# CONSTITUTIVE MODELLING OF MULLIN'S EFFECT IN SWOLLEN NITRILE BUTADIENE RUBBER UNDER CYCLIC LOADING

**IRMALISA BINTI SAMSURI**

**FACULTY OF ENGINEERING**

**UNIVERSITY MALAYA**

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**ABSTRACT**

Under cyclic loading, hyperelastic materials exhibit a particular stress softening behaviour called Mullin's effect. Few efforts have been done to propose a mathematical model to represent this behaviour in rubber material. However, all attempts are only focusing on dry rubber. The study of Mullin's effect in swollen rubber is quite important since a lot of parts or components made from rubber are exposed to aggressive solvent such as biodiesel. With the application of cyclic loading, the degradation of material becomes more rapid and leading to fatigue.

In this study, the constitutive modelling of Mullin's effect in swollen Nitrile Butadiene Rubber (NBR) is addressed. For this purpose, the viewpoint of Continuum Damage Mechanics by Chagnon et al. (2004) is considered and extended in order to take into account swelling level. The Fung strain energy density function is chosen to describe the mechanical behaviour of the hyperelastic rubber. The theoretical model developed is then plotted and the result is compared with the experimental. Results show a qualitative good agreement between the model and experiment. Although the model is able to capture the Mullin's effect phenomenon, further study needed in order to determine this behaviour in compressible material.

**ABSTRAK**

Dibawah aplikasi daya kitaran yang dikenakan keatas bahan hiperelastik, fenomena pelembutan tegasan didapati berlaku dan biasanya dirujuk sebagai kesan Mullin. Beberapa usaha kajian telah dilakukan untuk menghasilkan model matematik yang dapat menggambarkan fenomena kesan Mullin keatas bahan ini. Walaubagaimanapun, kebanyakan kajian hanya menumpukan keatas getah kering Kajian perlu dilakukan juga keatas getah kembang (getah yang terendam ke dalam cecair) kerana ia juga tidak kurang pentingnya. Kebanyakan peralatan menggunakan getah sebagai salah satu komponen. Kadangkala komponen ini terdedah kepada persekitaran yang mengandungi cecair contohnya seperti biodiesel. Keadaan ini memberikan impak yang lebih buruk dan menyebabkan bahan getah tersebut mengalami kerosakan yang cepat sehingga membawa kepada kegagalan peralatan.

Didalam kajian ini, penyiasatan kesan Mullin dilakukan keatas getah Nitrile Butadiene (NBR) yang kembang. Untuk tujuan ini, model yang diadaptasi oleh Chagnon et al. (2004) iaitu Kontinum Mekanik Kerosakan digunakan dengan mengambilkira kadar pengembangan getah tersebut. Dalam kajian ini, fungsi ketumpatan tenaga terikan, Fung digunakan untuk menggambarkan ciri-ciri mekanikal bahan ini. Model yang dihasilkan dari adaptasi ini berjaya menggambarkan kesan Mullin ke atas getah dan memberikan keputusan yang hampir sama dengan keputusan ujikaji. Namun begitu, ujian lanjutan perlu dilakukan sekiaranya bahan getah ini mempunyai ciri-ciri kebolehmampatan

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**Nomenclatures**

| | |
|---|---|
| $\boldsymbol{\sigma}$ | Stress tensor |
| $\varepsilon_{max}$ | Maximum strain |
| $\alpha$ | Scalar measure deformation rate |
| $\lambda$ | Principal stretch |
| $\beta$ | Swelling |
| V2 | Volume Rubber Fraction |
| $V2_{eq}$ | Equilibrium condition of volume fraction |
| *Wo* | Undamaged strain energy function |
| *d* | Damage parameter |
| *p* | Lagrange multiplier |
| $I_1$ | First stress invariant |
| $I_2$ | Second stress invariant |
| **B** | Left Cauchy-Green tensor |
| $\sigma^{1up}$ | Stress at first uploading |
| $\sigma^{2up}$ | Stress at second uploading |
| SR* | Stress Ratio |
| SS | Stress Softening |
| RSS | Ratio of Stress Softening |

# *CHAPTER 1 :* INTRODUCTION

## 1.1 Background

Recently, the interest in biodiesel has been increasing due to high petroleum prices and environmental consideration. Generally, biodiesel refers to any diesel fuel which is domestically produced from renewable biomass such as vegetable oils (soybean, corn, canola, rapeseed etc.) animal fats and alcohol normally called alkyl esters of fatty acids (John et al, 2007). In order for biodiesel to become an alternative transportation fuels, a really strict quality standard must be followed. The physical properties of biodiesel are almost the same with petroleum diesels, but bio-diesel giving cleaner environment during the combustion activity.

Biodiesel can be used alone in the standard engine system and can also be mixed in different concentration with petroleum diesel. The pure biodiesel is called B100 which contains 100% of biodiesel. Other concentration such as: B10, it contains 10% biodiesel and 90% petroleum diesel, B20, it contains 20% biodiesel and 80% petroleum diesel and B5, it contains 5% biodiesel, 95% and petroleum diesel. B20 is the common type of blend used because it complies with the Energy Policy Act (EPAct) of 1992. The usage of B20 biodiesel or a lower percentage is better since it does not require major modification in a standard engine system. Usage of pure biodiesel, B100 can cause performance failure or damage if modification is not done (Jon et.al, 2007)

Biodiesel also has an excellent energy security balance. Since the commodity prices in agricultural is lower compared to petroleum prices, we can fully utilize domestic excess of vegetable oil and therefore can increase energy security. Option to use the biodiesel will help to save the cost of importing petroleum from the foreign country. This cost can be used in biodiesel production which is cheaper since it can be done using the conventional equipment (Jon et al, 2007).

Compared with petroleum diesel, less emission produces when using biodiesel in a conventional engine system. This is another area of interest because of the emission is an important factors which contributing to a global warming effect. The data from the Environmental Protection Agency, USA (EPA, 2002) reported that the emission of incomplete combustion of hydrocarbons (HC), carbon monoxide (CO), sulfates, polycyclic aromatic hydrocarbons, nitrated polycyclic aromatic hydrocarbons, and particulate matter (PM) can be reduced effectively when using biodiesel especially in blended concentration. The more amount of biodiesel mix with petroleum diesel, the more emission can be reduced. B20 biodiesel showing the most effective biodiesel which can do this function.

In an automobile engine fuel system, there are a lot of parts or components made either from metal (ferrous and non-ferrous alloy) and elastomer which directly in contact with the fuel. These materials will interact chemically with the fuel. The interaction with biodiesel is different compared to the conventional petroleum diesel. It can cause corrosive and tribological attack on metallic components and degrade elastomer parts rapidly. Few researches have been done to present an overview of the work done so far on the compatibility of biodiesel with automotive materials.

In the case of elastomeric component, a lot of study has been done to see the compatibility of this material in contact with biodiesel. One of them is Haseeb et al. (2010) which study the compatibility of elastomer in palm biodiesel. When the elastomer is in contact with fuel, it will change chemically and physically. The changing is depending on the ability of the material to absorb the fuel or being dissolved by the fuel. It will also affect the physical characteristic of the material including swelling, shrinkage, embrittlement and changes in tensile properties. The allowable limit of physical change varies with different application but still can be tolerated at a certain degree of change. Under static mechanical loading for example, the material that swell in the fuel will suffer from a hardness problem but still can be continually use for a long time. However, in dynamic applications, the swelling may give more serious effect. It will increase the friction and wear and finally impact the engine durability

By considering the compatibility of elastomer material for example, in seal and hose, especially when in contact with biodiesel, it can be used as a recommendation or guideline to the elastomer manufacturer. Experience has shown that under this environment, the elastomer (seals, gaskets, hoses etc) will degrade more rapidly especially when it is exposed to pure type of biodiesel (B100). However, the study of the effect of this material with blended biodiesel with petroleum fuel is still not being established.

## 1.2 Problem statement

Elastomer is one of the important materials and has been used as a part or component in the engine fuel system. The study of compatibility of elastomer is required to see the durability of this material. It is also important to study the behaviour of material under mechanical loading especially in the cyclic loading environment. In nature, the fluctuating load will cause more serious effect compared to static loading. For example, it will lead to a problem like fatigue and crack. Few studies have been done to address the changes in elastomer physical characteristic. During the first couple of load under cyclic loading, an elastomer tends to encounter a significant softening phenomenon. After few cycles, it will disappear and material responses then become repeatable. Diani et al. (2008), refer this phenomenon as the Mullin's effect.

With the presence of biodiesel in contact with elastomer under cyclic loading, the effect becomes worse. Swelling and further degradation is some of the consequences. Under cyclic loading, swollen rubber exhibits inelastic response such as hysteresis, stress softening and permanent set. With this effect, the material is not more suitable to be used as part or component of equipment since it will require frequent replacements which also involve cost. The understanding of the above response is essential for the durability study of elastomer under this environment.

If many models available in dry elastomer to represent the mechanical behaviour in material, there are still no study focusing on developing model in swollen elastomer. Therefore, it is necessary to develop a model which can capture the mechanical characteristic under this condition.

## 1.3 Objective

The objective of this study can be defined as follow:

1. To develop a simple continuum mechanical model in order to capture the Mullin’s effect in swollen Nitrile Butadiene Rubber (NBR) under cyclic loading. A mathematical equation will be developed based on the result of experiment.

2. To compare the result of constitutive modelling with the experimental data. Numerical simulation will demonstrate the ability of the model to describe and predict the Mullin’s effect phenomenon.

## 1.4 Scope of Study

The purpose of the present work only covers the construction of a mathematical equation model to capture the Mullin's effect in the swollen state of NBR under compressive cyclic loading. The experimental data is obtained from Chai et al. (2011). As the objective of the present work is to identify the Mullin's effect, other characteristic which is observed during the experimental such as hysteresis, permanent set and stress relaxation will not be considered. It is also noted that the experimental works only focuses on stress-free swelling. Investigations on the effect of the multi-axial stress state in the swelling rubber are not being covered. Further study needed to see the mechanical response of material under this condition. The effort in developing the mathematical model also limited by an assumption that the material is homogenous, isotropic and remain incompressible either in the dry or swollen state. The incompressibility of material is not being verified during the experiment.

# *CHAPTER 2:* LITERATURE REVIEW

## 2.1 Biodiesel as an alternative fuel

Biodiesel can be produced in quantities as an alternative fuel but not to fully replace the conventional fuel. Petroleum diesel will still become the primary fuel for transportation engines and there is no necessity to design the engines specifically for biodiesel. This is advantage of biodiesel because it can be used with the current engine system without any modifications or the specific requirement.

Another advantages of biodiesel is, it able to protect the engine system by providing better lubrication. This can avoid the moving part especially metal to metal contact from wearing prematurely. Several investigations reported that, at low concentration, biodiesel improves lubrication of low sulphur diesel fuel. In addition, some research showing that when using biodiesel, it can prolong the engine lifespan and reduce the possibility of wear. However, since biodiesel contains of organic acids, water and/or methanol which is an agent of corrosive material, it may contribute to vehicle operability problems.

There are also some other limitations and issues arise when using biodiesel: storability, elastomer compatibility, cetane number, and solvent action.

Storage of biodiesel is one of the main issues. Biodiesel contains a high level of unsaturation which makes it susceptible with oxygen. It will contribute to the formation of acids, aldehydes, peroxides and also viscosity increasing polymers. Used of inhibitor such as anti-oxidant should be considered to stop this process. Additional issues arise when the biodiesel need to be store for longer period. It can be attacked by water to create the acids. With the presence of water, biodiesel become a good medium for microbial growth. To avoid this problem, the tank should be clean and free from water, and must be kept in the dark environment to prevent water condensation from humidity in the inner wall of a tank.

The cetane number is important in the engine system since it is use to measure the ignition quality of diesel fuel. Biodiesel have a low cetane number compared to petroleum diesel. This can cause difficulty in the initial starting of engines especially in cold weather.

The excellent solvent properties of biodiesel also able to give an impact on system engine durability. With this characteristic, it will cause any deposit especially in the engine delivery system and filters easily dissolve and clog the fuel lines. Due to the excellent solvent properties, other fuel-system problems also discovered. Some component in the fuel system especially in older vehicles and machinery may be not compatible with biodiesel, which may need frequent replacement of those parts.

Investigation reported that performance of biodiesel will decrease in a low temperature environment (John et al, 2007). At this temperature the biodiesel tend to appear cloudy and begin the formation of wax crystal. This phenomenon is called the "cloud point". Biodiesel performance will become worse at even lower temperature. Up to one point, the fuel will start to stop flowing and become gel. This stage is called the "pour point" .The formation of gel and wax crystal can cause clog at the fuel lines and filter. Finally it will affect the performance and durability of the engine system. Conventional petroleum diesel also shows this characteristic but not as much as biodiesel.

## 2.2 Elastomer in Engineering

Elastomers are amorphous polymer to which various ingredients are added and normally refer as a compound by chemist. This material will become rubber after the process of heating and vulcanization. It has low modulus of elasticity and capable to support deformation up to 1000 percent (Ronald, 1994). During the application of such deformation, elastomer tends to go back to its original dimensions after the removal of the load. Some elastomer has a high regularity in their backbone structure. With the application of strain, the backbone structure will crystallize and align resulting in high tensile properties. Reinforcement of elastomer will be needed for the elastomer which does not strain-crystallize in order to increase its tensile strength.

Elastomer can be processed into a variety of shape. Normally, it is used as a part or component in many applications for example, in the vehicle engine system as a seal, filters or mounting plates. In order to improve the properties, it also can be compounded. One of the advantages using the elastomer is, it will not corrode and normally no lubrication is required. The type of elastomer used depends on the function of the part and the environment in which the part is placed. To choose an elastomer for a certain application, consideration must be made by determining the suitable temperature limit. Elastomer must be able to operate in such environment. In high temperature, elastomer tends to increase its hardness. Further study also needed to determine the characteristic of elastomer when it is in contact with solvent or gas during a normal operation.

The characteristic of this material is not only elastic and rubbery but they also dissipate energy because of the viscoelastic characteristic. Under conditions of shear and compression, this material will have a very high strength. Failure still can occur in term of fatigue when the material is mechanically loaded, thus, the long term durability of rubber has to be predictable. Simple design criteria should be made available.

It is important to study the basic behaviour of elastomer under stress-strain since the materials are deal with the engineering design. There are few factors need to be considered which make the engineering design with the materials are so challenging.

Cyclic property change behaviour is important and should be considered during the design. Elastomer will change its stress-strain curve radically with the application of load and continue to change its behaviour. The second important behaviour is a large deformation response of rubber which is seen in its soft or low modulus response to applied deformations or load. Commonly, this behaviour is most considered before selecting an elastomer to be used as a part or component. The third behaviour is a non-linear stress-strain response, which is not only unique features of rubber behaviour, but they also are the most challenging for the design engineer. Another thing that also needs to be considered is the behaviour of elastomer when it deals with temperature or when it is exposing in aggressive fluids. The deterioration of rubber mechanical properties will be more vulnerable when it is presence in this environment. More unique behaviour of elastomer under stress strain was discussed further.

## 2.3 Characteristic of Elastomer under Stress-Strain

### 2.3.1 Low Elastic Modulus and Non-Linearity

During the application of uniaxial loading, elastomers tend to exhibit a purely elastic and non-linear behaviour under the stress-strain curve. It will have lower modulus elasticity at the initial curve and will increase with increasing strain up to the point of failure. The average elastic modulus of an elastomer is highly dependent upon the degree of cross-linking in rubber. The desired level of cross-linking is usually achieved through a process called vulcanization, in which a non-reversible chemical reaction is promoted between adjacent elastomer chains at an elevated temperature

### 2.3.2 Creep

Creep is one of the significant phenomenon in elastomer. All elastomer exhibits increasing deformation with time when subjected to load either in tension, compression or shear loadings (Judson, 2008). The creep behaviour will be varies with each type of loading. By using low working stress and avoiding high temperature, we can minimize the creep. Creep cannot be measured since there is no way to find out the accelerating time without introducing inaccuracies in the predicting rate of creep.

In engineering application, the rubber component should be designed to avoid creep especially in tension and shear load since during those modes, creep can easily lead to failure by rupture.

### 2.3.3 Stress Relaxation

Stress relaxation is the phenomenon occurs when a constant strain is applied to an elastomer will cause the force necessary to maintain that strain is not constant but decreases with time. This phenomenon occurs during both cyclic and constant deformation. In term of molecular chain, there are loosening entanglements of polymer network which cause this phenomenon. Therefore, during engineering design, the stress relaxation should be considered especially during the first few cycles of deformation.

### 2.3.4 Permanent Set

A unique feature of elastomer behaviour is set. According to Diani et al. (2009), Set designates as a permanent residual deformation after the applied force has been released. Since the duration of force application also produce stress relaxation and creep, it is always difficult to measure the permanent set.

Diani et al. (2009) also noted that this permanent set behaviour is actually not permanent and the effect will increase with increasing time in the deformed state and also with maximum deformation held.

### 2.3.5 Strain Crystallization

At higher strain, some elastomer will demonstrate crystallization behaviour. This phenomenon is often observed in un-reinforced material. The stress-strain curve will become steeper during the crystallization and resulting in increasing of strength failure. In term of molecular network, the chain will be arranged next to each other by the large extension to form a regular crystalline. A rapid and simultaneous rupture is required to break the van der Waals bonding between these chains. The crystallized group normally have a higher strength compared to non-crystallized. This is because the non crystallized chain is easy to get failure loading one chain at a time.

### 2.3.6 Hysteresis

In stress-strain curves (figure 2.1), the area between the loading and unloading curves correspond as a hysteresis loop. According to Chai et al. (2011) this phenomenon is representing the amount of energy dissipated during the cyclic loading. Under cyclic loading which involve both extension and contraction of a force, hysteresis present because of internal friction. From the previous work of Chai et al. (2011), it is found that, hysteresis will not disappear under stress-strain curves but it will stabilize after five cycles of loading.

Hysteresis can be defined as energy per unit volume which released as heat in each loading cycle. The specimen's temperature will increase accordingly to the magnitude of an internal heat generation and the rate at which the heat can be removed by conduction within the material and convection from the specimen surface (Roylance, 2001).

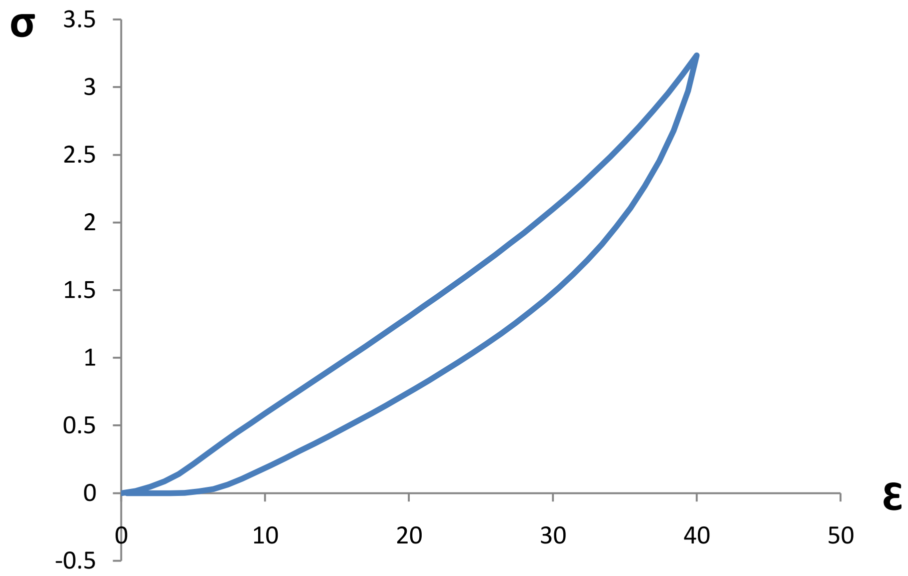


Figure 2.1: Hysteresis loop

Different elastomer will have different behaviour of hysteresis. Un-reinforced elastomer will have less hysteresis compared to elastomer with reinforcing material.

### 2.3.5 Mullin's Effect

According to Diani et al. (2009), Mullin's effect is a stress softening phenomenon observed in material when subjected to cyclic loading. During the first loading, materials will deform up to the maximum strain value. This material will exhibit a lower stress for the second and subsequent loading at the same applied strain. From the figure 2,2, this phenomenon can be observed by the path for the second loading which is not the same with the first loading.

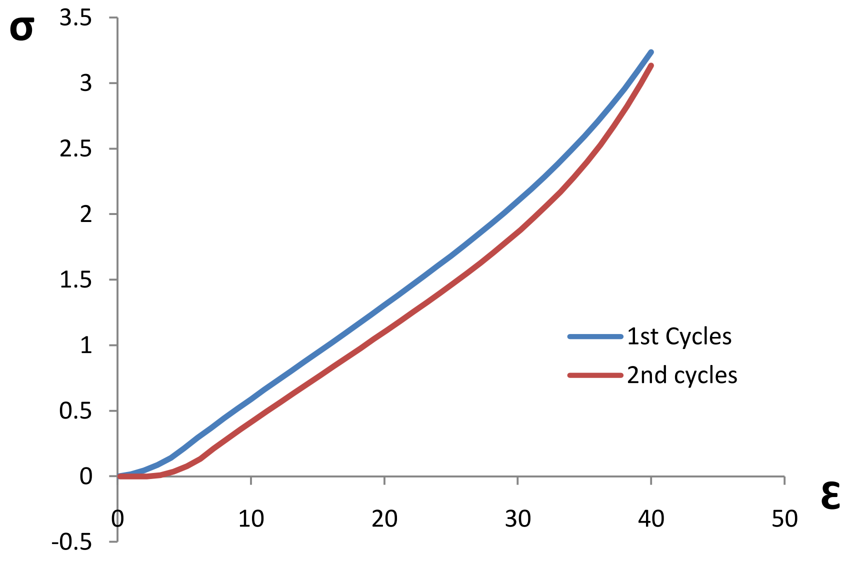


Figure 2.2: The Mullin's Effect phenomenon

The pattern of decreasing in stress value for the second and subsequent loading can be defined in term of material's molecular chain. During the first loading, the molecular chain of the material will break or damage corresponds to the particular strain. At the next loading, the broken chain will increase and no longer able to support the extension resulting the lower stress. According to Bueche (1960,1961) quoted by Diani et al, (2009), this is called a stress softening phenomenon. These happen due to polymer network chains under deformation entangle each other or with the reinforcement particle try to rearrange itself.

Mullin's effect also can be defined as a damage mechanism (Marckmann et al, 2001). This phenomenon can be observed in figure 2.3(a) and (b) which show the behaviour of Mullin's effect in rubber under static loading without influence of strain rate and visco-elastic phenomena. When the material is subjected to uniaxial strain as in figure 2.3 (a), the virgin material is stretched to $\lambda_I$, the stress will follow the *I* paths as in figure 2.3 (b). Then, after unloading from $\lambda_I$, the stress will follow the path *I'*. It goes the same in the second uploading where, when the material is stretched to $\lambda_{II}$ The stress will follow the path *II* which is same as a path *I* but during unloading, it will not follow the same path as *I'*. At a given stretch, the stress at *II'* is lower than the stress at *I'*. The phenomenon also observed when the stretch is extended until $\lambda_{III}$, the unloading will not following *I'* and *II'* path.

The stress softening effect will disappear after five cycles of loading according to Chai et al. (2011). The effect is different with hysteresis where it will not disappear but will stabilize after five cycles of loading. Diani et al. (2009), also reported that the effect of stress softening will increase in reinforced material.

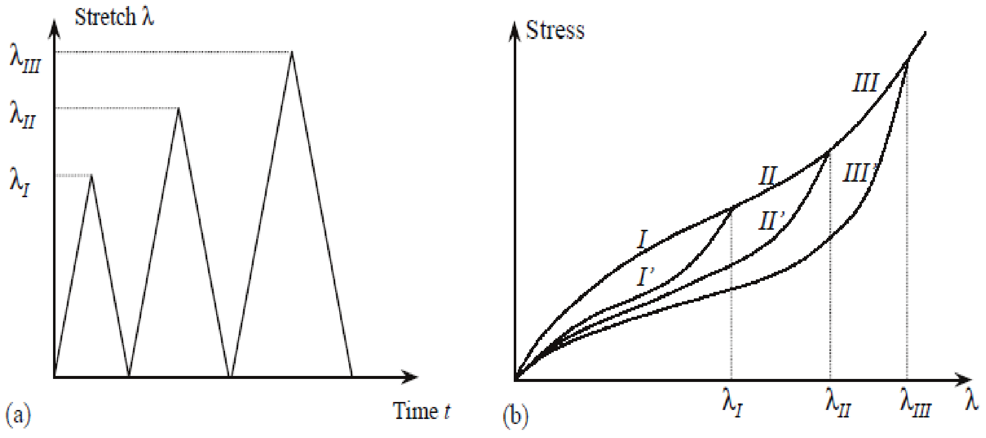


Figure 2.3: Macroscopic description of the Mullin's effect. (a) Stretch history. (b) Stress.

(Source: Marckmann et al, 2001)

### 2.3.7 Factor Affect Elastomer Characteristic under Stress-Strain

#### 2.3.7.1 Temperature

All the characteristic of elastomer which discussed earlier are temperature dependant. It is important to consider the effect of temperature since it will greatly affect on mechanical properties change of the material and also able to lead to permanent degradation. Increasing temperature for example, will show the following effect (Judson, 2008)

- Decreasing of hysteresis magnitude
- Materials become more fatigue
- Creep, stress relaxation and recovery process take place more rapidly

#### 2.3.7.2 Immersion Effects

When the elastomer exposed in a solvent for example; biodiesel, it will accelerate to rapid degradation and can cause fatigue. The immersion will cause swelling of the material and therefore will change its physical property. It is important to study the durability of elastomer under mechanical loading in this environment. For example, in the vehicle engine system, elastomer has been used as a part or component where it is exposing with the engine fuel. Durability study important to predict the lifetime of this part before it need the replacement.

### 2.3.7.3 Reinforcement

The study conducted by Diani et al. (2009) reported that, the phenomenon of Mullin's effect and hysteresis increase in the reinforced elastomer compared to un-reinforced. The function of reinforcement in elastomer is usually to increase the stiffness of the material. The common material use for reinforcement is carbon black, but the most popular and cheaper material called "fillers" is normally used to save cost. During design, elastomer normally reinforced before vulcanization by adding this fine particle to improve the physical properties of the material.

## 2.4 Strain Energy Density

This is the scalar function that relates the strain energy density of material with the deformation behaviour. The strain energy density is representing by the area under the stress-strain curves. It is assumed that the amount of stress in the material can be obtained by the derivation of the respective strain.

Through the strain energy density function, a constitutive modelling equation can be developed to represent the mechanical characteristic of elastomer. In the phenomenological approach, materials are treated as a continuum and the strain energy function is defined through either strain invariants or stretch ratios. Currently, most of the available hyperelastic material models are phenomenological based and have been mathematically justified.

## 2.5 Developing a Constitutive Modelling

There are a lot of studies to construct a constitutive modelling of hyperelastic material stress-strain relation which can fit with the experiment data. Two options phenomenological approach can be used to describe the behaviour of rubber elasticity. The first theory is using the continuum mechanics viewpoint and second is using statistical or kinetic theory by modelling the structure of vulcanised rubber.

Strain energy density function (*W*) can be used to develop a model which describes the elasticity behaviour. The most common and established strain energy model used is Neo-Hookean and Mooney Rivlin. To avoid complexity of a mathematical equation during developing a model, elastomer normally assumed to be homogenous, isotropic and incompressible. In general, the material parameters for a particular model are determined by fitting an experimental data with the theoretical model developed.

Once the strain energy function is chosen, the Cauchy stress can be obtained by

$$\boldsymbol{\sigma} = -p\mathbf{I} + 2\mathbf{B}\left(\frac{\partial W}{\partial \boldsymbol{B}}\right) \tag{2.1}$$

where **B** is the left Cauchy–Green stretch tensor and $p$ stands for the hydrostatic pressure introduced by the incompressibility assumption. *W* is generally expressed as a function of the first and second strain invariants, respectively, given by the following equation

$$I_1 = \text{tr}\,\mathbf{B} \text{ and } I_2 = \frac{1}{2}\left[I_1^2 - \text{tr}(\mathbf{B}^2)\right] \tag{2.2}$$

or as a function of the principal stretch ratio. Since the material is assumed as incompressible, the third invariants value is considered as 1. Therefore the principal stretch ratio can be shown as;

$$\lambda_1\lambda_2\lambda_3 = 1 \qquad (2.3)$$

The forms of the strain energy function W can be derived using phenomenological approach as a function of the strain invariants $I_1$ and $I_2$ or as principal stretch ratios (Marckmann et al, 2002). All of these constitutive equations are based on experimental observations and mathematical developments.

Several works have been done to develop constitutive modelling to capture the Mullin's effect. Some of them are research by Guo et al. (2008) which using the Gao's elastic law to simulate Mullin's effect and Chagnon et al. (2006) on modelling of Mullin's effect using network alteration theory. However, those studies only capturing the effect on a dry rubber. The Mullin's effects in swollen rubber still have not been covered yet.

# *CHAPTER 3:* METHODOLOGY

There are a lot of attempt to develop theoretical stress-strain that fits an experimental result for hyperelastic materials. One of them is a study on Continuum Damage Mechanic (CDM) by Chagnon et al. (2004) to describe the Mullin's effect phenomenon in elastomer. As most of study to describe the Mullin's effect phenomenon only deals with dry rubber, we would like to extend this study to include the swelling effect of the material.

On this research, we will adopt the study of Continuum Damage Mechanic (CDM) from Chagnon et al. (2004). In this CDM model, stress response in an incompressible and isotropic hyperelastic material is given by the following equation:

$$\boldsymbol{\sigma} = -p\mathbf{I} + (1-d)\left[2\left(\frac{\partial Wo}{\partial I_1} + I_1\frac{\partial Wo}{\partial I_2}\right)\right]\mathbf{B} - 2\,\frac{\partial Wo}{\partial I_2}\,\mathbf{B^2} \qquad (3.1)$$

Where $p$ is Lagrange multiplier, $I_1$ and $I_2$ is stress invariant, $Wo$ is a strain energy density function of undamaged material, and **B** is Left Cauchy-Green strain tensor. Assume that the equation is showing a damage phenomenon where the strain energy is referred by a scalar quantity of damage parameter, $d$. Diani et al. (2009) reported that, this damage mechanism is an unknown physical parameter which cover microstructural damage, multi chain damage or micro-void formation. Stress response can be entirely determined once the form of $Wo$ is known.

According to CDM model, a damage phenomenon is only occurred during the first cycle of deformation strain. If the cyclic loading is continuously applied below maximum effective strain energy, it will not contribute to this Mullin's type of damage.

In the case of dry rubber, the Mullin's effect depends on maximum strain ever experienced by the materials. Scalar *d* can be defined as a function of strain. For the swollen rubber, the effect of swelling must take into consideration in developing the constitutive modelling. We can say that, in the case of swollen rubber, *d* can be defined as a function of swelling and strain. In this study, the term of volume fraction, $V_2$ is used to describe the swelling effect. $V_2$ can be defined as follow:

$$
\begin{aligned}
\text{Rubber Volume Fraction } (V_2) &= V_{\text{dry rubber}} / V_{\text{gel}} \\
&= V_{\text{dry rubber}} / (V_{\text{dry rubber}} + V_{\text{liquid}}) \\
&= V_{\text{dry rubber}} / V_{\text{swollen rubber}} \\
&= V_o / V_i \qquad (3.2)
\end{aligned}
$$

We can now define swelling, β as a function of a rubber volume fraction:-

$$
\begin{aligned}
\text{Swelling } (\beta) &= (V_i - V_o)/V_o \\
&= (V_i/V_o) - 1 \\
&= (1/V_2) - 1 \qquad (3.3)
\end{aligned}
$$

It is known that the rubber volume fraction is inversing proportional with swelling. For dry rubber, $V_2$ is equal to 1 since there is no volume change. The volume changes will increase with longer immersion of a specimen. Therefore, the shorter duration immersion of a specimen, the higher value of $V_2$ obtained.

$$V_2^{\text{2 days}} > V_2^{\text{5 days}} > \ldots\ldots V_2^{\text{30 days}}$$

## 3.1 Experimental Result

All the experiment data is obtained from Chai et al. (2011), which using Nitrile Butadiene Rubber (NBR) as a material. To see the Mullin's effect phenomenon in swollen rubber, the NBR is immersed in biodiesel until it reaching the desired duration (2 days, 5 days, 10 days, 20 days and 30 days). The material is then subjected to a compressive cyclic loading at the different level of strain. To simplify the modelling, we only consider two condition of swollen state which is NBR in 5 days and 30 days of immersion

To develop a constitutive model to capture the Mullin's effect in swollen rubber, a few assumptions have been made:

1. The material remains incompressible. There is no volume change in both dry and swollen material during mechanical testing.
2. All material are considered isotropic either in dry or swollen state
3. The damage of material is considered as isotropic damage

## 3.2 Strain Energy Function

To begin the modelling of Mullin's effect, we have decided to choose the Fung model to describe the undamaged strain energy density function. The choice is based on the experimental observation where the Fung strain energy density function is the appropriate to describe the experimental plot. The Fung model can be defined by a following equation:

$$W\mathrm{o} = \mathrm{K}_1/\mathrm{K}_2\ [\exp \mathrm{K}_2\, (I_1 - 3) - 1] \qquad (3.4)$$

Considering the undamaged material of first stress uploading for the uniaxial compression test, the stress-strain relationship can be simplified as follow:

$$\sigma = 2\left(\lambda - \frac{1}{\lambda^2}\right)\left(\frac{\partial Wo}{\partial I_1} + \frac{1}{\lambda^2}\frac{\partial Wo}{\partial I_2}\right) \tag{3.5}$$

We will not take into consideration of $I_2$ since the measure of deformation is only depending on $I_1$. The equation (3.5) then becomes:

$$\sigma = 2\left(\lambda - \frac{1}{\lambda 2}\right) \mathrm{K}_1 \exp\{\mathrm{K}_2 (I_1 - 3)\} \tag{3.6}$$

$K_1$ and $K_2$ is material constant to be fitted from stress-strain curve for stress at the first uploading of undamaged material. It is noted that, the equation (3.6) is only applicable on dry rubber since the stress is only considering the strain and not the swelling. Therefore, the equation refers to the stress at first uploading for dry rubber.

## 3.3 Modelling of the Mullin's Effect

To model the first uploading stress for swollen rubber, we simply plot the stress ratio (SR*) over the strain from the experiment data. The stress ratio can be calculated by following:-

$$\text{Stress Ratio (SR*)} = \sigma^{1up\ (swollen)} / \sigma^{1up\ (dry)} \tag{3.7}$$

The stress value for the first uploading of swollen rubber can be obtained by multiplying the SR* with stress for the first uploading of dry rubber. The theoretical graph then plotted to fit with experimental and to identify the material constant. The result will be discussed in the next chapter.

In order to develop a theoretical model for the second uploading stress for swollen rubber, we have to consider the stress softening effect of the material. Stress softening (SS) can be obtained from the experiment data by the following equation:

$$SS = \frac{\text{Stress at first uploading} - \text{Stress at second uploading}}{\text{Stress at first uploading}}$$

$$= (\sigma^{1up} - \sigma^{2up}) / \sigma^{1up} \qquad (3.8)$$

The stress softening for swollen rubber ($SS^{swollen}$) can be defined as follow:

$$SS^{swollen} = (\sigma^{1up(swollen)} - \sigma^{2up(swollen)}) / \sigma^{1up(swollen)}$$

$$= 1 - \sigma^{2up(swollen)} / \sigma^{1up(swollen)} \qquad (3.9)$$

Therefore;

$$\sigma^{2up(swollen)} = \sigma^{1up(swollen)} (1 - SS^{swollen}) \qquad (3.10)$$

$SS^{swollen}$ also can be defined as;

$$SS^{Swollen} = (SS^{Swollen}/SS^{dry}) \text{ x } SS^{dry}$$

$$= RSS \text{ x } SS^{dry} \qquad (3.11)$$

Replace (3.10) into the equation (3.11),

$$\sigma^{2up(swollen)} = \sigma^{1up(swollen)} \{1 - RSS \text{ x } SS^{dry}\}$$

$$= \{ \sigma^{1up(dry)} \text{x } SR^*\} \{1 - RSS \text{ x } SS^{dry}\} \qquad (3.12)$$

The theoretical model of stress at the first and second uploading of swollen rubber is then plotted to identify all the material constant. The Mullin's effects in the theoretical model will also being discussed in the next chapter. Finally, the theoretical model plot is then compared with the experiment data.

As the above equation illustrated, this mathematical model has its own limitations. Since the modelling developed only considers one maximum strain representing a one-dimensional problem which is only happen in special uniaxial case, it is not applicable in real engineering application. The different way of measuring deformation state by adopting the 8-chain model of Arruda-Boyce is used. The parameter of this model can be simply replaced the function of maximum stretch ratio in order to incorporate with modelling of Mullin's effect. In this model, we used $\alpha$ instead of strain. $\alpha$ is defined by the following equation:

$$\alpha = \sqrt{(I_1/3)} - 1 \tag{3.13}$$

The stretch of diagonal cube is represented by $\sqrt{(I_1/3)}$ which is able to represent a simple three-dimensional deformation conditions.

$$I_1 = \lambda^2 + \frac{2}{\lambda} \tag{3.14}$$

Equation (3.13) become;

$$\alpha = \sqrt{[(\lambda^2 + \frac{2}{\lambda})/3]} - 1 \tag{3.15}$$

By using the developed model, the new material constant K is now can be defined from the new plot of theoretical as a function of $\alpha$. The result will be discussed in the following chapter.

*CHAPTER 4:* **RESULTS AND DISCUSSION**

In this chapter, we will be discussing on equation derivation to develop constitutive modelling to capture the Mullin's effect, material constant identification and finally the comparison result of the model developed with the experimental result. The discussion will also cover a different way of measuring the deformation state by using the Arruda-Boyce 8-chain model.

## 4.1 Development of modelling equation in special uniaxial case

In previous chapter, we have been discussed that damage material, *d* for swollen rubber is the function of swelling and strain. It also noted that the use of maximum strain experienced by the material which represents the damage criterion is not enough to accurately describe the Mullin's effect in swollen rubber. Thus, the development of the equation of stress softening variable should also include the swelling characteristic.

### 4.1.1 Stress Ratio (SR*).

The stress ratio of swollen rubber in 5 days and 30 days is calculated by dividing the first uploading stress of swollen rubber with the first uploading stress of dry rubber.

$$\text{Stress Ratio (SR*)} = \sigma^{1up\ (swollen)} / \sigma^{1up\ (dry)} \qquad (4.1)$$

The value of experimental SR* then plotted over strain as in the following figure:

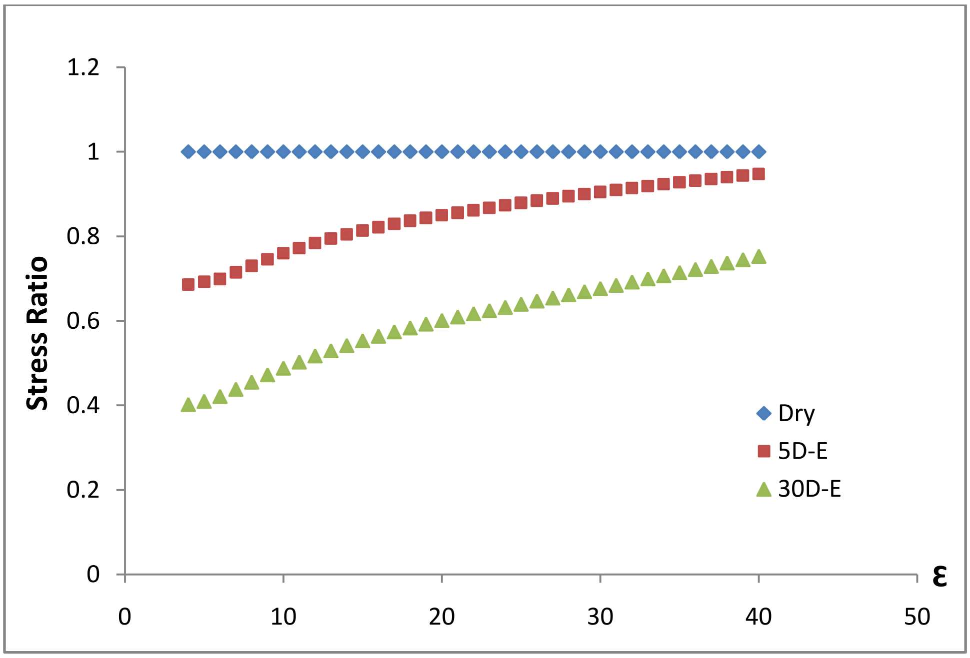


Figure 4.1: Experimental Stress Ratio

From the graph, we can observe that, the curve is in the shape of inverse exponential-like which can be represented by the following equation:

$$SR^* = 1 - K_3 \exp(-K_4\, \varepsilon/\varepsilon_{max}) \quad (4.2)$$

$K_3$ and $K_4$ are the material constant to be identified and $\varepsilon_{max}$ is the maximum strain applied. In order to include the swelling characteristic, equation (4.2) will become:

$$SR^* = 1 - K_3 V_{2eq}\,(1/V_2 - 1)\exp(-K_4\, \varepsilon/\varepsilon_{max}) \quad (4.3)$$

Where, $V_{2eq}$ is the highest value of swelling for the material (equilibrium condition). Nitrile Butadiene Rubber (NBR) having a $V_{2eq}$ value of 0.71 which is obtained from experimental. Consider the stress ratio ($SR^*$) as follow:

$$SR^* = 1 - f(\varepsilon) \quad (4.4)$$

Where,

$$f(\varepsilon) = K_3 V_{2eq}\,(1/V_2 - 1)\exp(-K_4\, \varepsilon/\varepsilon_{max}) \quad (4.5)$$

If V2 = 1, then f (ε) = 0 which represent the condition for dry rubber and if $V_{2eq}<V_2<1$ then f (ε) > 0 which represent condition for the swollen rubber.

### 4.1.2 Stress Softening

The stress softening equation for dry rubber is derived in order to develop a modelling of second uploading stress for swollen rubber. It is calculated by dividing the difference between first and second uploading stress with the first uploading stress.

$$\text{Stress Softening (SS)} = (\sigma^{1up} - \sigma^{2up}) / \sigma^{1up} \qquad (4.6)$$

It is known that from experimental plot in figure 4.2, stress softening is the decreasing function of strain exponentially. Since we only develop an equation for dry rubber, the effect of swelling is ignored. Therefore, the following equation is proposed. $K_5$ and $K_6$ is a material constant to be defined so that the theoretical plot will have a good agreement with the experimental plot:-

$$\text{Stress Softening} = K_5 \exp(- K_6\, \varepsilon/\varepsilon_{max}) \qquad (4.7)$$

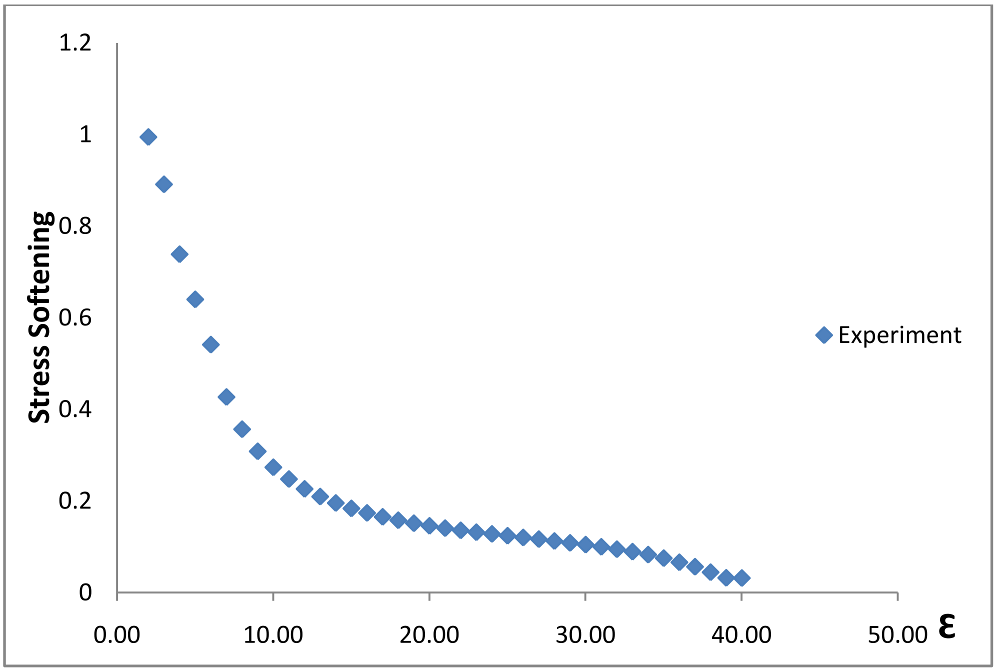


Figure 4.2: Experimental stress softening for dry rubber

### 4.1.3 Ratio of Stress Softening (RSS)

Ratio of stress softening for 5 and 30 days of immersion is defined from the stress softening data and the value is then plotted over the strain. To get the value of the ratio of stress softening, we simply divide the stress softening of swollen material to the value of stress softening of dry material:

$$RSS = SS^{swollen} / SS^{dry} \quad (4.8)$$

The figure 4.3 had shown the experimental plot for RSS over a strain for both dry and swollen rubber.

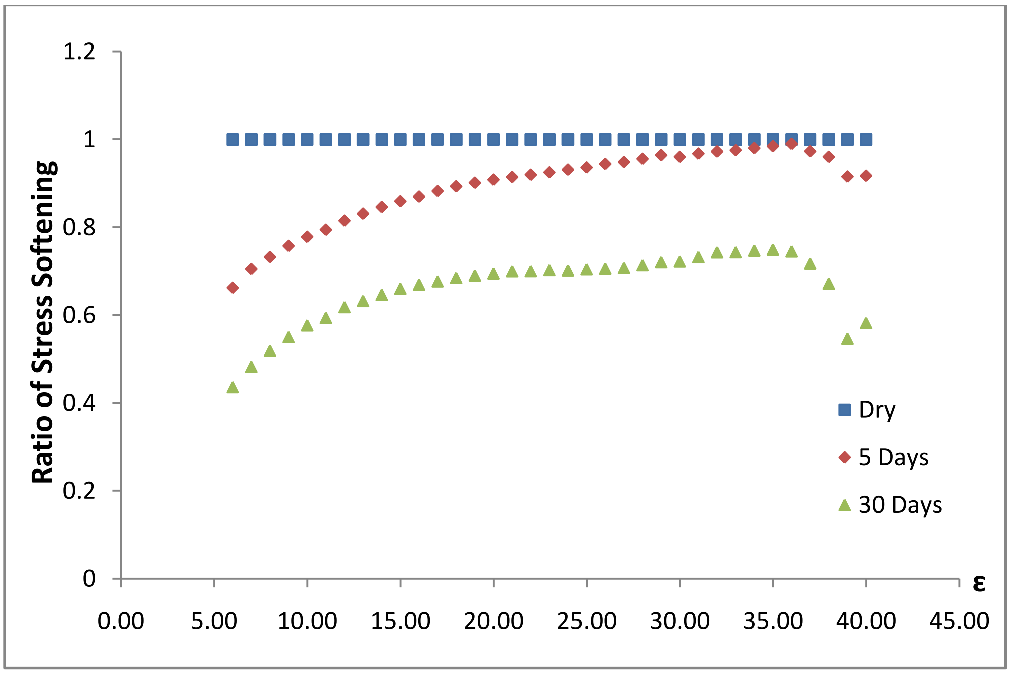


Figure 4.3: Experimental Ratio of Stress Softening

From the graph, we can observe that, the RSS curve is similar to the stress ratio (SR*) curve which is in inverse exponential shape. Since RSS equation is developed for swollen rubber, the effect of swelling must be considered. Therefore, we propose the same model as SR*.

$$RSS = 1 - K_7 V_{2eq} \left(1/V_2 - 1\right) \exp\left(-K_8\, \varepsilon/\varepsilon_{max}\right) \qquad (4.9)$$

$K_7$ and $K_8$ are material constants defined by fitting the experimental with the theoretical plot.

## 4.2 Fitting result and material constant determination

From the Fung strain energy density function discussed in the previous chapter, the experimental curve for the stress at the first uploading of dry rubber is plotted along the theoretical model proposed:-

$$\sigma^{1up\,(dry)} = 2(\lambda - \frac{1}{\lambda^2})\, K_1 \exp\{K_2\,(I_1 - 3)\} \qquad (4.10)$$

From figure 4.4, the value of $K_1$ and $K_2$ which give the best agreement with experimental is 0.775 and 0.001.

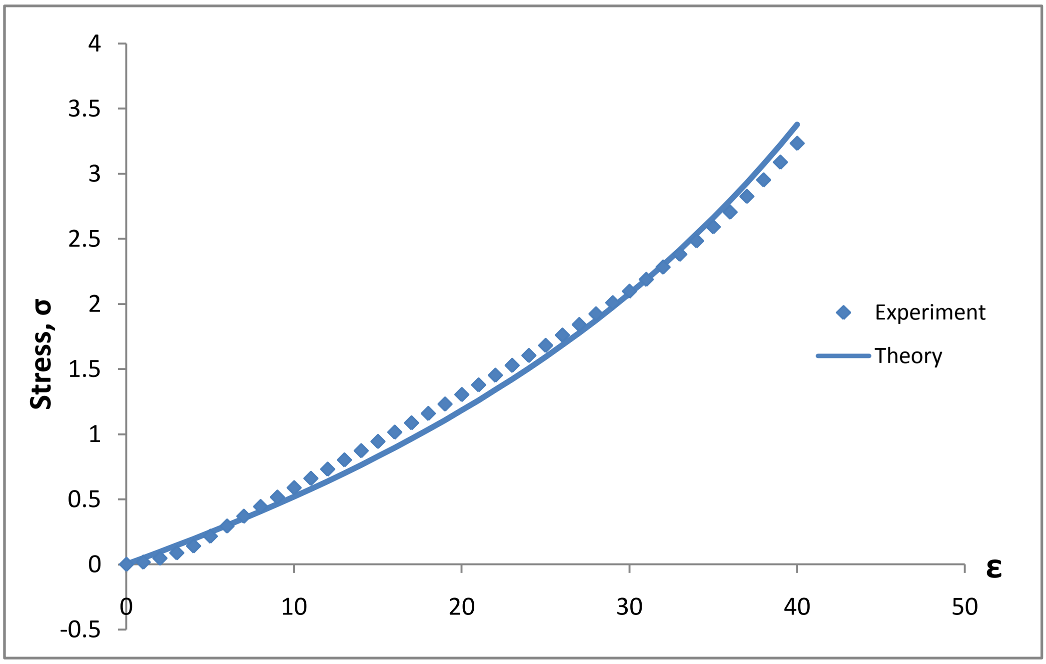


Figure 4.4: Stress at first uploading for dry rubber

For the stress ratio (SR*), the following equation is used to plot the theoretical. The value of $K_3$ and $K_4$ obtained is 3.15 and 0.75.

$$\text{Stress Ratio (SR*)} = 1 - K_3\, V_{2eq}\,(1/V_2 - 1)\, \exp\,(-K_4\, \varepsilon/\varepsilon_{max}) \qquad (4.11)$$

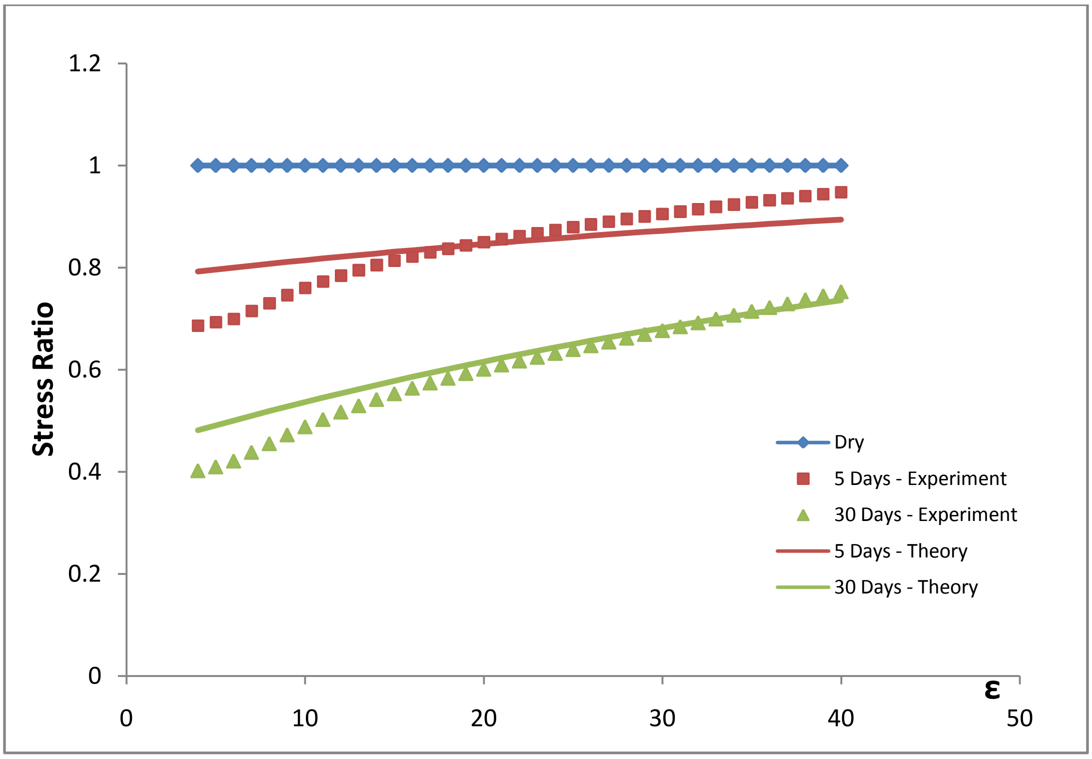


Figure 4.5: Stress Ratio of experimental and theoretical for dry and swollen rubber

To obtain the value of $K_5$ and $K_6$ from the stress softening equation model proposed, the theoretical and experimental graph is plotted as in figure 4.6. The value which can give the best fitting for both curves is 0.5 for $K_5$ and 2.5 for $K_6$.

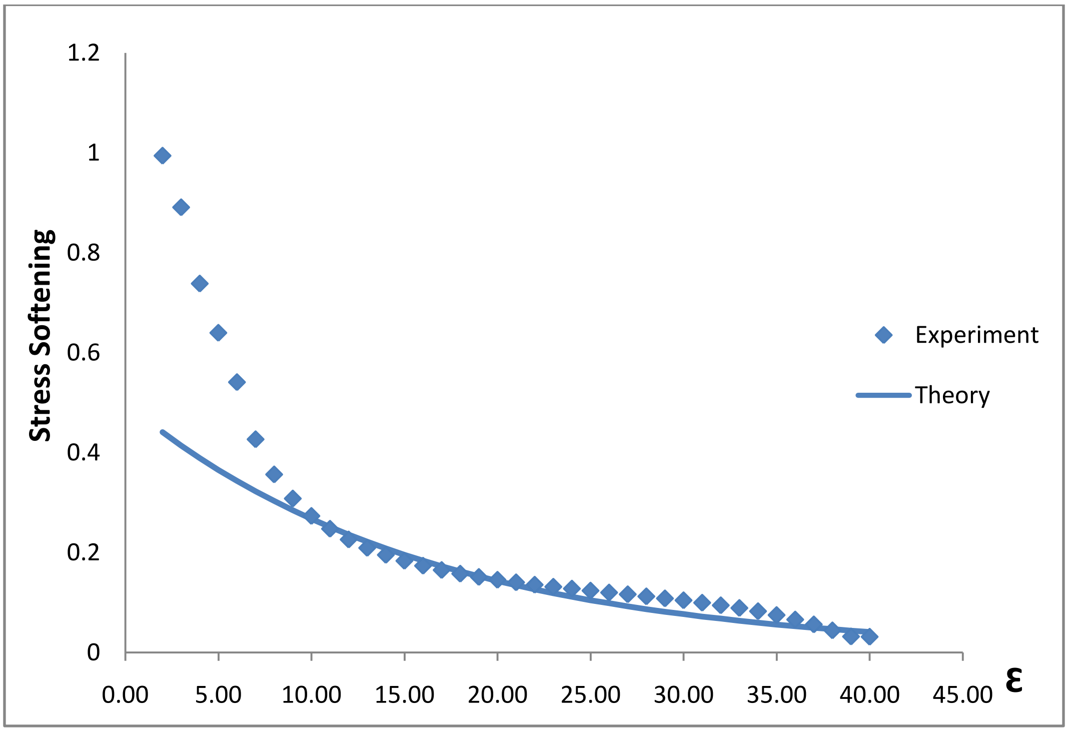


Figure 4.6: Experimental and theoretical stress softening curve for the dry rubber

The ratio of stress softening for theoretical is then plotted using the following equation:

$$RSS = 1 - K_7 V_{2eq} (1/V_2 - 1) \exp(-K_8\ \varepsilon/\varepsilon_{max}) \qquad (4.12)$$

From the graph, the value obtained for material constant $K_7$ and $K_8$ is 5 and 1.5.

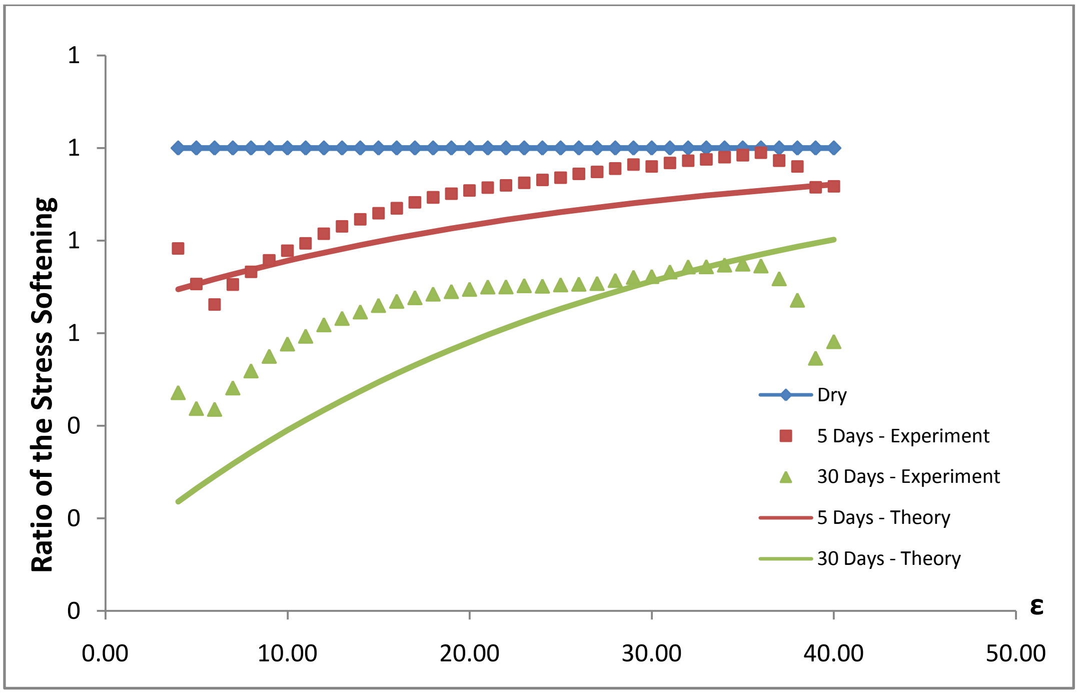


Figure 4.7: The experimental and theoretical curve for ratio of the stress softening

Value for the material constants obtained are summarizes in the below table:

Table 4.1: The value of material constant

| Parameter | K1 | K2 | K3 | K4 | K5 | K6 | K7 | K8 |
|---|---|---|---|---|---|---|---|---|
| Value | 0.775 MPa | 0.001 | 3.15 | 0.75 | 0.5 | 2.5 | 5 | 1.5 |

### 4.3 Comparison with experimental result

From all the constant value of K obtained, the theoretical stress of first and second uploading for dry and swollen rubber is plotted and compared with experiment result. For the first uploading stress, the equation (4.13) used as per discussed in the previous chapter:

$$\sigma^{1up(swollen)} = SR^* \times \sigma^{1up(dry)} \tag{4.13}$$

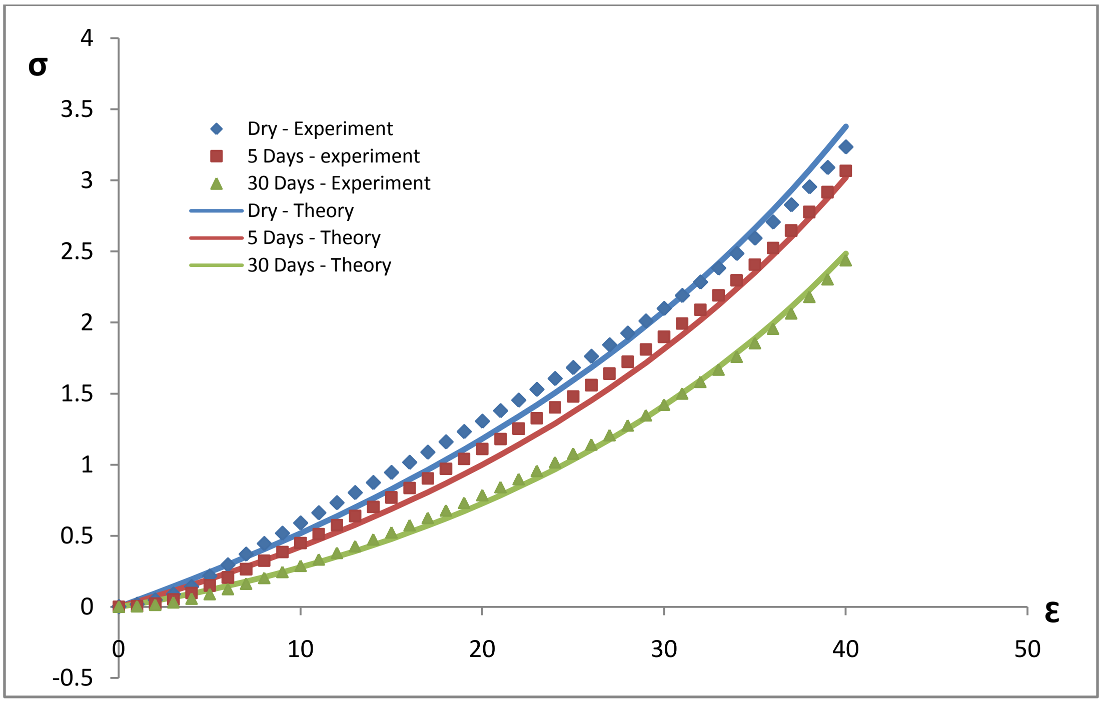


Figure 4.8: Stress at first uploading

The second uploading stress for both dry and swollen are plotted as in figure 4.9. The equation (4.14) is used to plot the theoretical graph:

$$\sigma^{2up} = \{ \sigma^{1up(dry)} \text{ x SR*}\} \{1 - \text{RSS x SS}^{dry}\} \quad (4.14)$$

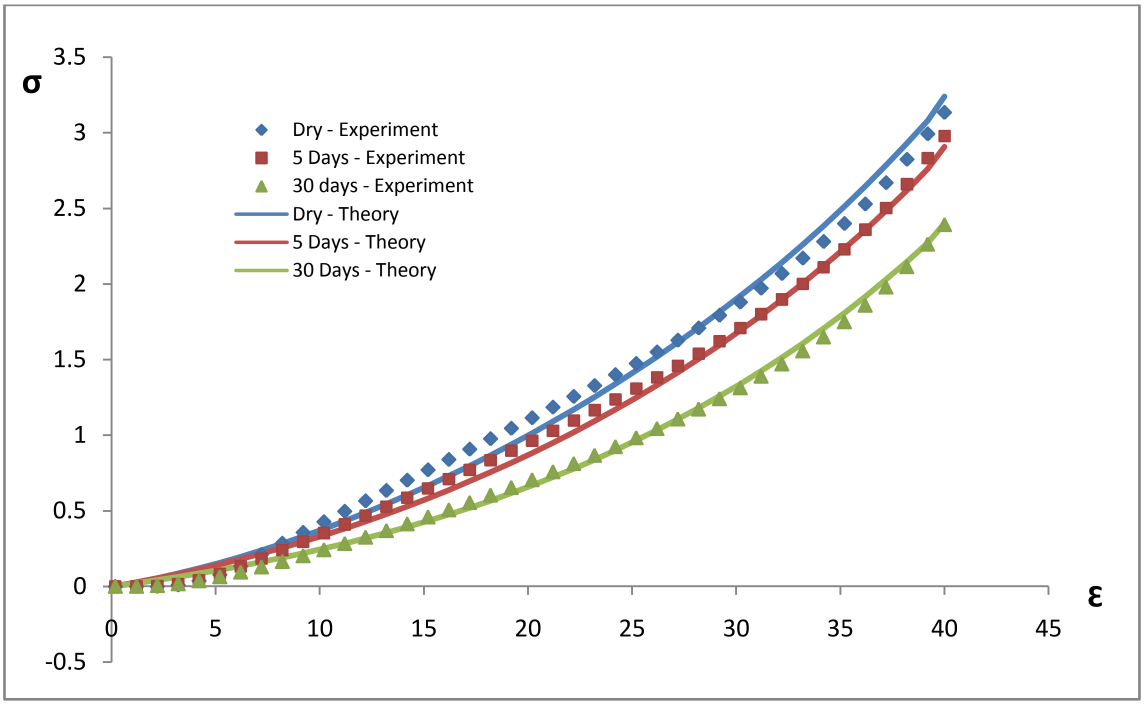


Figure 4.9: Stress at second uploading

From figure 4.8 and 4.9, we can now conclude that the modelling equation developed giving the good agreement with the experimental data.

### 4.4 Measuring Deformation State by the 8-chain model

By using the model proposed in section 4.1, the theoretical graph is plotted as a function of α. Figure 4.10 showing the best curve fitting between modelling and experimental for the dry NBR at first uploading stress. The value of $K_1$ and $K_2$ obtained from this curves is 0.775 and 0.001

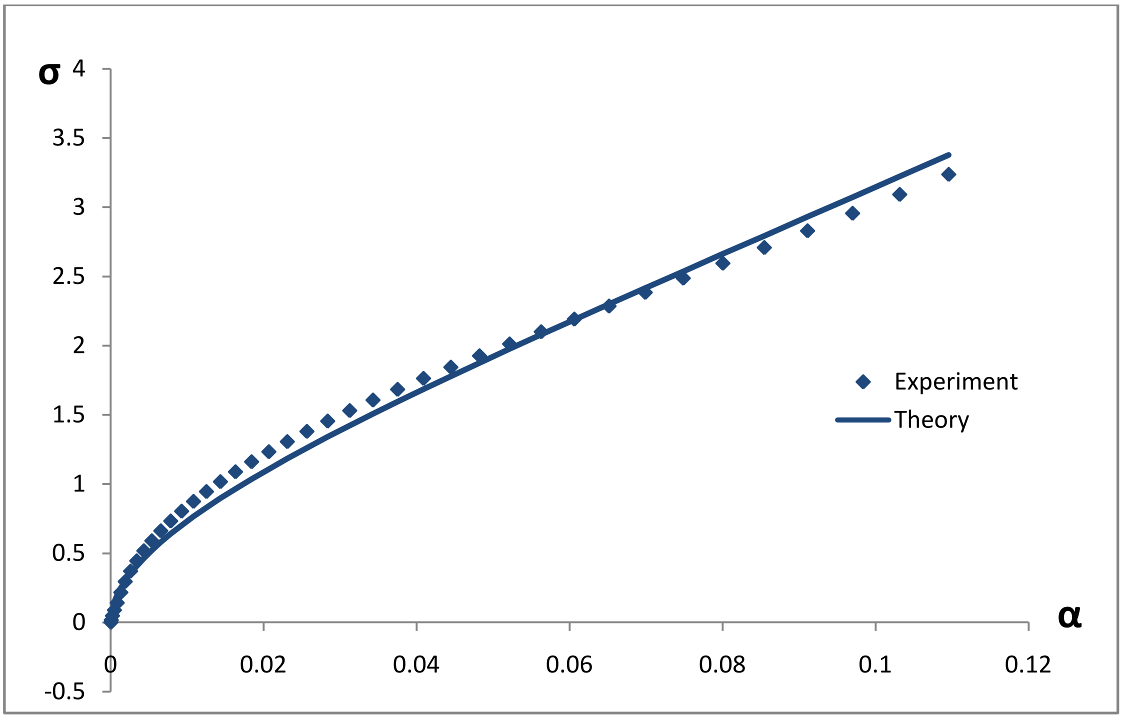


Figure 4.10: First uploading stress curves for dry NBR as a function of α

Figure 4.11 show the stress ratio graph as a function of α plotted by using the equation (4.3) and compared with the experimental. Value of $K_3$ and $K_4$ obtained is 3 and 0.75.

$$\text{Stress Ratio (SR*)} = 1 - K_3 V_{2eq} (1/V_2 - 1) \exp(-K_4 \alpha/\alpha_{max}) \quad (4.15)$$

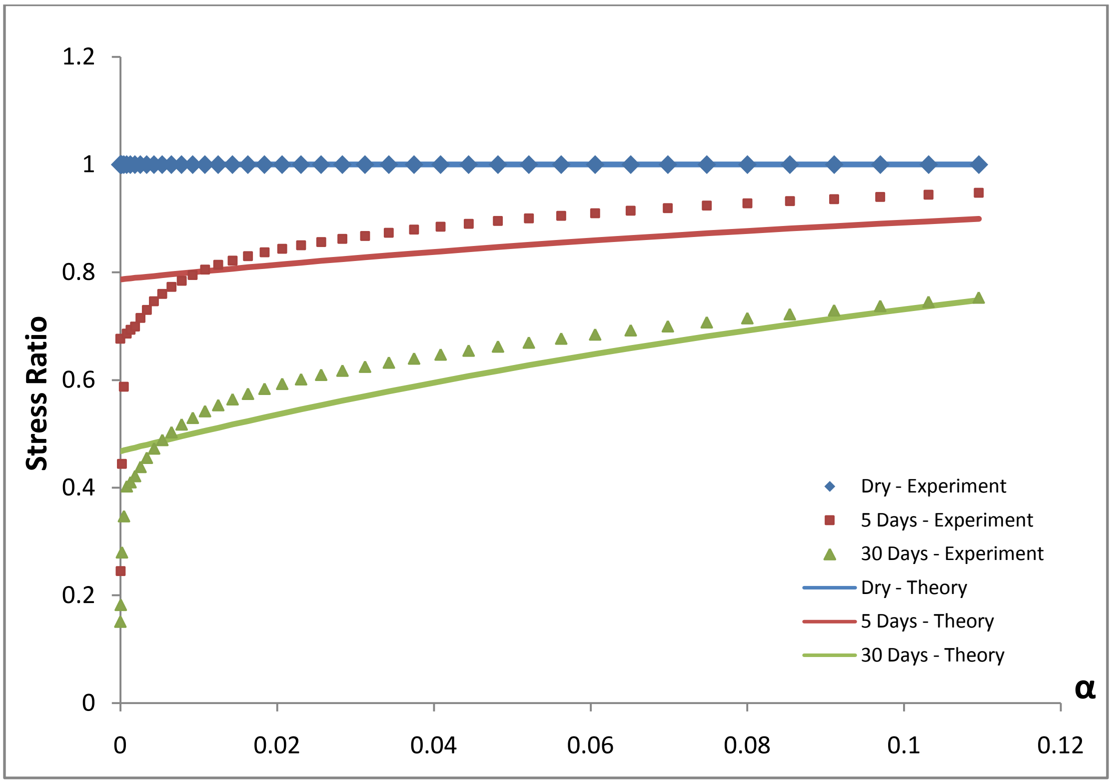


Figure 4.11: Stress Ratio as a function of α

In figure 4.12, the stress softening graph is plotted as a function of α and compared with the experimental. The value of $K_5$ and $K_6$ obtained is 0.2 and 1.7.

$$\text{Stress Softening} = K_5 \exp(- K_6\, \alpha/\alpha_{max}) \quad (4.16)$$

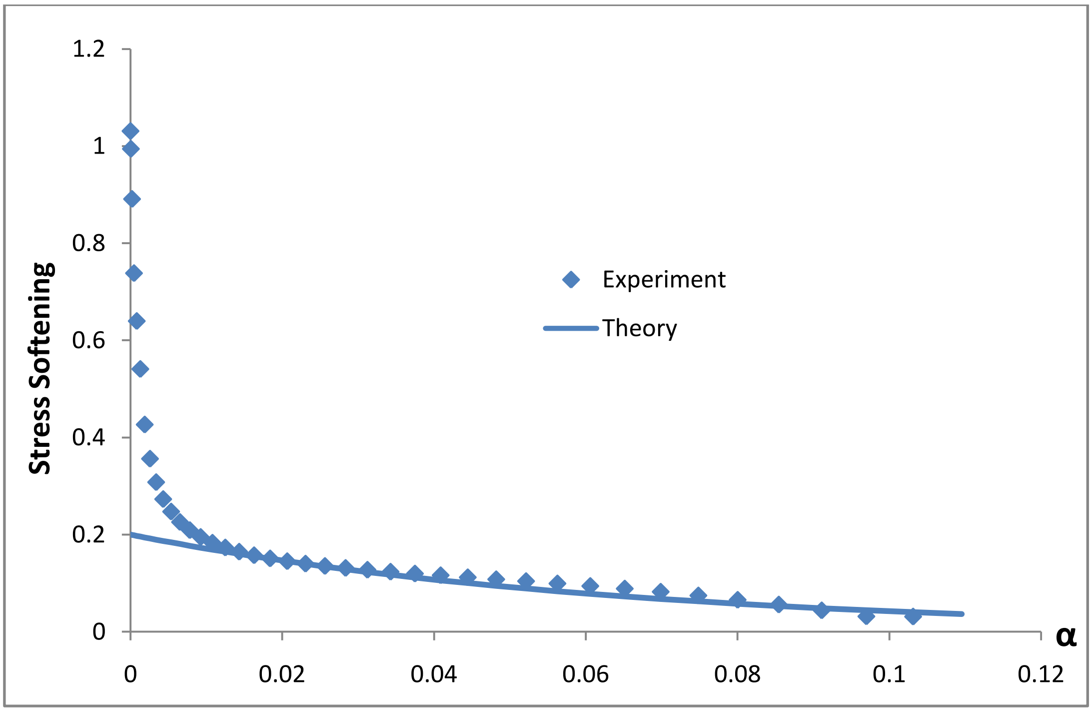


Figure 4.12: Stress softening for dry rubber as a function of α

The theoretical ratio of stress softening graph for NBR is then plotted as a function of α. The material constant $K_7$ obtained is and $K_8$ is 5 and 1.5.

$$RSS = 1 - K_7 V_{2eq} (1/V_2 - 1) \exp(-K_8\, \alpha/\alpha_{max}) \qquad (4.17)$$

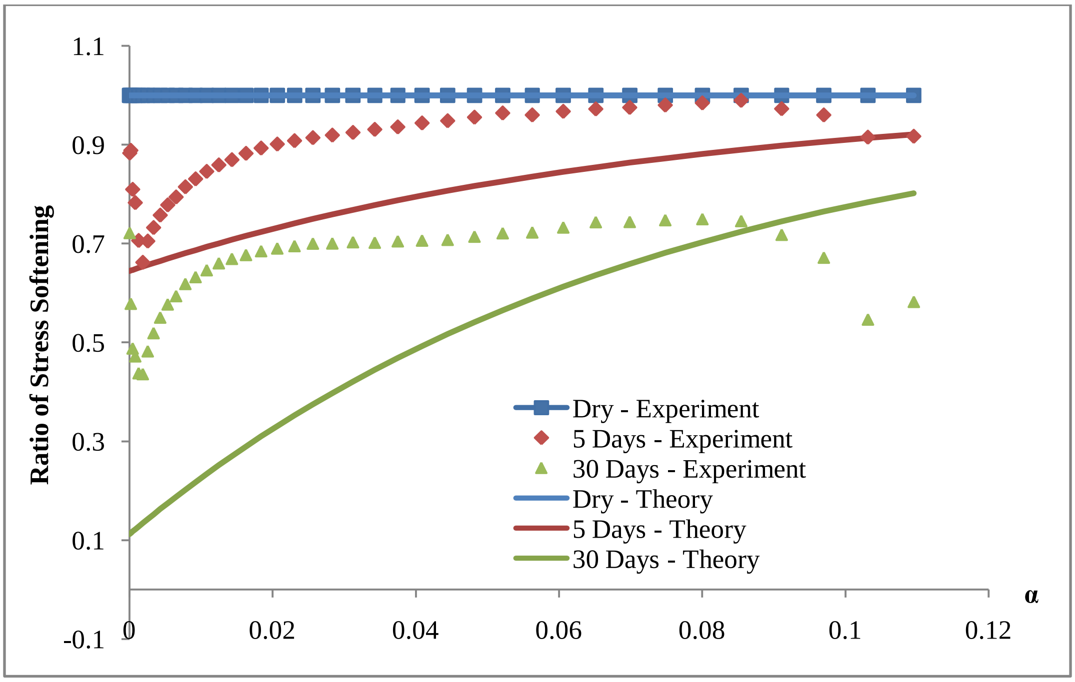


Figure 4.13: Ratio of stress softening as a function of α

The summary of all constant value is shown in table 4.2:

Table 4.2: Summary of material constant value in 8-chain model

| Parameter | K1 | K2 | K3 | K4 | K5 | K6 | K7 | K8 |
|---|---|---|---|---|---|---|---|---|
| Value | 0.775 MPa | 0.001 | 3 | 0.75 | 0.2 | 1.7 | 5 | 1.5 |

By using all value of material constant, K obtained the stress at first and second uploading as a function of α is plotted as shown in figure 4.14 and 4.15. It is shown that from the figure, the experimental and theoretical curve showing the good agreement with each other.

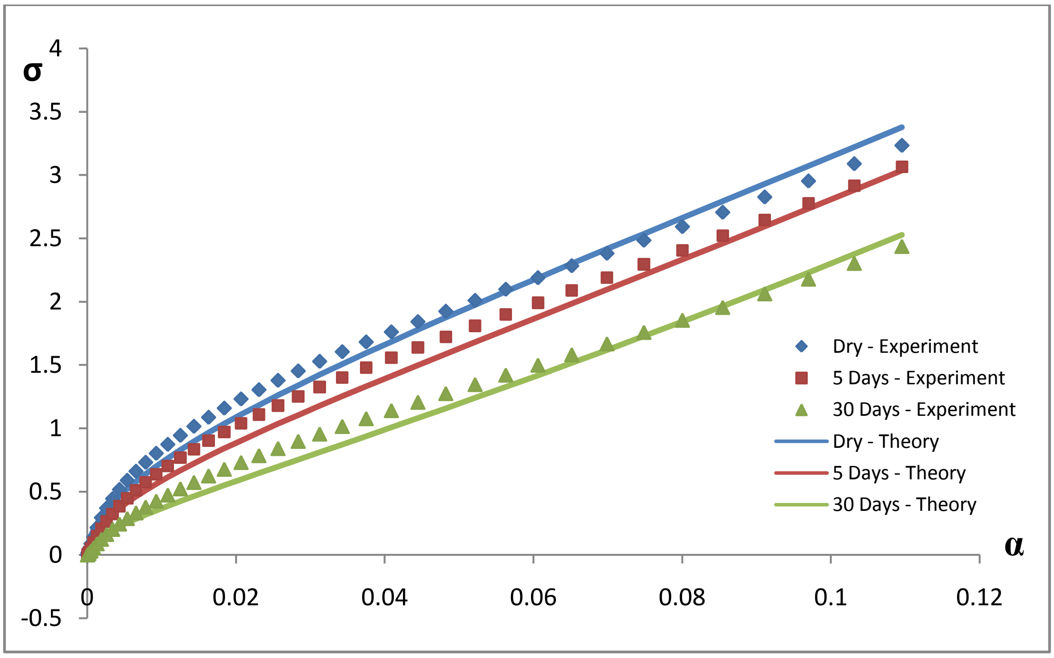


Figure 4.14: Stress at first uploading as a function of α

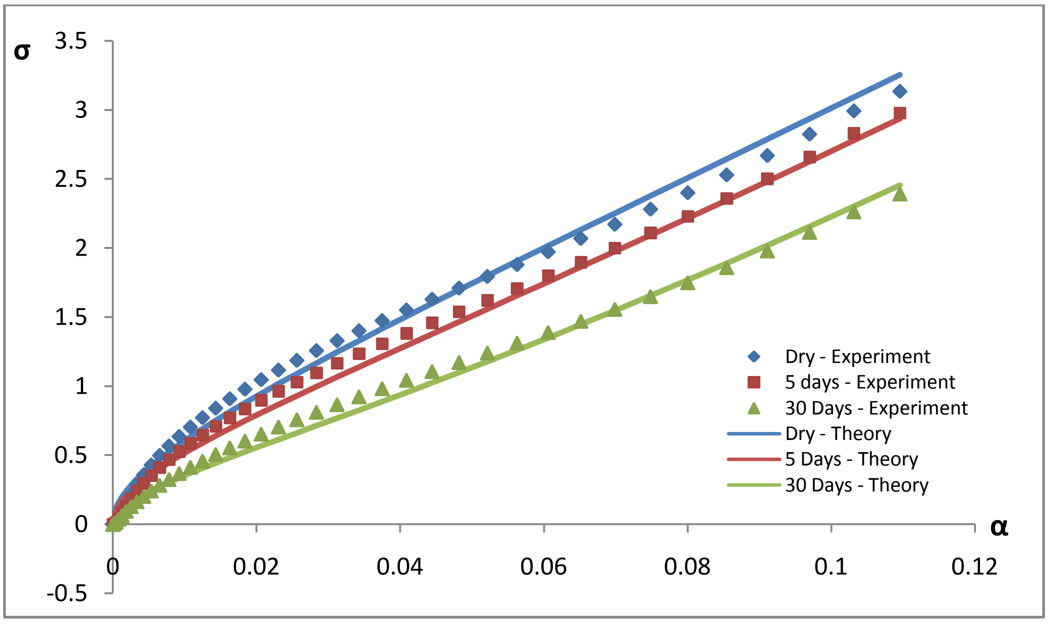


Figure 4.15: Stress at second uploading as a function of α

## 4.5 Discussion

It had been shown from figure 4.8 and 4.9, the theoretical model plot fit well qualitatively with experimental result. The modelling for 30 days immersion rubber showing a good agreement with the experimental result for both stress. 5 days immersion rubber showing a lower stress at the middle of applied strain but giving a good match at lower and higher strain. It is also shown that, NBR which exposed in longer immersion period will experience more swelling effect and resulting a lower stress in stress-strain curves.

It is also has been observed that, the accuracy of curve fitting between experimental and theoretical modelling is largely affected by the value of $K_1$ and $K_2$ which is refered to a stress at the first uploading curve for dry rubber. It means that, the selection of strain energy function is important in order to get a good conformation with experiment data. Fung model has been proved to be the appropriate strain energy function to be used during this study.

Both stress at first and the second uploading from theoretical model is then plotted as in figure 4.16.

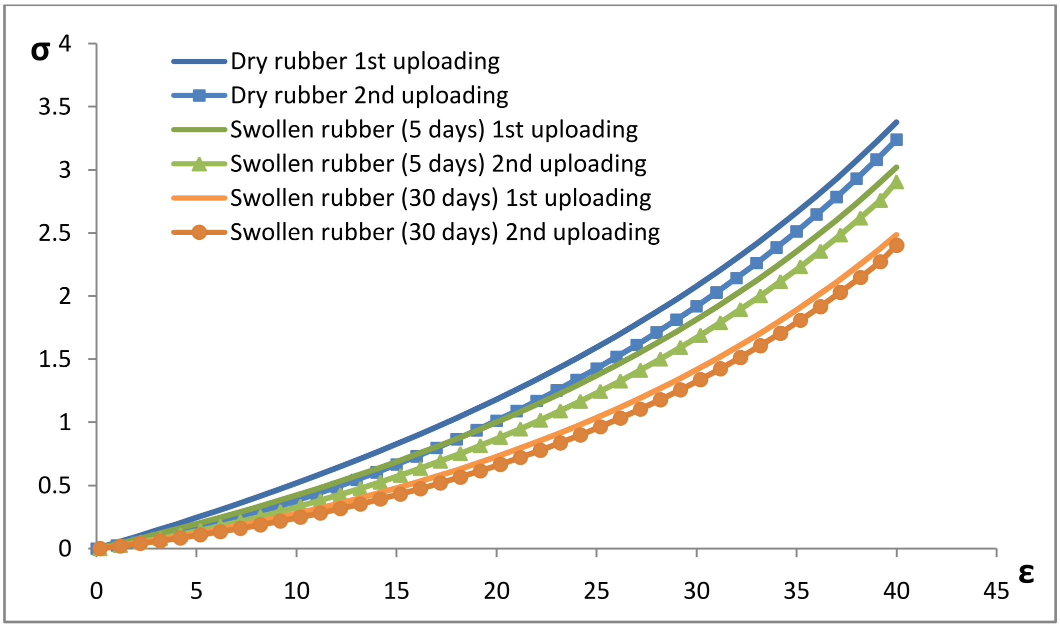


Figure 4.16: Theoretical stress at first and second uploading

From the observation in Figure 4.16, we can see the stress path for the second uploading is different with the stress at the first uploading. This stress softening phenomenon is called the Mullin's effect. It is also observed that swollen rubber having a lower value of stress at the same applied strain. By measuring deformation state using the 8-chain model, it is also shown that theoretical curve is tie with the experimental plot as shown in figure 4.14 and 4.15. With this result, we can conclude that the developed model is able to capture the phenomenon of Mullin's effect.

As discussed earlier, CDM model by Chagnon et al, (2004) showing in equation (3.1), is a damage phenomenon which the strain energy is referred by scalar quantity of damage parameter, *d*. In swollen rubber, *d* is a function of strain and swelling.

$$\boldsymbol{\sigma} = -p\mathbf{I} + \left(1 - \tilde{d}(\tilde{\varepsilon}, v2)\right)\left[2\left(\frac{\partial Wo}{\partial I_1} + I_1\frac{\partial Wo}{\partial I_2}\right)\right]\mathbf{B} - 2\,\frac{\partial Wo}{\partial I_2}\,\mathbf{B}^2 \qquad (4.18)$$

By adopting the Kachanov type of equation which proposed by Simo, quoted by Diani et al. (2006), the damage parameter is refer to the different path of uploading stress. The following equation is used to see the relationship between the Mullin's effect and damage phenomenon:

$$\sigma^{2up} = (1 - d)\, \sigma^{1up} \qquad (4.19)$$

Then,

$$(1 - d) = \sigma^{2up} / \sigma^{1up} \qquad (4.20)$$

Stress ratio can be defined as follow:

$$\text{Stress Ratio} = \sigma^{2up} / \sigma^{1up} \qquad (4.21)$$

Therefore;

$$(1 - d) = \text{Stress Ratio} \qquad (4.22)$$

Damage material can be defined as a stress softening by following:

$$\begin{aligned} \text{Stress Softening (SS)} &= (\sigma^{1up} - \sigma^{2up}) / \sigma^{1up} \\ &= 1 - (\sigma^{2up} / \sigma^{1up}) \\ &= 1 - \text{Stress Ratio} \\ &= 1 - (1 - d) \qquad (4.23) \end{aligned}$$

We can now define *d* as:

$$1 - d = 1 - \text{SS}$$

$$d = \text{SS} \qquad (4.24)$$

From the above derivation we can conclude that the damage phenomenon in this model is a stress softening phenomenon which refers to the Mullin's effect. If value of $d = 0$, there is no damage which mean there is no Mullin's effect in the material.

By using the stress softening calculation as in equation (4.19), the graph for stress softening in swollen rubber is plotted and compared with dry rubber. It is observed from the graph, the stress softening value which represents the damage mechanism is lower in swollen rubber compared with dry rubber at a given strain. The illustration can be seen at figure 4.17.

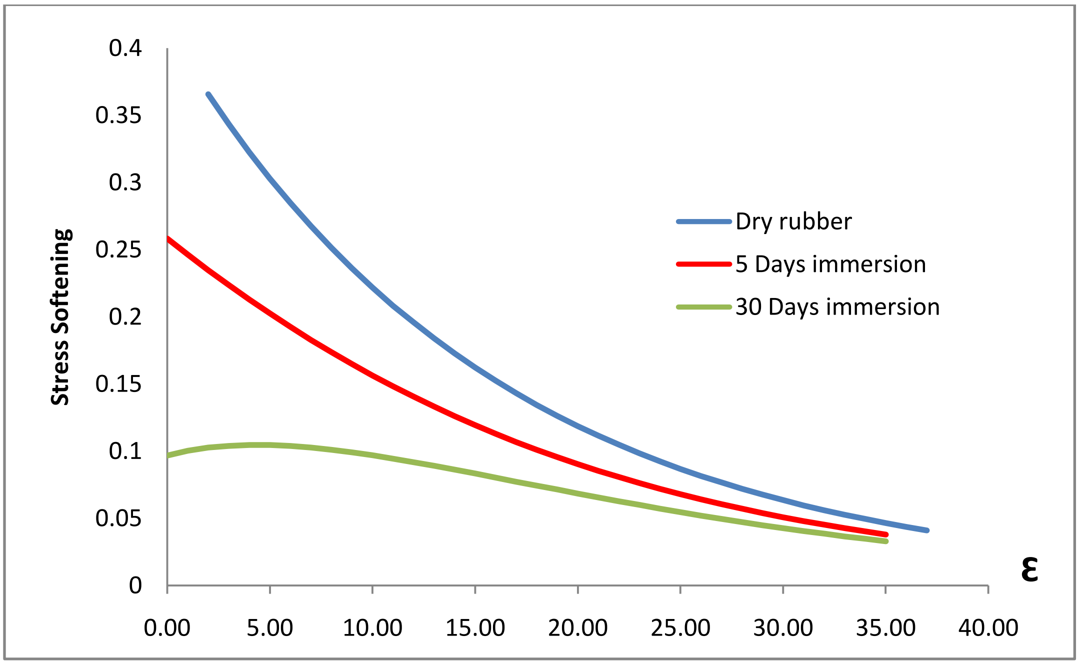


Figure 4.17: Stress softening of swollen rubber compared to dry rubber

# *CHAPTER 5:* CONCLUSION AND RECOMMENDATION

The present work demonstrates the development of constitutive modelling to capture the Mullin's effect in swollen rubber. During this research, Nitrile Butadiene Rubber (NBR) is used as a specimen. From the experimental result which taken from Chai et al. (2011), the experimental curve is plotted. By observation of this experimental plot, the behaviour of stress-strain curve is studied and mathematical equation is developed.

Fung model is chosen to describe the undamaged strain energy function. By adopting a Continuum Damage Mechanics (CDM) model by Chagnon et al. (2004), damage phenomenon is used to describe a Mullin's effect. The theoretical model developed is then plotted and compared with experimental plot. It had been shown that the theoretical curve fit well with the experimental.

Since the above model is only applicable in special uniaxial case, the 8-chain model adopted from Arruda-Boyce model is used as a different way of measuring deformation state. This model is chosen to represent a three-dimensional deformation state which is more applicable in the real engineering application. A new material constant is determined from the model developed and the new theoretical plot is then compared with experiment. The result from the curve fitting for both experiment and theoretical plots showing a good agreement between each others.

In conclusion, the comparison result of theoretical model and experimental data had shown that the constitutive modelling developed is able to capture the Mullin's effect in swollen rubber.

## 5.1 Recommendation

In order to describe the Mullin's effect phenomenon in hyperelastic material, it is assumed that the material is homogenous, isotropic and remains incompressible either in dry or swollen state. The incompressibility is not verified during this study. In the case of compressible material, the model developed in this study is not more suitable to be used to predict the Mullin's effect. Therefore, further study needed to determine the modelling equation which can capture the Mullin's effect in a mentioned case.

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