**SCHOOL OF MATERIALS AND MINERAL RESOURCES**

**ENGINEERING**

**UNIVERSITI SAINS MALAYSIA**

# STRUCTURE-PROPERTIES RELATIONSHIP OF WATER-BLOWN EPOXIDIZED NATURAL RUBBER FOAM

By

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Dissertation submitted in partial fulfilment
of the requirements for the degree of Bachelor of Engineering with Honours
(Polymer Engineering)

Universiti Sains Malaysia

**JUNE 2017**

# DECLARATION

It is hereby acknowledge and confirmed that the final year project entitled **“Structure-Properties Relationship of Water-Blown Epoxidized Natural Rubber Foam”** by Nur Haziqah binti Mohd Harnizi with matric number 122034 has been examined and matrix all the correction suggested was done. The final reports is submitted to the School of Materials and Mineral Resources Engineering as part of the requirements for a Bachelor of Engineering (Hons) Polymer, Universiti Sains Malaysia.

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Date : 20 June 2017

# ACKNOWLEDGEMENTS

Foremost, I would like to express my deepest gratitude to Universiti Sains Malaysia (USM) for giving us, students pursuing Bachelor of Engineering (Hons) Polymer the opportunity to undergo our research successfully. This project giving me the opportunity to experience the hands-on skill which is good starting for me before working in the industry.

My greatest thank are extended to my supervisor, Assoc. Prof. Dr. Zulkifli bin Mohamad Ariff for inspiring me and constantly guide me all the way through this project. Sincere thanks for this great learning opportunity.

I am particularly grateful for the assistance and constant supervision is given by technician for their constructive comments, guidance, encouragements and advice in order to help me complete my experimental work. They giving me much attention, time and willingly helped me out with their abilities and knowledge.

Last but not least, I would like to thank my family and all of my friends for their kindness and willingness of sharing their knowledge with me. Their encouragement makes me have an incentive to work harder for my thesis.

Once again, I hereby express my sincere gratitude to everyone for helping me in completing my project.

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| | |
|---|---|
| $G$ | Peak deceleration |
| $R$ | Relative density |
| $\rho_f$ | Foam density |
| $N$ | Number of cell per unit volume |
| $\rho_r$ | Rubber density |
| $\rho_s$ | Density of solid rubber |
| $H_f$ | Height after foaming |
| $H_o$ | Initial height before foaming |
| $M_L$ | Minimum torque |
| $M_H$ | Maximum torque |
| $t_{s2}$ | Scorch time |
| $T_{90}$ | Optimum cure torque |
| $t_{90}$ | Optimum cure time |
| $V_r$ | Volume fraction of rubber in swollen sample |
| $X$ | Interaction constant characteristic between rubber and toluene |
| $V_o$ | Molar volume of toluene |
| $M_c$ | Physical crosslinking concentration |

# LIST OF ABBREVIATION

| | |
|---|---|
| ENR | Epoxidized Natural Rubber |
| ASTM | American Standard for Testing and Materials |
| BR | Butadiene Rubber |
| CBAs | Chemical Blowing Agents |
| CBS | Benzothiazyl-2-cyclohexyl-sulfenamide |
| CR | Chloroprene Rubber |
| EPDM | Ethylene Propylene Diene Terpolymer |
| MDR | Moving Die Rheometer |
| NBR | Acrylonitrile Butadiene Rubber |
| NR | Natural Rubber |
| ODR | Oscillating Disc Rheometer |
| PBAs | Physical Blowing Agents |
| pphr | Part Per Hundreds Rubber |
| PS | Polystyrene |
| PU | Polyurethane |
| SBR | Styrene-butadiene Rubber |
| SEM | Scanning Electron Microscopy |
| TMTD | Tetramethyl Thiuram Disulphide |
| TMQ | 2, 2, 4-Trimethyl-1,2-Dihydroquinoline (TMQ) |

# HUBUNGAN ANTARA STRUKTUR-SIFAT BUSA GETAH ASLI TEREPOKSIDA DAN AIR SEBAGAI EJEN PENIUPAN

## ABSTRAK

Hubungan antara struktur dan sifat busa getah asli terepoksida dan air suling sebagai ejen peniupan fizikal telah dikaji. Jumlah air suling divariasikan untuk menentukan pengaruhnya terhadap morfologi dan sifat mekanik busa getah asli terepoksida. Busa getah asli terepoksida telah disediakan dengan memvariasikan jumlah air suling sebagai ejen peniupan. Penyelidikan ini melaporkan sifat mekanik dan perilaku morfologi busa getah asli terepoksida yang bervariasi kepekatan ejen peniupan. Eksperimen telah dijalankan dengan penyediaan empat formulasi kompaun getah yang berbeza dan berbeza jumlah air suling dari 0 hingga 3.0 bahagian per seratus getah. Sampel getah yang dikembangkan telah disediakan dengan menggunakan penggiling bergulung dua dan mengembang melalui ketuhar gelombang mikro. Telah didapati bahawa sifat mekanikal busa getah asli terepoksida berubah dengan ketumpatan relatif busa yang semakin meningkat ketumpatannya, akan mengurangkan nilai set mampatan. Busa getah asli terepoksida telah dicirikan sehubungan dengan ketumpatan sambung silang, ketumpatan relatif busa, saiz sel dan set mampatan. Hasil kajian menunjukkan bahawa struktur dan sifat busa boleh dikawal dengan jumlah ejen peniupan.

# STRUCTURE-PROPERTIES RELATIONSHIP OF WATER-BLOWN EPOXIDIZED NATURAL RUBBER FOAM

## ABSTRACT

The relationship between structure and properties of Epoxidized Natural Rubber (ENR) foams and distilled water as the physical blowing agent were varied to determine their effects on the morphology and mechanical properties of ENR foams. ENR foam were prepared by varying the amount of distilled water as the blowing agent. This investigation reports the mechanical properties and morphological behaviour of ENR foam by varying with the amount of blowing agent, which controls the foam architecture. The experiment was conducted by prepared four different formulation of compounding rubber which is different amount of distilled water from 0 to 3.0 parts per hundred rubber (pphr). The expandable rubber samples were prepared by using a two roll mill and expanded via a microwave oven. It was found that the mechanical properties of the ENR foam changed with the relative density of foam which is increasing the relative density, will decreasing the value of compression set. The ENR foams were characterized with respect to their crosslinking density, relative density, cell size and compression set. The results showed that the structure and properties of the rubber foams can be control by the amount of blowing agent.

# CHAPTER 1

# INTRODUCTION

## 1.1 Introduction and Problems Identification

Today, polymeric foams are highly demanded on the market. By using advance technology, foam has many unique properties such as lightweight, good thermal insulation properties, and energy absorption. According to Weaire (2007), foam is low cost compares to solid polymer indirectly make it highly demanded in comfort properties where these properties cannot be found in other material. Polyurethane (PU), polystyrene (PS), ethylene propylene diene (EPDM) terpolymer and acrylonitrile butadiene rubber (NBR) are the most commercial foam produced in industry (Metaxas, 1983). Epoxidized natural rubber (ENR) foam is being highlighted throughout this research.

Rubber foams are found in wide range of applications and being used everywhere in our everyday life. Foams contribute in the area of construction, automotive safety, sports, and packaging. Foam is a sponge like material which have small dispersed spherical air or gas bubbles inside a solid or liquid. Cell size distribution, structures and properties of the foam should be focused to obtain good foam for desired application. Foam are lightweight cellular engineering materials well-suited for exterior application in construction and automotive contacting with atmospheric particulates and chemicals, while interior applications demand durability and excellent performance (Bhowmick, 1994).

Epoxidized natural rubber (ENR) is a type of modified natural rubber comprised of randomly distributed epoxide group along the polymer chain. According to Ariff et. al (2010), ENR can be considered environmental friendly materials for the rubber product manufacturing industry as it was produced from renewable resources. There are several types of ENR that are commercially available in the market. The popular grades of ENR are ENR25 and ENR50. The types of different ENR is according to their percentage of epoxidation. ENR25 is the more popular rubber that has been used widely in tire tread to reduce fuel consumption because of its best performance on balancing of wet grip and rolling resistance. ENR also has been used as footwear sole, adhesives and vibration isolation devices due to high damping properties of ENR itself.

Blowing agent is a chemical added to plastic in the production of polymeric foams. There are two types of blowing agents which are chemical blowing agent (CBA) and physical blowing agent (PBA). Further, the chemical blowing agent can be classified into two types which are organic and inorganic. The blowing agent is one of the important ingredients in foaming process because it will create cellular structure during process and formation of inert gas at the processing temperature. It also affects polymer system which produces cellular structure, stiffness, rigidity and light weight. Different blowing agent concentration can also give different properties of the product performance. High concentration of curing agent and blowing agent, will larger cell size and thickness of the cell wall decrease (Choe, 2004).

This research involves a process of foaming the epoxidized natural rubber (ENR) compound using distilled water as blowing agent. ENR foam is rarely demanded because of the high cost needed in its production. By using water as the blowing agent probably may induce better structure of the epoxidized natural rubber foam thus increasing the properties of the product produce. Water is considered as a physical blowing agent is an organic substance that can be fit together harmoniously without harm either human or non-human. In manufacturing, bad side effect have to consider to the environmental so that the factors should be analyze either it is positive or negative influence. Thus, this method bring it the positive control to the environment and ease of processing in manufacturing because it only use water which is an abundant resources.

If the compound does not homogenously mix during compounding because of natural rubber is non-polar molecules (hydrophobic) that repel the water molecules, this will lead agglomeration of the compound which will create stress concentration point and will affect the accuracy of the test result. To avoid this problem from occurring, stearic acid which has a hydrophilic head was used, allowing it to act as a carrier for the water.

## 1.2 Research Objectives

This project involves research on structure and properties of epoxidized natural rubber foam by using distilled water as a blowing agent. To achieve the main objectives or goals in this research, all preparation are made clearly.

The objectives of this project are:

a. To produce range of epoxidized natural rubber foam using distilled water as blowing agent.
b. To investigate the effect of varying the blowing agent content on foam structure and its subsequent properties.
c. To evaluate the structure-properties relationship of the produced ENR foams.

Overall, it can be stated that the main objective is to study the structure-properties relationship of epoxidized natural rubber foam using distilled water as blowing agent. This will enable a production of foam with the best properties.

## 1.3 Scope of Study

This research will focus on processing and the structure-properties of the resulting ENR25 rubber using microwave foaming technique. Processing parameters that will be studied is amount of water loading and the effects of the parameter towards the foaming process will be evaluated based on the foam morphology, density of the foam and average cell size formed at the end of the processing.

Formulations are prepared by mixing using laboratory two-roll mills. For the result presented, physical blowing agent (distilled water) was used in the production of foam. The microwave frequency used in this study is fixed at 2.45 GHz (Yizong, 2013). The test conducted to determine the properties were compression set and crosslink density test. Portable digital microscope (Dino-Lite Pro) will be used to determine the average cell size of the foam.

# CHAPTER 2

# LITERATURE REVIEW

## 2.1 Epoxidized Natural Rubber (ENR 25)

Epoxidized natural rubber (ENR) was developed during this period. Epoxidized natural rubber (ENR) is a modified natural rubber (NR). According to Bhowmick (1994), epoxide is an organic chemical that contain group consist of an oxygen atom bound to two already connected atoms, usually carbon (epoxy group). Conceptually, epoxidation is a relatively old form of modification, but the new form purposely set out to establish a commercially practicable material. Although the material is based upon natural rubber and retains many of that material’s excellent characteristics, some of the new material’s properties are distinctly similar to several of the specialty synthetics.

Various degree of epoxidation of NR is available. For examples, ENR-25, ENR-50, and ENR-75. ENR-25, ENR-50, and ENR-75 have a different percentage of epoxidation. ENR-25 have the mole percentage of double bond in the polymer chain of ENR sufficient for effective vulcanization occur. ENR-25 and ENR-50 have -45℃ and -20℃ of glass transition temperature and 0.97 and 1.03 of specific gravities respectively (Bhowmick et. al., 1994).

ENR has high glass transition temperature, $T_g$ and specific gravity compared to NR. High glass transition temperature, also increase the polarity, improve oil-resistance, damping characteristics. NR less permeable to gas or air thus having lower resilience. ENR can be vulcanized by sulphur or peroxide vulcanization system. Vulcanization is important to stabilize bubble during foam expansion and preventing the formed cells from collapse under heat which subsequently improve mechanical properties of the rubber foam. In this research, ENR-25 with 25 mol% of epoxidization was chosen because of the mole % of double bond in polymer chain of ENR is high enough for effective vulcanization to occur by using sulphur vulcanizing system (Rosniza et. al., 2012). A typical formation of ENR from isoprene employing peracetic acid as shown in Figure 2.1.

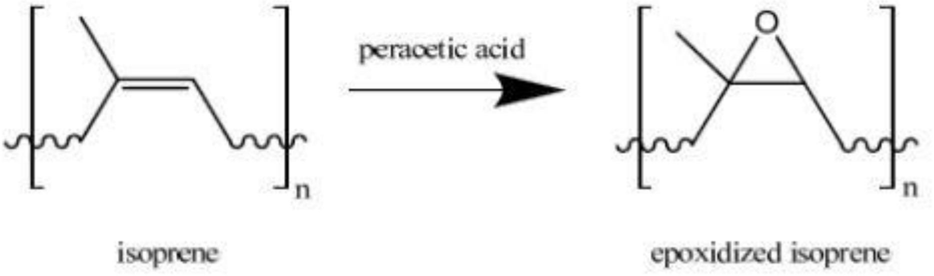


Figure 2.1: Chemical modification of NR to ENR (Rosniza et. al., 2012)

## 2.2 Foam

Most foams are formed by a process of growing or creating gas bubbles in a polymer matrix which can be in a liquid or solid form. Eaves (2004) suggest that, as the bubbles produced, the foam structure changes through stages which are at first, small dispersed spherical bubbles contained by the polymer matrix, with a small reduction in density. While the bubbles grow but still remain spherical, the lowest foam density is achieved when bubbles reach close-packed structure. For further growth of the bubbles, distortion of cells involved. A final stage involves rupture of cell walls and result in an open cell foam.

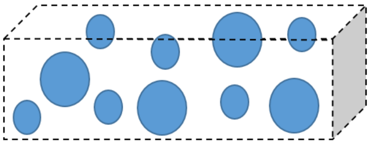


Figure 2.2: Gaseous bubbles in a liquid or solid form (Lee et. al., 2006)

Methodology of foaming is usually consist of a gaseous phase into a melt, then forming the gas, and solidifying the melt before gaseous bubbles condense or collapse back into liquid state. Gas bubble are generated in a spherical shape as shown in Figure 2.2. Since the bubble in spherical form which has lowest surface energy for a given volume thus it is an ideal shape for the weak (gaseous) phase to sustain within a dense (liquid or solid) phase (Lee et. al., 2006).

A polymeric foam has unique physical, mechanical and thermal properties, which are governed by the polymer matrix, the cellular structure, and the gas composition. It is known that foaming in the polymers involves delicate scientific mechanisms, fine processing accuracy, unique morphology transformation and structure formation Polymeric foams ride on the future polymer industry high route to a fascinating success. Today, it is viewed not only as a technique but also a well-established industry. Through challenges, such as ozone depletion, recycling, and environmental regulation, in addition to upgrades, it becomes a strong industry (Lee et. al., 2006).

### 2.2.1 Structures and Properties of Foam

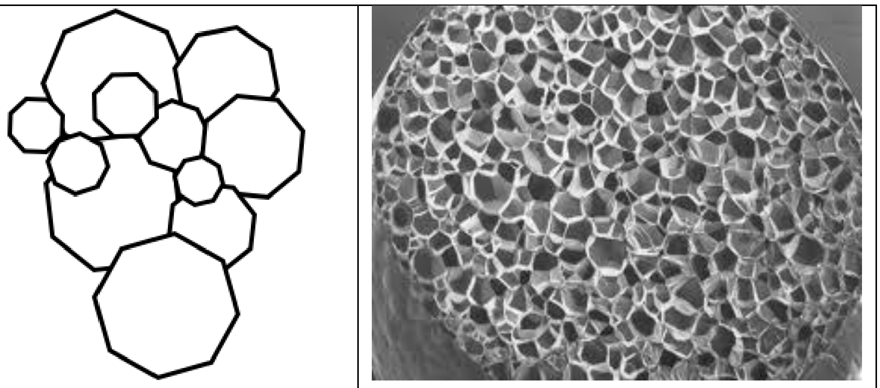
The characteristics of polymeric foams are determined by the following structural parameters which are cell density, expansion ratio, cell size distribution, open-cell content and cell integrity. These cellular structural parameters are organized by the foaming technology used in processing, and the foaming technology which often heavily depends on the type of polymer to be foamed.

Different polymer foams exhibit different properties depending on the characteristics of foams which can range from soft to stiff, resilient to tough, low to high hysteresis, and mono to multi-model cell distribution (Lee et. al., 2006).

### 2.2.2 Open and Closed Cell Foams

Solid foams are an important class of lightweight cellular engineering materials. These foams can be classified into an important division of solid foams based on their pore structure, i.e. closed-cell and open-cell foams. In a closed-cell foam, the gas forms discrete pockets and each of the pockets completely surrounded by the solid material. In an open-cell foam, the gas pockets connect with each other (Bibikov, 1997). A bath sponge is an example of an open-cell foam which is water can easily flow through all the structure. A camping mat is an example of a closed-cell foam which is the gas pockets are sealed from each other so the mat cannot absorb water.

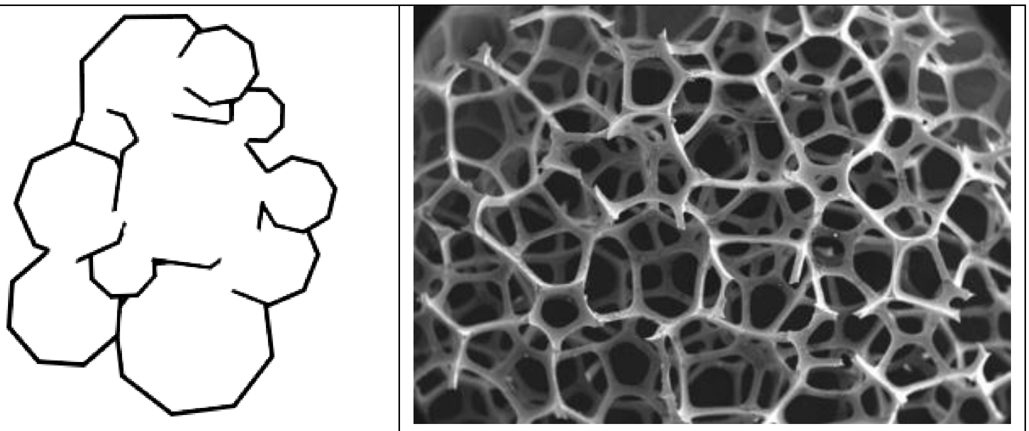
According to Bibikov (1997), closed-cell foams do not have interconnected pores. The closed-cell foams normally have higher compressive strength due to their structures. However, closed-cell foams are denser, require more material, and more expensive to produce. The closed cells can be filled with a specialized gas to provide improved insulation. The closed-cell structure foams have higher dimensional stability, low moisture absorption coefficients, and higher strength compared to open-cell-structured foams. An example of closed cell foam were shown in Figure 2.3.



(a) (b)

Figure 2.3: Image of closed cell foam by (a) drawing and (b) SEM image (Bibikov, 1997)

Open-cell-structured foams contain pores that are connected to each other and form an interconnected network that is relatively soft. Open-cell foams will fill with whatever they are surrounded with. If filled with air, a relatively good insulator is the result, but, if the open cells fill with water, insulation properties would be reduced. Foam rubber is a type of open-cell foam. The open-cell structure plays mixed roles in various applications. Open-cell foams are very good in gas exchange, absorption and sound deadening. An example of open cell foam were shown in Figure 2.4 where air can be freely passed through the cell (Mills, 2007).



(a) (b)

Figure 2.4: Image of open cell foam by (a) drawing and (b) SEM image (Bibikov, 1997)

Open cell or closed cell ratio can be determined by water absorption or permeation. All types of foam are widely used as core material in sandwich-structured composite materials. Various types of specially manufactured solid foams came into use. The low density of these foams makes them excellent as thermal insulators and flotation devices, and their lightness and compressibility make them ideal as packing materials and stuffing.

### 2.2.3 Cell Size Distribution

At a given expansion ratio, cell size may cause significant effects in mass and heat transfer due to the cell wall thickness and convection in the cell. For instance, cell size effects on thermal flow depicted as in Figure 2.5. It indicates that the thermal properties of the foam are strongly affected by the cell size and the way the cells are dispersed throughout the occupied volume. According Lee et. al., (2006), at medium and low expansion ratios, a spherical cell shape and a uniform cell size, whereas for high expansion ratios, the cell size tends to show a distribution due to insynchronization of nucleation and cell coalescence.

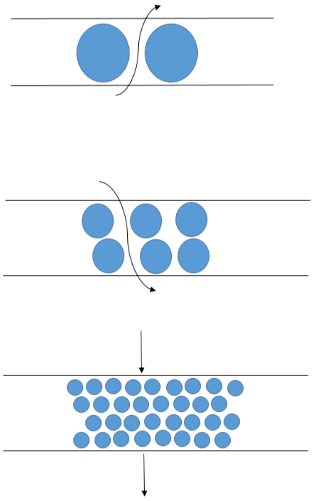


Figure 2.5: Heat flux for different cell size foam (Lee et. al., 2006)

Cell nucleation is an energy controlled process in which stable nuclei gather an energy large enough to overcome the surrounding confinement to develop bubbles into the unstable growth state governed by transport and thermodynamic properties. At instantaneous nucleation and low-degree expansion, the cell size should be uniform. However, in reality, an even energy distribution is difficult to control, and, as a result, "stage" nucleation often occurs (Lin et. al., 1996).

Characterization of cell foam size (diameter) is usually conducted because of its simple and easier way to classify rubber foam. Only suitable regular geometry of solid such as foam with a spherical and ellipsoids shape of bubbles can be classified the cell size. This cell size were depending on polymer grade and foaming conditions. According to Eaves (2004), cell size were important and have to measure in order to evaluate the effectiveness of blowing agent. Cell size were depends on loading, particle size and type of blowing agent. Different amount or concentration of blowing agent can affect the cell properties of the foam.

### 2.2.4 Mechanical Properties

All foams show a typical compression stress-strain curve as show as in Figure 2.6 which may be split into three zone:

i. Zone 1: Linear 'Hooke' behaviour
ii. Zone 2: Collapse plateau
iii. Zone 3: Densification

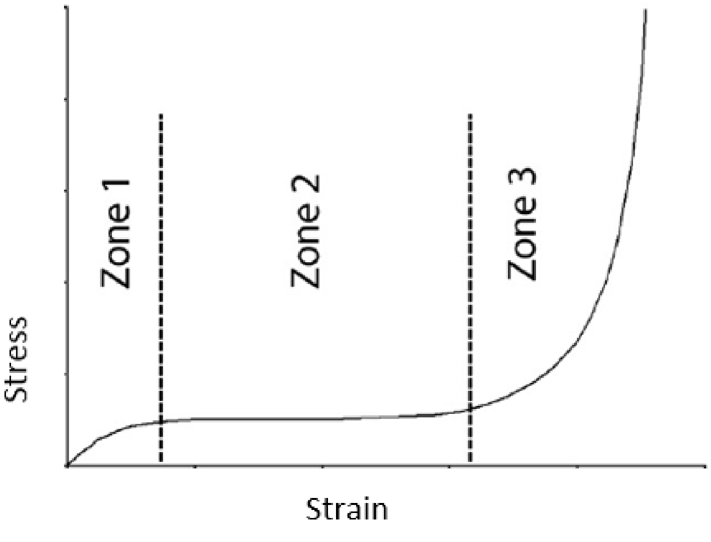


Figure 2.6: Stress-strain curve for a foam (Eaves, 2004)

In zone 1, linear elastic behaviour is controlled by cell wall blending and, in closed cell foams, by cell wall stretching due to the contained gas pressure. In zone 2, the cells collapse through cell wall buckling, or in brittle foams, by cell crushing and cell wall fracture. In zone 3, densification occurs. As foam density increases, Young’s modulus increases in zone 1, the plateau stress value increases and the strain at which densification starts reduces. In closed cell foams, the compression of gas in the cells also contributes more in zone 2 and 3 than 1. In a typical stress-strain curve, the area under the curve represents the energy required for the strain.

At large compressive strains the stress-strain curve increases sharply due to densification, and tends towards a limiting slope which is very considerably higher than the initial modulus at a limiting strain. This strain is lower than can be calculated by assuming it is the point at which all porosity has been eliminated, as the cell walls join together at a somewhat lower strain (Eaves, 2004).

The rubber industry has traditionally paid more attention to measuring the recovery after removal of an applied stress or strain, i.e. compression set, than creep or stress relaxation. This is partly because relatively simple apparatus is required but also because it appears at first sight that compression set is the important parameter when judging sealing efficiency. Compression correlates with relaxation only generally and it is actually the force exerted by a seal that usually matters, rather than the amount it would recover if released. There are two international standards for compression set which are ISO 815 for use at ambient and elevated temperatures and ISO 1653 for use at low temperatures although at the time of writing a draft revision is circulation which combines the two (Chandrasekaran, 2007).

Compression set is defined as the residual deformation of a material after removal of an applied compressive stress. Resistance to compression set is the ability of an elastomeric material to recover to its original thickness after having been compressed for an extended period. According to Chandrasekaran (2007), low set values mean that the material has recovered nearly to its original height, and there is very little residual deformation. This is particularly important in applications where a rubber parts is expected to provide a seal under a compressive force and the sealing force is removed and reapplied repeatedly. Compression set tests are usually run at elevated temperatures, to simulate conditions or aging effects. If the end product is expected to perform at low temperatures, compression set is measured at the expected service temperature (Ciullo, 1999).

### 2.2.5 Foam Applications

Based on properties of foam which are recognized as an outstanding material for different applications, the usage of foam has increased dramatically. It can be used in transportation, packaging and specialty applications. Rubber foam is used for seating, components (such as head and arm rests), sound absorption and energy management. Automotive foams tend to require durability, high and low-temperature resistance.

## 2.3 Microwave Heating

### 2.3.1 Principle of Microwave Heating

The basic principle of microwave heating of foam is the same as that used in household microwave oven. Microwaves energy is absorbed by dielectric materials such as polymers and water. Microwave frequencies are 896, 915 and 2450 MHz, which are preferred frequency for the operation of industrial heat. To allow preheating or curing practically the full range of molded rubber goods, the preferred frequency is 2450 MHz. Magnetrons transmit radio waves with a frequency of 2450 MHz which cause rotate currents in electrically conductive materials and oscillate polar molecular structures in the material.  Using microwaves as the source of heating can reduce processing time, produce large rubber profile and non-contacting heat which can reduce overheating of material surfaces because microwave heats material volumetrically, heat transfer from interior to outer wall of material. Microwave heating has been used for pre-heating blanks for compression molding. Conventional heating process is one of the sources of heating but overheating will occur to heat large rubber which can over-cured the rubber.

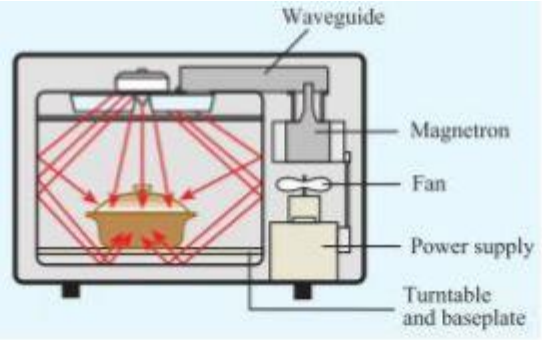


Figure 2.7: Microwaves oven (Vollmer, 2003)

Hence, microwaves more excitable for the polar component. This system is suitable to an elastomer which contains polar group. Microwave heating occurs by dipole rotation of polar groups present in rubbers. When rubber was placed into the microwave, the microwaves will heat the rubber molecules and soften it then heat up the air and dielectric material inside the rubber molecules (Bhowmick et. al., 1994). Microwave heating occurs as the molecules are brought into vibration and this happen in a polar group. The dielectric constant and loss factor of a compound give some indicator of the degree of polarity. For example, the degree to which the molecules are able to leave and to place themselves in the field. The vibration of the molecules causes a molecules friction and leads to a temperature rise. The intensity of these vibrations also depends on the strength and frequency of the electromagnetic field. Special formulations will have to be developed for microwave curing. As polarity is primary importance, nitrogen, oxygen, halogen or sulfur containing rubber are suitable candidates (Gorshenev, 1997).

According to Jenkins (2013), this volumetric heating will cause water to evaporate and the air to expand, pushing the softened rubber causing them to expand to become the foam. There is no chemical reaction occurs, meaning that there are no harm substances being produced from the process. There is only a change of states that occur are the melting of rubber molecules and the vaporization of air present. Charles' law has stated that the volume of gas is dependent and directly proportional to the temperature. The increase in temperature within the rubber will increase the gas content inside the rubber profile. The microwave gives energy to the rubber, being absorbed by rubber, and by dielectric material present in the rubber. The energy absorbed causing the molecules of rubber to move in higher velocity and this results to the molecules being further apart from each other and expand to produce foam (Shangzhao, 2003).

There are two principle mechanisms of microwave heating which were dipole rotation and ionic polarization as shown in the Figure 2.8. The dipolar component present inside the rubber is the one that will be responsible for the dielectric heating. In alternating current electric field, the polarity of the field is varied with the frequency of microwave. These dipoles will line up with the changing field and as the microwave field alters, the molecules moves to keep the dipoles in phase with the fields. The movement of the molecules in alternating field was the contributing factor to the conductivity. Polar molecules failed to keep in phase with the electric field at high frequency as the results in the portion of the energy are converted to a very fast which called as kinetic energy. According to Metaxas and Meredith (1983), when the frequency are too high, it will stop the motion of a polar particle before it follows a field resulting in inadequate interaction. When the frequency are too low, it allow sufficient time for polar molecules to align themselves in phase with the applied electric field.

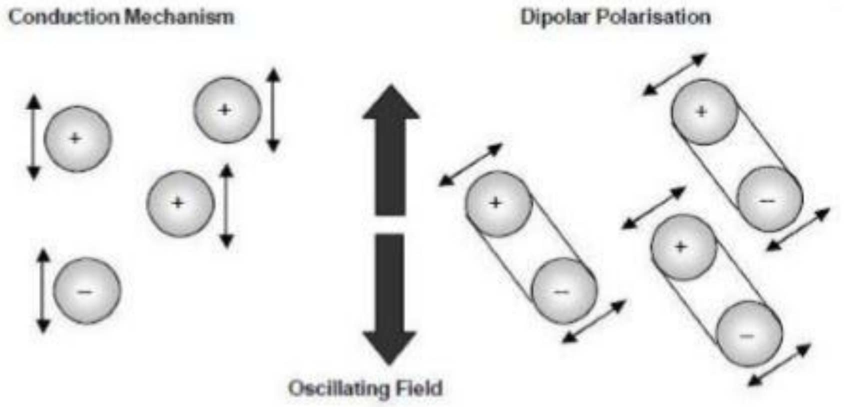


Figure 2.8: Dielectric polarization mechanism (Jenkins, 2013)

Dielectric polarization is defined as a result from moving of ionic molecules back and them trying to line up with oscillating electric field. Bound ions have a much lower ability to absorb microwave energy as compared to free ions. This ionic polarization is depends on the atomic or molecular nature of the material. There are three subdivisions of dielectric polarization. The displacement of electrons around the nuclei is electronic polarization. Relative displacement of the atomic nuclei due to unequal charge distribution in molecule formation is atomic polarization. Permanent dipoles in polar dielectrics reorientation under the influence of changing electric field is dipolar orientation (Metaxas, 1983).

### 2.3.2 Advantages of Microwave Heating

Some advantages from microwave heating are reaction acceleration, yield improvement, enhanced physicochemical properties and the evolvement of new material phases (Shangzhao et. al., 2003). Microwave heating can reduce processing time by indirectly accelerating the reaction. The movements created in the molecules produce heat. Microwaves are capable of penetrating a few centimeters into the rubber material, which is then heated from the inside out of the rubber itself (Bhowmick et. al., 1994). This make the microwave heating special because of quick and uniform vulcanisation can be achieved even for large articles. Table 2.1 shows the differences between microwave heating technique and conventional heating technique.

Table 2.1: Differences between microwave heating technique and conventional heating technique (Nieftagodien, 2013).

| | Microwave | Conventional |
|---|---|---|
| Source | Energy transfer | Heat transfer via conduction |
| Start up | Immediately | Depending on heating chamber |
| Rate | Rapid heating possible | Depends on thermal diffusivity |
| Uniformity | Volumetric and selective heating | Temperature gradient from the surface |
| Energy loss | Waveguide to energy loss | Loss due to radiation externally |

The microwave heating technique is usually being used to vulcanize small rubber part, preheating thick rubber part before post vulcanization and to cure rubber in a continuous vulcanization process and tire treads. Curing in a continuous vulcanization process using microwave can be achieved by appropriate turntable and stirring. However, metal mould cannot be used as they tend to reflect microwave energy in the curing process (Bhowmick et. al., 1994).

Other advantages for microwave heating are (Vollmer, 2003):

i. The product has a good surfaces finish which does not require cleaning.
ii. There is little deformation during curing.
iii. The thermal efficiency is high and only a short time is needed for preparation start up.
iv. The system is effective for polar rubbers and ingredients.
v. Microwaves generate higher power densities, enabling increased production speeds and decreased production costs.
vi. Microwave energy is precisely controllable and can be turned on and off instantly, eliminating the need for warm-up and cool-down.
vii. Microwave energy is selectively absorbed by areas of greater moisture. This results in more uniform temperature and moisture profiles, improved yields and enhanced product performance.
viii. The use of industrial microwave systems avoids combustible gaseous by-products, eliminating the need for environmental permits and improving working conditions.

## 2.4 Blowing Agent

In a polymer mass, a substance that produced a cellular structure is defined as a blowing agent (Lee et. al., 2006). According to Vasile (2000), blowing agent can be in the state of solid, liquid or gasses where it can produce a cellular structure. If a hollow structure is formed through physical changes of the materials, as an example of a compression of gas, evaporation or dissolving liquid, it will be defined as a physical blowing agent. For chemical blowing agent, the cell structure is produced by the formation of gas from thermal decomposition of the materials.

Water is physical blowing agent which is will use in this research. The cell size of foams produced with chemical blowing agent is higher than physical blowing agent (Lee et. al., 2006). If high water content in foam formulation of flexible foam,

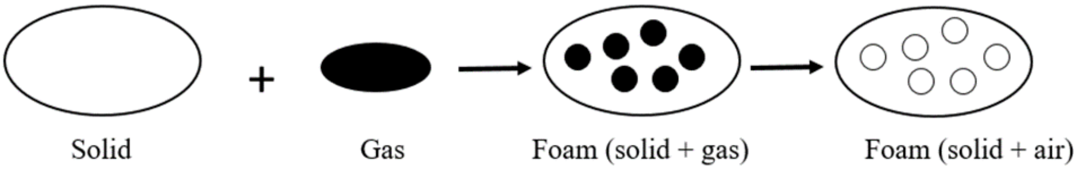


Figure 2.9: Foaming path (Lee et. al., 2006)

Most blowing agents is replaced by air as time passes when the foam is formed and exposed to air. Foaming process has been done by three steps:

1. Implementation
2. Liberation
3. Evacuation

Implementation is the process used to fix the quantities of outside gasses from entering the polymer matrix to form a polymer or gas solution. Liberation refers to the transformation of the polymer or gas solution which is distinguished by non-differentiated structural elements, into the fully differentiated cellular structure. Evacuation suggests the conversion of the polymer foam from a blowing-agent-filled to an air-filled state. In general, chemical reactions and physical mixing are the main methods of introducing a blowing agent into the polymeric melt (Lee et. al., 2006).

### 2.4.1 Physical Blowing Agents

Physical Blowing Agents (PBAs) are gases that do not react chemically in the foaming process. Therefore, PBAs are not harmful to environment. It inert to the polymer forming the matrix. However, the physical blowing agents don’t take part in a chemical reaction, the volatile liquids in the rubber compound will evaporate and make the foam expand (Thirumal et. al., 2007).

## 2.5 Rubber Compound

It was necessary to masticate the raw rubber in order to soften it. The mastication has a reduction of the molecular weight of the rubber and a change on its distribution. Mastication can take place in a two-roll mill where the rolls rotate at different speeds and generate a shear force on the rubber as it passes between the nips between the rolls.

Rubber require compounding prior to vulcanization. This is a process of blend the rubber with vulcanizing agents and other substances to produce a homogenous mix. Mixing of the compounding ingredients with rubber is like mastication and usually carried out on a two-roll mill or in an internal mixer. In this research, two-roll mill is used. The quality of the final mix is important to determine the final product properties. The efficiency of the process includes the type of mixer, the way it is used, the order of adding the ingredients, the control of times and temperature, and other parameters (Ciullo, 1999).

### 2.5.1 Raw Elastomer

Selection of an elastomer or raw rubber are the most important and usually the first step in compounding. All elastomers are elastic, flexible, tough and relatively impermeable to both water and air. The selection of elastomers should be based on properties, processability and price. The raw elastomer use in this research is Epoxidized Natural Rubber 25 (ENR-25). This type of rubber is the standard grade rubber for used in industrial application (Ciullo, 1999).

### 2.5.2 Vulcanizing Agent

Vulcanizing agent are ingredients which must be present to cause the chemical reaction which was resulting in crosslinking of elastomer molecules. According to Ciullo (1999), crosslinking achieved when an elastomeric compound is converted from a soft, tacky thermoplastics to a strong temperature stable thermoset. Sulfur is the most used vulcanizing agent and it was used in this research.

### 2.5.3 Zinc Oxide and Stearic Acid

A cure system consisting of sulfur and accelerators usually requires the presence of an amount of zinc oxide and stearic acid to attain the good crosslinking. Zinc oxide act as an activator to activate the accelerator and its effectiveness in the crosslinking process. Zinc oxide will react with stearic acid to form zinc stearate to speed up the sulfur vulcanization occurs. The curing process may take an hour with sulfur alone but with this curing system it can be reduced to a minutes (Ciullo, 1999).

### 2.5.4 Accelerators

Accelerators were ingredients used to reduce the vulcanization time or cure time which can be done by increasing the speed of vulcanization. The accelerator used in this research is thiuram disulfides (TMTD) also known as sulfur donor materials. It provide monosulfidic crosslink which improve compression set. This TMTD consists of fast curing and low scorch. It less scorch in the absence of sulfur. In this case, its function would be the crosslink agent rather than an accelerator and it gives good compression set (Najib, 2009).

# CHAPTER 3

# RESEARCH METHODOLOGY

## 3.1 Overview

This research work can be divided into three stages. The first one was sample preparation where all the materials were combined and prepared properly according to the formulation of the compound. Next, the process of vulcanization were conducted to determine cure characteristics and foaming process was performed after curing. Finally, the prepared samples are cut according to the standard dimension for the testing and characterization stage. The work outline can be referred to Figure 3.1:

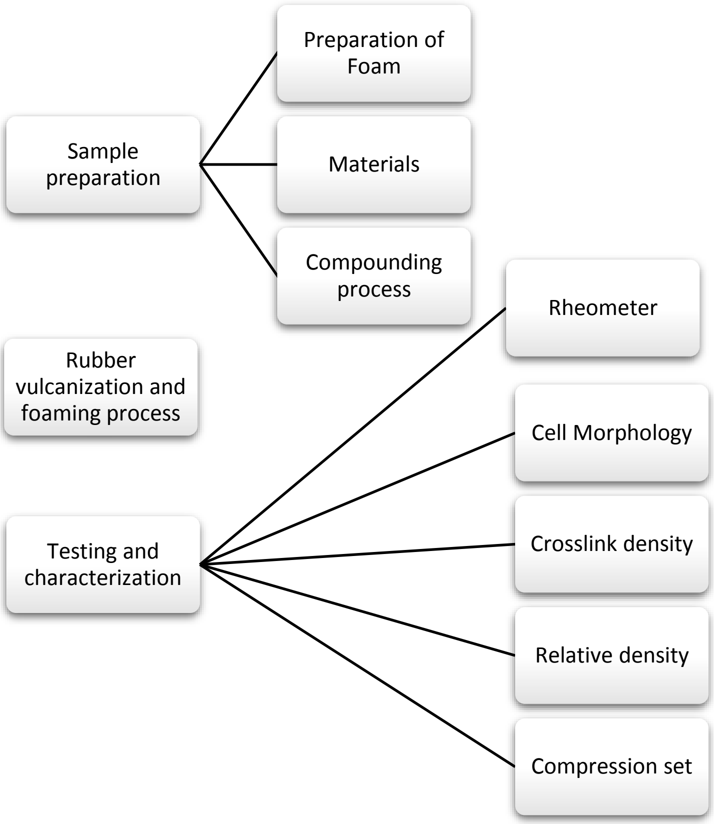


Figure 3.1: Outline work for research methodology

## 3.2 Sample Preparation

### 3.2.1 Materials

Ingredients used in rubber compound may be classified as vulcanizing agents, accelerators, activators, fillers, processing aids, protective agent and additional ingredients that can be used for specific purposes. Vulcanizing agents are ingredients which must be present to cause a chemical reaction and resulting in crosslinking of rubber molecules. Sulfur is the most used vulcanizing agent. Accelerators are ingredients used to reduce the vulcanization time or cure time by increasing the speed of vulcanization. Most accelerators being used today are organic substances containing both nitrogen and sulfur. Activators are ingredients used to activate the accelerator and improve its effectiveness. The most widely used activators are zinc oxide, stearic acid, magnesia, and amines.

Materials that are used in the epoxidized natural rubber foam compounding are:

a) Epoxidized natural rubber (ENR25) produced by Malaysian Rubber Board and supplied by Zarm & Chemical Sdn. Bhd.
b) Distilled water
c) Zinc oxide was supplied by Bayer Co., Ltd.
d) Stearic acid was supplied by Bayer Co., Ltd.
e) Tetramethyl thiuram disulphide (TMTD) was supplied by Bayer Co., Ltd.
f) 2,2,4-Trimethyl-1,2-Dihydroquinoline (TMQ) was supplied by Bayer Co., Ltd.
g) Benzothiazyl-2-cyclohexyl-sulfenamide (CBS) was supplied by Bayer Co., Ltd.
h) Sulphur was supplied by Bayer Co., Ltd.

Each of the materials has their own function and each has an impact on properties, processability, and price. Table 3.1 shows each of the material with their function.