheologists to use the fabricated parallel plate rheometer in determining cure characteristic of thermoset material.

2.0 LITERATURE REVIEW

2.1 SILICONE SEALANT MATERIALS

Silicone sealants consist of polymers containing simultaneous inorganic groups (silicon atoms and oxygen) in their backbones chains with various organic groups in their side chains. Their unique properties are acquired from the Si-O-Si backbone (which exhibit silica properties). Majority of silicone sealants in the construction industry use monomers based on silanol-terminated polydimethyl siloxanes or known as silanols.

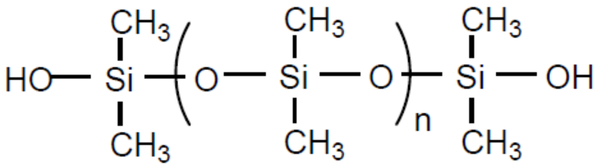


Figure 2.1: Chemical structure of silanol-terminated polydimethyl siloxanes (silanols)

2.1.1 Polymerization of Silicone Sealant

There are two ways where the silanols can turn into silicone polymer in order to produce a silicone sealant with a sealing ability. Firstly, the silanols groups are end-capped with a hydrolysable crosslinking group such as organosilane to form a one part sealant that vulcanize when in contact with ambient moisture at room temperature. These types of sealants are generally known as one-component Room Temperature Vulcanizing Silicone (RTV-1).

Secondly, by mixing two parts system, the first part contains the silanol group and the second part contains the curative agent plus a catalyst. These systems are typically referred as two-component Room Temperature Vulcanizing Silicone (RTV-2).

Most silicone sealants in the market are based on RTV-1 systems. Thus, in this study only RTV-1 systems will be discussed in this chapter although RTV-2 systems offer the benefits of fast curing. The used moisture reactive end-capping groups commonly in RTV are trifunctional silanes. RTV silicones are generally classified according to the by-product emitted during the curing reaction. These by-products emitted process are called crosslinking by condensation.

Moisture curing RTV silicones basically depends on chemical reactions with water moisture. These silicones are crosslinking at room temperature by reacting with ambient moisture at atmospheric pressure and it is also adsorbed on the surface (adsorption). The cure rate depends on the room temperature and relative humidity of the environment. Sometimes, in cold temperatures (below 10°C), moisture levels in the atmosphere at relative humidity drop significantly.

Basically, adhesives and sealants silicone-based types cure relatively fast, developing skin within a minute, becoming tack-free within minutes to hours and turning to an elastic rubber (fully elastic) in approximately 24 hours. However, due to the nature of being a one-component, it is impossible to get a fast cure speed of deep section because the system has to react with the air therefore curing from the top of the surface to bottom. Silicone products basically require a bond line width or depth that is lesser than 10-15mm so that moisture can diffuse in and out, thus is able to react with the material in the centre of the joint. During crosslinking, a by-product is released. This is called condensation process. Depending on the trifunctional silanes, it may release by-products which are acidic (e.g. acetic acid), basic (e.g. amine), neutral (e.g. oxime or alcohol) or other volatile reaction products (Fink, 2013). Full cure through thick sections of silicones sealant may take up to 72 hours. If greater depths are needed, two-component RTV-2 type are typically used. However, Allen et al., 1994 stated that due to the nature of silicone chemistry, it should be noted that the adhesive strength may start to regain for 1-2 weeks after the silicone has been applied.

The basic type of RTV-1 are acetoxy sealants using methyl triacetoxy silane end-cappers and releasing acetic acid. In the synthesize process, the hydrolysable crosslinking group which is organosilane reacts with the silanol end-groups in the presence of a catalyst as shown in the figure 2.2. Examples of catalysts used for this reaction are stannous octoate and dibutyltin dilaurate (Dunn, 2003).

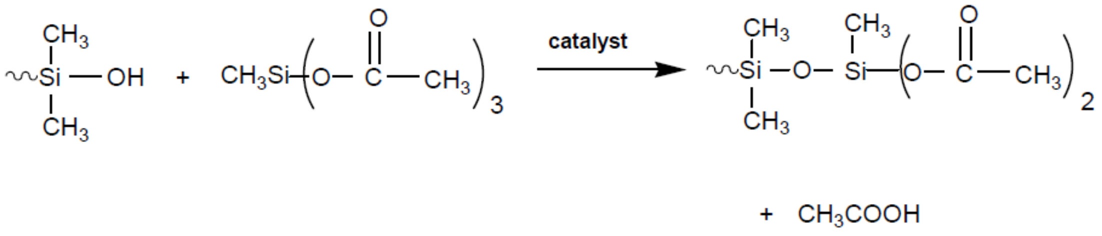


Figure 2.2: Synthesis of organosilane and silanol with presence of catalysts to produce methyl triacetoxy silane (Dunn, 2003).

The crosslinking reaction with atmospheric moisture at ambient temperature initiate reactions between the ends capped chains together to form a vulcanized elastomer and releases the by-product:

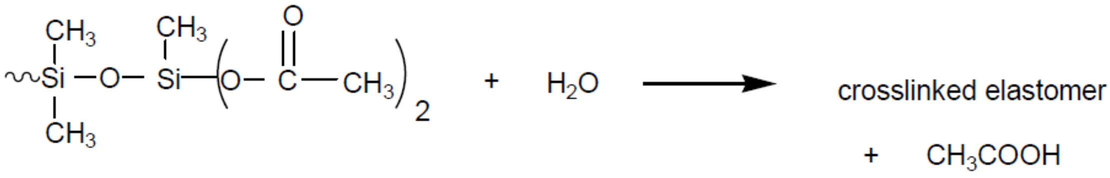


Figure 2.3: Crosslinking reaction of acetoxy with presence of water moisture to liberate a cross-linked elastomer with acetic acid as by product (Dunn, 2003).

2.1.2 Viscoelastic Behaviour of Silicone Sealant

Polydimethyl siloxanes (PDMS) is the polymeric materials in the silicone sealant. It has siloxane group as its backbone chain that provides overall flexibility of the PDMS molecular structure Viscoelasticity theory has the good explanation for the flexibility.

The only materials properties that disclose both viscous and elastic characteristics when undergoing affliction is Viscoelasticity. The viscous part dissipates energy, while the elastic part stores it. Mechanical energy is dissipated by conversion to heat in the deformation of viscoelastic materials. Polymeric materials under certain circumstances exhibit unusual properties that somehow fall in between the properties (viscous and elastic) of traditional materials (Cowie & Arrighi, 2007).

For better understanding, mechanical models for linear viscoelastic response have been developed by researchers. The nature of the viscoelastic properties of polymers can be obtained by analysing the stress and strain response of mechanical models using an ideal spring that obeys the Hooke’s law and a dashpot that obeys the Newtonian fluid.

$$\sigma = E\varepsilon \tag{2.1}$$

$$\tau = \eta\dot{\varepsilon} \tag{2.2}$$

Where

$\sigma = \text{stress}$

$E = \text{modulus}$

$\varepsilon = \text{strain}$

There are two type of models that can represent well the viscoelastic behaviour of rubber. First is known as Maxwell model. This model contains a series combination of a spring and dashpot as shown in figure 2-4.

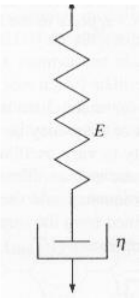


Figure 2.4: Maxwell model

The total strain, ε, is a summation of the individual strains of the spring and dashpot. Meanwhile the stress is constant throughout the deformation. By differentiating the strain, we get the strain rate of the deformation which is essential in determining the creep and stress relaxation time of the sealant.

$$\varepsilon = \varepsilon_1 + \varepsilon_2 \tag{2.3}$$

$$\sigma = \sigma_1 = \sigma_2 \tag{2.4}$$

$$\varepsilon = \varepsilon_1 + \varepsilon_2$$

$$\frac{d\varepsilon}{dt} = \frac{d\varepsilon_1}{dt} + \frac{d\varepsilon_2}{dt}$$

$$\frac{d\varepsilon}{dt} = \left(\frac{1}{E}\right)\left(\frac{d\sigma}{dt}\right) + \frac{\sigma}{\eta} \tag{2.5}$$

The other model of viscoelasticity is Voigt-Kelvin model. This model is consists of a parallel combination of a spring and dashpot as shown in figure 2-5.

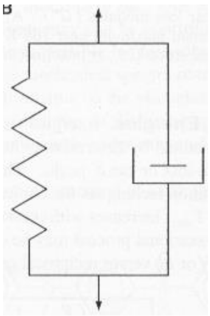


Figure 2.5: Voigt-Kelvin model

$$\varepsilon = \varepsilon_1 = \varepsilon_2 \tag{2.6}$$

$$\sigma = \sigma_1 + \sigma_2 \tag{2.7}$$

$$\sigma = \sigma_1 + \sigma_2$$

$$\sigma = E\varepsilon + \eta\frac{d\varepsilon}{dt}$$

$$\frac{d\varepsilon}{dt} = \frac{\sigma}{\eta} - \frac{E\varepsilon}{\eta} \tag{2.8}$$

The total stress, ε, is a summation of the individual stress of the spring and dashpot. Meanwhile the strain is constant throughout the deformation. By differentiating the stress, we get the strain rate of the deformation which is essential in determining the creep and stress relaxation time of the sealant.

However, in application of sealant, it involves cyclical deformation. Instead of applying a constant stress, the mode of testing should be in oscillating stress or oscillating strain that will be discussed further in section 2.3.

Macroscopically, viscoelasticity can be separated into three basic components; two of which are reversible and one which is irreversible. The three components described by Cook (1965) were:

a) Instantaneous elasticity which was a straightening out or uncoiling of the main polymer chain.

b) Delayed elasticity which consisted of orienting the polymer chains in the direction of stress.

c) Viscous flow which occurred as the polymeric chains begin to slip past one another due to the stress.

These viscoelasticity properties play a vital role in the cure characteristics of the silicone sealant as high viscous portions in the sealant will yield low softening point as it dissipates energy upon deformation and heating.

2.1.3 Type of Curing System

Selecting the right curing system of the sealant is a key in determining the final properties of the silicone sealant. It determines the silicone sealants cure characteristics properties. Curing system such as acetoxy has quickest cure time compared to other type of curing system. Thus, selection of curing system is really essential in obtaining the optimum cure time.

Acetoxy sealants can be recognized by their distinguishing vinegar odour and are used broadly as household and construction sealants. They have good adhesion to many substrates and relatively fast cure and short tack free time.

However, their disadvantages are their unpleasant odour released to surrounding and the fact that the acetic acid can introduce corrosion to metal substrates. These negatives factors have motivated the development of low odour sealants based on alternative silanes groups, however it has drawbacks which are low cure time and poor adhesions to substrates.

$$CH_3Si\left(O- \ CH_3\right)_3$$

Figure 2.6: Chemical structure of Acetoxy

Besides, oxime cure systems are usually one component, thin section, and ambient moisture cure sealants. The cure mechanism is the hydroxyl end-blocked silicone reacted with an oxime functional cross-linker in the presence of tin catalyst and relative humidity. The by product, methyl ethyl ketoxime, is released which is non-toxic substance.

Oxime cure system is well known as an excellent oil and temperature resistance. It is also a non-corrosive sealant. It can be neutral or non-acidic systems depends on the hydrolysable crosslinking functional group. However, oxime cure system may take longer tack-free and cure time then acetoxy or alkoxy cure system.

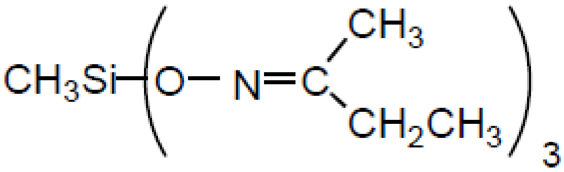


Figure 2.7: Chemical structure of oxime

Alkoxy or also known as alcohol cure systems are normally used in construction applications which requires a greater thickness. These silicones can be cured in thicker section greater than other curing systems such as acetoxy. The curing system be made of a tetra-alkoxysilane crosslinker and a tin catalyst. Similar to the acetoxy cure system, water moisture is required to proceed for crosslinking. Contrast to the acetoxy system, the by-product is an alcohol, which is non-corrosive and do have very little odour of alcohol compared to acetic acid.

However, these alkoxy need 7 days or more to obtain whole cure relying on the humidity and thickness factors of the silicone section. Alkoxy cure system takes longer tack-free time and longer cure time compared to acetoxy. In addition, it is also has poor adhesion to substrate compared to acetoxy. There are two types of alkoxy, which are methoxy (figure 2.8) and ethoxy (figure 2.9).

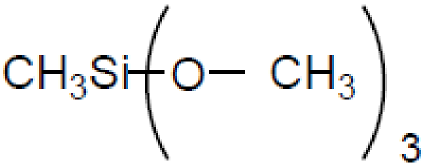
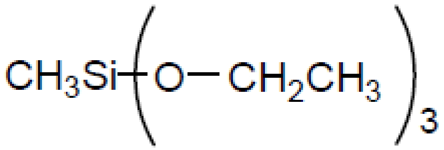


Figure 2.8: Chemical structure of Methoxy



$CH_3Si\left(O-CH_2CH_3\right)_3$

Figure 2.9: Chemical structure of Ethoxy

2.2 EXISTING TECHNIQUES

There are various approaches existing in the sealant industry today to characterize the cure time of sealant products. Some major methods, their advantages and drawbacks, are outlined in this chapter. This chapter also provides an insight to the need for a new study of parameters that affect the cure characteristics of a sealants.

Literature study gives an insight into the approaches that have been developed previously to solve the problem of characterizing the exact optimum cure time.

(Allen et al., 1994) have suggested that the state of cure of the sealant can be determined by using tensometer to measure modulus variance of the sealant and Dynamic Mechanical Thermal Analysis (DMTA) to measure glass transition temperature (T_g) of the materials. As the sealant cures its long polymeric chains crosslink and extend. This consecutively increases the load-carrying capability of the sealant but decreases its movement capability hence modulus increases with cure time. The T_g of a polymeric material is directly related to the internal free volume and can be defined as the temperature at which segmental motion, wagging and rotation of polymeric chains starts to occur. The reactions of molecular chain crosslinking and extension between themselves results in reduction of internal free volume, thus the polymer molecular chains become bulkier, less mobile and increases in steric hindrance. These factors combine together, resulting in an increase in T_g with cure time. The results show that both modulus and Tg are beneficial constraints for evaluating the state of cure of the sealants, with Tg measurement being mostly elegant. Six weeks curing seemed to be the minimum cure time required to provide an adequately high degree of crosslinking for the sealant to be tested, nevertheless of curing condition or sealant type used.

2.2.1 Curemeter

Curemeter is a vital instrument that are used comprehensively in both academic and industry purposes. The equipment plots a graph of torque versus time for any specified vulcanization temperature. There are two types of curemeters, which are oscillation disk rheometer (ODR) and moving die rheometer (MDR).

2.2.1.1 Basic Principle of Curemeter

The basic principle of the oscillating disk rheometer is a rubber compound sample is put in a closed mould equipped with a rotor that oscillated at a constant angular displacement. The magnitude of the oscillation is measured in degrees of arc, 1°and 3°. The rate of oscillation is suggested as 1.7 Hz (Ciesielski, 1999). This action creates a shear strain on the rubber molecular chain and the torque (force) required to oscillate the cavity varies upon stiffness (also known as shear modulus) of the rubber compound. The shear modulus of the rubber molecular chains increases when the rubber molecular chains start to vulcanize forming a three dimensional network during curing (Jaunich et al, 2009). Thus, increase in shear modulus will increase the demand of the torque required to oscillate the disc contained rubber compound that is undergoing vulcanization. A study by Nitzsche/Wolf proposes the relationship between shear modulus and crosslinking density based on the statistical theory of rubber elasticity in order to yield vulcanization curve. It gives the equation as below:

$$G = v.R.T. \tag{2.9}$$

where

G is shear modulus, in n/MM²

v is cross linking density, in Mol/MM3.

R is the universal gas constant, 8.313 J/(Mol.k)

T is the thermodynamic temperature, in K

If strain is directly proportional to the force applied, then:

$$\tau = G.y = v.R.T.y \tag{2.10}$$

where

y is shear strain, equal to the tangent of the shear angle.

τ is the shear stress in n/MM².

if T and y are constant, then τ is proportional to v.

At a constant temperature, technically specified as isothermal condition is the function of time which purposely to measure the level of the cross linking reaction. In perspective of rheometry, the isothermal crosslinking is the function of time, of the oscillating shear force, F occurring at a specified temperature as a result of crosslinking and expressed as

$$F = f(t) \tag{2.11}$$

Where t is vulcanization time.

The torque reading is sensed by a torque sensor mounted directly on the torque shaft bearing. Thus, reading of the torque will be received directly. This torque signal is then converted to voltage value and then will yield graph of torque against time (W. Hoffman, 1989). The measurement data then will be automatically computed by the computer using certain software to execute vulcanization curve. There are two types of measurement data that are transmitted from the machine, which are torque and time values. These will be discussed further in the next subtopic.

2.2.1.2 Vulcanization Curve

Generally, study of curing characteristics can be explained using vulcanization curves such as that shown in Figure 2-10. The common types of equipment used to yield vulcanization curves are the oscillating disk rheometer (ODR) and the moving die rheometer (MDR). There are also known as curemeters (Deniz et al, 2008). The curemeter is used to determine the cure characteristics is specified in ASTM D 2084 (ASTM D 2084, 1995). In this study, only oscillating disk rheometer will be discussed comprehensively in order to study the viscoelastic nature of the silicone sealant.

Basically, there are three regions clearly can be presented by a vulcanization curve as shown in Figure 2-10. The first region is known as the induction period, commonly occurred due to the slow chemical reaction between elastomer and the additives. It promotes excellent flow of the rubber compound inside a mould cavity and act as a safe indicator for technologist during processing. The second region is vulcanization stage where crosslinking of rubber molecular chains starting to occur to form three dimensional networks structures. The last region, which is over cure region, the rubber molecular chains start to show increasing and decreasing curing reactions, depending on the rubber type, vulcanization agent and temperature. In an ideal case, an equilibrium rate of crosslinking is obtained and the torque versus time graph plateaus. However, some compounds may yield reversion behaviour due to extensive heating during the test that corresponds to major deterioration of elastomeric three dimensional networks. Conversely, additional vulcanization may occur (due to the induced reaction of very unstable vulcanization agent such as hyperoxides) to produce a marching trend. It is also well known in rubber industry that overcure of a rubber compound generally will have poor quality product. For that reason, determination of optimum cure time is crucial to make sure the production having maximum performance and economical cost without neglecting the quality of the final product (Aggarwal, 1990).

Besides, a comprehensive understanding of factors that determine vulcanization factors are important in determining the optimum cure time. This is due to the different formulations of rubber compounds may produce the different network density. Example of crucial factors that influence the cure time are formation of sulphur bonds, incorporation of fillers and thermal instability of sulphur linkage. The effect of cure time is clearly seen in the rubber compound with incorporations of filler due to the rubber-filler interactions (Leblanc, 2002). For elastomers that do contain fillers, the cure time is usually shorter than elastomers that do not contain fillers and the maximum torque value increases as part hundred rubber of filler in the formulation increases.

2.2.1.3 Minimum and Maximum Modulus

The minimum modulus (M_L) is proportioned to the viscosity of the uncured rubber compound. When the rubber compound is heated and sealed under pressure, the viscosity decreases, thus the resistance of rotor to rotate is lower and the torque value falls. The lowest value of Torque recorded throughout test running is called M_L. Generally, it is a value of stiffness and viscosity of unvulcanized rubber compound.

If the M_L value is outside the allowed range of common M_L value, it might show indications as following: High phr amount of carbon black or too little amount of processing oil in the formulations of the rubber compound, it will yield high M_L value. However, too low phr amount of carbon black or too high amount of processing oil in the formulations of the rubber compound would give the opposite trend. Some green elastomers tend to reduce their viscosity with compounding, especially natural rubber. If the rubber compound is excessively mixed, such as too long mastication or compounding time, the viscosity may drop adequately thus will yield anomalously low $M_{L.}$

Meanwhile, the maximum modulus (M_H) is the value when torque continues to up rise, until there is no more significant increase. At this stage, the rubber molecular chain in compound is crosslinking to form three dimensional networks and this maximum torque value is designated by the symbol M_H. Depending upon the type of the rubber compound, the slope of significant rising of torque varies. In a moment, the torque generally achieves maximum torque value and it shows constant value. It is called Plateau Curve. Meanwhile, if ODR test is prolonged for sufficient time, the torque tends to fall tremendously result in a descend trend of torque. This type of curve is known as Reversion Curve. At some times where the torque shows continuous rising trend of torque versus. This type of curve is called Marching Curve. M_H is the highest torque value recorded in plateau curve. However, in reversion curve, the M_H is abbreviated as MHR.

Moreover, a constant value for M_L will give the indications to the rubber technologist just referring to the M_H trend. It gives information regarding the curative system and curative agents. At the same time, the degree of cross-linking of the elastomer can be determined (Ciesielski, 1999). Insufficient of curatives in the rubber formulations of the compound can be detected when the value of M_H is low. Meanwhile, excessively high amount of curatives will give the result vice versa.

2.2.1.4 Scorch time

Scorch can be defined as premature vulcanization of rubber where the compound becomes partly vulcanized before the product turns its final form and ready for vulcanization. It reduces the plastic properties of the rubber so that it is irreversible process. Scorching is due to the temperatures reached during processing and period of time the compound is exposed to elevated temperatures. This period before crosslinking starts is typically referred to as scorch time. Since scorching alters the compound, it is essential that crosslinking does not start until processing of rubber is complete.

Before the rubber compound reach scorch time, during the time closure of the rubber compound in the cavity, there is an induction time, ts2 where the viscosity of rubber compound rises 2 units above M_L. Meanwhile when 5 units above M_L is taken, this period is called scorch time, ts5. Similarly, both scorch time are measures of initial gradient of vulcanization phase of a vulcanization curve that act as indicators of processing safety.

Establishment of a minimum scorch time is important to obtain safe processing of an elastomeric compound. A huge complex mould takes longer time to fill with uncrosslink rubber chains in the compound thus it might need a long scorch time. In this case, a short scorch life could result in premature vulcanization, before the mould has properly filled, resulting in a high level of scraps.

2.2.1.5 Cure time

Time to reach complete vulcanization, known as the cure time. The symbol for this property is t90. This can be defined technically as the time required for the curve to reach a value of M_H plus a percentage of the difference between M_H, and M_L. This percentage value is taken sometimes 50% and sometimes 90%. If 50% is used, the symbol of cure time will be t50. Meanwhile if 90% is taken, the symbol of the cure time will be t90. Mathematically, cure time can be calculated as $0.9(M_H - M_L) + M_H$. These t50 and t90 represents the degree of vulcanization at that time respectively which are 50% and 90%. In addition, the value of cure time is also gives some hints on the curative system of the rubber compound.

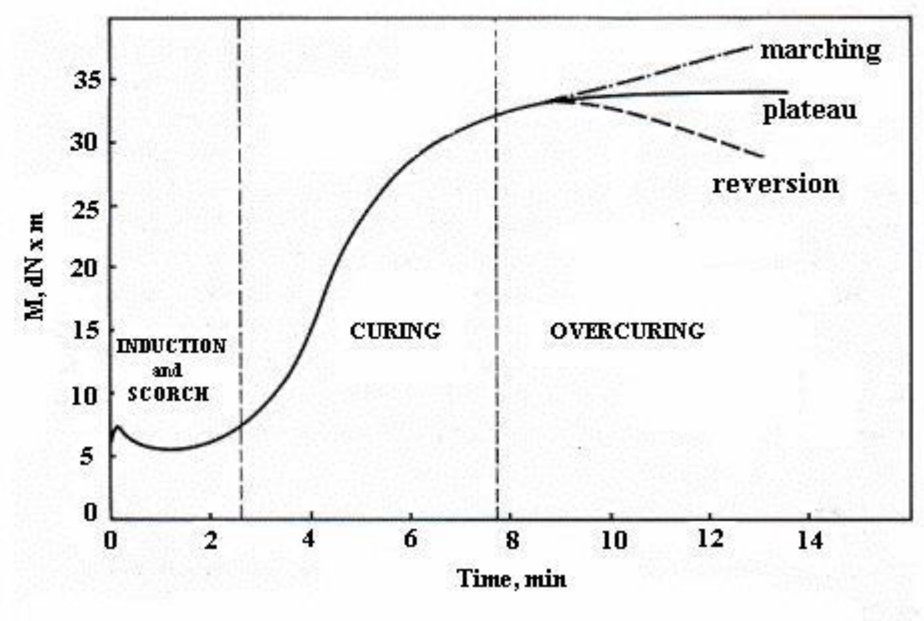


Figure 2.10: Typical oscillating disk curemeter curve (Ciesielski, 1999)

2.2.2 Rheometer

Knowledge of cure characteristics of thermoset polymer is essential in determining the rheograph of silicone sealant, in order to obtain scorch and cure time. Silicone sealant is a thermoset polymer, thus will yield same trend graph of torque versus time with solid rubber compound. However, due to the soft paste of silicone sealant, it may not suitable to use available ODR in its disk geometry and the different rheological properties and applications of silicone sealants are also restrict the measurements of rheological properties thus a parallel plate rheometer is suggested to study its cure characteristics.

2.2.2.1 Principle of Rheometer

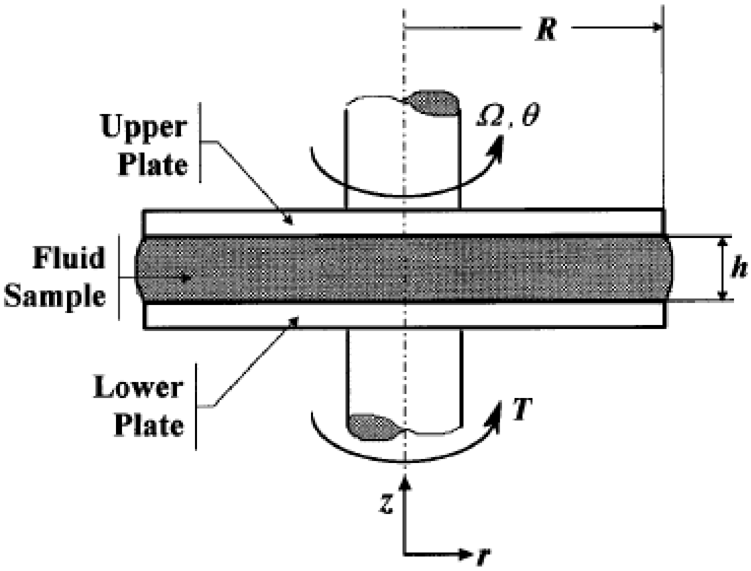


Figure 2.11: Parallel Plate Geometry (Leblanc et al .,1999)

Parallel-plate geometries are chosen instead of cone-and-plate since silicone sealant has high viscosity and particle size thus requires big gap separation between samples and two parallel plates to avoid potential test errors that will be discussed comprehensively in 2.4.4. These are to ensure that results obtained are correct and the scorch and optimum cure time can be measured from the parallel plate rheometer.

The following equation shows the relationship between rheological data and the measurement data that are obtained from the rheometer.

$$\eta = \frac{\sigma}{\dot{\gamma}} = \frac{M.K_\sigma}{\Omega.K_\gamma} \tag{2.12}$$

The rheometer measures stress (τ) by means of torque (M) and measuring measures strain rate ($\dot{\gamma}$) by means of velocity (Ω). K_σ and K_γ is the instrument's geometrical factors. Factor K_σ is used to translate the torque (M) into stress (σ) and K_γ is utilized to translate velocity (Ω) into strain rate ($\dot{\gamma}$).