

**SCHOOL OF MATERIALS AND MINERAL RESOURCES ENGINEERING  
UNIVERSITI SAINS MALAYSIA**

**ROOM TEMPERATURE SELF-HEALABLE NATURAL RUBBER**

**By**

**NUR SYAMSINAR BINTI SARDI**

**Supervisor: Dr. Raa Khimi bin Shuib**

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

**Universiti Sains Malaysia**

**JUNE 2018**

## DECLARATION

I hereby declare that I have conducted, completed the research work and written the dissertation entitled “Room Temperature Self-Healable Natural Rubber”. 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.

Name of Student : Nur Syamsinar Binti Sardi

Signature :

Date : 25 June 2018

Witness by

Supervisor : Dr. Raa Khimi bin Shuib

Signature :

Date : 25 June 2018

## **ACKNOWLEDGMENTS**

It would not have been possible to complete my final year project and write the thesis without the help and support of the kind people around me. First of all, I am grateful to God for giving me sustained patience and good health to complete this investigation. I would like to express the deepest appreciation to my supervisor, Dr. Raa Khimi bin Shuib who has tirelessly assisted me with every step of my final year project and thesis writing and was never short of good advice and direction when it was needed most.

I also take this opportunity to acknowledge the help, support and encouragement rendered by technicians from School of Materials and Mineral Resources Engineering at Engineering Campus of Universiti Sains Malaysia who have spent their time and effort to guide me on how to operate the machine properly and safely. I also thanks to all my coursemates for their help and encouragement.

Last but not least, I would like to thank my family especially my parents for their continual encouragement and support at all times. I would not have made this far without them.

## TABLE OF CONTENTS

Contents	Page
DECLARATION.....	ii
ACKNOWLEDGMENTS.....	iii
LIST OF TABLES.....	viii
LIST OF FIGURES.....	ix
ABBREVIATIONS.....	xi
LIST OF SYMBOLS.....	xiii
ABSTRAK.....	xiv
ABSTRACT.....	xvi
CHAPTER 1 INTRODUCTION.....	1
1.1 Research Background.....	1
1.2 Problem Statement.....	4
1.3 Research Objectives.....	6
1.4 Thesis Outline.....	6
CHAPTER 2 LITERATURE REVIEW.....	7
2.1 Overview of Self-Healing.....	7
2.2 Self-Healing Polymers.....	8
2.2.1 Self-Healing Thermoplastic Materials.....	8
2.2.2 Self-Healing Thermoset Materials.....	10
2.2.3 Self-Healing Elastomer Materials.....	11
2.3 Self-Healing Approaches.....	12
2.3.1 Extrinsic Self-Healing.....	13

2.3.2	Intrinsic Self-Healing .....	16
2.4	Self-Healing Concepts for Natural Rubber.....	19
2.4.1	Dynamic Exchange .....	19
2.4.2	Ionic Interaction.....	22
2.5	Impact of Self-Healing Natural Rubber .....	22
2.6	Applications Self-Healing Elastomer.....	23
2.6.1	Tire .....	23
2.6.2	Other Potential Applications .....	25
CHAPTER 3	METHODOLOGY .....	26
3.1	Materials .....	27
3.1.1	Natural Rubber (SMR L).....	27
3.1.2	Zinc Oxide.....	27
3.1.3	Stearic Acid.....	27
3.1.4	Carbon Black (N330).....	28
3.1.5	Zinc Thiolate .....	28
3.1.6	Dicumyl Peroxide (DCP) .....	28
3.1.7	Toluene.....	28
3.1.8	Ethanol.....	28
3.2	Equipment.....	29
3.3	Preparation of Self-Healing Rubber.....	30
3.3.1	Formulation of Self-Healing Rubber .....	30
3.3.2	Rubber Mixing Two Compounding .....	31
3.3.3	Cure Characteristics.....	33

3.3.4	Shaping and Curing .....	33
3.4	Characterization .....	34
3.4.1	Healing Efficiency Test.....	34
3.4.2	Swelling Test.....	34
3.4.3	Morphological Characterization .....	35
3.4.4	Elemental Characterization .....	36
3.4.5	Thermal Analysis.....	36
CHAPTER 4	RESULTS AND DISCUSSIONS .....	37
4.1	Stage One : To Develop Self-Healing Natural Rubber Based On Zinc Thiolate Exchange That Able To Heal By Itself At Room Temperature .....	37
4.1.1	Characterization of Self-Healing Network in Natural Rubber .....	37
4.1.2	Cure-Curve Analysis .....	39
4.1.3	Fourier Transform Infrared (FTIR) .....	40
4.1.4	Crosslink Density .....	41
4.1.5	Visual Observation .....	42
4.1.6	Healing Efficiency.....	44
4.1.7	Scanning Electron Microscopy (SEM) Observation .....	45
4.1.8	Tensile Strength.....	48
4.1.9	Elongation at Break.....	49
4.2	Stage Two : To Assess The Effect of Carbon Black on The Self-Healing Capability of Natural Rubber .....	51
4.2.1	Effect of Carbon Black Content on Healing Efficiency of Natural Rubber.....	51
4.2.2	SEM images.....	54
4.2.3	Crosslink Density .....	57

4.2.4	Thermogravimetric Analysis (TGA) .....	58
CHAPTER 5	CONCLUSION.....	60
5.1	Conclusions .....	60
5.2	Recommendation for Future Work .....	61
REFERENCES	.....	62

## LIST OF TABLES

	<b>Page</b>
Table 2.1 : Self-healing approaches for thermoplastic materials	8
Table 2.2 : Common self-healing approaches for thermoset materials	10
Table 2.3 : Common self-healing approaches for elastomeric materials	12
Table 3.1 : Typical properties and specification of SMR L	27
Table 3.2 : List of equipment used in this research	29
Table 3.3 : Formulation used for intrinsic self-healing natural rubber in Stage 1	30
Table 3.4 : Formulation used for intrinsic self-healing natural rubber in Stage 2	31
Table 3.4 : Steps of mixing intrinsic self-healing natural rubber	32
Table 4.1 : Char residual based on TGA data at different carbon black content in natural rubber	58



## LIST OF FIGURES

	<b>Page</b>
Figure 2.1 : Categories of self-healing approaches	13
Figure 2.2 : Schematic illustrated mechanism of self-healing material based healing	14
Figure 2.3 : Schematic concept of intrinsic self-healing polymer by presence of external	17
Figure 2.4 : Example of thiolate/nanoparticles exchange network performed healing process	20
Figure 2.5 : Example of aromatic disulphide exchange network performed healing process	21
Figure 2.6 : Example of gold (I) thiolate/disulfide exchange network performed healing process	21
Figure 2.7 : Simplified representation of ionic interaction healing process	22
Figure 2.8 : Representation of self-healing based on reversible ionic association	25
Figure 3.1 : Research flow chart of self-healing fabrication and characterization process	26
Figure 3.2 : Conceptual of hot press	33
Figure 4.1 : Sketch for fundamental network forming	38
Figure 4.2 : Torque-time curve for 0 phr zinc thiolate and 30 phr zinc thiolate	39
Figure 4.3 : FTIR spectra of the 0 phr and 30 phr zinc thiolate	40
Figure 4.4 : Crosslink density for samples with different levels of ionic cross-linker 10 phr, 20 phr, 30 phr and 40 phr of zinc thiolate content	41

Figure 4.5	: Illustration self-healing behaviour at room temperature : (a) cut strip-shape sample, (b) healed sample at room temperature for 10 minutes, (c) Manual stretching of healed sample	43
Figure 4.6	: Healing efficiency based on tensile strength at 30 phr zinc thiolate content	45
Figure 4.7	: SEM images with 150 x magnification for self-healing natural rubber with different levels of zinc thiolate (a) 0 phr, (b) 10 phr, (c) 20 phr, (d) 30 phr and (e) 40 phr at fracture surface	48
Figure 4.8	: The effect of zinc thiolate content on tensile strength and healing efficiency	49
Figure 4.9	: The effect of zinc thiolate content on elongation at break and healing efficiency	50
Figure 4.10	: Healing efficiency of tensile strength with different carbon black content	51
Figure 4.11	: Schematic presentation of carbon black filler network	51
Figure 4.12	: Healing efficiency of elongation at break with different carbon black content	54
Figure 4.13	: SEM images with 100 x magnification for self-healing natural rubber with additional of carbon black (a) 5 phr, (b) 10 phr and (c) 30 phr at fracture surface	56
Figure 4.14	: Crosslink density vulcanized natural rubber with different carbon black content	57
Figure 4.15	: Thermogravimetric analysis of self-healing natural rubber containing different carbon black content	59

## ABBREVIATIONS

BR	Polybutadiene Rubber
BIIR	Bromobutyl Rubber
XNBR	Carboxylated Nitrile Butadiene Rubber
ENR	Epoxidized Natural Rubber
NR	Natural Rubber
PE	Polyethylene
PP	Polypropylene
PMMA	Polymethyl Methacrylic
PBAE	Poly(Bisphenol A-Co-Epichlorohydrin
PVC	Polyvinyl Chloride
Cl	Chlorine
FRP	Fiber-Reinforce Polymer
PUU	Poly(Urea-Urethane)
PDMS	Thiol-Functionalized Polydimethylsiloxane
DCPD	Dicyclopentadiene
UF	Urea-Formaldehyde
UV	Ultraviolet
pH	Potential of hydrogen
DA	Diels-Alder
AgNPs	Silver Nanoparticles
BIIR	Bromobutylene Rubber
SEM	Scanning Electron Microscopy
FTIR	Fourier Transform Infrared
TGA	Thermogravimetric Analysis
ZnO	Zinc Oxide

DCP	Dicumyl Peroxide
CB	Carbon Black
TS	Tensile Strength
EB	Elongation At Break
ATR	Attenuated Total Reflectance
PZT	Polymerized Zinc Thiolate
ZT	Zinc Thiolate

## LIST OF SYMBOLS

%	Percentage
phr	Part per hundred rubber
min	Minimum
max	Maximum
g/cm <sup>3</sup>	Gram per centimetre cubic
mm	Milimeter
°C	Degree celcius
g	Gram
psi	Pound per square inch
mm/min	Milimeter per minute
$\Phi_r$	Volume fraction of swollen rubber
$V_0$	Molar volume
cm <sup>3</sup>	Cubic centimeter
m	Meter
$\rho_1$	Density
X	Crosslink density
mol/cm <sup>3</sup>	Molar concentration per cubic centimeter
$\chi$	Interaction parameter
cm <sup>-1</sup>	Number of wavelengths per centimeter
°C/min	Degree celcius per minutes

## **PENYEMBUHAN SENDIRI GETAH ASLI PADA SUHU BILIK**

### **ABSTRAK**

Sifat getah adalah dapat menahan pesongan besar dengan sedikit perubahan bentuk. Walau bagaimanapun, getah masih gagal melalui patah dan keletihan sepanjang tempoh perkhidmatan mereka. Dengan kewujudan penyembuhan sendiri dapat mengesakan keretakan pada peringkat awal dan dapat mengelakkan kegagalan pada bahan. Tujuan kajian ini adalah untuk menghasilkan penyembuhan diri getah asli yang mempunyai keupayaan untuk menyembuhkan diri mereka secara spontan dan autonomi pada suhu bilik.

Dalam kajian ini, zink thiolate digunakan sebagai ejen penyembuhan diri melalui pemvulkanan yang disebabkan oleh peroksida untuk menghasilkan campuran kedua-dua kovalen dan ikatan terbalik dengan getah asli dan dieksploitasi sebagai bahan-bahan yang boleh sembuh sendiri. Jumlah zink thiolate diubah pada empat tahap yang berbeza (10 phr, 20 phr, 30 phr dan 40 phr) untuk menilai jumlah optimum zink thiolate yang diperlukan bagi mencapai keupayaan penyembuhan yang tertinggi. Sifat tegangan sembuh sebelum dan selepas proses penyembuhan diukur menggunakan penguji tegangan untuk mendapatkan kecekapan penyembuhan bahan. Hasilnya menunjukkan bahawa kecekapan penyembuhan diri getah asli mampu menghasilkan 60% -80% sifat mekanik awalnya dalam masa beberapa minit dan hampir 100% dalam 10 minit pada suhu bilik tanpa bantuan sumber luar. 30 phr zink thiolate menunjukkan kecekapan penyembuhan yang tertinggi. Bukti dari Pengimbasan Mikroskop Elektron (SEM) menunjukkan bahawa kawasan patah telah pulih sepenuhnya setelah penyembuhan diproses.

Kesan karbon hitam pada keupayaan penyembuhan diri getah asli juga dikaji. Jumlah karbon hitam diubah pada tiga tahap berbeza (5 phr, 10 phr dan 30 phr). Ciri-ciri penyembuhan bahan diukur menggunakan rheometer (MDR 2000). Ujian tegangan, ketumpatan silang, pencirian unsur dan analisis termal telah dijalankan untuk menyiasat kecekapan penyembuhan getah asli menyembuhkan diri. Keputusan menunjukkan bahawa penambahan karbon hitam mengurangkan kecekapan penyembuhan sebanyak 20% -30%. Imej SEM menunjukkan bahawa kawasan patah telah pulih selepas proses penyembuhan.

# ROOM TEMPERATURE SELF-HEALABLE NATURAL RUBBER

## ABSTRACT

Indeed to the properties of rubber which can sustain large deflection with little deformation. However, rubber still fail through fracture and fatigue over their service period. Emerging self-healing provides capability to arrest crack propagation at early stage and thereby preventing catastrophic failure. The aim of this work was to produce self-healing natural rubber that have capability to heal themselves spontaneously and autonomously at room temperature.

Firstly, there were 2 stages implemented zinc thiolate was employed as self-healing agent with peroxide induced vulcanization to developed formation of covalent and reversible bonds with the natural rubber and exploited it as a potential self-healable materials. The amount of zinc thiolate was varied at four different levels (10 phr, 20 phr, 30 phr and 40 phr) to assess the optimum amount of zinc thiolate to achieve highest healing capability. Tensile properties of cured rubbers before and after healing process were measured using universal tensile tester to obtain healing efficiency of the materials. The results revealed that the developed self-healing natural rubber able to recover 60%-80% of its initial mechanical properties in a minutes and almost 100% in 10 minutes at room temperature without the aid of any external resources. It was also found that 30 phr zinc thiolate produced samples with highest healing capability. Evidence from Scanning Electron Microscopy (SEM) showed that the fracture area was fully recovered after the healing processed.



Secondly, the effect of carbon black on the self-healing capability of the developed self-healing natural rubber was also investigated. The amount of carbon black was varied at three different levels (5 phr, 10 phr and 30 phr). Cure characteristics of the materials were measured using rheometer (MDR 2000). Tensile testing, crosslink density, elemental characterization and thermal analysis were carried out to investigate the healing efficiency of developed self-healing natural rubber filled with carbon black. The results revealed that addition of carbon black reduced the healing efficiency by 20%-30% but material with and without carbon black showed a stable thermal properties. SEM images showed that the fracture area was recovered after the healing process.

# CHAPTER 1

## INTRODUCTION

### 1.1 Research Background

Self-healing rubber is one of the growth interest groups of smart materials in engineering products that have ability to repair themselves and to recover functionality when they are damaged without the need for detection or repair by manual intervention of any kind. At present, rubber materials being developed for various applications such as tires, cable, hoses, belting, bearing, mounting and footwear. Indeed to the properties of rubber materials which can sustain large deflections with little or no permanent deformation, rubbers still fail through fracture and fatigue processes. Emerging self-healing rubber provides capability to arrest crack propagation at an early stage thereby preventing catastrophic failure. Until now, numerous of self-healing rubber being developed with the aim of improving its performance in challenging applications in order to drive the need of materials with excellent reliability and extended lifetime.

Self-healing rubber can be classified into two different group based on approach to the self-healing mechanism, intrinsic and extrinsic (Blaiszik et al., 2010). In extrinsic system, the healing chemistries are usually separated from the polymer matrix and contain in microcapsules or vascular network which if the material crack, the healing agent released into the crack plane, reacting and restore the functionalities of the materials (Zhang and Rong, 2013; Peponi et al., 2017; Keller and Crall, 2018). In intrinsic system, the material is inherently able to restore its integrity. Intrinsic self-healing often require an external trigger for the healing to take place such as temperature, pH, UV light and moisture (Guimard et al., 2012).

The purpose of self-healing is to reconnect the chemical bonds which are broken when a material fractures and restoring the mechanical integrity. However for many applications, autonomous healing of the material without any external stimuli is desirable. An ideal self-healing rubber should be recovered without any human intervention and promotes reshuffling of such reversible bonds at ambient conditions. Among covalent bonds that are susceptible to undergo reversible exchange to provide self-healing capability of rubber at room temperature are dynamic sulphur chemistry using metathesis of aromatic disulphides and thiol-disulphide exchange offers unique opportunities due to its simplicity and availability (Martin et al., 2016). However, to the best of our knowledge these reactions have not been exploited so far for the preparation of self-healing natural rubber.

At present, several approaches for introducing self-healing concept in synthetic rubbers such as polybutadiene rubber (BR), bromobutyl rubber (BIIR) and carboxylated nitrile butadiene rubber (XNBR) have been explored and various reviews have been published on this field (Hernández et al., 2016; Xu et al., 2016). The testing results of the final applications is promising, however, no self-healing rubbers has direct potential for final applications. This could be due to limitation of synthetic rubbers when compared with natural rubber. Natural rubber has the highest failure strain of any rubber, resistance to wear, creep and cyclic deformation. It can be compounded with different additives to produce widely varying properties. Furthermore, it can be processed into a variety of shapes and can adhere to metal inserts or mounting plates. It is apparent that final application would become possible if self-healing concept can be introduced to natural rubber.

According to the author knowledge, there is limited work was dedicated to investigate the capability of natural rubber to be developed as self-healing materials. Natural rubber is a non-polar rubber that have no availability of functional groups which is one of the reason lack of self-healing studied using natural rubber. Besides, stable

crosslinks molecular structures of natural rubber cause it not has self-healing capability due to presence non-reversible bonding. Instead of sulphur, peroxide also can be used as vulcanization agent for natural rubber. It is believed that peroxide reacts with rubber chains through a radical mechanism. Rubber radicals can be formed by two mechanisms which are through additional to double bonds or abstraction of hydrogen atom from rubber chains. Abstraction of hydrogen atom not only from rubber but also from other additives used in rubber compounding. The cleavage of peroxide crosslinks is influences by rubber structure, peroxide type, concentration and reaction temperature which leads to temporary local mobility of the rubber chains and offers the potential of self-healing mechanism through renewal of cross links across damage surface by exchange reactions. Chain mobility is important because chain mobility can determine the healing capability of materials (Grande et al., 2015).

Most of the researchers designed self-healing system for example through aliphatic disulphide exchange or hydrogen bonding interaction that required external stimulus to allow chain mobility and trigger healing response towards damage area (Rekondo et al., 2014; Imbernon et al., 2015). However, it is the best if the healability of rubber can be fulfil without any external stimuli to realize the effect of applications natural rubber in service life. Therefore, ionic association in natural rubber become another approaches to generate self-healing capability of natural rubber due to it autonomous healing mode at room temperature. This work focused on development of a new generation of intrinsic self-healing natural rubber through ionomeric interactions which have good mechanical and dynamic properties leading to enhanced durability and reliability of potential products. In addition, the effect of reinforced fillers such as carbon black on mechanical performance of self-healing natural rubber is also investigated.

## 1.2 Problem Statement

Traditionally, rubber structures and product require human attention to identify and repair the damage. In most cases a routine inspection and periodically maintenance results in identification of the damage. Without this maintenance, the damage goes undetected until failure occurs. When the damage is detected, it requires human intervention to replace or repair the system. Development of materials that can detect and heal themselves appear to be possible way to reduce human interaction with the system, minimize down time and reduce the need for part replacement. Furthermore, for some applications such as bridge bearing, dock fender, dynamic seals and rail or road system considerably required high cost and a lot of labour to replace the damage system. The ability of the materials to heal damage might significantly reduce the chance of failure and reduce the maintenance costs.

To date, 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. Conventional vulcanized natural rubbers do not have such a self-healing capability due to the presence of non-reversible stable three-dimensional crosslinking structure which derive their excellent mechanical properties (Hernández et al., 2016; Xu et al., 2016).

In an earlier attempt to develop self-healing natural rubber, researchers mainly focused on epoxidized natural rubber (ENR), taking advantage of the polar oxirane groups presents in the rubber chains. It has been reported that the materials exhibited a self-healing behaviour at high temperature. The self-healing take place because of reversible hydrogen bonding through molecular interdiffusion and effective polar interactions when the fractured ENR surface are brought in contact. However, the strength of non-covalent hydrogen interactions is much weaker and the hydrogen

bonding had poor creep resistance and lacked a long term stability at ambient temperature.

More recently, introduction of ionic groups in rubbers has been demonstrated to be another approach to fabricate self-healing natural rubber. The reversibility of ionic crosslinking between rubber molecular chains induce the healing process to enable a fractured sample to regain its original properties. Unfortunately, most commercial rubbers are non-polar with no available ionic functional group. Generation of ionic associations in rubber molecular chains could offer potential to introduce self-healing mechanism in natural rubber (Xu et al., 2016).

Therefore, a substantial study on natural rubber based on ionic associations in rubber molecular chains will be carried out in this work in order to develop a new generation of natural rubber with self-healing ability. Furthermore, this work will also investigate the effect of reinforced fillers such as carbon black on mechanical performance of self-healing natural rubber in order to realise the full potential of the materials for industrial application.

### **1.3 Research Objectives**

The objective of this research is to develop new self-healing natural rubber that can heal at room temperature without external stimulus in order to generate the healing process. The specific research objectives are as follows:

- i. To develop self-healing natural rubber based on zinc thiolate exchange that able to heal by itself at room temperature.
- ii. To assess the effect of carbon black on the performance of self-healing natural rubber.

### **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 the research, extensive review of methods to introduce self-healing ability on materials and testing that conducted to the self-healing materials.

Chapter 3 : State the detail of raw materials that used in this research, experimental procedures and machine handling that were involved in generated experimental data for this research.

Chapter 4 : Data and results obtained as well as charts discussion on mechanical, morphological and thermal 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

Degradation, damage and failure are the most common consequences that happened to polymeric materials either thermoplastic, thermoset or elastomer over a period of service time. Therefore, emerging self-healing ability provides the polymer with capability to arrest crack propagation at an early stage thereby preventing catastrophic failures. Self-healing polymeric materials are new class of smart materials that have the capability to repair themselves and to recover functionality when they are damaged without the need for detection or repair by manual intervention (Hager et al., 2010). Emerging self-healing capability able to extend lifetime of the material as well as restoring the material performance that contribute to safety and durability of the components. Furthermore, development of self-healing materials would reduce the maintenance and replacement cost which also save the energy. At present, these capability seems offers great opportunities for broadening in various sector such as construction, automotive, medical devices and household appliance.

Self-healing polymeric materials can be classified into two kinds which are intrinsic and extrinsic self-healing. In extrinsic system, the healing chemistries are usually separated from the polymer matrix and contain in microcapsules or vascular network which if the material crack, the healing agent released into the crack plane, reacting and restore the functionalities of the materials (Zhang and Rong 2011, Peponi, Arrieta et al. 2017, Keller and Crall 2018). In intrinsic system, the material is inherently able to restore its integrity. Intrinsic self-healing often require an external trigger for the healing to take place such as temperature, pH, UV light and moisture (Guimard et al., 2012). However, employing extrinsic self-healing for natural rubber is quite difficult because the capsules or vascular network might be rupture during compounding process in two roll mill.



Furthermore, another drawback of extrinsic healing process only leads to a singular local healing site which cause development of intrinsic self-healing (Cuvellier et al., 2017).

## 2.2 Self-Healing Polymers

### 2.2.1 Self-Healing Thermoplastic Materials

Thermoplastic materials is a class of polymeric material which can be heated, reshaped into desired shape and can be recycled. There are two types of thermoplastic which are commodity thermoplastic and engineering thermoplastic. Commodity thermoplastic is a group of plastic material such as polyethylene (PE) and polypropylene (PP) which widely used in daily life and produced in large quantity. Engineering plastic is used for special purposes for example nylon due to it their excellent properties in term of mechanical or heat resistance. Table 2.1 show thermoplastic materials with few healing approaches. Regarding to table below, most of thermoplastic materials used encapsulation method to trigger the healing capability. Encapsulation method is one of extrinsic self-healing approach that stored healing agent for example epoxy in capsule reservoir (Ahangaran et al., 2017).

Table 2.1 : Self-healing approaches for thermoplastic materials

<b>Materials</b>	<b>Healing Approach</b>	<b>References</b>
Polymethyl methacrylic (PMMA)	Encapsulation	(Zhang and Rong, 2013; Celestine et al., 2015; Ahangaran et al., 2017)
Polyurethane	Diels-Alder reaction	(Feng et al., 2017)
Poly(bisphenol A-co-epichlorohydrin (PBAE)	Encapsulation	(Jones et al., 2015)
Polyvinyl chloride (PVC)	Encapsulation	(Zhu et al., 2015)
Acrylic Resin	Hollow Fiber	(Yerro, et al., 2016)

Capsule healing approach required capsule reservoir that have high flexibility, brittle and good survival rate during mixing as the properties requirement (Araújo et al., 2017). Brittle capsule is required to ensure it break when a crack formed and heal the crack area (Ahangaran et al., 2017). High flexibility properties is important for capsule reservoir in order to protect the healing agent inside the capsule. Furthermore, material with good survival rate during mixing is considered due to the mixing condition may subjected to friction, force and shear that can rupture the capsule. Therefore, low glass transition temperature ( $T_g$ ) material should be chosen to fulfil this requirement because at high temperature the capsule will act as rubbery material which increase it toughness that can bend during process at high temperature (Chakrabarti et al., 2004).

Polymethyl methacrylic (PMMA) is a most commonly used thermoplastic for self-healing approach because PMMA compatible with various healing agent. Generally, PMMA is brittle amorphous thermoplastic material that have low  $T_g$  about  $100^\circ\text{C}$  which suit with the requirement of encapsulation method (Shonaik and Simon 1999). However, polyvinyl chloride (PVC) also brittle thermoplastic and the  $T_g \sim 100^\circ\text{C}$  which also suitable for making capsule but the different between PVC and PMMA that made it more commercial used is due to their processability (Chakrabarti et al., 2004). PVC has low thermal stability compare with PMMA due to chlorine atom, Cl.

### 2.2.2 Self-Healing Thermoset Materials

Thermoset material forming irreversible bonding once it cured which cannot be recycle, reshaped or melt. This type of polymer is widely used in fiber-reinforce polymer (FRP) composite applications. Table 2.2 show thermoset materials with a few healing approaches. According to table below, epoxy is a common thermoset material that be used for self-healing thermoset. Epoxy can be used as reservoir or healing agent in healing system due to its low cost and high healing efficiency (Jin et al., 2012). In addition, epoxy have excellent chemical, mechanical and physical properties cause it widely used in industry (Chowdhury et al., 2015). Epoxy also is a brittle material that suitable to be used as reservoir of healing agent. Therefore, healing capability of epoxy can be achieved through vascular and encapsulation methods.

Table 2.2 : Common self-healing approaches for thermoset materials

<b>Materials</b>	<b>Healing Approach</b>	<b>References</b>
Polydimethylsiloxane	Encapsulation	(Rule et al., 2007)
Epoxy	Encapsulation	(Jin et al., 2012; Varley and Charve, 2012)
Epoxy	Vascular	(Cuvelier et al., 2017)
Polyurethane	Reversible covalent bond	(Cao et al., 2017)
Polyketone	Covalent and hydrogen bonding interaction	(Araya-Hermosilla et al., 2016)

### **2.2.3 Self-Healing Elastomer Materials**

Natural rubber consists of hydrocarbon atoms that forming crosslinking by presence of vulcanization agent such as sulphur. Irreversible bond of natural rubber impart the mechanical properties of the rubber but lack of healing ability. This is because the formation of crosslink in rubber matrix provide stable network. Since NR is cured using sulphur vulcanization agent, the formation of disulphide and polydisulfide bonds within the rubber matrix are there. Number of sulphide bond is depend on amount of accelerator and sulphur used (Hernández et al., 2016). The sulphide bond offer the potential of healing ability to natural rubber but required external stimulus to trigger the damaged. The stimulus for example heat is presence in order to allow temporary local mobility to the rubber forming new linkage. In other word, natural rubber required modification of crosslinking to impart healing ability. Therefore, natural rubber difficult to being used as healing material.

Epoxidized Natural Rubber (ENR) and Poly(urea-urethane) (PUU) elastomer are commonly used materials designed for self-healing elastomer as shown in Table 2.3. ENR made up with epoxide group lead to healing capability (Xu et al., 2016). ENR have low degree of crosslinking which allowed interdiffusion of rubber chain with oxirane group to form new linkage as a result of healing process. PUU consist with hard and soft segment. It can formed healing ability based on hydrogen bonding due to presence of N-H from urea and urethane. Hydrogen bond is considered as weak bond that highly dynamic which can be used as designed interaction for healing ability (Zechel et al., 2017).

Table 2.3 : Common self-healing approaches for elastomeric materials

Rubber	Healing Approach	References
NR	Ionic and hydrogen bonding interaction	(Canadell et al., 2011; Hernández et al., 2016; Luo et al., 2016; Grande et al., 2015)
PUU elastomer	Dynamic crosslink	(Martin et al., 2014; Martin et al., 2016)
ENR	Ionic Interaction and Dynamic crosslink	(Rhaman et al., 2011; Rahman et al., 2013; Imbernon et al., 2015)
PDMS	Hydrogen bonding	(Zhang et al., 2017)
Polyurethane elastomers	Ionic and hydrogen bonding interaction	(Daemi et al., 2016; Comí et al., 2017)

### 2.3 Self-Healing Approaches

To date, self-healing capability of polymer can be achieved based on two approaches which are extrinsic and intrinsic system as illustrated in Figure 2.1. Some of well-known extrinsic self-healing is capsule-based self-healing and vascular network self-healing. Self-healing also can be achieved via intrinsic approach based on covalent bond, ionic interaction and dynamic bonding.

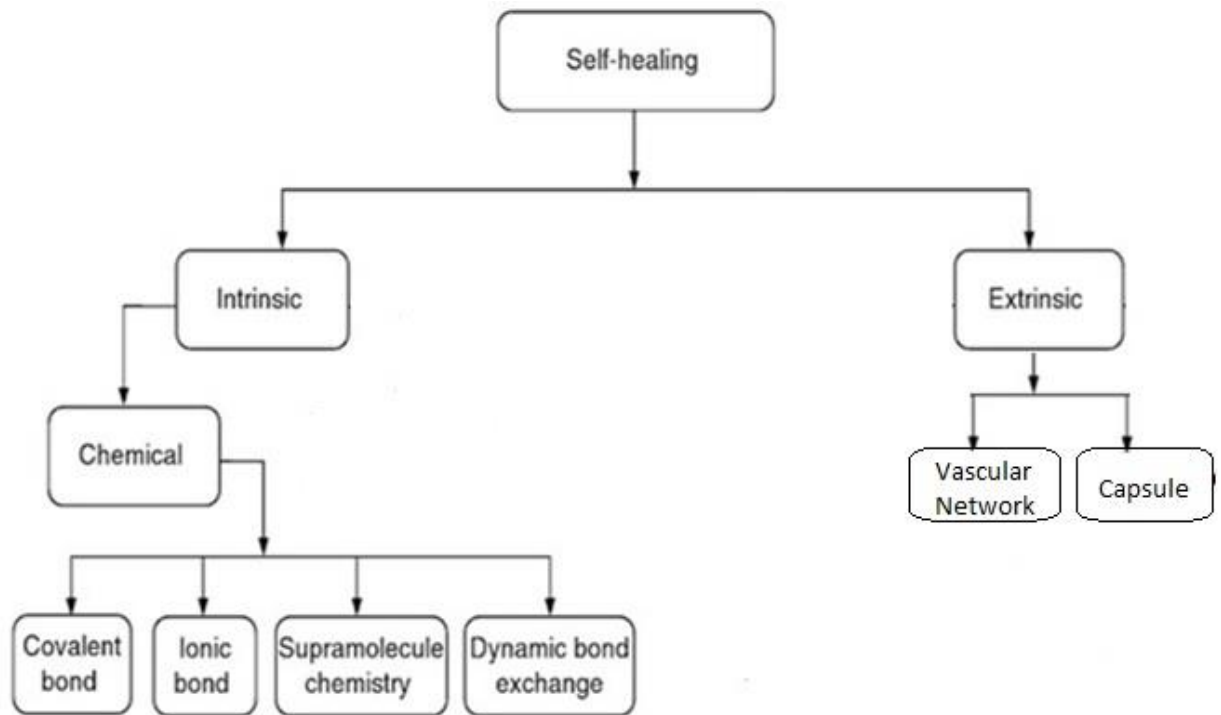


Figure 2.1 : Categories of self-healing approaches (Li 2014)

### 2.3.1 Extrinsic Self-Healing

Extrinsic self-healing system is the system where the healing agent is stored in structure either in form of microcapsule, hollow fiber or vascular network that embedded inside the polymer matrix (Blaiszik et al., 2010). General concept in this approach is once the damage occurs, the structure containing healing agent for example dicyclopentadiene (DCPD) will be broken realising healing agent at the particular network area (Canadell et al., 2011). The damage area is considered heal after the healing agent solidified through physical and chemical interaction between healing agent and polymer matrix as shown in Figure 2.2. As a result from this mechanism, the crack growth can be minimize and prevent failure happened to structure which allow the longer service life of product.

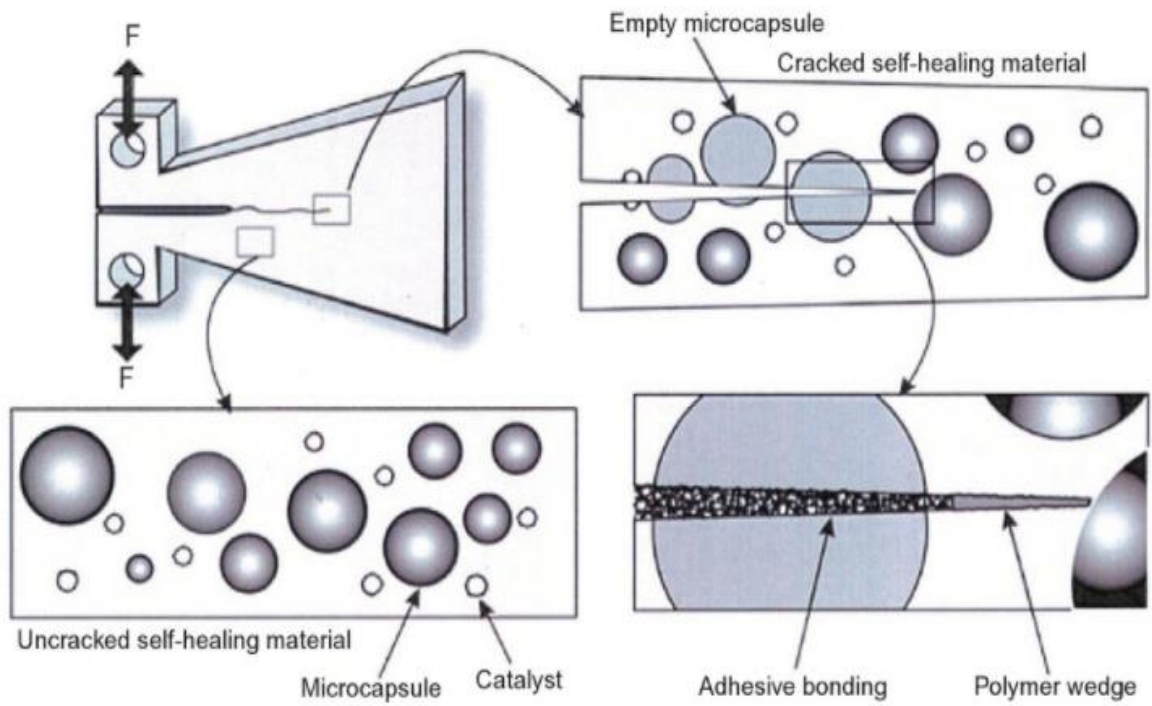


Figure 2.2 : Schematic illustrated mechanism of self-healing material based healing agent (Hughes 2015)

### **2.3.1.1 Capsule-based Self-Healing Materials**

The most commonly used structure for extrinsic self-healing is microcapsules because it is easy to embed the microcapsules healing agent in the polymer matrix using a conventional processing technique and does not require changing in molecular structure to enhance self-healing ability. The healing agent can be stored in an encapsulated reservoir such as a reactive chemical, suspension, solvent or low melting point metal (Zhu et al., 2015). Generally, microencapsulated healing agent is embedded inside a matrix that contains a catalyst where the catalyst will react with the healing agent. During the damage, the microcapsule will break and release the healing agent.

Microencapsulated healing agent can be produced through polymerization processes such as in-situ polymerization, interfacial polymerization and emulsification. According to Keller and Crall (2018), the first microcapsule was synthesized through an emulsification process based on urea-formaldehyde (UF). It is interesting to note that the microcapsule can be made in spherical or irregular shapes and the size may vary from nano-size to micro-size. However, to design a microcapsule for self-healing applications, a few parameters of the microcapsule should be considered such as wall thickness, stiffness and the interface with the polymer matrix in order to get better self-healing efficiency (Awaja et al., 2016). The important factors that influence the development of capsule-based self-healing materials are due to an inexpensive manufacturing process and exhibit room temperature polymerization (Ghosh 2009).

This encapsulation method has some limitations where multiple repairs cannot be performed at the same location due to a lack of the healing agent contained in the microcapsule. An insufficient quantity of healing agent cannot trigger the healing capability of the material (Ghosh 2009). Encapsulation can be performed for thermoplastic and thermoset materials but not for elastomeric materials because during the compounding process, the elastomer is subjected to high shearing forces which will break and rupture the capsule (Binder 2013).



### **2.3.1.2 Vascular Network**

As mention before in Section 2.3.1.2, encapsulation method does not allow the repeating healing to be happen due to rupture of capsule structure and insufficient healing agent stored. Therefore, the vascular network was design to overcome the problems (Yuan et al., 2008). Vascular network is a self-healing network that used hollow fibres or mesoporous network as reservoir (Dry and Sottos, 1993; Toohey et al., 2009). The principle used in vascular network is similar with capsule approach where the healing agent is embedded in fiber or network capillary and released when damaged occurs. . However, the system used by vascular network is opposite with capsule-based system. The vascular system introduced the healing agent after the network has been integrated into matrix while the capsule system directly dispersed in a melt polymer.

Vascular system required accurate choice of healing agent in term of surface wettability, chemical reactivity and viscosity. High viscosity or unfavourable wetting properties prevent efficient filling of the network since the network has been integrated into the matrix. These properties should be considered to prevent damaged on vascular design since the vascular used to transport the healing agent.

The most common approach is the use of individual hollow fiber due to it behaviour. It has both microcapsule-based and hollow fiber-based self-healing (Mookhoek et al., 2012). Furthermore, using this type of fiber can activated localized healing response.

### **2.3.2 Intrinsic Self-Healing**

Intrinsic self-healing system is a system that is capable to repair damage through reversible bonding in polymer matrix and most commonly required external trigger such as heat, pH or UV light to allow the healing process to occur as shown in Figure 2.3. However, mechanical, electrical, magnetic and photo stimulus also can be applied (Hager et al., 2010). Presence of external stimuli is to enhance polymeric chain mobility and allowed restoration bond at damage area as a heal process (Das et al., 2016).

Intrinsic self-healing can be achieved through reversible covalent bond, ionic interaction and hydrogen bonding multiple times at particular area (Yang et al., 2015; Ghosh, 2009). Furthermore, this approach can be applied to thermoplastic, thermoset and elastomeric materials.

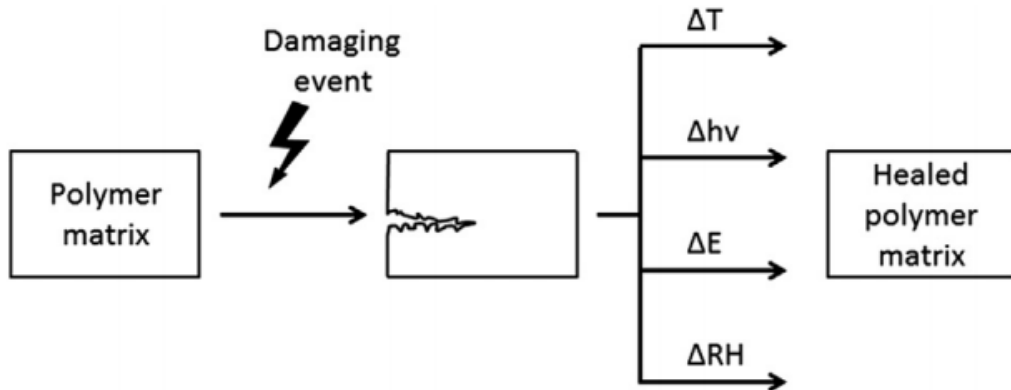


Figure 2.3 : Schematic concept of intrinsic self-healing polymer by presence of external stimuli (Peponi et al., 2016)

### 2.3.2.1 Reversible Covalent Bond

Crosslinks is irreversible bonds that produced in order to impart excellent mechanical properties to polymeric material. However, highly crosslinks in material cause brittleness and lead to formation of crack. Irreversible bond also cause difficulty in reprocessability. Therefore, a new approach is to produce reversible crosslink that can exhibit self-healing properties. In general, reversible bond chemistries need to be trigger by external stimuli such as heat and UV light. The most widely used of reversible bond for self-healing materials is based on Diels-Alder (DA) reaction. Generally, once the damaged is detected, the heat is applied to increase the mobility of damage area to allow bond reformation and heal the damaged. Bis-maleimide tetrafulan as an example of DA crosslinks reaction polymer created self-healing through thermal at low temperature (Das et al., 2016). The healing accomplished by bonding between maleimide group with furan

group in matrix. Disulphide exchange reaction is another type of reversible bond that normally applied for elastomeric material (Martin et al., 2016).

### **2.3.2.2 Supramolecular Interaction**

Intrinsic self-healing approach that can be used is supramolecular interactions. Ionic interaction and hydrogen bonding are examples of supramolecular interactions that designed to form strong association in self-healing. Types of supramolecular interaction are discussed in the following section.

#### **2.3.2.2.1 Ionic Interaction**

Ionic interaction is due to formation of ion pairs associated from metallic cation (Ghosh 2009). Polymer that containing ion species for example metal salt will aggregate and formed cluster. Therefore, the mobility of the polymeric network is changes due to cluster formation that allowed self-healing to be happened. These cluster can be activated by applied external stimuli to the damage area that lead to healing process. Ballistic is an application that used ionic interaction to achieve the healing ability where the heat to trigger the healing process is generated during projectile damage (Rahman et al., 2013). Interesting to note that this interaction allowed for multiple healing event to occur at same damage area due to reversible cluster formation (Yuan et al., 2008).

#### **2.3.2.2.2 Hydrogen Bond**

The most popular supramolecular interaction is based on hydrogen bonding. To perform self-healing capability, the chain should able to performed remodeling of network after damage. Concentration of hydrogen bonds, length and rigidity of polymer backbone are the factors to obtain network remodeling. The idea behind this, when the damage occurred on polymeric material, the hydrogen bond will be broken and cause high density of non-associated hydrogen bonds at the surface. This hydrogen bonds will contact with other cutting surface to form new hydrogen bonding and heal.

## **2.4 Self-Healing Concepts for Natural Rubber**

### **2.4.1 Dynamic Exchange**

Dynamic exchange reaction is an example of reversible covalent bond. Disulfide exchange reaction are the current dynamic covalent systems but required external trigger likes thermal energy, pH change, irradiation or catalytic additives (Garcia 2014). Disulfide bond is commonly used in healing elastomeric materials. However, disulfide bond still required external trigger to allow the healing process to be happened. According to Martin et al. (2014), to allow healing of elastomeric materials to be performed in room temperature without any presence of stimulation, the design of elastomeric network of disulphide exchange should be changes.

#### **2.4.1.1 Thiolate/Nanoparticle Exchange**

Thiolate/nanoparticles exchange is a new design of self-healing system for polymeric material. The principle of this system is that for example silicone rubber, the crosslink network is built between thiol-functionalized polydimethylsiloxane (PDMS) and silver nanoparticles (AgNPs) through synthesis (Martin et al., 2016). In Figure 2.4, it can be seen the healing process involving thiolate-silver interaction. Once damaged was detected, the silver(I)-thiolate species rearrange and bond with nearby AgNPs when the cutting surface place in contact and lead to full recovery of network in 24 hours after damaged.

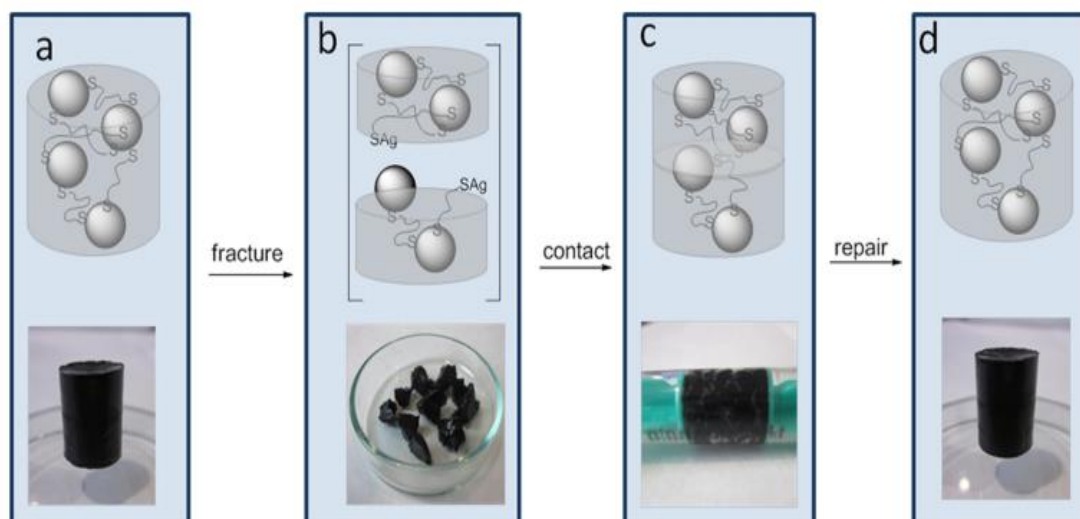


Figure 2.4 : Example of thiolate/nanoparticles exchange network performed healing process (Martin et al., 2016)

#### 2.4.1.2 Aromatic Disulfide Exchange

Aromatic disulphide exchange is one of the changes made to alter the healing capability of elastomer. Aromatic disulphide was proposed in designing elastomeric networks to allow the healing to be happened in room temperature without presented any stimulus. This aromatic disulphide was first applied in poly(urea-urethane) (PUU). The mechanism of this method is based on reshuffling of dynamic crosslinks. Once the damage is detected, the aromatic disulphide bonds undergo homolytic cleavage to form free radicals due to lowest bond energy dissociation. The sulphides are rearrange to form new disulphides group with adjacent chains. With presence of dynamic crosslink, it promoted to interfacial reshuffling of disulphide. The fracture heal after reach the equilibrium condition. The aromatic disulphide reaction is illustrated in Figure 2.5. This approach is widely used in industrial applications such as sealants, paints and coatings.

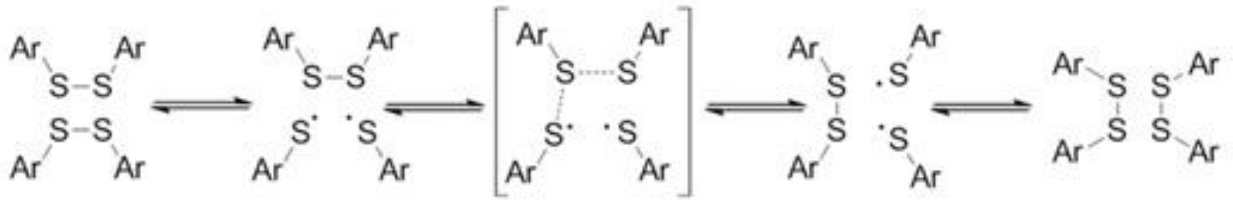


Figure 2.5 : Example of aromatic disulfide exchange network performed healing process (Martin et al., 2016)

### 2.4.1.3 Gold (I) Thiolate/Disulfide Exchange

Gold(I)-thiolate/disulfide exchange also been introduced in order to introduce self-healing for elastomer that consist with disulfide bridge and gold(I)-thiolate as shown in Figure 2.6. The thiolate is blocked with gold to prevent oxidation happened which can reduced concentration of reactive thiolates. If this situation occurred, the self-healing capability of material in room temperature will lose. The idea behind this is to reconnect gold(I)-thiolate/disulfide exchange after damaged by rearrange disulfide bond with neighboring sulfur in order to form new network as a resulted of healing process.

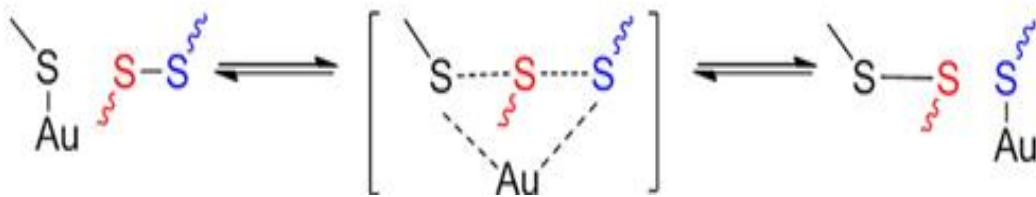


Figure 2.6 : Example of gold (I) thiolate/disulfide exchange network performed healing process (Martin et al., 2016)

### 2.4.2 Ionic Interaction

Electrostatic interactions can be created through ionomer where the polymeric systems containing acid groups neutralized in form of ionic metal salts to form interaction. These ionic metal salts are bonded to hydrocarbon backbone for example natural rubber. As a result, the electrostatic interaction is formed as shown in Figure 2.7 (Garcia 2014). Electrostatic interaction containing ion pair (positive and negative charges) restricted the mobility of rubber chains. Restriction of ionic crosslink to rubber network is due to salt-bonding and multiplets formation of ion pairs into rubber network. All these restriction cause the new kind of crosslinking action. The crosslink created is form of physical crosslink that are reversible in nature which allowed the healing process to be happened.

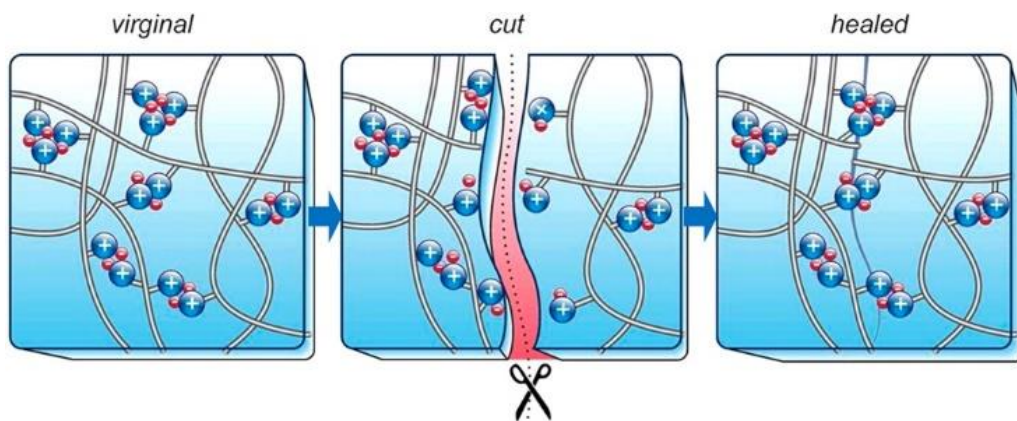


Figure 2.7 : Simplified representation of ionic interaction healing process (Das et al., 2015)

### 2.5 Impact of Self-Healing Natural Rubber

Development of natural rubber based product with self-healing capability may cause significant impacts toward economy, social and environment. Traditionally for some application such as tire, bridge bearing, dock fender and dynamic seals required human intervention to identify, modify and repair the damage. In most cases a routine inspection and periodically maintenance results in identification of the damage; without this maintenance the damage goes undetected until failure occurs. When the damage is

detected, it requires human intervention to replace or repair the system. Development of materials that can detect and heal themselves appear to be possible way to reduce human interaction with the system, minimize down time and reduce the need for part replacement. Furthermore, for some applications, it required high cost and a lot of labour to replace the damage system. The ability of the materials to heal damage might significantly reduce the chance of failure and reduce the maintenance costs.

Besides, in social, self-healing capability helps in enhanced safety of product. For example in tire application, if the tire puncture during driving, the puncture area will be healed autonomously and the vehicles still can continue moving without tire flat. This able to reduce accidents to be happened.

Waste has been a major environmental issue around the world especially when the industrial become important. The world is faced with the increases amount of waste especially involving tires. Waste can comes in many sizes and types such as liquid, solid and hazardous. Since the rubber consists with crosslinking, it cannot be melt or burn. This may cause problems to the earth. Thus, self-healing capability become more important for rubber applications. By presence of self-healing capability of natural rubber, it able to prevent environmental pollution by extend shelf life of rubber product which can minimize rubber waste. At the same time, this able to saving energy due to less consumption of natural rubber for manufacturing.

## **2.6 Applications Self-Healing Elastomer**

### **2.6.1 Tire**

Natural rubber is the main material in producing tire due to highest failure strain and unbeatable in terms of damping performance, resistance to wear, creep and cyclic deformation. Puncture is an often phenomenon that always occur on tire. It required replacement or repair where cause abundance of waste tire and also costly. Besides, if the tire puncture during driving, it will cause accident due to tire flat. By presence of self-healing for tire application, it able to overcome those problems. Due to this reason,



researchers at Harvard University have developed a potential self-healing rubber for flat tire. They were produce an imidazolium-modified BIIR that forms a cross-linked network by reversible ionic association to overcome the problem. The healing process is due to reversibility of ionic association trigger by heat as shown in Figure 2.8.

Furthermore, Goodyear also took a challenge to design built-in sealant for truck applications to allow the tire remain in service until it is retreaded. At the same time, the tire can be used even though it already puncture. Goodyear used DuraSeal Technology that consist with yellow gel-like rubber compound to recover puncture area (Zhang and Rong 2011). The advantages of this design where the healing action can be repeated, does not required reapplied sealant on tread and the life time of tire truck six times longer than conventional tire.

Continental AG, Finixx New Technology Co. Ltd and Tianyee Tire Co. Ltd are companies that already deal with self-healing for tire applications. Continental AG designed ContiSeal that cover inside tread with preapplied sticky. By right, this tire is fitted on Volkswagen Passat CC. Finixx is offered by Finixx New Technology Co. Ltd used Mix SIS material to allow healing process on tire during puncture. Interesting method of healing is used by Tianyee Tire Co. Ltd which the inner tire is sprayed by thin layer of rubber compound and the healing can be occurred at temperature range  $-35^{\circ}\text{C}$  to  $110^{\circ}\text{C}$ .