

# Determination of optimum cure state of elastomers

Master's thesis

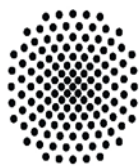
Submitted by

Ragini Rajarajan

(Matriculation Number – 3104437)

Institute for Materials Science

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**Universität Stuttgart**

Examiner: Prof. Dr. Joachim Bill



Supervisor – Dr. Ali Golriz

in cooperation with



Supervisors - Dr. Günter Auernhammer

Dr. Rüdiger Berger

# DECLARATION OF AUTHORSHIP

This master thesis report is written by Ragini Rajarajan under the supervision of Prof. Dr. Joachim Bill, Dr. Günter Auernhammer, Dr. Rüdiger Berger and Dr. Ali Golriz.

I, Ragini Rajarajan, hereby declare that this master thesis is a result of my own work and has not been submitted earlier in any other university or institute. The information derived from the published or unpublished works of others has been cited and all the references have been listed in the appended bibliography.

Stuttgart, 25 Oct. 17

Ragini Rajarajan

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Place and Date

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Signature

# TABLE OF CONTENTS

ACKNOWLEDGEMENTS.....	4
ABSTRACT .....	5
1. INTRODUCTION .....	6
1.1. MOTIVATION .....	7
1.2. MATERIALS – ELASTOMERS.....	9
1.2.1. Poly(dimethylsiloxane) (PDMS).....	9
1.2.2. Natural Rubber (NR).....	10
2. THEORETICAL BACKGROUND .....	13
2.1. EXISTING TECHNIQUES.....	13
2.1.1. Compression Set .....	13
2.1.2. Swelling Experiments .....	15
2.1.3. Rheometer .....	16
2.1.4. Other Methods in Literature.....	17
2.2. MICRO CANTILEVER SENSOR (MCS) TECHNOLOGY.....	19
2.3. PIEZORHEOLOGY .....	22
2.3.1. Flory – Rehner theory .....	22
2.3.2. Piezorheology.....	22
3. EXPERIMENT .....	26
3.1. SAMPLES.....	26
3.2. PIEZORHEOLOGY .....	27
3.3. SWELLING EXPERIMENTS .....	29
4. RESULTS AND DISCUSSION .....	30
4.1. POLY(DIMETHYLSILOXANE) (PDMS) .....	30
4.2. NATURAL RUBBER .....	34
5. CONCLUSION .....	44
6. FUTURE SCOPE .....	46
REFERENCES.....	48
APPENDIX A.....	50

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## **ABSTRACT**

The enhancement of an elastomer's functional properties like dimensional stability, resistance to solvents and to high temperatures is a result of the curing or crosslinking between the various chains of an elastomer [3]. One of the methods used in industry to predict cure state is the rheometer. The methods existing in the industry and in literature to measure the cure state have some advantages and disadvantages. The main objective of the master's thesis is to establish and evaluate one standard method that can be relied on, to measure the optimum cure state of an elastomer. This method should be fast, precise and help in predicting cure state of products with complex geometries.

Piezorheometers follow the set up and principles of classic oscillatory rheometers. Here, the excitation of piezoactuators is achieved by the principles of piezoelectric and inverse piezoelectric effect, contrary to the use of electro motors and capacitive transducers in conventional rheometers [18]. Evaluation was done for two elastomers – one reference and one real time sample. The reference was Poly(dimethylsiloxane) and the other sample was natural rubber. Results produced were evaluated and the method was tested for variations. Piezorheology is a reproducible and reliable technique which is easy to use and can be applied in the industry.

# 1. INTRODUCTION

Elastomers are viscoelastic materials that exhibit extraordinary elasticity. They are long chains of organic macromolecules, often cross-linked [1]. Elastomers are known for their nature of stretching and returning to their original shape in a reversible way [2]. The presence of heteroatoms such as fluorine, silicon, oxygen and nitrogen in the backbone chain are shown to extend an elastomer's chemical resistance [1]. Elastomers are flexible, with excellent oil and moisture impermeability, abrasion resistance and insulation, and are used in many applications like gaskets, shoe heels, tires, industrial belts, wire insulators and medical prosthetics [1].

The enhancement of functional properties like dimensional stability, resistance to solvents and to high temperatures is a result of the crosslinking between the various chains of an elastomer [3]. The main constituents of rubber are long macromolecular chains. In the non crosslinked state, the material exhibits plastic behavior as the chances of chain sliding are high. After crosslinking, a three dimensional network is formed and relative chain sliding is minimized, thus exhibiting elastic behavior [4]. The mechanical properties of an elastomer depend on crosslinking as much as they depend on compounding [4].

Crosslinking is often done by externally added crosslinking agents that form chemical bonds at functional sites [1]. Vulcanization or curing is the formation of chemical crosslinks between coiled and long elastomer chains with sulphur as a crosslinking agent, in order to improve their mechanical properties (tensile strength and modulus), and improve resistance to thermal and chemical degradation [2]. Vulcanization or crosslinking or curing is an essential part of processing of an elastomer product. It is the final stage in processing, and it helps in improving the elastic strength, solvent resistance and oxidation resistance of elastomers [1]. Vulcanization is done at high temperatures (110 - 210°C) and high pressures for most rubbers, inside the mold, or press in the case of compression molding [1]. However, there are also other rubbers that crosslink at room temperature, without sulphur. These room temperature vulcanization rubbers are usually Silicones like poly(dimethylsiloxane), and their crosslinking is catalyzed by Platinum. During vulcanization, various chemicals are mixed into the initial rubber and compounded. This includes a curing agent, accelerators, activators and retarders.

Sulphur is used as the most common curing agent, followed by organic peroxides [1]. The mechanism of sulphur vulcanization is strongly dependent on the components present, temperature and duration of the process. During the initial period, the structural fragments mainly include disulphide and polysulfide linkages and pendant polysulfide chains. These chains are terminated by an accelerator fragment. Isomerization of the double bonds is also believed to occur leading to the formation of conjugated diene and triene sequences [1].

For the process of vulcanization to be useful and successful, it should be controlled, and stopped at the right time. Premature vulcanization may create bubbles in the elastomer and make it unusable in some cases. Over curing or overexposure might lead to reversion of crosslinks, which occurs since the polysulphide linkages in crosslinks are susceptible to scission [1]. Vulcanization is controlled by the production unit to a certain point, such that the product produced fulfils the requirements expected out of it. Understanding cure chemistry can be beneficial in characterizing the exact time to stop vulcanization, as the process consumes a high amount of energy and time. To characterize the exact cure state has been a challenge to most rubber technologists. Curing or crosslinking of elastomers has been studied by researchers and industrialists, to understand the chemistry and process better. Some of the methods used in the industry and in literature to measure the cure state are outlined in the upcoming chapters.

### **1.1. MOTIVATION**

The main objective of the master's thesis is to establish one standard method that can be relied on, to measure the optimum cure state of an elastomer. It is important to know the cure state of an elastomer product, as this helps in stopping vulcanization at the right time, to save energy and time. The other advantage is that the performance of any product is enhanced as it reaches optimum cure state. The methods existing in the industry and in literature to measure the cure state have some advantages and disadvantages. The most widely used methods are outlined on the basis of test sample geometry, reversion detection, error and timing, in Table 1.1. From Table 1.1 it can be understood that there is not one standard method in the industry for optimum cure time measurement.

One of the other main methods used in the industry is the Moving Die Rheometer (MDR). This method is further explained in section 2.1.3. The  $t_{90}$  from MDR is used as an effective characterization of 90% cure state in the industry. This gives an insight to the cure state of the elastomer. This method is reliable and effective, but cannot be applied on complex sample parts. The die in the apparatus is usually of 25 mm diameter [5]. Some of the other methods include compression set, mass swelling, and porosity. Compression set and mass swelling require at least 22 – 24 hours as test time and the sample preparation for compression set from complex parts is not possible. Thus, every method existing has a disadvantage, and hence there is a need for a new method that has maximum advantages, and can be easily applied in the industry. The main focus of the thesis is to answer questions about the optimum vulcanization time, and to evaluate a new method regarding its feasibility and practicability for industrial applications.

## **1.2. MATERIALS – ELASTOMERS**

### **1.2.1. Poly(dimethylsiloxane) (PDMS)**

To assess the exact cure time of a crosslinked elastomer by a new method, a reference with a simple crosslink system had to be chosen. Poly(dimethylsiloxane) is selected as reference due to its simple chemistry, and the limited amount of compounding ingredients, as compared to conventional rubbers. PDMS is also used in this thesis due to the ease of breaking down the chemistry to understand the cure state. Another reason for choosing PDMS as a reference was the fact that swelling experiments are usually characterized on this elastomer. The following chapters discuss the different methods, and solvent swelling is one of the important ones. In this regard, PDMS is widely used by researchers to be characterized in terms of swelling experiments [6] [7]. Thus, it would be the most ideal reference substance for this thesis.

Poly(dimethylsiloxane) is a silicone elastomer with structure (Figure 1.1). PDMS is one of the largely used silicon-based organic polymers. It is most widely used as contact lenses and medical devices, caulking, lubricating oils and heat resistant tiles. PDMS is optically clear, non-toxic and non-flammable [8]. The mechanical properties of PDMS can be fine-tuned by varying the crosslink density in the polymer [6].



PDMS is a Room Temperature Vulcanization (RTV) silicone [8]. The presence of Silane precursors with fewer methyl groups like methyltrichlorosilane in reactive PDMS helps in crosslinking, as each site with such groups becomes a branch point [8].

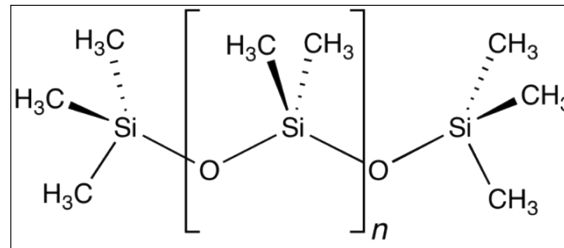


Figure 1.1– Structure of PDMS [8]

At each end of the long PDMS polymer chains, there are usually vinyl groups present. The short crosslinker is an oligomer, polymethylhydrosiloxane, which links the PDMS chains (Figure 1.2).

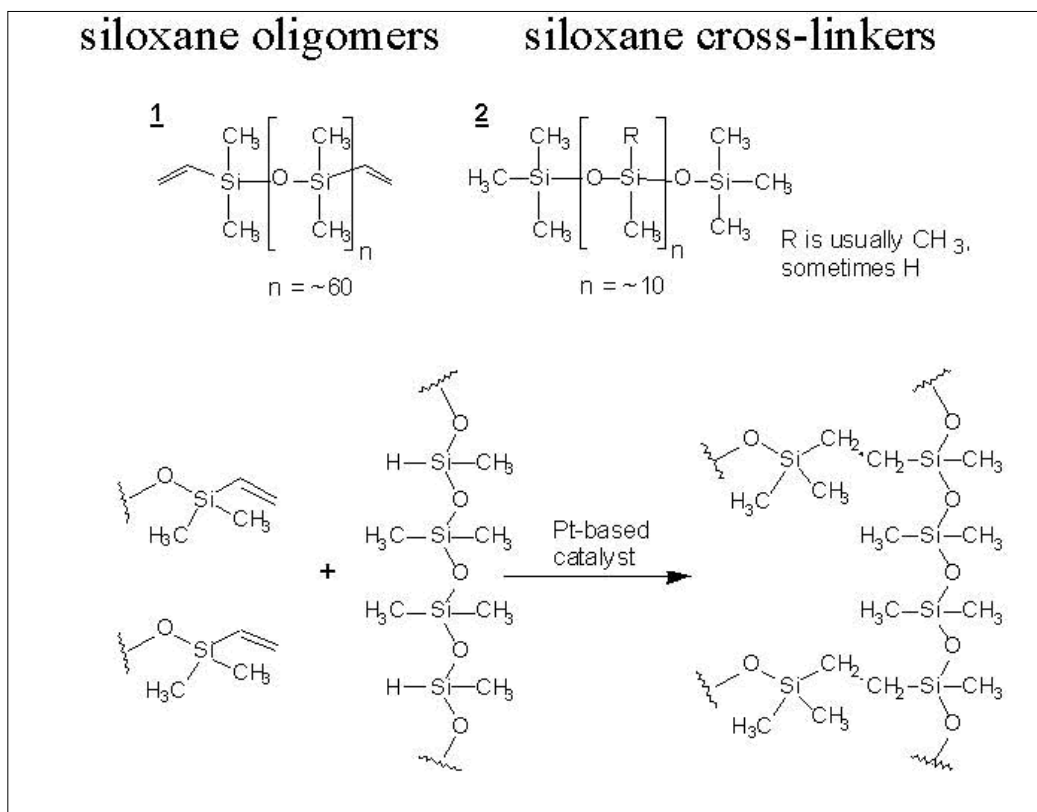


Figure 1.2 – Crosslinking of PDMS [8]

The main step of the platinum cure mechanism is hydrosilation with Platinum as catalyst. This type of curing requires the material to be post cured, to complete the crosslinking process [8].

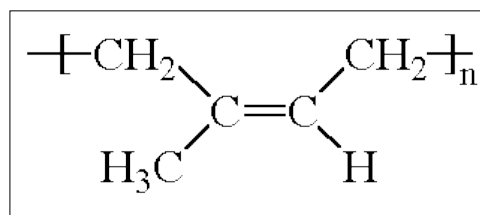
This reaction is catalyzed by platinum. PDMS is soft and gel-like at low crosslink densities. As the crosslink density is increased, it becomes more and more stiff. Stiffness can be varied by varying the ratio of base (PDMS long chains and short chains) to curing agent (Platinum) [8].

One of the main goals of this thesis is to characterize the cure behavior of PDMS network samples, and establish PDMS as reference.

### 1.2.2. Natural Rubber (NR)

Natural rubber (NR) is obtained as latex (polymer dispersion in aqueous medium) from the *Hevea Braziliensis* tree [1]. It is the only non-synthetic elastomer most widely used for various applications [1]. NR mainly constitutes of *cis*-1, 4-polyisoprene in its backbone chain. One of the special types of natural rubber available is in the form of ribbed smoked sheets [1]. The latex obtained from the *Hevea* tree contains many organic and inorganic impurities. This latex is then coagulated using an acid, and the concentrated rubber is formed into ribbed smoked sheets. These sheets are raw materials for various industries [1]. The main applications of natural rubber include in tires, conveyor belts, vibration isolators, seals, hose and tubing [1].

Apart from these applications, natural rubber is also used as a reference to rate other synthetic elastomers for their strength, resilience and hysterical properties [1]. This makes it an obvious choice for the experiments regarding cure state. For this Master's thesis, the natural rubber samples used were provided by Vibracoustic GmbH. The structure of the monomer unit of NR Vib 1 is shown in Figure 1.3.



**Figure 1.3 – Structure of the monomer unit of natural rubber (*cis* – polyisoprene) [1]**

To understand the cure state of an elastomer, it is important to understand the chemistry behind crosslinking and vulcanization. Natural rubber is vulcanized by Sulphur [1]. Sulphur forms crosslinks between the chains of natural rubber through the reactive double bonded carbon site. Chemical compounds called accelerators and activators are added in order to

increase the speed of vulcanization. Vulcanization proceeds by the formation of an active accelerator complex from the reaction of the accelerator and activator [9]. The active accelerator complex reacts with molecular Sulphur to form sulphurating species. These sulphurating species then form crosslink precursors after reaction with an unsaturated site, in particular an allylic carbon on the rubber chain [9]. The crosslink precursors are polysulfidic pendant groups attached to the rubber chain [9]. Polysulfidic crosslinks are formed when these crosslink precursors react with additional unsaturated sites on the rubber chain [9].



## 2. THEORETICAL BACKGROUND

### 2.1. EXISTING TECHNIQUES

There are numerous methods existing in the industry today to characterize the vulcanization time of elastomer products. Some major methods, their advantages and shortcomings, are outlined in this section (Table 1.1). This provides an insight to the need for a new standardized method to measure the cure time precisely.

**Table 2.1 – Comparison of existing methods and methods in literature [4] [10]**

Method	Need for specific sample geometry	Reversion detection	Error	Timing
Differential Scanning Calorimetry [4]	No	No	High	30 min
NMR t2 relaxation [4]	No	Yes	Low	1 min
Mass swelling [10]	No	Yes	High	24 h
Compression set [10]	Yes	No	Low	24 h
Hardness [4]	Yes	No	Low	1 min
Porosity [10]	No	No	High	1 min

#### 2.1.1. Compression Set

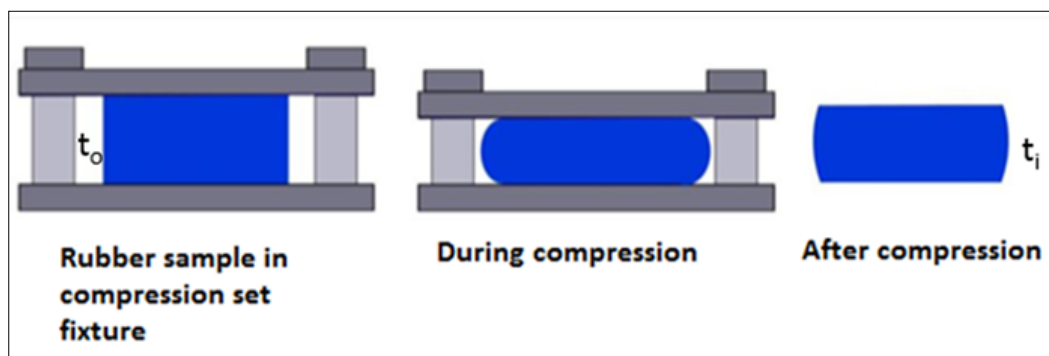
Compression set is the ability of rubber to return to its original thickness after prolonged compressive stresses. The behavior of rubber under predefined load for a specific time translates to the mechanical strength, in turn, giving useful information about cure state. According to ISO 815, DIN 53517, ASTM D395 and other International Standards, a rubber specimen is compressed over time between 2 flat parallel plates with a predefined preload and kept for a specific time at a certain temperature [1]. After a specific time of compressive

force, the elastomer loses its ability to return to its original thickness. This test method also characterizes the capability of an elastomeric product to perform elastically over a long period of time [11].

The compression set fixtures are usually made of stainless steel and feature stiff compression plates, as shown in Figure 2.1 [11]. The standard test specimen shall be a cylindrical disk cut from a laboratory prepared slab [11]. Specimens from each sample may be tested in duplicate (test method A) or triplicate (test method B) [11]. The thickness of specimen for test method A is  $12.5 \pm 0.5$  mm, and for test method B is  $6.0 \pm 0.2$  mm [11]. There is also a difference in test methods A and B in the cooling time after the specimen is removed from the fixture after testing, and before measuring the height. For most elastomer samples, a cooling time of 30 minutes is applied, except for samples whose compression set values are affected by moisture in the atmosphere [11]. For those samples, according to method A, cooling is done in a moisture controlled atmosphere of  $50 \pm 5$  % relative humidity [11].



(a)



(b)

**Figure 2.1– (a) Compression set fixture (b) A rubber sample being subjected to compressive force**  
[11]

The compression set is calculated for test method A below (2.1).

$$C_A = \left( \frac{t_o - t_i}{t_o} \right) \times 100 \quad (2.1) [11]$$

Where,

$C_A$  = Compression set (Test Method A) as a percentage of the original thickness

$t_o$  = original thickness, and

$t_i$  = final thickness

Compression set is a classic method used in the industry to help determine the cure state of an elastomer. The higher the crosslinking, lower is the chain mobility, and hence, lower the compression set. A low compression set elastomer performs better during application of compressive stresses than a high compression set elastomer. Since vulcanization is also done to enhance the mechanical performance of elastomers in the field, compression set is an ideal method to characterize the extent of cure in an elastomer.

Compression set requires at least 22 – 24 hours of testing time, during which the samples are heated to a specific temperature [11]. The results are obtained after 24 hours of testing time and 30 minutes of cooling time, which is a drawback, considering an industry setup where production runs for 24 hours a day. The method is highly dependent on sample preparation, sample mounting and pre-loading. Measurement of height after the test is done manually, usually with a dial gauge, which might induce human error and can become unreliable. The preparation of samples from complex geometries is not possible. Hence, the need for a new method that optimizes the measurement time and is also reliable and reproducible is prominent.

### **2.1.2. Swelling Experiments**

Elastomers swell when they are in contact with a suitable solvent. This is a result of the elastomer imbibing the solvent [7]. In the case of a linear non-crosslinked chain of an

elastomer, the swelling is limited to the availability of solvent. When the elastomer is crosslinked, and possesses a network structure, the amount of solvent absorbed, will reach saturation, beyond which swelling will not occur. As the number of crosslinks in an elastomer increases, swelling in a solvent decreases. The concept of swelling can be explained as the effect of osmotic forces between the elastomer and the solvent. Swelling or expansion of the elastomer is analogous to elastic deformation. When the elastic response of the network structure is balanced by the osmotic forces, equilibrium between solvent in the gel and excess solvent is attained [7]. Flory *et al* explained in his work on configurations theories that to reach swelling equilibrium, the partial molal free energy of the solvent in the gel and the molal free energy of the unabsorbed solvent should be equal [7]. Hence, for a crosslinked system, swelling equilibrium is reached far earlier than for a linear non-crosslinked gel.

The classical swelling experiment used to determine cure state in the industry. In a standard swelling experiment, a sample of the elastomer is made to come in contact with a suitable solvent for 24 hours [12]. The elastomer sample swells in the due to the solvent. The sample is weighted before the experiment and the swollen sample is weighted after exposure to the solvent [12]. The swelling ratio is the ratio of initial and final weights of the sample, before and after immersion. It is calculated using the formula below.

$$\text{Swelling ratio} = \frac{W_f}{W_i} \quad (2.2) [12]$$

$$\text{Swelling \%} = \frac{(W_i - W_f)}{W_i} \times 100 \quad (2.3) [12]$$

Where,  $W_i$  is the initial weight of the elastomer, and  $W_f$  is the weight of the elastomer after swelling in the solvent.

Swelling experiments are a simple and inexpensive way to characterize polymer networks. They are essentially used for quality control and aid as an indexing tool for polymer systems with different levels of crosslinking in the industry [12]. Swelling experiments are done manually, and mostly with a liquid solvent. This makes handling and measurement of weight after immersion tricky. Also, the removal of excess solvent from the sample can be done by various methods like wiping or blow drying. This produces discrepancies. The elastomer is immersed in the solvent for at least 24 hours, which makes the experiment time consuming.



### 2.1.3. Rheometer

The study of flow and deformation of materials under applied forces is called rheology [1]. Rheology tests of polymers study the relationship between the stress and deformation with respect to flow properties. Laboratory methods to study rheology can help in deciding optimal processing conditions, which save costs and minimize waste. Rheology tests could also give an insight to cure state of an elastomer [7].

The rheometer can be used to analyze the vulcanization characteristics of elastomer compounds [1]. A sinusoidal strain is applied to the uncured elastomer sample in a sealed and pressurized cavity [1]. Due to the viscoelastic nature of elastomers, the applied strain is out of phase with the measured complex torque response. The out of phase response is quantified by the phase angle  $\delta$  [1].

The elastomer sample cures in the cavity of the rheometer under high temperature and pressure, and the values of torque start to vary. The Moving Die Rheometer (MDR) employs a set of dies between which the uncured sample is mounted. The torque is measured and plotted against time for which the sample is cured between the die. Figure 2.2 is a typical schematic obtained from a Rheometer for a natural rubber sample.

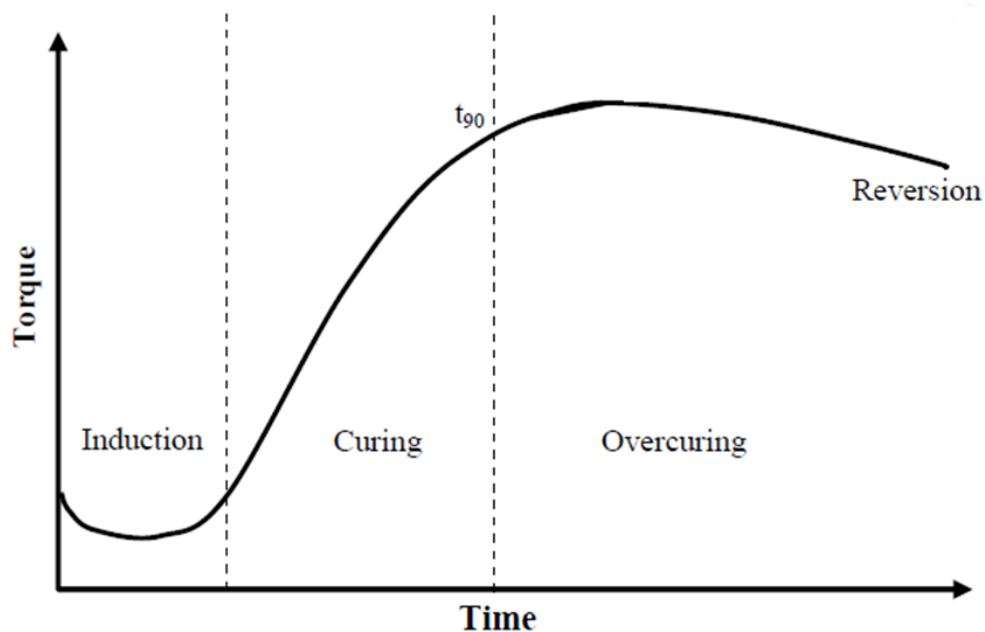


Figure 2.2 – Rheometer curve [13]

There are three stages represented in a vulcanization curve. In the first stage, there is a slow chemical reaction between the rubber and additives, this is the induction phase. During this phase, the rubber is not scorched, and starts to flow. This is also called scorch safety. During the second stage, curing proceeds in the elastomer and networks start forming. The rate of vulcanization can be calculated from this stage. The optimum cure of the sample is observed at  $t_{90}$ , which is defined as the time necessary for the torque to attain 90% of the maximum achievable torque. In the final stage, there is a chance of over curing to occur, based on the rubber type, temperature and curing agent [13].

#### **2.1.4. Other Methods in Literature**

Literature study gives an insight into the methods that have been developed before to solve the problem of characterizing the exact cure time. Methods like Nuclear Magnetic Resonance (NMR) Spectroscopy and Porosity tests have been long used in the industry to solve this problem. Some of their disadvantages were outlined in Table 2.1.

Kirchhoff *et al* have explored into ultrasound techniques to determine the cure state in their work [14]. The method uses ultrasound waves that are passed through the isolated sample and the reflected waves are measured by a detector. Speed of sound in the sample and attenuation coefficient are correlated to the mechanical properties of the elastomer. The attenuation coefficient and phase velocity were used to calculate complex moduli and dynamic loss factors. Frequencies between 0.5 to 10 MHz were used to test elastomer samples. The tests were also done on samples with fabric layers to check the applicability of the technique. The main advantage of this method is that the results are immediately available and the waiting time is short. It can be highly reproducible and is non-destructive to the sample. Some of the disadvantages outlined in the paper include that it requires high resolution and cannot be used at elevated temperatures due to the dependency of attenuation coefficient on temperature. The reproducibility of the measurement of attenuation for thin samples with fabric layers is very low. The resolution of the technique is dependent on temperature [14].

Liebers *et al* have researched further into the ultrasonic methods of cure testing [15]. In a conference for the German Aerospace Centre (DLR), they presented that the most innovative, time saving and advantageous way of measuring cure state of composites would be by the use

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of in situ sensors that measure the cure time during production. The role of process integrated sensors in quality assurance, process optimization and automation was explained. One of the methods include the adaptation of an ultrasonic transducer into the mould using a vacuum bag. This would require access from both sides of the mould for detection of the cure state using ultrasonic waves. The installation of transducers requires preparation as they have to be placed in an adapter and sealed into the vacuum bag which might also be a leakage risk [15].

Zaimova *et al* studied the use of Differential Scanning Calorimeters (DSC) in cure time characterization [4]. The standard DSC is used to study phase transitions and measure the glass transition temperature. DSC measurements were done on molded test sheets of natural rubber to study the cure state. The results showed 20 % error due to the low sensitivity of the method. Three levels of state of cure were detected using this method. The precision of this method was low, and reversion could not be detected [4].

Pickering *et al* used the Dynamic Mechanical Analyser (DMA) to understand the vulcanization state of elastomers, and then compared it to standard rheometer (MDR) measurements [13]. The DMA is used to analyse the elastomer's response to sinusoidal deformation. The glass transition temperature, loss and storage moduli, and viscosity can be determined by using the DMA. An isothermal time sweep was done on natural rubber samples with different ratios of compounding ingredients. The results from DMA were compared to standard rheometer tests and the three major stages of vulcanization as understood from the rheometer curve (Figure 2.2) were observed [13].

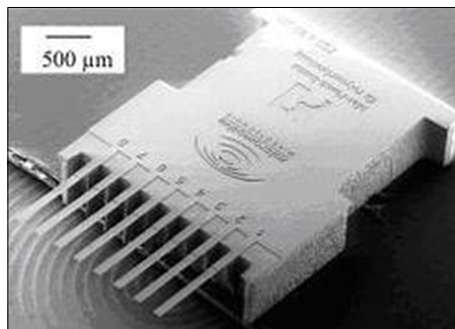
From literature study, it became evident that there is need for a new method that helps in characterizing the cure time with the following advantages

- Small sample – the advantage of testing parts with complex geometries
- Short time – a method that can be incorporated in the production line and does not consume a high amount of time
- Reliable and precise measurement of cure state

A method with the above mentioned advantages is an essential step to solving the problem of cure state characterization.

## 2.2. MICRO CANTILEVER SENSOR (MCS) TECHNOLOGY

Micromechanical cantilever sensors are made from Silicon wafers with dimensions in the order of approximately 750  $\mu\text{m}$  or above. These cantilevers have applications in several sectors such as telecommunications, consumer electronics, transportation, building automation and healthcare [16]. Their initial important application was as force probes in atomic force microscopy (AFM). The silicon probes in AFM are extremely sensitive to various factors like acoustic noise, temperature, humidity, and ambient pressure, which may be an interference during measurement with an AFM. Later research led to the observation that the same mechanisms that caused unwanted interference in an AFM can be converted into a platform for a new family of sensors. The new family of sensors relies on measuring the shifts in resonance frequencies of the micro cantilevers. They are mass sensitive devices that can be used in place of conventional piezoelectric sensors due to their high sensitivity, and small size [17].

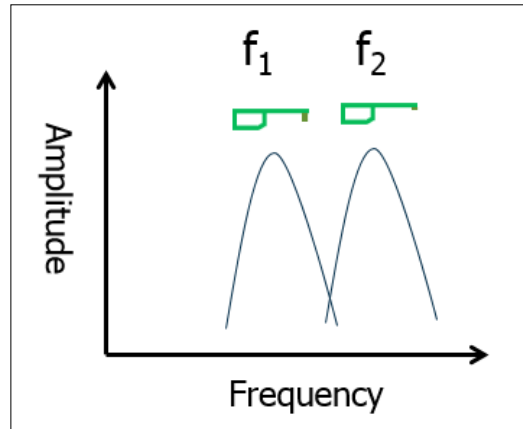


**Figure 2.3– Micro cantilever sensor [17]**

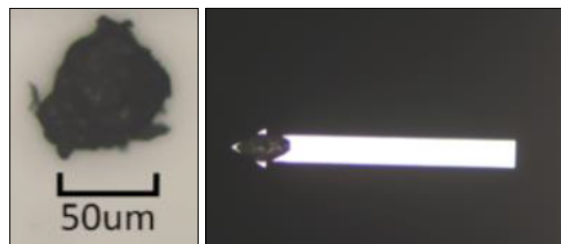
The mass sensitivity of micro cantilevers can be very well exploited by the rubber industry in the area of cure time characterization. A simple and standard experiment used in the industry to measure the optimum cure time is the swelling experiment. As explained in section 2.1.2, a small sample of elastomer (macro scale) is immersed in solvent solution for 24 hours. The sample is weighted before and after immersion. The swelling ratio is calculated from the difference in weight of the elastomer before and after immersion. The swelling ratio is inversely proportional to the cure state. This same concept can be applied to the micro cantilevers and the mass sensitive resonance frequency can be a measure of the cure state.

The main advantage of such a technique is the sample size of about 50  $\mu\text{m}$ , and a weight of  $10^{-11}$  g. A highly magnified sample is a benefit while studying cure states of products with

complex geometries, as there is only need for a smaller area of the sample. The micro sample is carefully mounted on the cantilever and exposed to solvent vapor. The resonance frequencies during exposure to solvent are measured. A steady decrease in resonance frequency is expected as the mass increases due to absorption of solvent by the elastomer. The resonance frequency difference corresponds to the mass difference and helps in measuring cure state of the sample.



(a)



(b)

**Figure 2.4 – (a) A 50  $\mu\text{m}$  particle is mounted on the cantilever before testing. The change in mass occurs due to solvent swelling. (b) The shift in resonance frequency occurs as a result of change in mass of swollen elastomer.**

The change in resonance frequency corresponds to the change in mass due to swelling. The change in mass can be calculated by using the following formula.

$$\Delta m = \frac{K}{4\pi} \left( \frac{1}{f_2^2} - \frac{1}{f_1^2} \right) \quad (2.4)$$

Where,  $f_1$  is the resonance frequency before exposure to solvent,  $f_2$  is the resonance frequency after exposure to solvent, and  $K$  is the spring constant of the cantilever.

The huge advantage is that of obtaining results in a relatively short period of approx. 30 minutes, as opposed to 24 hours for classical swelling experiment. This is feasible due to the small size of the sample that takes less time to swell when exposed to solvent. The mass resolution of the sample is a boon to test cure states throughout the thickness of the elastomer product. In addition to determining the vulcanization extent, this method can also be used to understand the swelling – de-swelling behavior of the elastomer.

## 2.3. PIEZORHEOLOGY

### 2.3.1. Flory – Rehner theory

Elastomers with crosslinks in their chains can assume various configurations depending on the free rotation about the carbon-carbon bonds in their main chain. In November 1943, Flory and Rehner [7] developed a statistical mechanical theory of chain configuration. This theory aids in explaining the elasticity of rubbers and other long chained macromolecules. According to this theory, the rubber chains in the non-deformed state assume configurations close to their most probable state. Deformation displaces the configuration and decreases entropy of the chain. This explains the elastic nature of rubber. Various theories of chain configuration propose the relation between elastic properties and the structure of a crosslinked system.

Swelling of crosslinked networks can be understood as the osmotic dilution opposed by the elastic response of the swollen network. The Flory–Rehner equation describes the equilibrium swelling of a crosslinked polymer in terms of crosslink density. The theory considers forces arising from three sources – the change in entropy due to mixing, the change in entropy due to swelling (reduction in number of possible chain conformations), and the heat of mixing [7].

The equation is given as,

$$-\left[\ln(1 - v_2) + v_2 + \chi_1 v_2^2\right] = V_1 n \left(v_2^{\frac{1}{3}} - \frac{v_2}{2}\right) \quad (2.5) [7]$$

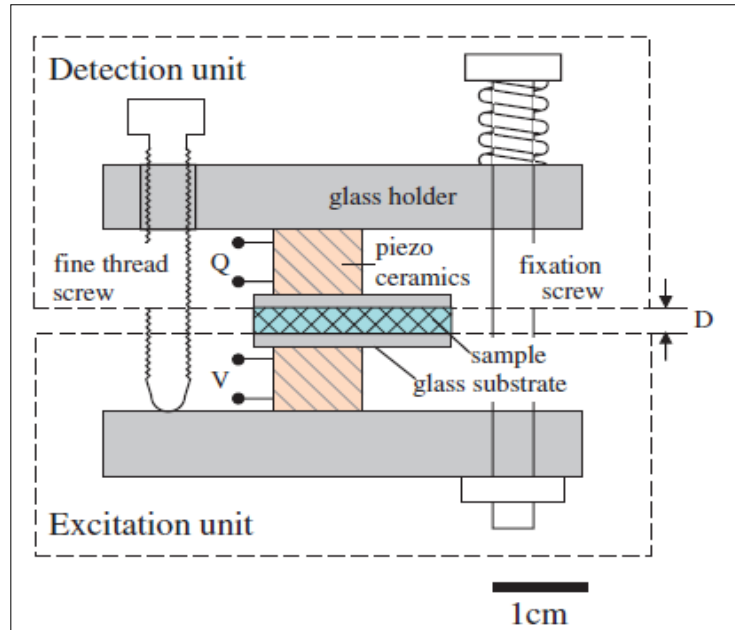
Where,  $v_2$  is the volume fraction of polymer in the swollen mass,  $V_1$  is the molar volume of the solvent,  $n$  is the number of network chain segments bounded on both ends by crosslinks, and  $\chi_1$  is the Flory solvent-polymer interaction term [7].

### 2.3.2. Piezorheology

The rheological behavior of a complex network system possesses many unanswered questions [18]. In this thesis, the focus is on the mechanical properties as a function of frequency. For this, a homemade piezorheometer is used [19].

Piezorheometers follow the set up and principles of classic oscillatory rheometers. Here, the excitation of piezoactuators is achieved by the principles of piezoelectric and inverse piezoelectric effect, contrary to the use of electro motors and capacitive transducers in conventional rheometers [18]. The strain amplitudes for conventional rheometers are in the range of  $10^{-2}$  or higher, while the minimum strain amplitudes of piezorheometers are about  $10^{-4}$  [19]. The applied strain on the sample is very small, owing to the mechanical excitation by piezoelectric actuators. At these small strains yielding is avoided for fragile materials, which makes piezorheometers suitable for measurements in the linear regime. The low deformations can contribute to the device being reproducible [18]. The frequency dependent shear moduli can be measured from 0.1 to 1000 Hz. Moreover, compact design can be achieved by the use of piezoelectric actuators [19]. The upper frequency limit is shifted to 1 kHz due to the reduced inertia moments [18]. Beyond 1 kHz, resonance effects prevent an accurate determination of the shear modulus [18].

Durand *et al* brought together a piezorheometer for the first time, to study smectic liquid crystalline phases [20]. In the first piezorheometer, small strains were crucial as the deformation energies required were low. Yamamoto *et al* and others made further developments in the piezorheometer, but kept the original design intact (13). The master thesis also uses similar design as made by M. Roth *et al* in the analysis of colloid liquid crystal composites [18].



**Figure 2.5 – Schematic of Piezorheometer. Scale bar indicates dimensions [18].**

The piezorheometer operates in shear mode, and follows the principles of construction, as mentioned by Durand *et al* [20]. Figure 2.5 illustrates the important elements of the set up. There are two piezoceramic stacks (PICA™ Shear Piezo Actuators; PICeramic, Lederhose, Germany), both the stacks are glued on to a glass substrate on one end and a glass holder on the other end [18]. The gap between the two glass holders is between 10  $\mu\text{m}$  and 5 mm, where the sample is placed [18]. This gap is confined by three fine thread screws that have an accuracy of 3  $\mu\text{m}$  [19]. The dimensions of the glass substrates were (12  $\times$  20  $\times$  2)  $\text{mm}^3$ , and that of the whole cell were (55  $\times$  58  $\times$  100)  $\text{mm}^3$  [19].

The piezoelectric stack was excited electronically by using a frequency generator (33220A; Agilent), that applied a sinusoidal voltage  $V_E(t)$  [18].

$$V_E(t) = V_{E0} \sin(\omega t) \quad (2.6) [18]$$

In this experiment, the frequency was varied between 0.1 to 1000 Hz, and the amplitude  $V_{E0}$  was in the range of 0.5 to 10  $V_{pp}$ . From the understanding of inverse piezoelectric effect and specific polarization of ceramics, it can be said that this voltage is transferred to shear deformation  $s(t)$  of the sample [18].

$$s(t) = d_{15} V_E(t) \quad (2.7) [18]$$



The proportionality constant in this case is  $d_{15} = (3.4 \pm 0.1) \times 10^{-18}$  m/V, with absolute deformations in the range,  $s_{\min} = 7$  nm, and  $s_{\max} = 600$  nm. In this range, the proportionality is preserved [18]. The deformation is transmitted into the sample through the complex shear modulus  $G^*(\omega)$ . Free charges  $Q_D(t)$  are generated by piezoelectric effect on the piezoactuators, as a result of the stress  $\sigma(t)$  in the upper glass substrate [19].

$$Q_D(t) = d_{15} \cdot \sigma(t) = d_{15} \cdot G^*(\omega) \cdot \frac{s(t)}{D} \quad (2.8) [18]$$

A charge sensitive amplifier (Type 2635; Brüel and Kjaer) is used to collect these generated charges and convert them into a voltage  $V_D(t)$ . An oscilloscope (DSO6044; Agilent) records  $V_D(t)$  at the same time with the excitation voltage. Since the stress is directly proportional to  $V_D(t)$ , the ratio of amplitude and the phase difference of  $V_E(t)$  and  $V_D(t)$  give a direct measure of the complex shear modulus [19].

At low levels of signal the detection of deformation by the piezo could be approximately 0.2 pm. The charges generated are in the order of 0.1 pC, which is equal to a stress of  $\sigma_{\min} = 1$  Pa [19]. The minimum shear modulus, with respect to the thickness  $D$ , can be calculated by Equation 8, below.

$$|G_{\min}^*| = \frac{\sigma_{\min}}{s_{\min}} \cdot D \approx 5 \text{ Pa}/\mu\text{m} \cdot D \cdot A \quad (2.9) [19]$$

Where,  $A$  is the empirical scaling factor, whose value depends on the recorded data [18]. The data set was processed by Fourier transformation to obtain averaged values for the shear moduli. The piezoceramic stacks were comprised of single sheets arranged in the order of alternating crystal orientations and electric contacts. This cancelled all effective long wavelength electromagnetic radiation. Hence, electromagnetic isolation was achieved as an intrinsic feature of the piezoceramic stack [19]. All the cable connections to the actuators were shielded using metal, which is not shown in Figure 2.5 [18].

M. Roth *et al* made gauging measurements as part of calibration of the device [19]. Measurements were made for absolute values of complex shear modulus, with the help of two calibration fluids that behaved as pure Newtonian liquids over a broad frequency range [19]. The frequency dependence of loss modulus  $G''$  was measured at different temperatures.

The viscosity was derived from fitting. The overall error of viscosity data amounted to less than 3% [18].

### 3. EXPERIMENT

#### 3.1. SAMPLES

Poly(dimethylsiloxane) (PDMS) samples were synthesized using Sylgard®184, a commercially available two part Silicone elastomer by Dow Corning. Samples were made for three mixing ratios of base to crosslinker or curing agent. The ratios were decided as a basis to distinguish between the three different crosslink densities. The number of parts of crosslinker was changed accordingly, as shown in Table 3.1. For the mixing ratio of 1:10 by weight, 1 part of elastomer was taken and mixed with 0.1 parts of curing agent, for 1:20, 0.05 parts of curing agent was used, and for 1:30, 0.033 parts of curing agent was used. The mixture was mixed on a magnetic stirrer in the laboratory for 15 minutes. The mixture was then transferred to rectangular Teflon molds of 2 mm thickness. Curing was done at room temperature as PDMS used in this study was a room temperature vulcanization (RTV) elastomer. To accelerate the process, and to study post curing time required, the elastomer was cured in a laboratory convection oven at 100°C, for 18, 48 and 132 hours. The elastomer was then removed from the molds and cut into rectangular samples of approximately 5 × 2 mm<sup>2</sup> dimensions and 2 mm thickness.

**Table 3.1 – PDMS sample details**

PDMS Mixing Ratio – Elastomer : Curing agent	Cure time (hours)	Cure temperature (°C)
1:10	18, 42, 132	100
1:20		
1:30		

Natural Rubber sample plates were supplied for the thesis by Vibracoustic GmbH (NR Vib 1). Natural rubber for sample plates was compounded, and the plates were prepared by compression molding at 170°C. The plates were approximately 2 mm and 6 mm thick and had

dimensions of  $200 \times 200 \text{ mm}^2$ . The natural rubber plates were cured from 1.5 minutes to 15 minutes (Table 3.2).

**Table 3.2 – NR Vib 1 Sample details**

Thickness	Cure time	Number of sample plates	Cure Temperature (°C)
2 mm	1,5	1	170
	2	1	
	4	2	
	6	2	
	10	2	
	12	1	
	15	2	
6 mm	2	2	
	4	2	
	6	2	
	10	2	
	12	2	
	15	2	

The 2 mm sample plates were used to prepare samples for Piezorheology. The samples were cut out from the plates, using a circular cutter and hammer. The cut samples were of 10 mm diameter. These samples were then cleaned with ethanol, to remove any surface residues before being used in the piezorheometer.

### 3.2. PIEZORHEOLOGY

Poly(dimethylsiloxane) samples were tested in the piezorheometer to obtain values of loss modulus  $G''$ , and storage modulus  $G'$ . The device was first aligned in such a way that the glass substrates touched each other. The gap size was completely reduced for this, with the help of fine thread screws, as in Figure 2.5. Plate parallelism was checked by Newton rings due to multiple reflections from the interface of air and the glass substrates [18]. Then, all three fine thread screws were adjusted in order to increase the gap between the glass substrates. M. Roth *et al* estimated the quality of parallelism to be better than  $0.1^\circ$  [18]. The difference between total distance of the glass holders at the centre and the distance when the glass substrates touch each other gives the absolute gap size [19]. The thickness of the PDMS samples was measured using a screw gauge, and the gap size was set equal to the measured thickness. The PDMS samples ( $5 \times 2 \text{ mm}^2$ ) were placed in such a way that they had a plain, flat and clean surface in contact with the glass plates of the piezorheometer. The set up was then screwed tight using three fixation screws (Figure 2.5), by hand. After every measurement, the surface of the glass substrates was cleaned with ethanol in the laboratory.

Natural rubber (NR Vib 1) samples were tested in the piezorheometer in a similar way. The samples were round, and of 10 mm diameter. They were cut from the centre of the sample plate initially, and later from other places for extensive analysis. The samples were placed on the glass substrates using the method detailed above. The thickness of the samples was measured with the same screw gauge. The surface of the natural rubber samples was cleaned with ethanol solution, in order to remove all the contaminants from blooming. Blooming of rubber is caused by the migration of compounding chemicals like antioxidants, wax and anti-degradants to the surface, due to their poor solubility in the rubber matrix [1]. It was essential to remove the “bloom” in order to avoid variations caused due to bad contact between the sample and the glass substrates.

The dynamic measurements were made for each sample for typically ten periods, and 20000 points per period. The data was measured from 0.1 Hz to 1000 Hz, at an input voltage of 2 V ( $V_{pp}$ ). Measurements were made to analyze the effect of the input voltage, by varying the input voltage to 0.5, 2, 5, and 10 V. All the measurements were made for at least 3 consecutive

times on the same sample, to help calculate the error due to noise in the setup. The measurements were saved and the values of  $G'$  and  $G''$  are then post processed.

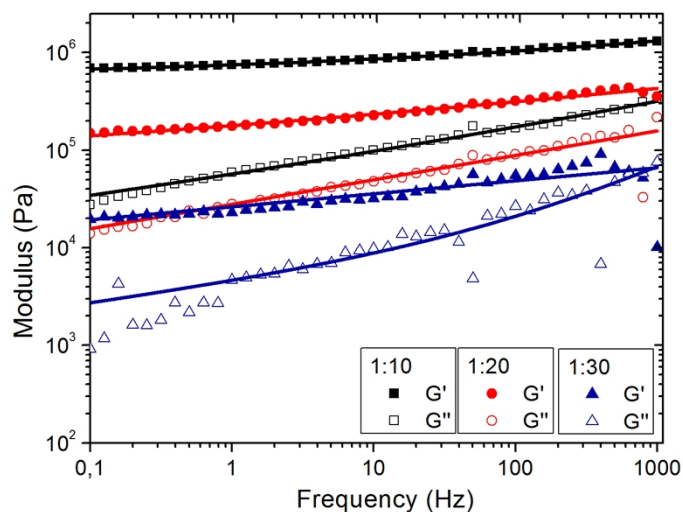
### **3.3. SWELLING EXPERIMENTS**

Classical swelling experiments were done on the reference (PDMS) and on natural rubber to be compared to the results from piezorheology. The samples were cut out from sheets and immersed in liquid toluene for 72 hours. The weight of the samples was calculated before and after immersion. The swelling ratio was then calculated from the weights (equation 2.2).

## 4. RESULTS AND DISCUSSION

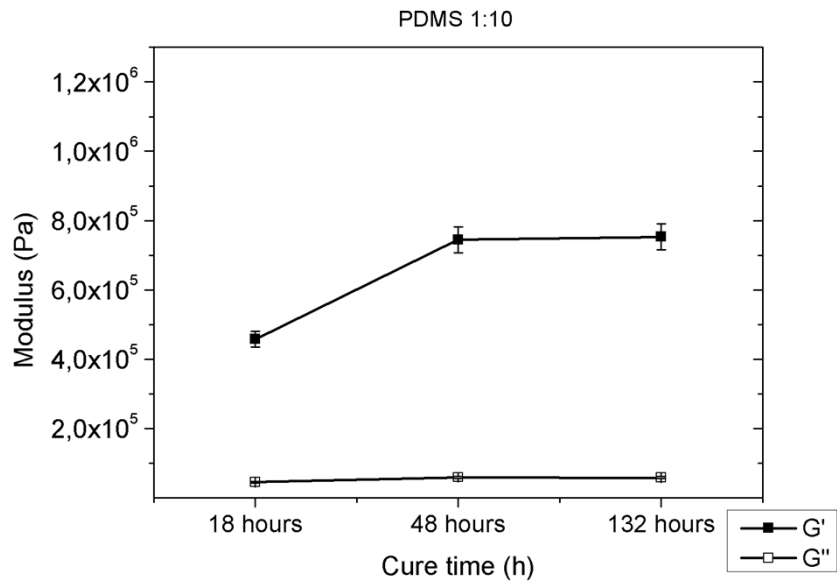
### 4.1. POLY(DIMETHYLSILOXANE) (PDMS)

The results from piezorheology for the reference are evaluated in this section. Three different crosslink ratios of PDMS were used (Table 3.1). The initial mechanical spectra are plotted as modulus against frequency curves. The obtained spectra is represented in Figure 4.1.

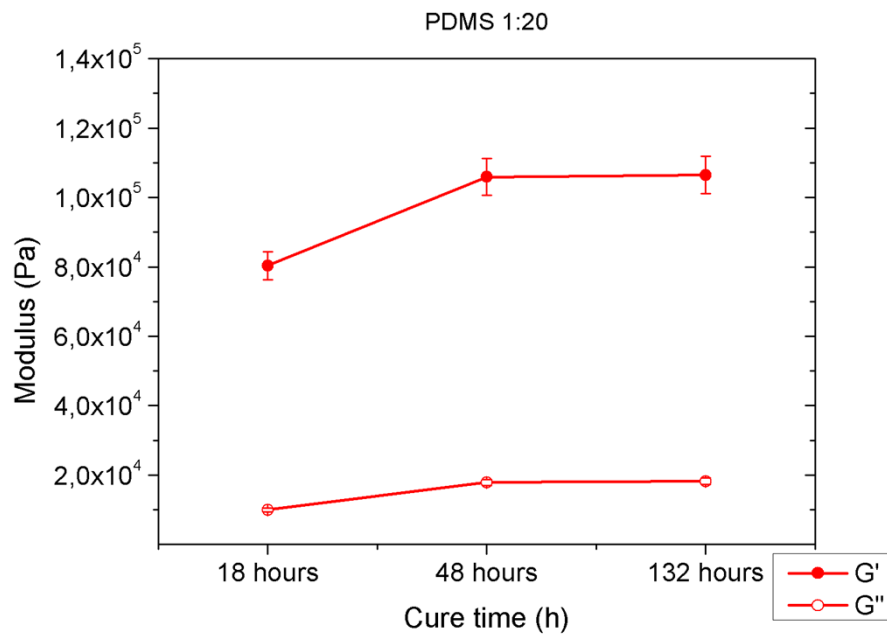


**Figure 4.1 – Modulus against Frequency curves for PDMS mixed at three ratios and cured for 48 hours at 100°C, plotted in a log-log graph. Points were acquired from measurement and lines were fit using a power law.**

The storage modulus  $G'$  and loss modulus  $G''$  increase with increasing crosslink density. The lowest moduli is for 1:30 and increases as the mixing ratio reaches 1:10. The loss moduli from measurement are almost 1.5 orders smaller than the storage moduli, which is comparable to values in literature [21]. From the initial spectra (Figure 4.1), evaluation was done at 1 Hz to understand the dependencies of modulus on frequency and also to differentiate the crosslink ratios based on the values of  $G'$  and  $G''$ . The curves at 1 Hz for different mixing ratios of PDMS, cured for 18, 48 and 132 hours at 100°C are evaluated below (Figure 4.2).

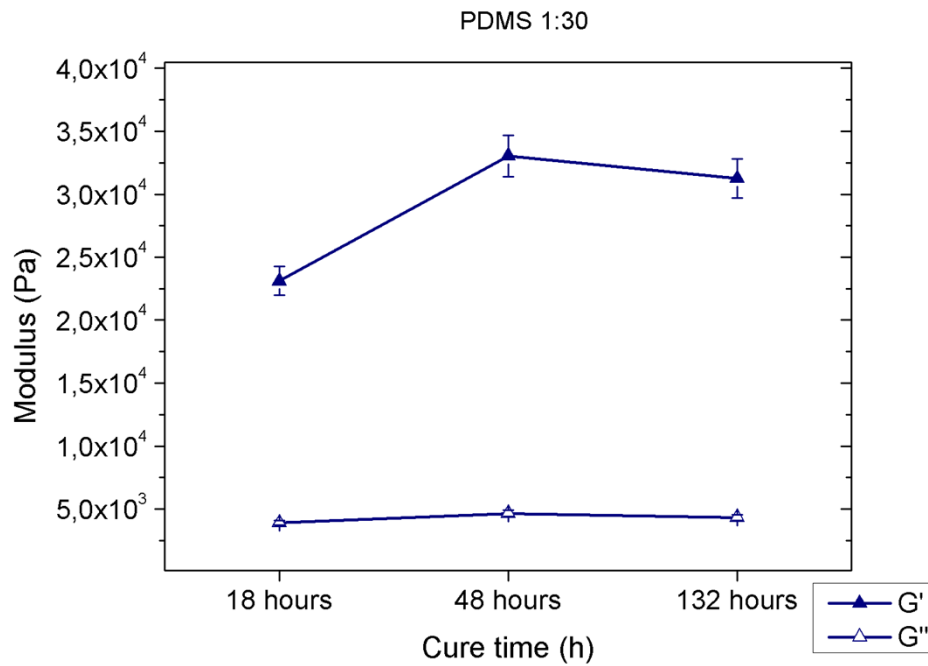


(a)



(b)





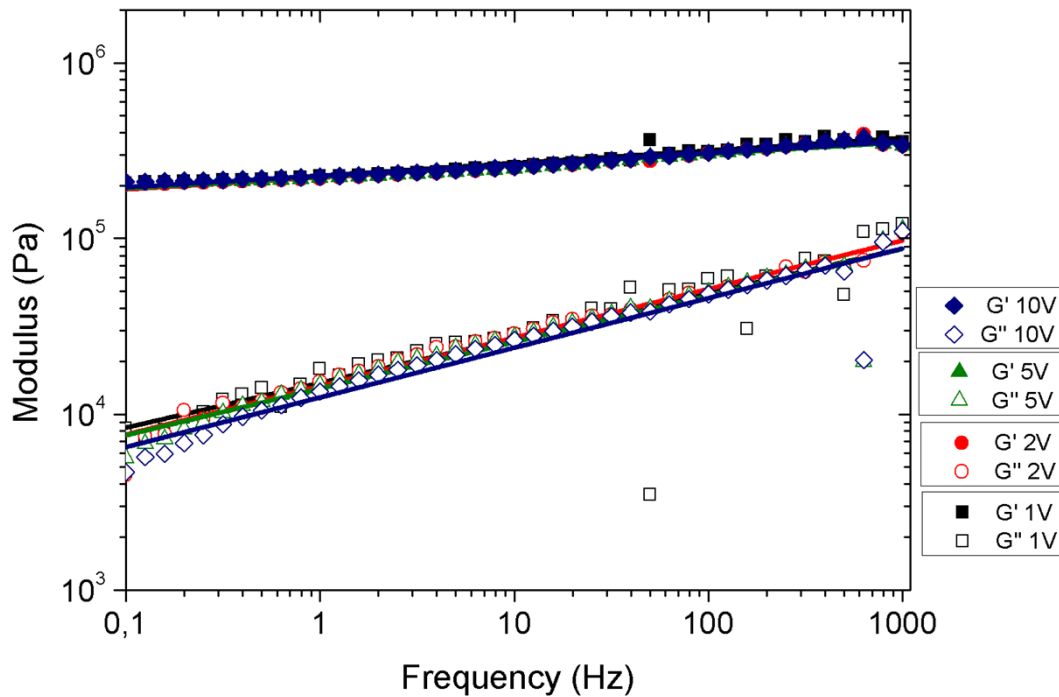
(c)

**Figure 4.2 – Modulus values of PDMS of all mixing ratios plotted against different cure times. (a) For 1:10, the  $G'$  values are highest out of the three, ranging between  $4 \times 10^5$  to  $8 \times 10^5$ , (b) For 1:20, the  $G'$  values are between  $8 \times 10^4$  to  $1.2 \times 10^5$ , (c) For 1:30, the  $G'$  values are between  $2 \times 10^4$  to  $3.5 \times 10^4$ , thus making it the lowest of the three.**

The storage modulus  $G'$  increases with curing time, and then stabilises at about the same value for all three mixing ratios. From these graphs it can be understood that post curing of PDMS is completely done for the samples cured for 48 hours. After 48 hours at  $100^\circ\text{C}$ , PDMS is stable. The error bars are calculated based on noise of the setup.

#### ***A. Variation of Input Voltage***

The input voltage is directly proportional to the amplitude of the force exerted on the sample. Changing the input voltage changes the deformation through the sample (section 2.3). Voltages of 1, 2, 5 and 10 V were used to do this test. The resultant modulus was plotted against the frequency (Figure 4.3).

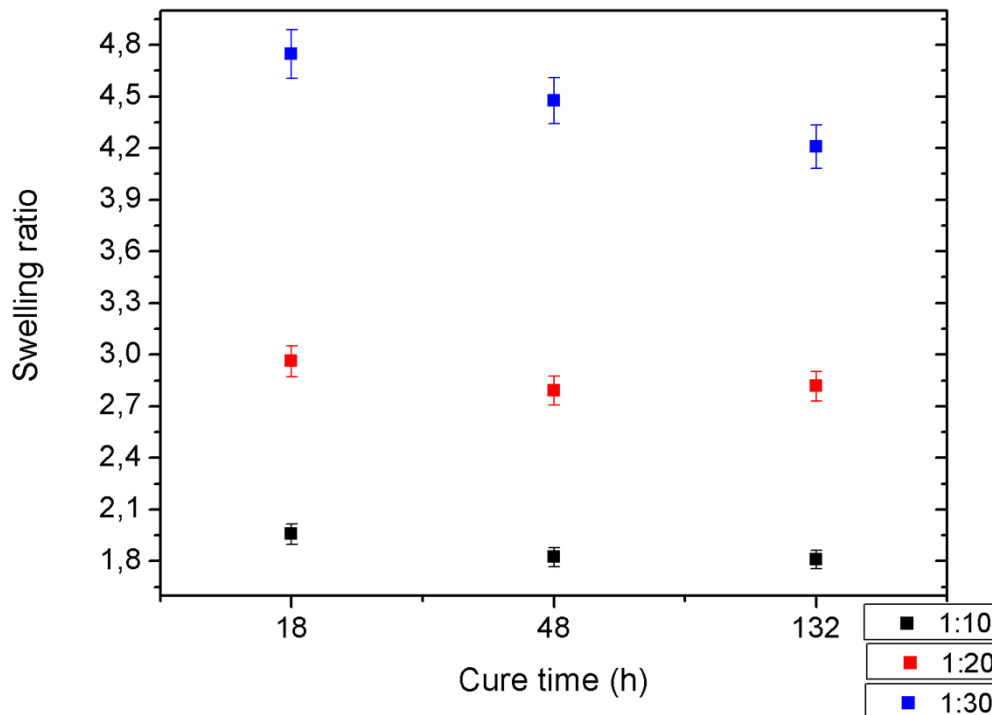


**Figure 4.3 – PDMS 1:10 cured for 18 hours and tested with input voltages at 1 V, 2 V, 5 V and 10 V. Variations in  $G''$  are observed at 10 V.**

The results gave an insight into the ideal input voltage that can be used on the samples. The variation in  $G''$  at 10 V is more pronounced than in  $G'$  (Figure 4.3) due to the higher sensitivity of the loss modulus, and also since it is in the lower range than  $G'$ . Based on the results, an input voltage as high as 10 V is not ideal, owing to the small size of the sample. Voltage of 2 V is ideal for the sample size used in this measurement.

### ***B. Swelling Experiments***

To study the cure state of PDMS better, the classic swelling experiment (section 2.1.2) was done on the samples. Results show the swelling behaviour of PDMS cured at 18, 48 and 132 hours (Figure 4.4). The results from swelling can be compared to the modulus values obtained from piezorheology. As explained in section 2.1.2, osmotic swelling is an indirect measure of the elastic modulus of the system [7].

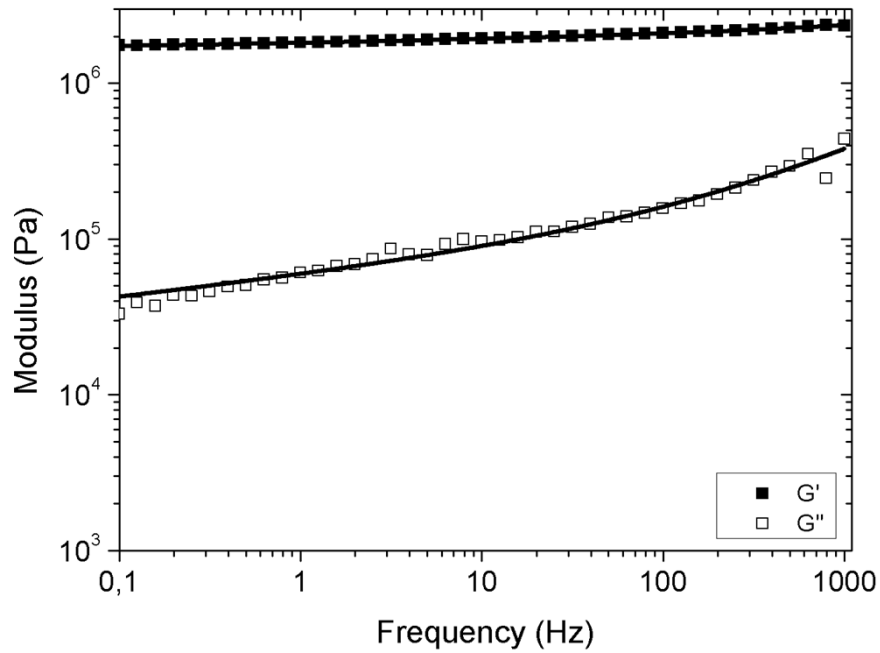


**Figure 4.4 – Swelling results of PDMS. PDMS samples were immersed in toluene for 72 hours and weighted before and after immersion. Error bars were calculated based on repeatability of the measurement.**

Swelling measurements clearly indicate that the highest swelling are the samples with 1:30 mixing ratio, at all temperatures and cure times (Figure 4.4). The  $G'$  and  $G''$  of mixing ratio 1:30 is the lowest (Figure 4.2). The highest swelling polymer has the lowest crosslinking [7]. It can be thus characterized that the results from piezorheology are comparable to the classic swelling experiments.

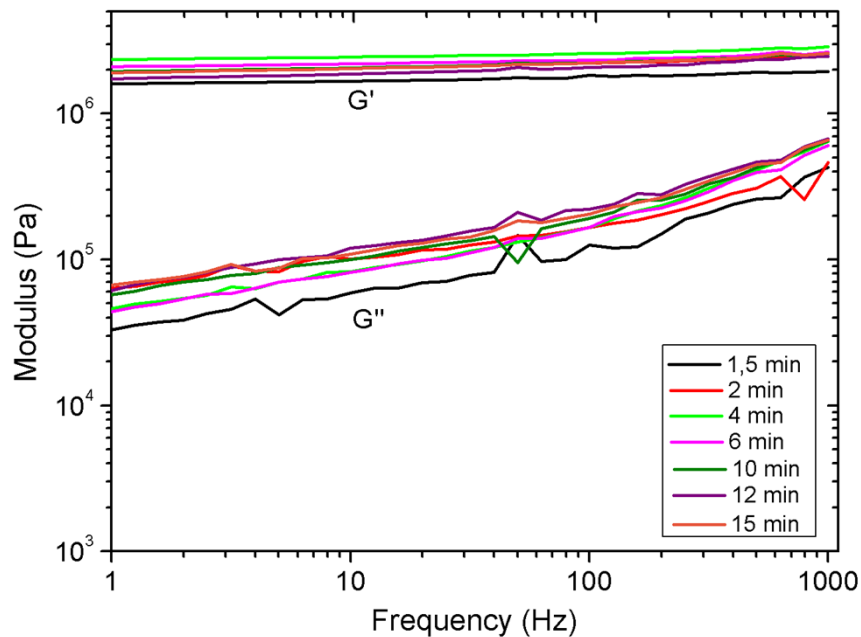
## 4.2. NATURAL RUBBER

After tests with PDMS, natural rubber from Vibracousitc was tested on the piezorheometer. PDMS was the reference substance due to its simple chemistry and the absence of compounding ingredients. In a real time natural rubber elastomer, there are various other compounding ingredients present. It would be interesting to evaluate piezorheology on such a complex system. The natural rubber samples cured for different times from 1.5 minutes to 15 minutes were all tested at an input voltage of 2 V. The initial mechanical spectrum for the sample cured for 2 min is shown below (Figure 4.5). All fitting of curves is done based on the same power law fitting used for PDMS reference.



**Figure 4.5 – Natural rubber (NR Vib 1) cured at 170°C for 2 minutes, tested on piezorheometer.**

The initial mechanical spectra of all the samples of natural rubber are plotted the same way. At frequencies below 0.5 Hz, the noise due to the electronic components of the set up cause some deviation in measurement. So in the following graph, frequencies from 1 Hz are considered (Figure 4.6). The loss moduli are almost one order smaller than the storage moduli.



**Figure 4.6 – Loss and storage moduli of natural rubber (NR Vib 1) cured for 1.5 minutes to 15 minutes. The lines indicate the different cure times.**

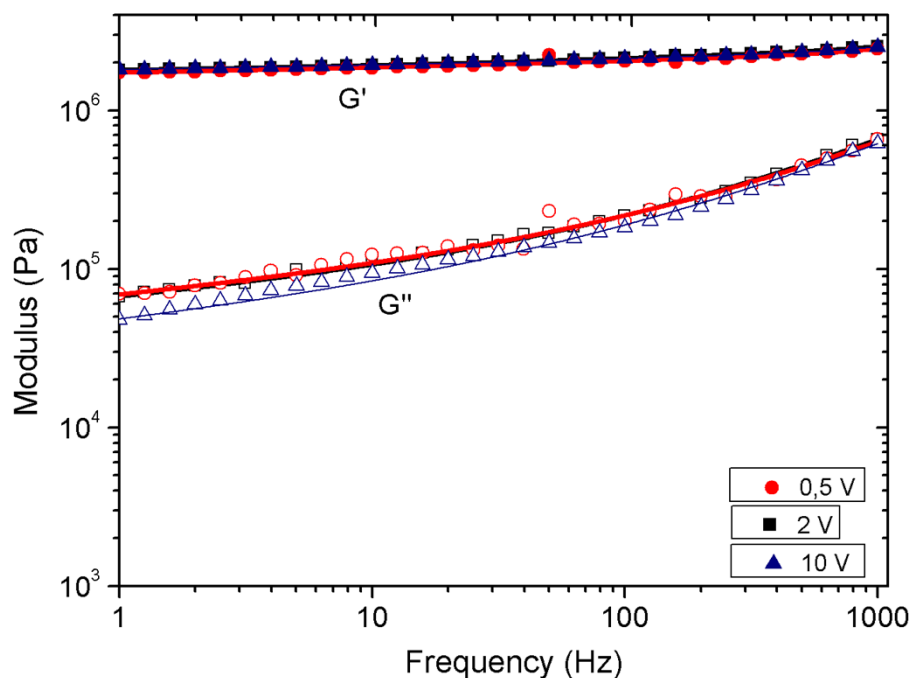
The measurements show that there is a variation in modulus values for samples cured at different times. This is further analysed in the coming sections (Figure 4.6).

After the first measurements, the following variations were tested in order to assess the reproducibility, ease of use, error dependencies and the possible industrialization of the method. The dependency of moduli on

- Effect of different input voltages
- Effect of screw tightening of device
- Sample mounting variations
- Variations due to samples from same sample plates
- Variations due to samples from different sample plates

#### ***A. Variation of Input Voltage***

The effect of different input voltages was also tested on a natural rubber sample. From the results of the PDMS reference, it was understood that 10 V was not ideal for PDMS. The same was expected for natural rubber. The plot for natural rubber indicates a variation in  $G''$  when tested at 10 V (Figure 4.7).

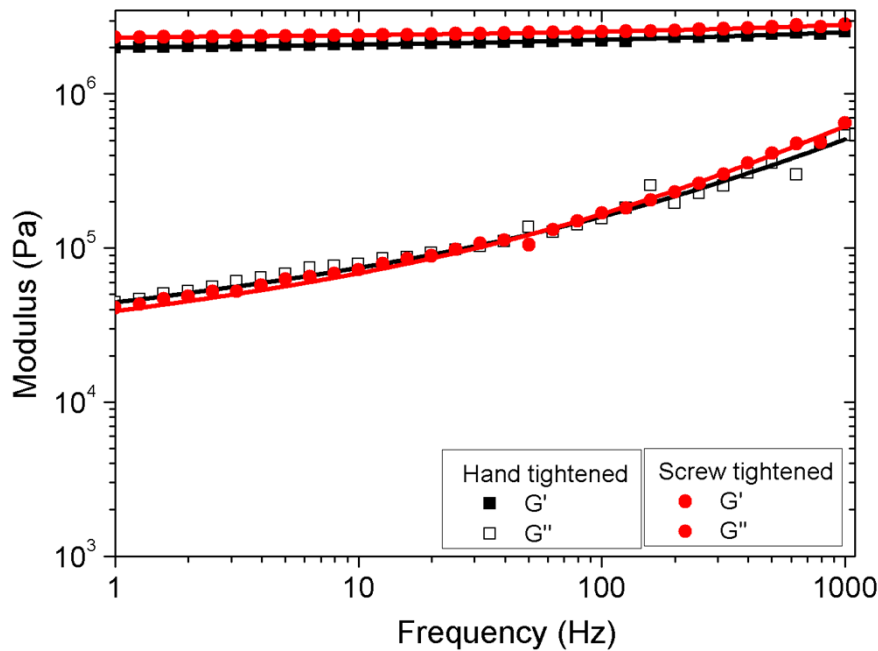


**Figure 4.7 – Natural rubber cured for 15 minutes tested at input voltages of 0.5 V, 2 V and 10 V.**

The loss modulus at 10 V indicates a clear variation from 0.5 V and 2 V. This reiterates that the input voltage of 10 V could be high for an elastomer, and 2 V is an ideal voltage to test the samples.

### ***B. Screw tightening of device***

The initial measurements were done by tightening the device by hand. The measurements were then done by tightening the device with a screw driver, to measure the variations and suggest a precise way of usage of the device.

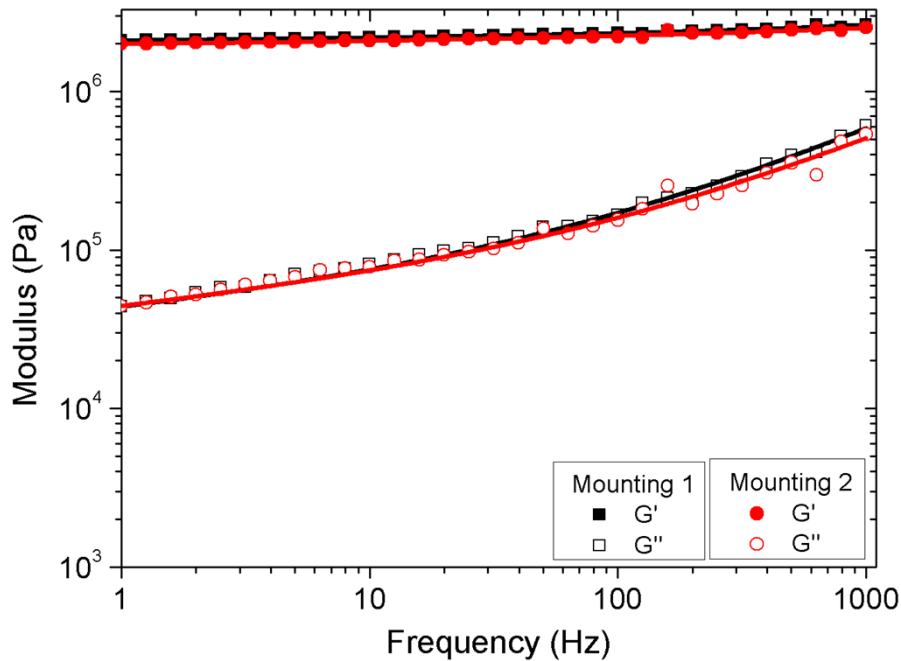


**Figure 4.8 – Natural rubber cured for 6 minutes, tested by tightening the device by hand, and then by a screw. Variation in  $G'$  is evaluated.**

From measurements (Figure 4.8), a percentage difference between hand and screw driver tightening was calculated. The percentage difference for storage modulus is 15.21 %, and for the loss modulus is 8.04 %. The use of screw driver to tighten the device will increase the precision of measurement and reduce the noise due to vibrations and resonance of the setup.

### ***C. Sample mounting variations***

Sample mounting is an essential part of any method that requires manual mounting of the sample. Tests were performed on the same sample after remounting it for a second time. The sample was mounted in contact with the glass plates both the times. This test was done to check for any influence of manual error while loading the sample.

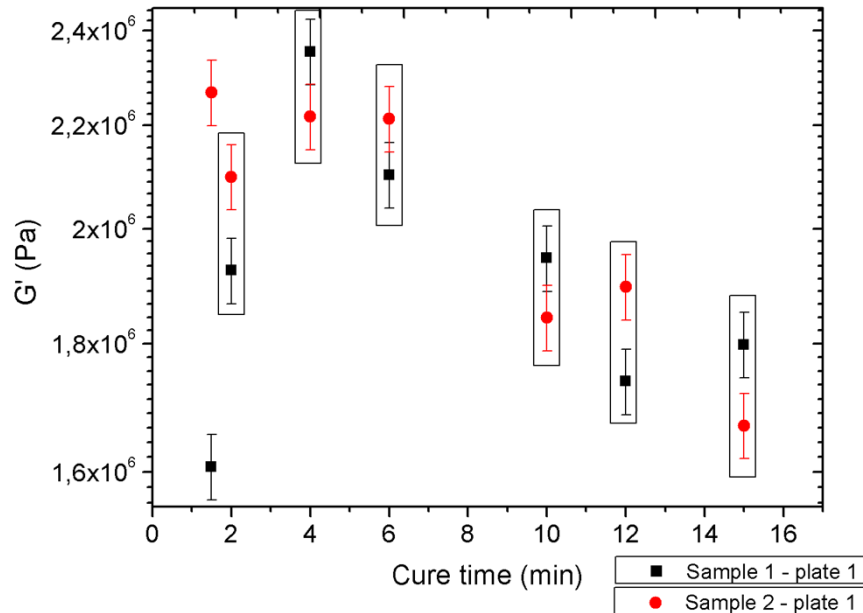


**Figure 4.9 – Natural rubber sample cured at 6 minutes, tested for error due to mounting. The two different mountings are numbered as 1 and 2.**

The error was calculated from the values of the loss and storage modulus of both the iterations of mounting. The percentage difference between the two ways of mounting for storage modulus was 4.81 % and that of the loss modulus was 0.73 %. The effect of sample mounting variations was thus evaluated. The percentage differences are quite low, in the order of  $10^1$  to  $10^2$  Pa. Thus, it can be summarized here that manual error due to sample mounting does not have a great influence in measurement, and the contact of sample surface to glass plates is critical.

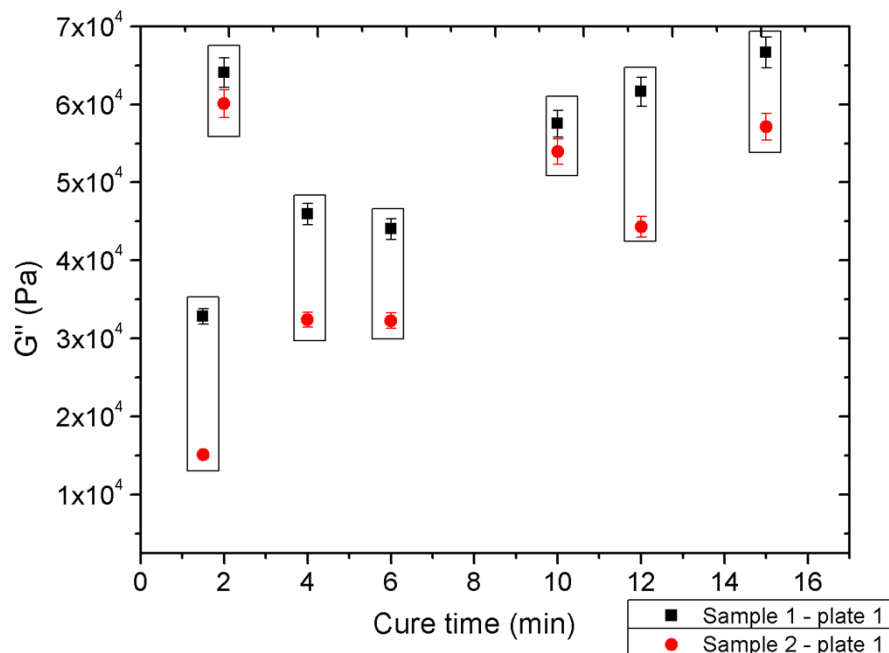
#### ***D. Samples from same sample plate***

The reproducibility of measurement was tested by comparing samples from the same sample plates. The samples were taken from the centre and one edge of the plates. Comparison of  $G'$  and  $G''$  of individual samples is done at 1 Hz.



**Figure 4.10 – Scatter plot of  $G'$  values at 1 Hz for samples from same sample plate. The box indicates the set of a couple from the same cure time. Error bars were calculated from repeated measurements.**

The highest value of  $G'$  is between the cure times of 4 to 6 minutes (Figure 4.10). The  $G'$  values start to decrease from 6 minutes, until 15 minutes. The storage modulus is directly proportional to the stiffness of the sample [1].



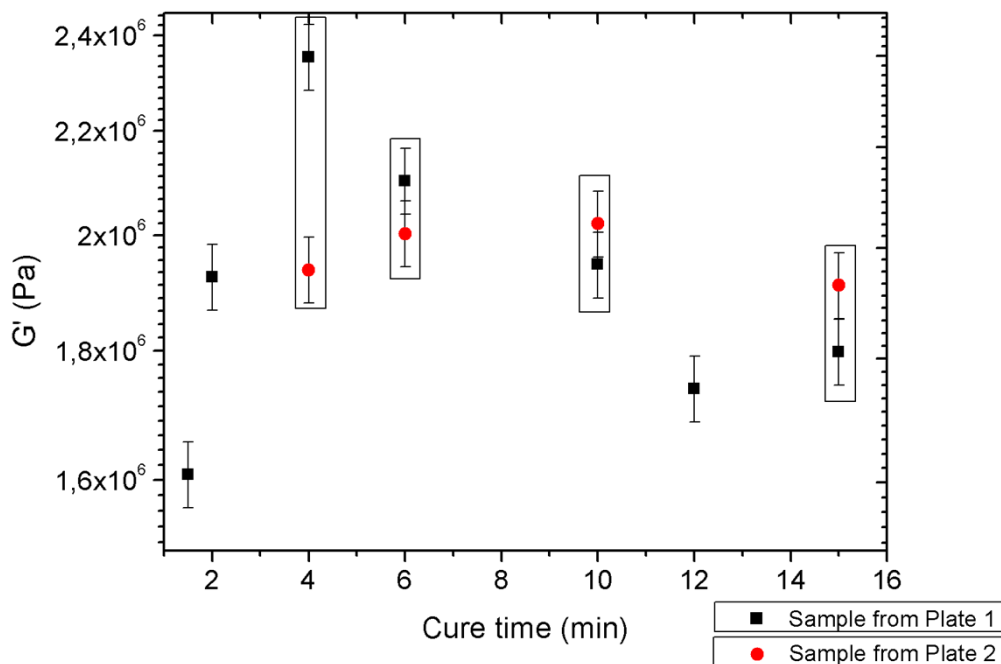
**Figure 4.11 – Scatter plot of  $G''$  values at 1 Hz for samples from same sample plate. Error bars were calculated based repeated measurements (iterations).**



The loss modulus corresponds to the viscous element of the sample. The lowest  $G''$  is at 4 and 6 minutes (Figure 4.11). The points at 1.5 minutes are neglected as a deviation, since the cure time of 1.5 minutes would be just enough to heat the sample and trigger the initial steps of vulcanization. The variations in the loss and storage moduli of samples from the same plate are higher than the previously discussed variations. This can be attributed to variations in mixing or non-uniform heat transfer from the compression mould surface to the plate, while fabrication of sample plates.

### *E. Samples from different sample plates*

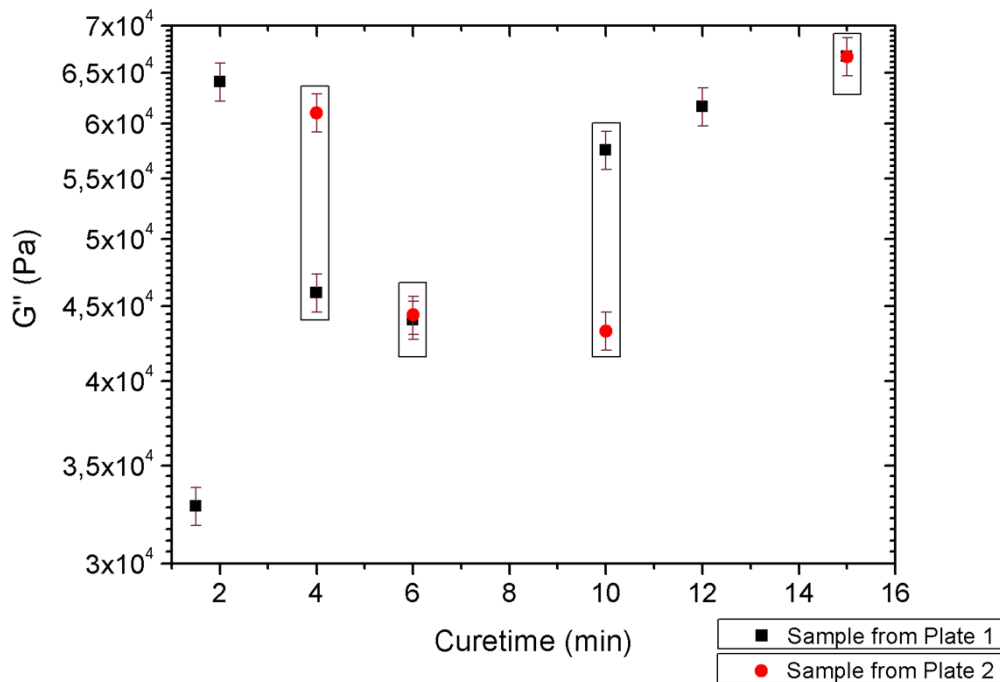
As previously mentioned, the natural rubber plates were provided by Vibracoustic for evaluation. There were two sample plates each for cure times 4 minutes, 6 minutes, 10 minutes and 15 minutes (Table 3.2). A comparison of data from samples of two different plates was done. The storage and loss moduli are plotted against the cure time.



**Figure 4.12 – Scatter plot of  $G'$  values of samples from different plates. There was one sample plate each of cure times 1.5 minutes, 2 minutes and 12 minutes, hence the single data point. Boxes indicate the set of data points for each cure time.**

Error bars were calculated from the noise in measurement. The highest  $G'$  values are estimated to be highest for the samples cured at 4 and 6 minutes. Similar to Figure 4.10, the storage modulus starts to decrease after 6 minutes (Figure 4.12). The error bars are bigger

than that of the previously seen variations. The difference in  $G'$  values between the two plates could be as a result of inhomogeneity in the compounding, or variations during fabrication of the plates.



**Figure 4.13 – Scatter plot of  $G''$  values of samples from different sample plates. Error bars were calculated based on the noise in measurement.**

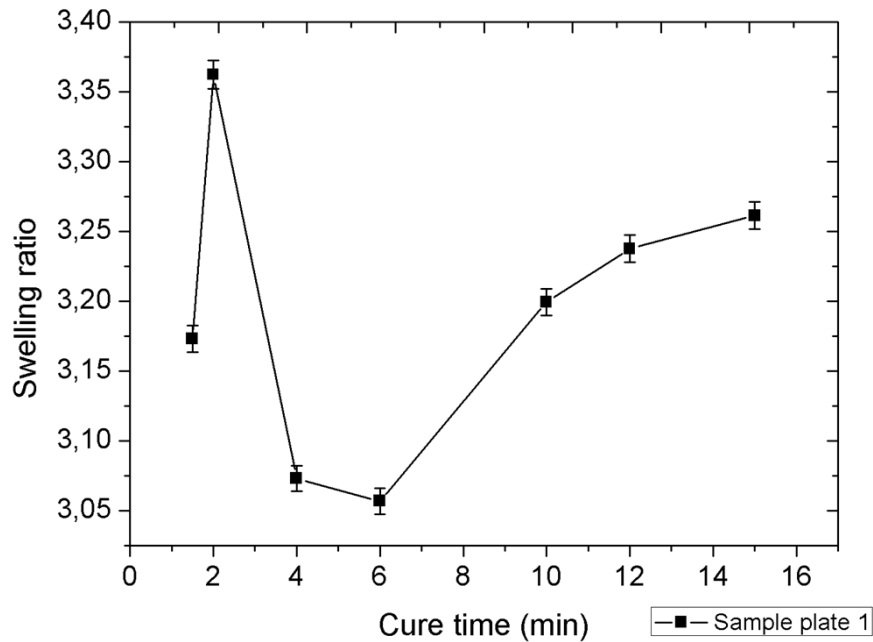
The values of  $G''$  are lowest for the sample cured at 6 minutes (neglecting sample cured at 1.5 minutes) (Figure 4.13). The loss modulus is a measure of the viscous nature of the sample [13]. The values of loss modulus can be compared to results of classic swelling experiments to draw a correlation.

#### ***F. Frequency dependence of moduli***

The storage modulus of samples tend to show similar behaviour as frequency is increased. The general storage modulus increases with increasing frequency, but the similar trend is displayed by all samples of all cure times (graphs in Appendix A). The frequency of 1 Hz was considered to compare different variations as below 1 Hz, the electronic components in the setup caused some noise and deviation in data. Above 500 Hz, the noise due to resonance of sample was present.

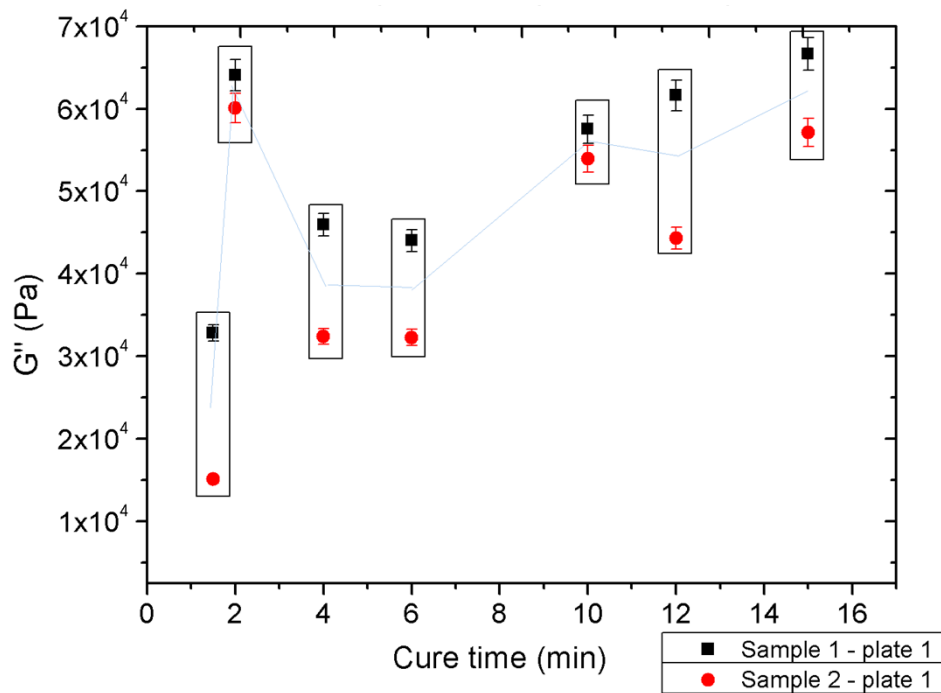
### G. Swelling Experiments

Natural rubber samples were immersed in liquid toluene for 72 hours. Swelling ratio was calculated from weight of sample before and after immersion.



**Figure 4.14 – Swelling ratio of natural rubber samples from plate 1. Error bars were calculated from repeated measurements of samples from plate 1.**

The lowest swelling samples are those cured at 4 and 6 minutes (Figure 4.14). This can be evaluated with the results of loss modulus for the same sample plate from piezorheology.



**Figure 4.15 –  $G''$  values of natural rubber samples from plate 1 at 1 Hz. The blue line is assumed as a guide to compare the trend in  $G''$  to the trend from swelling experiments.**

The comparison between loss modulus and swelling experiments shows a strikingly similar trend. The swelling ratio decreases higher crosslinking is achieved [7]. The swelling ratio is lowest for 4 minute and 6 minutes samples. The loss modulus is also lowest for these two cure times. Hence, it is comparable and can be deduced from swelling theories that the samples cured at 4 minutes and 6 minutes are closest to the maximum crosslinking.

## 5. CONCLUSION

The optimum cure state of rubber is an important parameter in rubber processing. Rheology, compression set, and classic swelling experiments are some of the techniques used in the industry to measure the optimum cure state. These techniques have many disadvantages (section 2.1), and are not used as standards in the industry. The importance of optimum curing reflects in the performance of the elastomer product, and thus, is an essential parameter that requires standard testing methods. This thesis evaluated a new technique, Piezorheology, to help in cure state characterization. From the tests made and the results obtained, the following conclusions can be derived.

### ***A. Reproducibility and Repeatability***

The results of PDMS from piezorheology are comparable to classical swelling experiments. The results of loss and storage moduli of natural rubber samples taken from the same plate indicate that the method is reproducible (Figure 4.10 and Figure 4.11). The difference in moduli of certain samples are attributed to the processing conditions. The sample plates were prepared by using a compression press, and the heat transfer from press surface to sample is not necessarily constant. This might have affected the crosslinking in the corners of sample plates. Piezorheology is repeatable since the values obtained by testing the same sample twice produced a negligible difference of 4.81 % for storage modulus and 0.73 % for loss modulus.

### ***B. Reliability***

The comparison of results from swelling experiments to the loss modulus at 1 Hz of natural rubber samples from same plates showed similar trends (Figure 4.14 and Figure 4.15). Classical swelling experiments have been a standard way of measuring the cure state of elastomers in industries. The results from piezorheology agreed with the classical theory of osmotic swelling [7]. Piezorheology is a reliable method even when the input voltage is altered, and clearly depicted artefacts when the voltage was too high for the used sample size.

### ***C. Ease of use***

Piezorheology is a simple technique that does not require highly skilled labour. The variations that arise due to mounting were studied, and results show that the difference is as small as

4.81 % for storage modulus and 0.73 % for loss modulus (Figure 4.9). The technique does not depend on the difference in sample mounting, although it is essential that the sample is in contact with the glass plates of the device. The device also produces best results when it is tightened by a screw. The error between hand tightening and screw tightening for loss modulus was  $\pm 0.46$  Pa, and that of loss modulus was  $\pm 0.95$  Pa.

As a conclusion, piezorheology is a technique that can be used in industries to help characterize the optimum cure of elastomers. The evaluation of piezorheology was done and it can be industrialized as a standard method to characterize the optimum cure of elastomers. Apart from being repeatable, precise, reliable and easy to use, the method also used small samples of at least 50  $\mu\text{m}$  thickness and an area of at least 5  $\text{mm}^2$ . Thus, it can be used to understand the cure state of products with complex geometries.

## 6. FUTURE SCOPE

Industrialization of piezorheology, and standardizing the technique for application is an important scope of this work. The piezorheometer can be used in the industry setup for quick and precise measurement and comparison of cure states.

Microcantilever sensor technology is a novel method that can be used in cure time characterization. Micromechanical sensors provide an advantage of using a sample with a mass resolution of  $10^{-11}$   $\mu\text{m}$ . The test provides results in approximately 30 minutes, and since it uses gaseous solvent, the swelling and de-swelling behaviour of the elastomer can be studied. The advantages and theory of the method were outlined in section 2.2. It is a precise method that can be experimented with, and industrialized.

Dynamic mechanical analysis (DMA) is another promising technique from literature, to help in cure time characterization. The values of  $\tan \delta$  from the rheometer are studied and compared to the values of  $\tan \delta$  from DMA. The DMA was tested in shear mode and isothermal tests were done to monitor changes that occur in the elastomer during vulcanization [13]. The DMA is a widely used method for analysis of glass transitions and moduli under temperature and stress. The measurement of cure time by DMA, if achievable, will be a great aid in industries.

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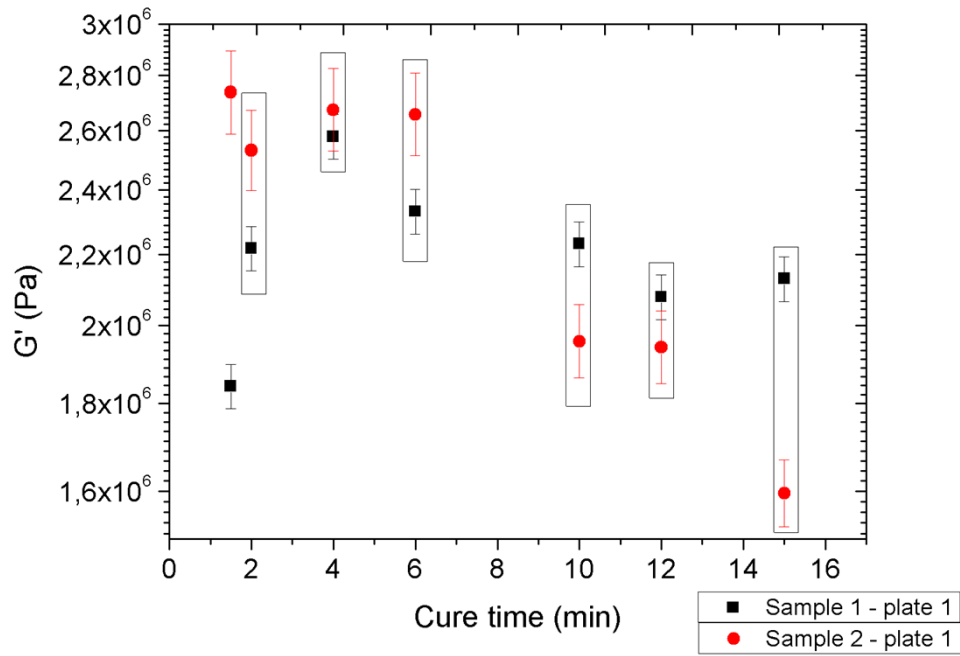
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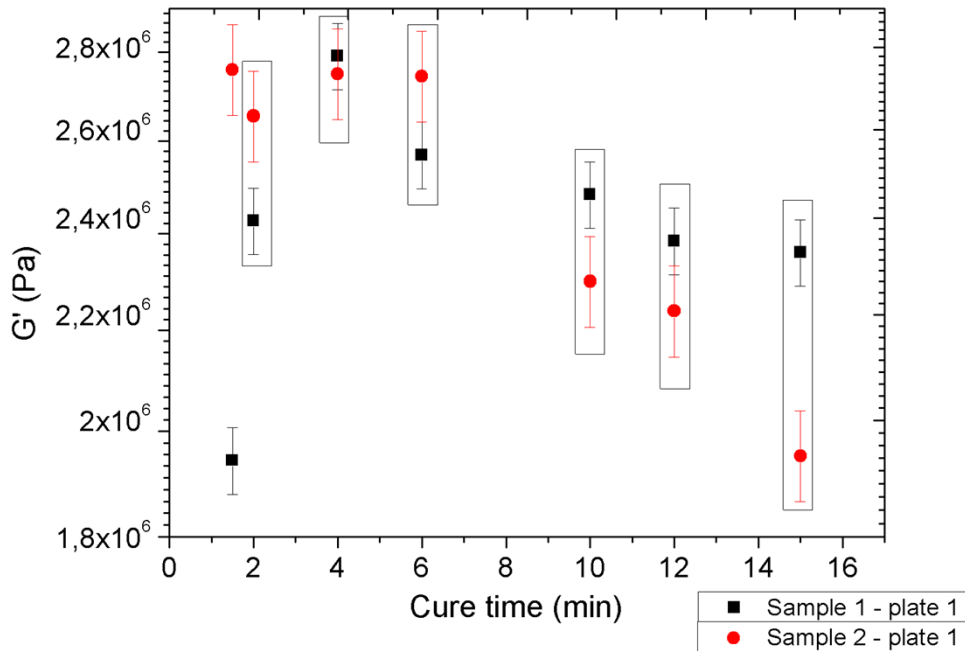
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# APPENDIX A

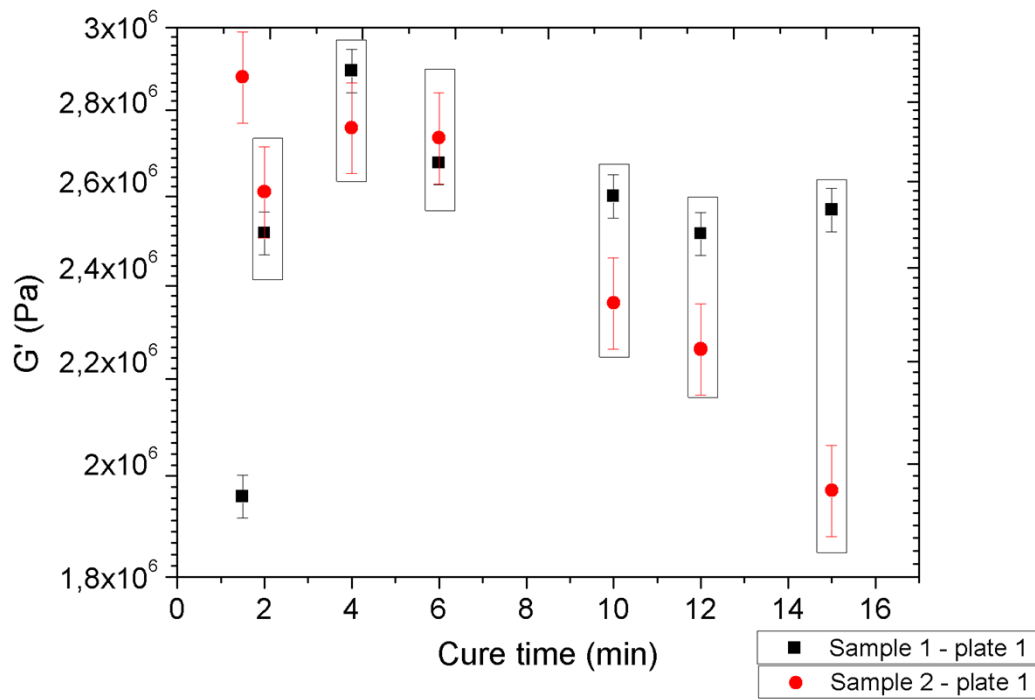
*Graphs at different frequencies for samples from same plate*



(a)



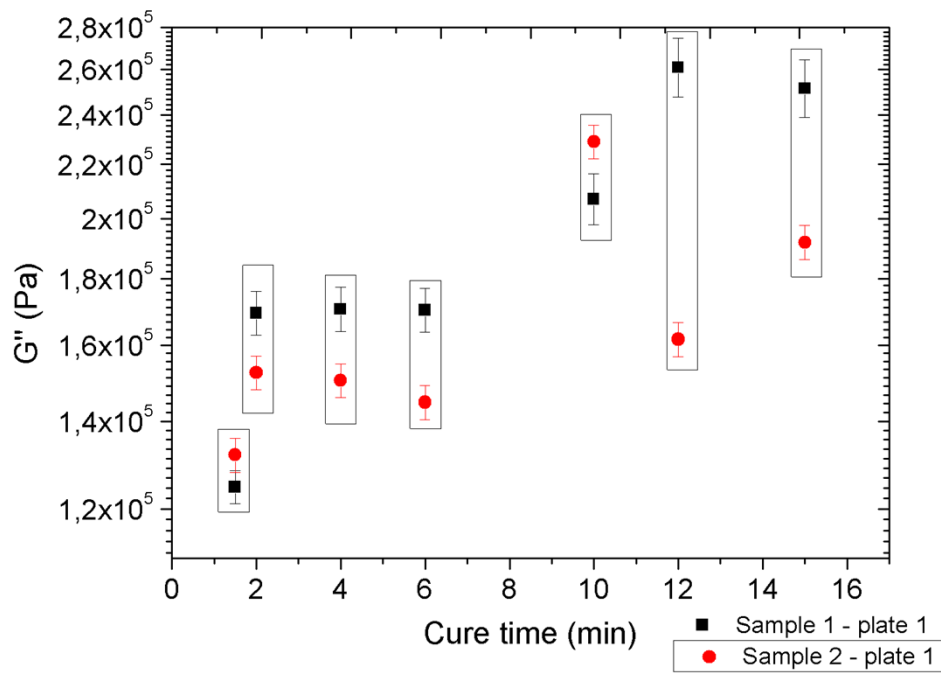
(b)



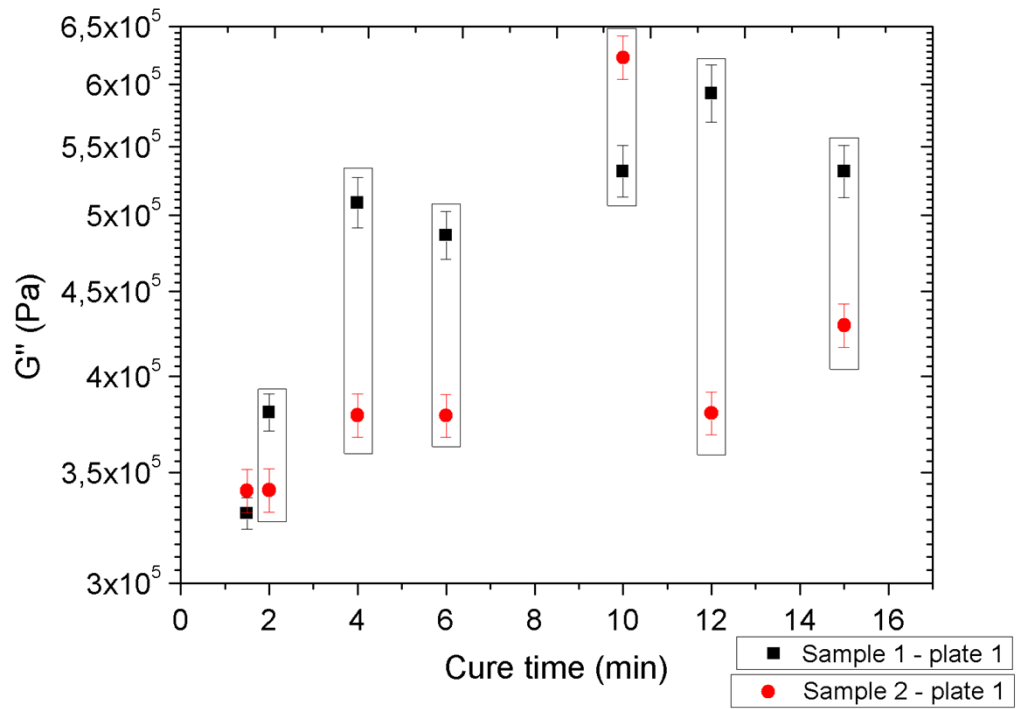
(c)

**Figure 1 – Storage moduli of samples from same plate at (a) 100 Hz, (b) 500 Hz and (c) 1000 Hz.**

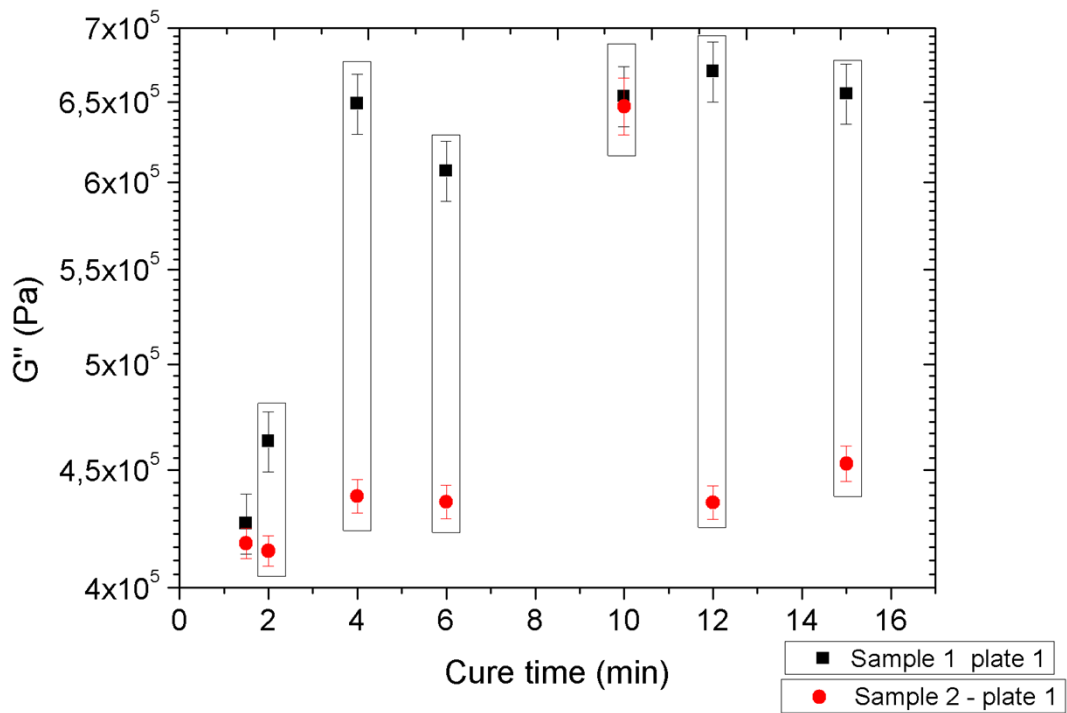
A similar trend is observed in the storage modulus at all frequencies, as explained in section 4.2 F.



(a)



(b)



(c)

Figure 2 – Loss moduli of natural rubber samples from the same plate at (a) 100 Hz, (b) 500 Hz and (c) 1000 Hz