SCHOOL OF MATERIALS AND MINERAL RESOURCES ENGINEERING

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SELF-HEALING NATURAL RUBBER:
PREPARATION AND CHARACTERIZATION

By

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DECLARATION

I hereby declare that I have conducted, completed the research work and written the dissertation entitled **"Self-Healing Natural Rubber: Preparation and Characterization"**. I also declare that it has not been previously submitted for the award of any degree or diploma or other similar title of this for any other examining body or university.

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Date	: 21 June 2017		

Witness by

Supervisor	: Dr. Raa Khimi bin Shuib	Signature	:
Date	: 21 June 2017		

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LIST OF ABBREVATIONS

PVC	Poly (vinyl chloride)
PMMA	Poly (methyl methacrylate)
PS	Polystyrene
GMA	Glycidyl methacrylate
CTE	Coefficient of thermal expansion
BIIR	Bromobutyl rubber
ENR	Epoxidized natural rubber
NR	Natural rubber
DA	Diels-Alder
rDA	Retro-Diels-Alder
DCP	Dicumyl peroxide
PC	Polycarbonate
PA	Polyamide
ATRP	Transfer radical polymerization
DCPD	Dicryclopentadiene
ROMP	Ring opening metathesis polymerization
PDMS	Polydimethylsiloxane
HOPDMS	Hydroxyl-functionalized polydimethylsiloxane
PDES	Polydiethyoxysilane
DBTL	di-n-dibutyltin dilaurate
DGDCA	Diglycidyl dicyclopentadienedicarboxylic acid ester
BR	Polybutadiene rubber
CR	Chloroprene rubber

TDS	Reshuffling of thiuram disulfide
PCL	Polycaprolactone
ZDMA	Zinc dimethacrylate
hBN	Hexagonal boron nitride
SEM	Scanning electron microscope
SMR	Standard Malaysia rubber
ZnO	Zinc oxide
CBS	N-cyclohexyl-2-benzothiazole sulfonamide
TMTD	Tetramethylthiuram disulfide
IPPD	N-isopropyl-N'-phenyl-p-phenylenediamine
Si 69	Silane tertasulfide
CV	Conventional vulcanization
EV	Efficient vulcanization
Semi-EV	Semi-efficient vulcanization
pphr	part per hundred rubber
ASTM	American society for testing and materials

LIST OF SYMBOLS

°	Degree
%	Percentage
°C	Degree Celsius
mol%	Percentage of molar concentration
Tg	Glass transition temperature
s	Second
min	Minutes
MP	Megapixels
mm	Millimeter
g	Gram
dNm	Decinewton meter
ts_2	Scorch time
t_{30}	Time to reach 30 % maximum torque value
t_{50}	Time to reach 50 % maximum torque value
t_{70}	Time to reach 70 % maximum torque value
t_{90}	Time to reach 90 % maximum torque value
M_L	Minimum torque
M_H	Maximum torque
psi	Pounds per square inch
kN	Kilonewton
mm/min	Millimeter per minutes
σ	Tensile strength
$\mathcal{E}$	Elongation at break

m	Weight
V_r	Volume fraction of rubber
V_o	Molar volume of toluene
ρ	Density
[X]	Crosslink density
mol/cm^3	Molar concentration per cubic centimeter
χ	Interaction parameter between rubber and toluene
min^{-1}	Cure rate index

GETAH ASLI PENYEMBUHAN SENDIRI: PENYEDIAAN DAN PENCIRIAN

ABSTRAK

Objektif kajian ini adalah untuk menghasilkan satu getah asli baru yang mempunyai keupayaan penyembuhan sendiri dengan motivasi untuk memperkenalkan intrinsik keupayaan penyembuhan sendiri dengan menggunakan kaedah konvensional dan bahan kimia getah yang biasa. Peringkat pertama dalam kajian ini bertujuan untuk menyiasat intinsik keupayaan penyembuhan sendiri dalam getah asli dengan pengubahsuaian sistem pemvulkanan. Getah asli dengan pelbagai jenis sistem pemvulkanan divulkankan pada masa pematang yang berbeza. Keputusan menunjukkan bahawa getah asli ditervulkan dengan sistem pemvulkanan (Semi-EV) separa cekap mempunyai kecekapan penyembuhan yang lebih tinggi. Walau bagaimanapun, kecekapan penyembuhan menurun apabila getah asli ditervulkan pada masa pengawetan yang lebih lama. Di samping itu, peringkat kedua dalam kajian ini bertujuan untuk menyiasat intrinsik keupayaan penyembuhan sendiri dalam getah asli yang divulkan dengan dua ejen pemvulkanan. Ia didapati bahawa kecekapan penyembuhan sendiri untuk getah asli yang divulkan dengan sulfur/Si 69 adalah lebih tinggi daripada yang divulkan dengan sulfur/DCP dan DCP/Si 69. Bukti disokongkan daripada mikroskop elektron (SEM) menunjukkan bahawa sampel divulkan dengan sulfur/Si 69 tiada ruang yang ketara pada permukaan retak yang disembuhkan.

SELF-HEALING NATURAL RUBBER:
PREPARATION AND CHARACTERIZATION

ABSTRACT

The objective of this research was to develop a new self-healing natural rubber with the motivation to introduce self-healing capability using conventional rubber processing equipment and ingredients. The research’s stage 1 investigated the intrinsic self-healing ability of the natural rubber by modification of vulcanization system. The natural rubber compounds were vulcanized with different types of vulcanization system at different curing time. The results showed that the rubber compound with semi-efficient (Semi-EV) vulcanization system have the higher healing efficiency of tensile strength and elongation at break. However, the healing efficiency decreased as the curing time increased from t_{30}, t_{50} to t_{70}. Research’s stage 2 investigated the self-healing capability of a natural rubber by using binary vulcanization agents. It was found that the healing efficiency of tensile strength and elongation at break for rubber compounds vulcanized with sulfur/Si 69 is generally higher than those vulcanized with sulfur/DCP and DCP/Si 69. Evidence from scanning electron microscopy (SEM) supported that the healed samples vulcanized using sulfur/Si 69 showed no obvious gap between the healed crack surfaces.

CHAPTER 1

INTRODUCTION

1.1 Research Background

Self-healing polymers are relatively new class of smart materials that have ability to partially or fully repair themselves when damaged and to recover functionality by using the resources inherently available to them. Generally, polymeric materials undergo degradation process over the time due to fatigue, environmental conditions, or damage incurred during their service time. Propagation of crack and other types of damage on microscopic level can lead to failure of the materials. Self-healing polymers initiate a repair mechanism that responds to the micro-damage in order to counter the degradation process. This increased the service lifetime and safety of materials with less maintenance.

Self-healing polymeric materials, can be categorized into thermoplastic, thermoset, and elastomer (Wool, 2008; Wu et al., 2008; Blaiszik et al., 2010). The most commonly used thermoplastic self-healing materials are poly (vinyl chloride) (PVC), poly (methyl methacrylate) (PMMA) and polystyrene (PS). The method used to introduce self-healing ability to these thermoplastic is by embedding microcapsules consist of healing agent into the polymer matrix during processing. Glycidyl metharcrylate (GMA) is one example of healing agent used in thermoplastics which can recover micro-crack by atom transfer radical polymerization (Wang et al., 2009) and reversible addition-fragmentation chain transfer (Yao et al., 2011; Zhu et al., 2013). However, there are some disadvantages of microcapsule embedment self-healing method. The cost to fabricate the healing agent capsules are very expensive. This might be due to the difficulty in fabricating the capsule as the healing agents need to be inserted into micro-sized capsules. Other than that, the healing process did not occur if the interfacial bonding between polymer matrix and microcapsule shell wall is weak (Ghosh, 2009). Furthermore, the system is ineffective if the microcracks do not rupture the microcapsule to release the healing agents (Zhang and Rong, 2011).

For thermoset polymers, epoxy-based thermoset is the most commonly used self-healing thermoset materials (Trask et al., 2007; Yin et al., 2007; Blaiszik et al., 2010). Embedding a hollow fiber in the epoxy matrix is one of the approaches to introduce the healing capability. The epoxy resin and healing agent are filled into the hollow fiber. When the crack ruptures the hollow fiber, the epoxy resin and healing agent will flow into the crack. Mixing of epoxy resin and healing agent will initiate the polymerization to heal the crack. However, this approach has some disadvantages. A high-viscosity of resin might unable to flow and fill the crack completely such that resulting in the poor properties of healed crack. Other than that, the use of hollow fiber in the fiber reinforced composites lead to mismatch of coefficient of thermal expansion (CTE). When the composites are subjected to heat, the delamination of hollow fiber with the polymer matrix occurs resulting in failure of microcracks to rupture the hollow fiber. The resin and healing agent are not released and healing not occur.

Elastomer is another type of polymeric materials that shows potential to be developed as self-healing materials. The elastomer with self-healing ability offers certain advantages. The self-healing elastomer prevent or mitigate the fatigue failure by recovering the micro-crack before crack propagation. It also offers unique development opportunities in development of both commercial and engineering applications, such as O-rings, tires, conveyer belts and earthquake bearings, to improve their safety, performance, and prolong their fatigue life.

The healing process of an elastomer can be achieved using intrinsic self-healing. The intrinsic self-healing without any external trigger, such as heat and pressure, is only available in few cases that the healing efficiency is time dependence. A thermoplastic elastomer, that synthesized by dimer and trimer fatty acids from vegetable oils, can recover their tensile properties by simply bringing together the fractured surfaces (Cordier et al., 2008).

Typically, intrinsic self-healing of an elastomer requires certain stimulation, such as heat and pressure. The healing process involves reformation of cross-links, such as supramolecular and chemical interactions, after network is damaged. The self-healing elastomer with supramolecular interaction are crosslinked by reversible non-covalent interactions, such as metal-ligand interactions, $\pi - \pi$ interactions, and hydrogen bonding (Blaiszik et al., 2010; Binder, 2013; Xu et al., 2016). The main challenge to introduce the intrinsic self-healing with supramolecular interactions is to find the right balance between the irreversible and reversible interactions. The lower the irreversible interaction, the better the reversibility but poor mechanical properties might obtain. Recently, the intrinsic self-healing ability with supramolecular interaction is introduced to a commercially available bromobutyl rubber (BIIR) by reacting with various amines which resulting in formation of reversible ionic associates. These ionic associates exhibit physical cross-linking which facilitates the healing processes by heating or stress-induced rearrangements (Das et al., 2015).

Other than that, intrinsic self-healing of an elastomer can be introduced by chemical interactions which involves the thermal reversible crosslinking based on Diels-Alder (DA) reaction (Xu et al., 2016). A highly crosslinked polymeric material was synthesized with multi-furan and multi-maleimide via DA reaction. Upon subjected to heat, the crosslinking linkages break down (retro-DA reaction) but then reform after cooling. This DA and retro-DA reactions is fully reversible and can be used to restore fractured surfaces.

In the field of self-healing natural rubber, researchers have mainly focused on epoxidized natural rubber (ENR) vulcanized with dicumyl peroxide (DCP). The presence of the oxirane groups in the rubber backbone might introduce self-adhesion properties to ENR. This self-adhesion properties assisted in the self-healing of the ENR. The higher the level of epoxidation of ENR, the better the self-adhesion assisted self-healing of rubbers (Rahman et al., 2011; Rahman et al., 2013).

According to the author’s knowledge, no comprehensive work was dedicated to investigate the capability of natural rubber to be developed as self-healing materials. In this study, intrinsic self-healing capability of a natural rubber is investigated by modification of vulcanization system. In addition, the self-healing capability of a natural rubber was also investigated by vulcanizing natural rubber using binary vulcanization system.

1.2 Problem Statement

Development of self-healing natural rubber in this work is a novel direction. Indeed at present, general research in self-healing natural rubber is still in its infancy. Most of the researchers focused on introducing and improving the self-healing ability of synthetic rubbers and limited work was carried out to develop self-healing natural rubber. To the author's knowledge, there is limited work carried out to study on the formulation, fabrication and healing method for natural rubber. Therefore, it is sensible to study the self-healing ability of vulcanized natural rubber in order to realize the full potential application and prolong the natural rubber service lifetime.

At present, researchers are mainly focused on introducing and improving the self-healing capability of epoxidized natural rubber (ENR) due to the presence of the oxirane groups which can form reversible hydrogen bonds (Rahman et al., 2011; Rahman et al., 2013; Imbernon et al., 2015). However, little work study about self-healing natural rubber. This could be due to the presence of stable three-dimensional crosslinking structure which are non-reversible bonding which limited the self-healing ability of a natural rubber. However, natural rubber has high potential to be developed as a self-healing materials because the cleavage of di- and poly-sulfide bonds under various stimuli, such as heat, light or redox conditions, leads to temporary local mobility of the polymer that may repair the crosslinks across damaged surfaces by exchange reactions. Therefore, a substantial study on the self-healing mechanism of a natural rubber is essential in order to develop and understand the self-healing mechanism of natural rubber.

1.3 Research Objectives

The objective of this research was to produce new self-healing natural rubber with the motivation to introduce self-healing capability using conventional rubber processing equipment and ingredients. The specific research objectives are as follows:

I. To investigate the self-healing capability of sulfur vulcanized natural rubber by modification of vulcanization system.

II. To investigate the self-healing capability of a natural rubber cured using binary vulcanization agents.

1.4 Thesis Outline

This thesis is covered all chapters that consist of:

Chapter 1:	Consists of background, problem statement and objective of the research.
Chapter 2:	Provide literature review of project, extensive review of methods to introduce self-healing ability on the materials, especially for elastomers, and testing that conducted to the self-healing rubber.
Chapter 3:	State the detail of the raw materials that used in this research, experimental procedures employed, and machine handling that were involved in generating experimental data for this research.
Chapter 4:	Data and results obtained as well as charts discussion on mechanical and morphological properties of self-healing rubber would be presented in detail.
Chapter 5:	Summary and conclusion on this present work as well as suggestions for the further research.
Chapter 6:	List of references that were used in this research.

CHAPTER 2

LITERATURE REVIEW

2.1 Overview of Self-Healing Polymers

Degradation, damage and failure are the most common consequences of material application over the time. Engineering research has been focused traditionally on either the design of new polymeric materials with increased properties or the development of nondestructive testing method for material inspection, but all engineered polymeric materials eventually fail after long term of usage. Fatigue lead to microcracking which result in failure and reduce the lifetime of the materials. One possible way to prolong the lifetime of materials is to introduce bio-concepts, such as self-healing, as the secondary function in engineered materials. Failure of polymeric materials occurred through the crack formation and propagation (Sheldon, 1982) and the ability to repair these micro- or nano-size cracks at early stage will prevent catastrophic failure, thus the lifetime of the polymeric material can be extended.

Self-healing polymeric materials are a new class of the smart materials that able to recover from mechanical damages, such as crack and cut, by themselves spontaneously or with the aid of a stimulus. Self-healing polymers are relatively new class of smart materials that have ability to partially or fully repair the crack or damage by themselves and recover functionality of the materials by using the resources inherently available to them. There are several types of self-healing polymeric materials, such as thermoplastic, thermoset and elastomer, that have been investigated in order to prolong the service lifetime and improve the safety and performance of the materials with less maintenance (Yin et al., 2007; Rahman et al., 2013; Zhu et al., 2015). In near future, it is believed that self-healing polymers will have massive impact on all industries, from the automotive industry to energy sector. The major application of self-healing polymers being developed today are in automobile (windshield seal, gaskets and fiber-reinforced soft touch surface for interior) (Nagaya et al., 2006), medical devices (syringe, medical tubing, packaging and medical wrapping) (Blaiszik et al., 2010; Binder, 2013), household appliance sector (sporting goods, footwear soles, toys and adhesives) (Wool, 2008; Wu et al., 2008) and aerospace industries (Blaiszik et al., 2010).

2.2 Self-healing Thermoplastic

The commonly self-healing thermoplastics was shown in Table 2.1. Poly (methyl methacrylate) (PMMA) is the most typical thermoplastic used for self-healing thermoplastic. The technique used to introduce self-healing in the thermoplastic can be either intrinsic or capsule healing method.

Table 2.1: Common self-healing thermoplastic.

Thermoplastic	Healing method	References
PMMA	Capsule	(Wang et al., 2009)
PMMA	Intrinsic	(Lin et al., 1990; Wang et al., 1994; Hsieh et al., 2001)
PC	Intrinsic	(Wu and Lee, 1994; Takeda et al., 2004)
PVC	Intrinsic	(Zhu et al., 2013; Zhu et al., 2015)
PA	Intrinsic	(Liu and Chen, 2007)
PS	Intrinsic	(McGarel and Wool, 1987)

Experiments carried out by using thermoplastics such as poly (methyl methacrylate) (PMMA) and polystyrene shown that promoting entanglement of polymer chains from each side of crack face result in intrinsic healing of the crack. The chain mobility is required for this kind of manually-induced healing either by heating the polymeric material above its Tg or using solvents, such as methanol and ethanol, to reduce the effective Tg to below the room temperature (Lin et al., 1990; Wang et al., 1994). The glass transition temperature of PMMA was reduced to a range of 40-60 °C and two distinctive stages for crack healing were found out. The first one related to the progressive healing due to wetting, while the second corresponding to enhancement of diffusion for the healing behavior. Similarly, the crack healing of PMMA induced by co-solvent of methanol and ethanol was studied. The healing efficiency of the crack was found out to be liner function to healing time under elevated temperature. The fracture stress increased with decreasing of co-solvent volume fraction. The hydrogen bond formed due to interaction between co-solvent with broken polymeric chain which increased the mechanical strength of the healed sample (Hsieh et al., 2001). In addition, crack healing in polycarbonate (PC) was observed at temperature range of 40-60 °C by using the same technique but with different type of solvent (carbon tetrachloride) (Wu and Lee, 1994).

The healing process via transfer radical polymerization (ATRP) technique between PMMA matrix and microencapsulated glycidyl methacrylate (GMA) as healing agent was also studied (Wang et al., 2009). When the crack propagates and ruptures the capsule shell wall, the polymerization reaction occurs as the healing agent in contact with the PMMA matrix. The formation of covalent bond from the polymerization reaction recovered the crack area. The healing process can be occurred repeatedly with the transfer radical polymerization technique. The healing efficiency increase with increased in healing time.

More recently, a new healing technique called “click chemistry” was used to produce self-healing poly (vinyl chloride) (PVC) composite that can automatically self-heals in response to mechanical damage. The self-healing agents were encapsulated separately before added into PVC. Crack ruptured the self-healing capsules and these self-healing agents form crosslinks between two crack surface which enable them to heal and join together (Zhu et al., 2015).

2.3 Self-healing Thermoset

Table 2.2 shows the commonly self-healing thermoset. Epoxy-based thermoset is the most common self-healing thermoset. The self-healing capability of an epoxy can be introduced using capsule, vascular and intrinsic healing methods.

Table 2.2: Common self-healing thermoset.

Thermoset	Healing method	References
Epoxy	Capsule	(White et al., 2001; Brown et al., 2004; Cho et al., 2006; Yin et al., 2007; Yin et al., 2007; Yuan et al., 2008; Yuan et al., 2009)
Epoxy	Vascular	(Dry and Sottos, 1993; Motuku et al., 1999; Bleay et al., 2001; Trask and Bond, 2006)
Epoxy	Intrinsic	(Chen et al., 2002; Chen, 2003; Brancart et al., 2014)
Crosslinked multifuran	Intrinsic	(Brancart et al., 2014)

An example capsule-catalyst self-healing system is the dicyclopentadiene (DCPD) as the liquid healing agent and Grubbs' catalyst as an internal chemical trigger. Both are encapsulated and dispersed in an epoxy matrix. This system proceeds on the basis of ring opening metathesis polymerization (ROMP) of DCPD via the Grubbs' catalyst. The healing reaction started upon the capsules are ruptured and a highly cross-linked tough polycyclopendiene is formed which seal the rupture zone (White et al., 2001). The healing efficiency can be increased by capsulated the catalysts and healing agents using wax.

Delamination and low-velocity impact damages in fiber reinforced epoxy composites were found to be successfully repaired by healing agent (Rule et al., 2005).

Moreover, a latent curing agent, $CuBr_2(2\text{-}MeIm)_4$, is used instead of solid phase catalyst, to replace the Grubb's catalyst to carry out healing process by using ROMP reactions. It is found out that the healing efficiency of this kind of latent curing agent is better than the original Grubb's catalyst. The healing efficiency was depend on the amount of the healing agent and degree of damage (Yin et al., 2007).

In addition, phase separation technique is also introduced in the capsule-based self-healing polymer. Cho et al. (2006) introduced this technique by phase-separating hydroxyl-functionalized polydimethylsiloxane (HOPDMS) and polydiethyoxysilane (PDES) in epoxy vinyl ester matrix. In this system, the tin catalyst, di-n-dibutyltin dilaurate (DBTL), were encapsulated and dispersed in the matrix. Once the matrix damage ruptured the capsules, tin catalyst will release and catalyze the reaction with the phase-separated HOPDMS/PDES.

Self-healing ability of thermoset can also be introduced by using vascular healing method. Dry and Sottos (1993) developed first vascular self-healing 1D systems. They examined the healing ability of epoxy with millimeter-diameter glass pipettes which preloaded with either cyanoacrylate or a separated two-part epoxy system. However, they have only achieved limited success using this approach. Motuku et al. (1999) further explored the use of pipettes which made from different materials to evaluate their suitability for incorporation into fiber-reinforced vinyl ester and epoxy resins. Large diameter capillaries/pipettes were embedded into resin, but the trials were unsuccessful as well. Smaller hollow glass fiber (15µm diameter) were adopted by Bleay et al. (2001) and were organized into unidirectional plies for composite laminates. Composites system formulated by using this kind of filled glass fiber are unable to deliver the resin into the crack zone due to the high viscous epoxy resin, which resulted in low recovery effectiveness. Trask and Bond (2006) further investigated the structural effects of pipettes integration on fiber-reinforced composites by fabricating quasi-isotropic (0 °/90 °) specimens with hollow glass fibers, which containing uncured resin or hardener, at the ply interfaces. The composites panel prepared by this method was reported can restore up to 97 % of its original flexural strength.

Moreover, thermally reversible reaction can also introduce the intrinsic self-healing system in thermoset, such as the Diels-Alder (DA) and retro-Diels-Alder (rDA) reactions. Chen et al. (2002) were the first to design the thermally triggered self-healing system based on DA reactions of synthesis furan-maleimide polymers. The first thermally triggered self-healing polymers showed a strength with 53 % recovery. Later, the recovery efficiency of mechanical strength has been improved to 83 %. Brancart et al. (2014) designed the reversible cross-linking network in epoxy based coating by investigating the ability of furan-maleimide building block. The reversible cross-linking of furan-precursors with a bis-maleimide was achieved. Thermal analysis of these composites showed that the modification of the polymer network structure allows the thermally triggered self-healing to occur.

2.4 Self-healing Elastomeric Materials

Table 2.3 shows the common self-healing elastomeric materials. It can be seen that most self-healing elastomeric materials are synthetic elastomeric materials. For the natural based elastomeric materials, the previous works are mainly focused on the epoxied natural rubber. The self-healing capability of an elastomeric materials can be introduced either intrinsic or extrinsic. This will further discuss in next section.

Table 2.3: Common self-healing elastomeric materials.

Elastomeric Materials	Healing method	References
PDMS	Capsule	(Rule et al., 2005; Keller et al., 2007; Rule et al., 2007)
PDMS	Intrinsic	(Roy et al., 2014)
Polyether rubber	Intrinsic	(Chen and Jiao, 1999)
Polyurethane rubber	Intrinsic	(Rivero et al., 2014)
BR and CR	Intrinsic	(Xiang et al., 2015; Xiang et al., 2016)
BIIR	Intrinsic	(Das et al., 2015)
ENR	Intrinsic	(Rahman et al., 2011; Rahman et al., 2013; Imbernon et al., 2015)
NR	Intrinsic	(Hernández et al., 2016; Xu et al., 2016)

2.4.1 Self-healing Techniques for Elastomeric Materials

Figure 2.1 shows the overview of self-healing techniques. Self-healing techniques can be categorized into either intrinsic or extrinsic self-healing systems. Intrinsic healing process is a process that enable the crack healing mostly under certain stimulation, such as heat, UV light and pressure. For extrinsic self-healing, the healing agents have to be stored in some media, such as microcapsules, and embedded into the polymer matrix. Once the crack damaged the media, the healing agent is released into the crack area and heal the crack.

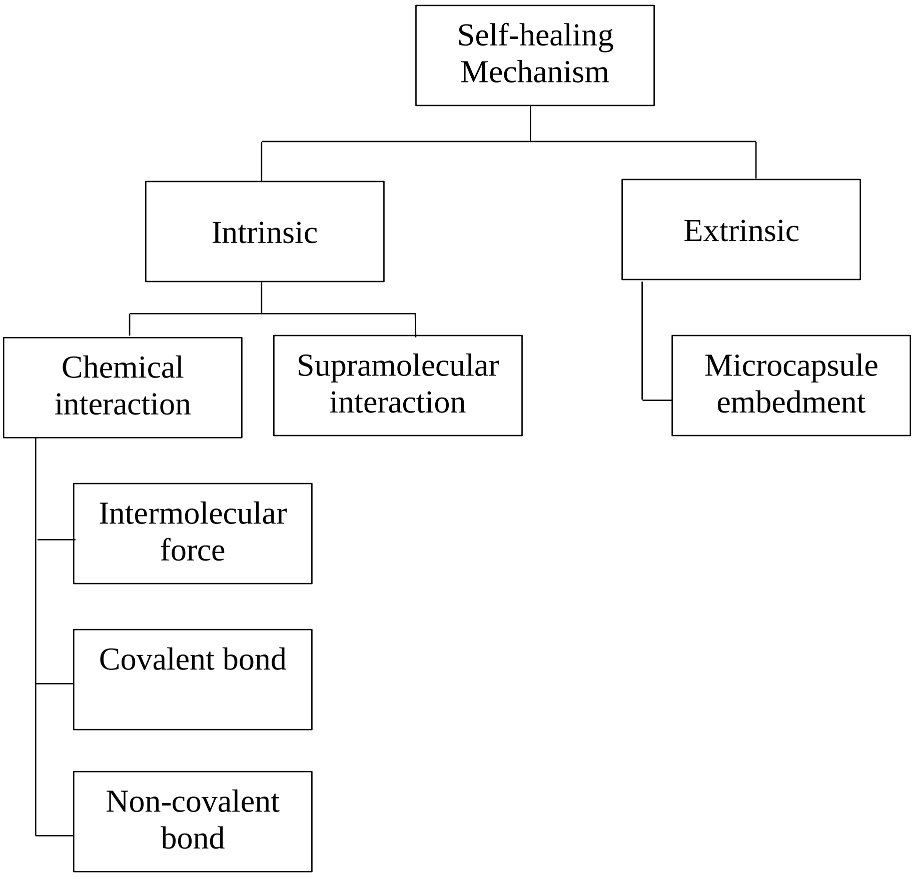

Figure 2.1: Flowchart representing self-healing approach (Subramanian and Varade, 2017).

2.4.1.1 Microcapsule Embedment

Microencapsulation is a process of entrapping micron-sized healing agents in a tiny sphere in order to isolate and protect them from the external environments. Microcapsules have two parts, namely the core and the shell. Both core and shell materials are no chemically reactive to each other. Microcapsules may have spherical or irregular shapes and may vary in size ranging from nano- to microscale. The self-healing microcapsules are dispersed in the matrix. The healing reaction occurred once the crack damaged the microcapsules. The self-healing strategy used by microcapsule embedment is shown in Figure 2.2.

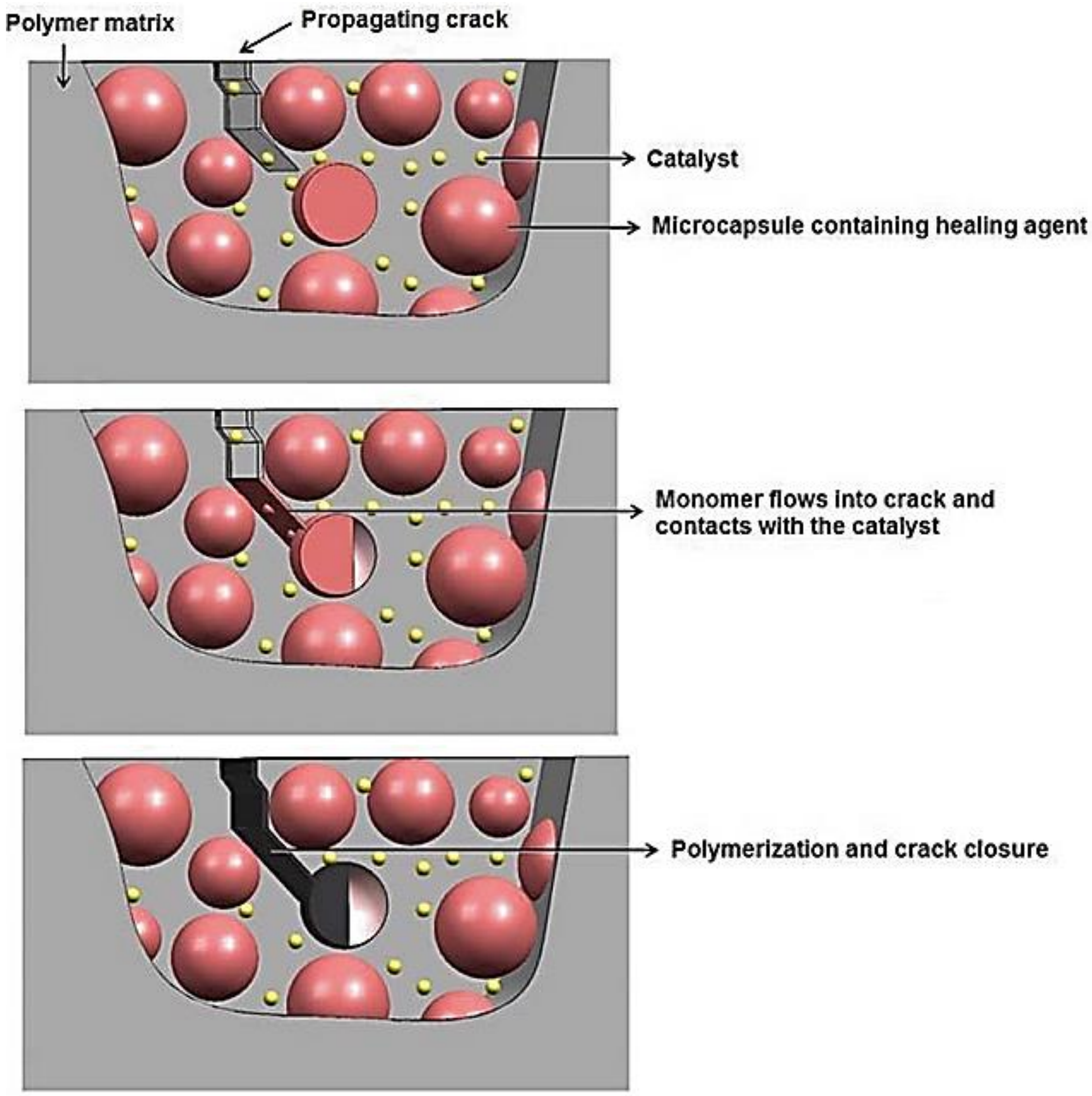

Figure 2.2: Schematic representation of self-healing concept using embedded microcapsules (Ghosh, 2009).

Keller et al. (2007) designed multicapsule self-healing in polydimethylsiloxane (PDMS) - based elastomers which are resin capsule and initiator capsule. In this system, the healing reaction is carried out by hydrosilylation of PDMS resin in the presence of platinum as catalyst. The effect of microcapsules size on the self-healing efficiency was further investigated by Rule et al. (2007). Encapsulation based-self healing have some disadvantages, as follow:

- The interfacial attraction must be strong between polymer matrix and capsule shell;
- Capsules must be broken to release the healing agents;
- Healing agents must have low viscosity to ease the filling of crack area;
- Cured crack must no induced shrinkage;
- Multistep fabrication is required.

2.4.1.2 Reversible Bond

Self-healing capability of elastomeric materials can also be introduced by reversible cross-links with the external trigger such as thermal, photo, or chemical activation (Chen et al., 2002). For example, a highly-crosslinked elastomer with self-healing ability was synthesized via Diels-Alder (DA) reaction. The thermally reversible crosslinking based on DA reaction is illustrated in Figure 2.3. Retro-DA reaction (cleavage of linkages) occurred when heating but reconnect upon cooling. These reactions is fully reversible and can be used to restore the crack (Chen et al., 2002). Later, the preparation of sample via Diels-Alder (DA) reaction was modified by Liu and Hsieh (2006). The multifunctional furan and maleimide compounds were prepared in a simpler route by using epoxy as precursors. This also resulting in furan and maleimide monomer are considered as epoxy-based compounds because they have similar characteristics of epoxy resin. Moreover, Rivero et al. (2014) also introduced self-healing capability in the polyurethane networks based on polycaprolactone (PCL) and furan-maleimide at ambient temperature conditions via one-pot synthesis. A combination of quick shape memory effect followed by reformation of covalent bonds (DA-rDA reaction) allows the self-healing process to occur at 50 °C resulting in complete recovery of rupture zone without fully melt the polymer.

In addition, the thermally reversible covalent bond polyether rubber is developed by Chen and Jiao (1999). Diglycidyl dicyclopentadienedicarboxylic acid ester (DGDCA) was used as a crosslinking monomer in alkyl aluminum system and copolymerized with epoxide monomer. The resultant polyether thermoplastic elastomer can be molded into sheets at 215 °C. The crack can be healed and become invisible under certain conditions. The decrosslinking of the crosslinked copolymer occurred at an elevated temperature (120 °C), leading to melting and plastic flow. The DA cycloaddition between side group cyclopentadiene rings reconstructed the elastic cross-linking networks upon cooling.

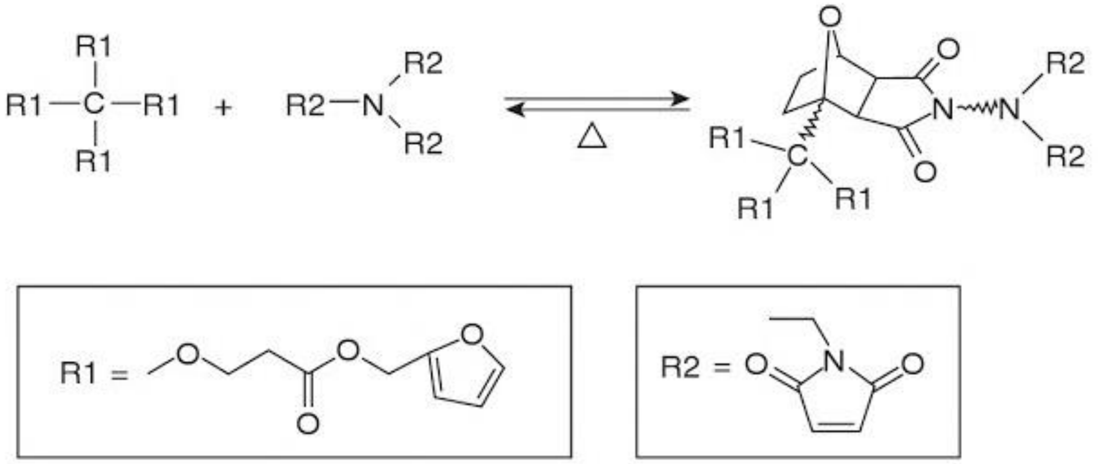

Figure 2.3: Thermally reversible crosslinking based on Diels-Alder reaction (Zhang and Rong, 2011).

Moreover, self-healing capability of PDMS can also be achieved by a reversible covalent linkages through imine bond formation with hydrogen bonds (non-covalent interactions) between urea-type groups inside the same polymer structure (Roy et al., 2014). A reversibility of carbinol (hydroxyl) terminated polydimethylsiloxane (PDMS) was produced through polycondensation reaction between siloxane-based diadehyde and carbohydrazide via the formation of bis-iminourea type subunits. Polymer capable of autonomous healing was produced via acylhodrazone units and lateral hydrogen bonding interactions which introduced to the polymer structure as reversible covalent and non-covalent linkages, respectively.

In current self-healing NR field, previous works mainly focused on epoxidized natural rubber (ENR) which the self-healing ability is dependence on the amount of presence of oxirane groups in the rubber backbone. Self-healing ENR was developed by vulcanizing ENR with different epoxidation levels (25 and 50 mol% epoxidation) and dicumyl peroxide. The self-healing capabilities of ENR on the damage or crack is investigated under different experimental conditions, such as high-energy impact and tear test (Rahman et al., 2011; Rahman et al., 2013). The self-healing capabilities of ENR was contributed by the inter-diffusion processes. A reprocessable ENR was later developed by using dithiobutyric acid as cross-linker in the presence of 1,2-dimethylimidazole acting as a catalyst. The self-healing process of this ENR can only be carried out under non-ambient conditions (Imbernon et al., 2015).

2.4.1.3 Supramolecular Interaction

The mechanical properties of an elastomeric material are influenced by the entanglement of long chains of the monomer, which are held together by covalent bond. Recently, a thermally reversible crosslinking rubber had been successfully developed by using supramolecular hydrogen bonding networks (Chino et al., 2002). The fractured surfaces can be healed due to the rearrangement of molecules during heating and reformation of network occurs when the material is cooled down.

Self-healing elastomers can also be designed to form strong end-group and/or side-group associations via reversible hydrogen bonds. Cordier et al. (2008) designed a rubbery material with self-healing ability via supramolecular assembly which is crosslinked with reversible hydrogen bond. The crack zones are healed by the reformation of hydrogen bond in close contact under room temperature when the rubbery self-healing materials are damaged.

The self-healing capability can also be introduced to an elastomer by using metal-ligand supramolecular interaction instead of the hydrogen bond. Copper (II) chloride ($CuCI_2$) was found as an effective catalyst for triggering healing process in sulfur vulcanized polybutadiene rubber (BR) (Xiang et al., 2016). Once $CuCI_2$-based catalyst was activated, the metathesis of disulfide and polysulfide bonds in the polymer matrix is enabled at 110 °C and mechanical properties is recovered. In addition, copper methacrylate (MA-Cu) catalyst was used in this similar catalyzed approach to promote the disulfide metathesis reaction in vulcanized chloroprene rubber (CR) at elevated temperature. MA-Cu based catalyst enabled the reshuffling of inherent sulfur crosslinks at 120°C while microstructure of the CR remained unchanged at lower temperature (typically lower than 100 °C). Sulfur bonds in vulcanized CR can be reversibly exchanged as well as across the surfaces at 120 °C which introduced the capabilities of repeated reshaping, self-healing and recycling for vulcanized CR (Xiang et al., 2016).

Furthermore, a self-healing elastomeric polymer have also been produced by reshuffling of thiuram disulfide (TDS) units (Amamoto et al., 2012). The self-healing process of this kind of polymer occurs under ambient conditions, such as visible light, air and room temperature, and in the absence of solvent. The reactive TDS were incorporated in the main chain of low Tg polyurethane in order to carry out the self-healing reaction under room temperature conditions.

2.4.1.4 Ionic Association

The self-healing process in an ionic rubber network is illustrated in Figure 2.4. The generation of ionic association in rubbers involved the inclusion of ionic groups in the carbon-carbon backbone chains where healing process is carried out by ionic bonds rearrangement. Das et al. (2015) converted bromobutyl rubber (BIIR) into a highly elastic material with self-healing capabilities by transforming the bromine functionalities of BIIR into ionic imidazolium bromide groups. The healing processes were induced by the reversibility of ionic association which enable a cut sample to recover partially or fully to its original properties.

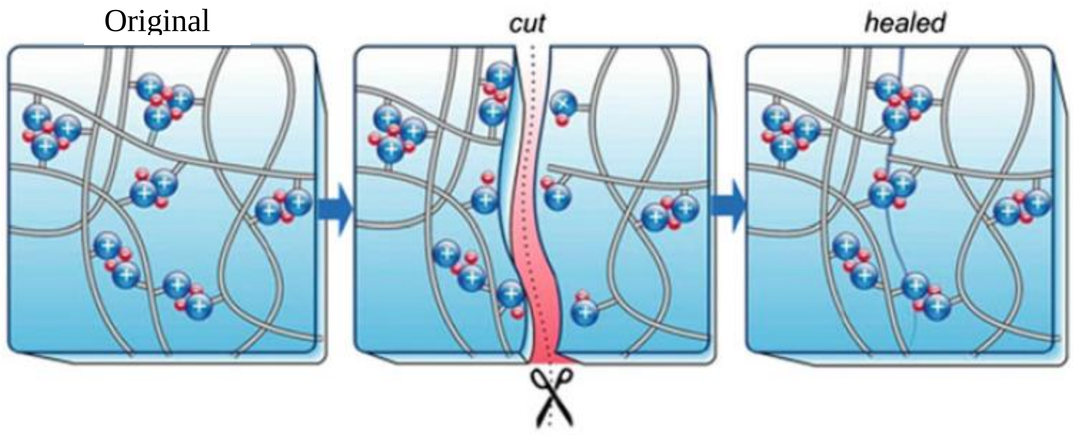

Figure 2.4: Schematic representation of self-healing process in an ionic rubber network by reformation of reversible ionic associates (Xu et al., 2016).

Introducing ionic associations is one of the most effective approaches to introduce self-healing ability on rubbers. However, natural rubbers are non-polar rubbers which did not have any available functional groups that can be converted into ionic groups. Therefore, it is still very challenging to introduce self-healing capabilities in vulcanized natural rubber (NR) even though natural rubber (NR) have the potential to be an autonomous self-healing materials. A controlled peroxide vulcanization of natural rubber to generate massive ionic crosslinks via polymerization of zinc dimethacrylate (ZDMA) is successfully developed as a potential self-healable material. Peroxide vulcanization process is controlled to limit the formation of irreversible covalent crosslink network in order to generate a reversible ionic network between the rubber molecular chains. The rubber molecular chains in ionic network had good flexibility and mobility. These ionic crosslinks can be easily reconstructed and rearranged when damaged natural rubber subjected to heat. It enables a fully cut sample to rejoin and retain to its original properties after a suitable self-healing process at ambient temperature (Xu et al., 2016).

Lafont et al. (2014) produced a multifunctional self-healing composite by mixing an uncured thermoset rubber with reversible disulphide bonds which load with thermally conductive graphite and hexagonal boron nitride (hBN) as fillers. When increasing in the healing temperature, better cohesion recovery of crack is obtained even for highly loaded self-healing composites. An et al. (2015) also reported a dual sulfide-disulfide crosslinked networks which have fast (30 s – 30 min) and effective self-healing ability under room temperature without any external stimuli. The synthesis of dual-sulfide-disulfide crosslinked network produced a sufficient density of disulfide crosslinking which is required to complete the self-healing process at room temperature.

2.5 Application of Self-Healing Elastomer

2.5.1 Tire

Punctures of tire for industrial vehicles are a regular and expensive occurrence due to downtime, missed schedules and hefty service and tire repair bills. Goodyear tackles the problem in an innovative way by incorporates a built-in sealant designed to allow truck operators to continue driving after a tire is punctured. The tire will remain in service until it is retreaded. When a nail puncture occurs, a yellow, gel-like rubber compound instantly surrounds the nail and seals the punctures. It stops the air from escaping from the tires, and it can repeat the healing action without replacing the tire or reapplying sealant. The self-healing tires can last up to six times longer than conventional truck tires before replacement.

Similarly, Continental AG offers self-healing tires which containing a preapplied sticky, viscous layer that covers the inside of the tread from shoulder to shoulder. It provides an almost instantaneous seals around the penetrating objects in the tread area. The air will trap inside the tires and the emergency roadside tire changes can be avoided.

Unlike above healing strategies, a new self-healing tire containing a sealant layer, that is bonded along the inner surface of the tire, is developed(Nagaya et al., 2006). The sealant layer consists of two rubber sheets covering polymer particles with sewn line to create lattices as shown in Figure 2.5. The polymer particles are a kind of hydrophilic material that can absorb about 400 times as much water as its own weight. The polymer particles expand and become gel-like, creating high pressure in the lattice. This polymer will mix with rubber adhesive to prevent the movement of the gels when automobile starts or stops suddenly. When a nail punctures the tire and is removed, the expanded sealant would seals the holes instantly. The polymer gels will become solid upon contact with air, the gel will not leak out from the puncture hole. Hence, the tire can be continued to service until the tire’s tread bald.

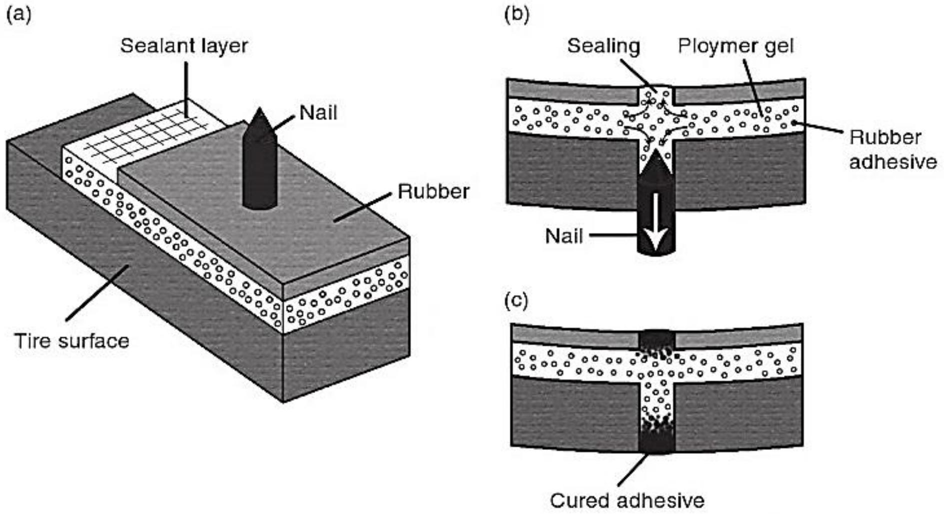

Figure 2.5: Schematic drawing of the drawing of self-healing tire based on water absorbing polymer: (a) cross-section of a punched tire; (b) removal of the sharp object lead to instant healing; and (c) tire cured (Nagaya et al., 2006).

2.5.2 Impact Barrier

Battelle Memorial Institute developed a self-healing impact barrier that produced by polyurethane for National Association for Stock Car Auto Racing (NASCAR) pit-stop walls. It can recover to its original shape within several minutes after a car crashes on it. The deformed materials do not rebound too quickly, which could cause a crashed car to bounce back into the lanes. Recently, Battelle is also working on highway-crash barrier and also military armor application.

2.5.3 Other Potential Applications

Arkema company is now working on the self-healing supramolecular polymer by introducing the reversible hydrogen bonds in the polymer. These supramolecular polymers are consisted of fatty acid oligomers which derived from the vegetable oil. The self-healing supramolecular polymer have high potential in the commercial, industrial and engineering applications, such as conveyer belt, insulation, sealing joints, gasket, shoes sole, earthquake bearing, shock-absorbing layers, industrial gloves, pastes and sealants.

CHAPTER 3

METHODOLOGY

The research flow for this study is illustrated in Figure 3.1. Two stages of investigation were carried out in this research. Stage one investigates the intrinsic healing capability of a natural rubber (NR) by modification of vulcanization system. Stage two investigates the self-healing ability of natural rubber (NR) by curing with binary vulcanization agents. The research flow diagram is illustrated in Figure 3.1.

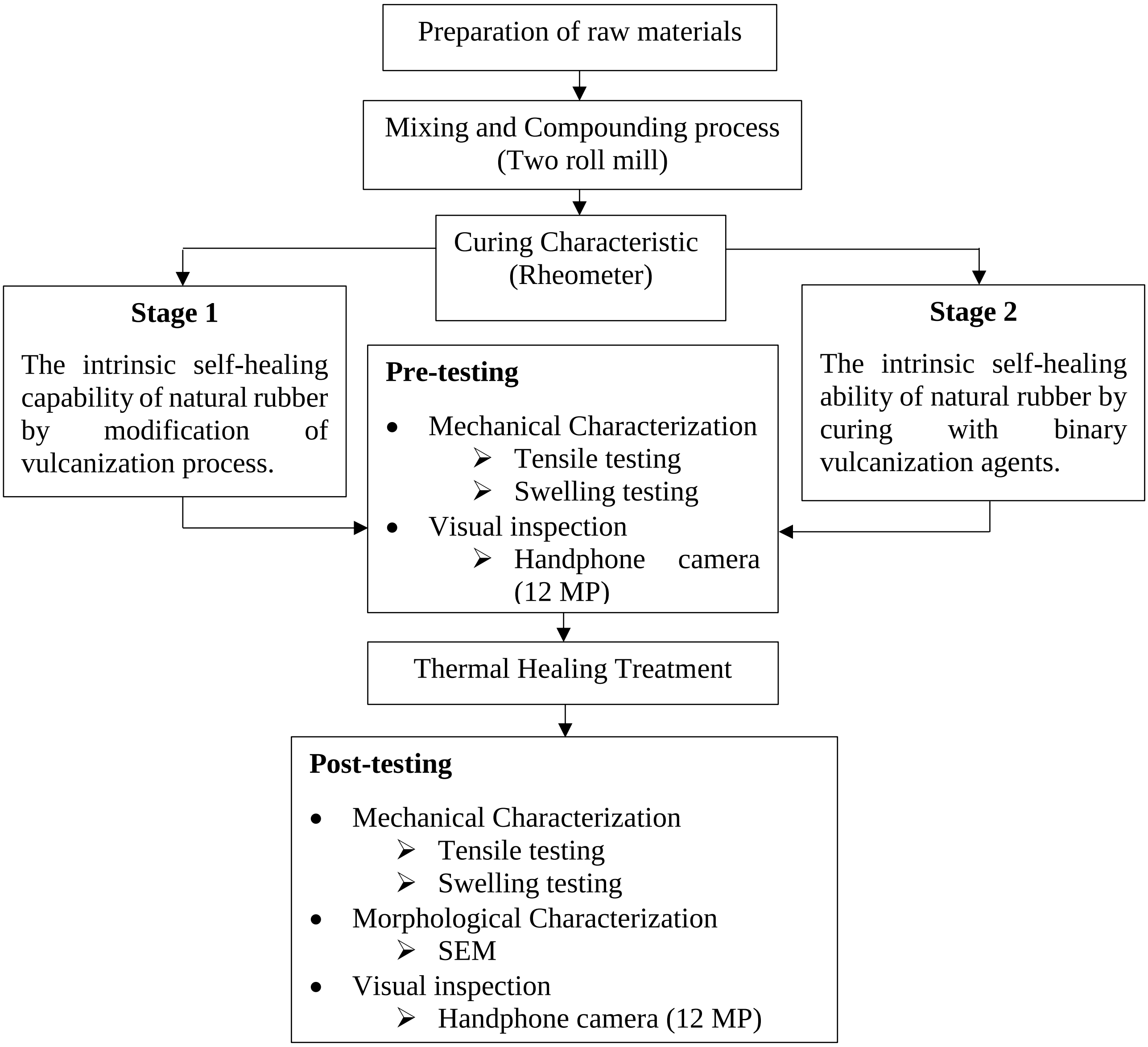

Figure 3.1: Flow diagram of self-healing rubber fabrication and characterization process.