PREPARATION AND PROPERTIES OF INTRINSIC SELF-HEALING NATURAL RUBBER

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PREPARATION AND PROPERTIES OF INTRINSIC SELF-HEALING NATURAL RUBBER

by

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LIST OF SYMBOLS

λ	Extension ratio
HE	Healing efficiency
X	Crosslink density
V_0	Molar Volume
Tv	Transition temperature
Φ_r	Volume fraction of swollen rubber
ρ_1	Density
phr	Part per hundred rubber
^{0}C	Degree Celcius
^{0}C/min	Degree Celcius per minute
cm^{-1}	Reciprocal centimeter
cm^3	Cubic centimeter
dNm	Deci newton metre
g	Gram
kJ/mol	Kilo joule per mole
m	Meter
mm	Millimeter
mm/min	Millimeter per minute
mol/cm^3	Molar concentration per cubic centimeter
MPa	Megapascal

LIST OF ABBREVIATIONS

AMI	Automic Materials
BIIR	Bromobutyl Rubber
BIS A	Bis (4-Aminophenyl) disulphide
BR	Polybutadiene Rubber
CR	Chloroprene
DA	Diel-Alders
DCP	Dicumyl Peroxide
DSC	Differential Scanning Calorimetry
EB	Elongation at break
EDA	Ethylenediamine
ENR	Epoxidized natural rubber
EPDM	Ethylene-propylene-diene Monomer
FTIR	Fourier-transform infrared spectroscopy
MAA	Methacrylic acid
NR	Natural rubber
OM	Optical Microscopy
PDMS	Polydimethylsiloxaneane
pH	Power of Hydrogen
PU	Polyurethane
SEM	Scanning Electron Microscopy
TEM	Transmittance Electron Microscopy
Tr	Tear strength
TS	Tensile strength
UV	Ultraviolet
XNBR	Carboxylated Nitrile Butadiene Rubber
XSBR	Carboxylated Styrene Butadiene Rubber
ZnO	Zinc oxide
ZT	Zinc Thiolate

PENYEDIAAN DAN CIRI-CIRI INTRINSIK GETAH ASLI PENYEMBUHAN DIRI

ABSTRAK

Getah sembuh sendiri adalah satu bahan kumpulan baru yang mempunyai keupayaan untuk memulihkan kerosakan tanpa proses baik pulih manual. Kerja-kerja yang dijalankan dalam tesis ini mengkaji potensi getah asli penyembuhan sendiri intrinsik berasaskan rangkaian ionik logam tiolate boleh balik, ikatan terma boleh balik garam Zn^{2+} dan penukaran terma boleh balik disulfida. Logam tiolate ditambah ke dalam getah asli (NR) dengan menggunakan sistem vulkanisasi peroksida dengan kandungan zink tiolate yang berbeza (0, 10, 20, 30, 40 phr). Spektroskopi inframerah transformasi Fourier (FTIR) dan analisis ketumpatan pembengkakan membuktikan pembentukan rangkaian ionik logam tiolate. Sifat tegangan dan kekuatan koyakkan masing – masing pulih 90 %, dan 132.6 % apabila sampel yang putus dicantum selama 10 minit pada suhu bilik. Jangka hayat lesu sampel meningkat sebanyak 60% berbanding dengan sampel yang tiada penyembuhan sendiri. Pendekatan ikatan terma boleh balik garam adalah berasaskan kepada interaksi antara ion Zn^{2+} daripada agen sambung silang zink tiolate dan kumpulan karboksi daripada asid metakrilik (MAA) yang dicantum pada rantaian NR pada kandungan berbeza (0.5, 0.7, 1.0, 1.5, 2.0 phr). Bukti ikatan garam Zn^{2+} diperolehi melalui analisis FTIR. Keputusan mendedahkan bahawa bahan tersebut pulih 76% di bawah mod tegangan dan 100% di bawah mod koyakkan dan ujian jangka hayat lesu. Untuk pendekatan penyembuhan sendiri melalui penukaran terma boleh balik disulfida, rantaian getah asli dicantumkan dengan Bisfenol A (BIS A) pada kandungan yang berbeza (0, 2, 5, 7 phr). Bukti pembentukan rangkaian disulfida diperolehi daripda analisis FTIR. Keputusan mendedahkan bahawa bahan tersebut pulih pada 150 ^{0}C.

PREPARATION AND PROPERTIES OF INTRINSIC SELF-HEALING NATURAL RUBBER

ABSTRACT

Self-healing rubber is a new group of smart material which has the ability to restore the damages without manual intervention. The work carried out in this thesis explored the potential of intrinsic self-healing natural rubber based on reversible metal thiolate ionic networks, thermo-reversible Zn^{2+} salt bonding and thermo-reversible disulphide exchange. The metal thiolate was added in natural rubber (NR) compound through peroxide vulcanization system at different zinc thiolate content (0, 10, 20, 30, 40 phr). Evidence for reversible metal thiolate ionic networks was obtained through Fourier-transform infrared spectroscopy (FTIR) and swelling density analysis. The tensile properties and tear strength recovered at 90 %, and 132.6 %, respectively when the broken sample was brought into contact for 10 minutes at room temperature. The fatigue lifespan of the materials increased by 60 % compared with the non-self-healing sample. Thermo-reversible salt bonding approach is based on the ionic interactions between Zn^{2+} ions from zinc thiolate crosslinker and carboxyl groups which were introduced by grafting different content of methacrylic acid (MAA) (0.5, 0.7, 1.0, 1.5, 2.0 phr) onto NR chains. Evidence for Zn^{2+} salt bonding was obtained from FTIR analysis. The results revealed that the materials able to recover up to 76 % under tensile mode and 100 % under tear mode and fatigue test. For self-healing approach through thermo-reversible disulphide exchange, the NR chain was rafted with different Bisphenol A (BIS A) content (0, 2, 5, 7 phr). Evidence for disulphide networks was obtained from FTIR analysis. The results revealed that the materials able to recover up at 150 ^{0}C.

CHAPTER 1

INTRODUCTION

1.1 Background of study

Rubber is widely used in engineering applications such as tyres, bearings, shoe soles, gaskets, hoses, and cables due to its outstanding dynamic performance, as well as resistance to wear, creep, and cyclic deformation. Normally, rubber products require humans to recognize, identify, and repair damages during service. In most cases, routine inspection results in the identification of the damage without this maintenance, the damage could go undetected until a catastrophic failure occurs. Furthermore, irreversible sulphur or peroxide cross-linked networks in vulcanized rubber could impede the possibility of reprocessing and recycling rubber products. This critical issue has resulted in the scrapping of hundreds and thousands of tonnes of rubber goods in the automotive industry, the construction industry, and daily occurrences, all of which threaten available resources and degrade the environment. A viable evolution to the rubber industry is therefore required to produce more sustainable rubber products (Thomas and Stephen, 2010). Integrating the self-healing concept to rubber is one of the captivating approaches in the recent development of smart materials. This concept refers to the ability of a product to recuperate spontaneously when it is damaged without undergoing any changes in structural reliability (Wang et al., 2016, Chakrabarti et al., 2004, Miwa et al., 2019).

In general, self-healing rubber can be fabricated using extrinsic and intrinsic methods. An extrinsic system involves a healing agent encapsulated and embedded in a rubber matrix. When the material cracks, the healing agent is released and covers the damaged site and restores its function; however, healing is limited to single localized damage. Moreover, the processing of rubber, which generally requires high shear forces during mixing and compounding, tends to break down the capsules (Blaiszik et al., 2010, White et al., 2001). In comparison, the intrinsic method consists of complex reversible chemical bonds within the material that permits multiple healing at the equivalent location (Zechel et al., 2017a, Bekas et al., 2016a). The reversible chemical bonds can be initiated via the Diels–Alder reaction (Chen et al., 2002, Chen et al., 2003), radical-based systems, disulphides exchanges (Nevejans et al., 2016, Martin et al., 2016, Lei et al., 2014), hydrogen or halogen supramolecular interactions as well as ionic interactions (Chen et al., 2012, Cordier et al., 2008b, Rahman et al., 2012, Hohlbein et al., 2015, Jiang et al., 2010, Wang et al., 2016, Zechel et al., 2017a). These reversible bonds have opened up an entirely new way to reshape and reconstruct cross-linked rubber (Zhong and Post, 2015a, Rahman et al., 2013).

1.2 Problem statement

At present, strategies for introducing intrinsic self-healing rubber are mainly focused on synthetic rubbers such as ethylene propylene diene monomer (EPDM), polydimethylsiloxane (PDMS), polyurethanes (PU), carboxylated styrene-butadiene rubber (XSBR), and bromobutyl rubber (BIIR) (Jia et al., 2020, Yu et al., 2019, Kim et al., 2020, Zechel et al., 2017b). The reversibility and self-healing performance of these rubbers has been extensively investigated, but the self-healing behaviour requires external stimuli to initiate the healing process. Furthermore, although test results have been positive, most of the self-healing rubbers that have been developed have failed to meet the specifications for end applications (Xu et al., 2016c, Zheng and McCarthy, 2012, Das et al., 2015, Hernández et al., 2016a), probably due to the long-term stability of the associated reversible network within synthetic rubbers.

Natural rubber is non-polar and has no available functional groups that can be converted into reversible physical or chemical interactions; hence, posing a challenge to the development of rubber-based materials that can self-heal at room temperature (Ghosh, 2009, Hernández Santana et al., 2018, Kohjiya, 2014, Speck et al., 2013). The challenge in developing self-healable rubber is to balance the self-healing function and mechanical properties of the materials without sacrificing any one of these two properties. The reason why it is difficult to obtain both desired properties at the same time is that self-healing behaviour of rubber depends on the flexibility of dynamic reversible crosslink networks while the mechanical performance relies on the rigid and stable covalent crosslink networks instead (Hernández et al., 2016b).

Xu et al. (Xu et al., 2016a) introduced a practical approach by integrating an ionic reversible network into natural rubber. However, the study provided no direct evidence to confirm that the ionic reversible network was successfully grafted onto the natural rubber molecular chains, which limits further research into the essence of reversible rubber network formation and the correlation between the properties and the molecular structure of the self-healing natural rubber. Although the material was able to recover its properties at room temperature, the tensile strength was lower at 0.63 MPa, so it is not suitable for practical application. In particular, Liu and et al. demonstrated the self-healing natural rubber by incorporating weaker sacrificial hydrogen bonds and more robust Zn-based units. The dynamic nature allows the sacrificial bonds to be ruptured and re-formed, but it cannot return to its original length and leave a notable residual strain. The recovery process is prolonged, and the stress−strain curve does not completely recover, including the reorganization of the re-formed bonds between the rubber chains (Liu et al., 2016). Recently, it has been demonstrated that the introduction of ionic association into the epoxidized natural rubber is an effective method for achieving rubber-based self-healing behaviour. Nevertheless, the self-healing functioning on epoxidized natural rubber at 80 ^{0}C is minimal as it requires heat-induced self-healing (Liu et al., 2019). Xiang et al. (Xiang et al., 2015a) studied the disulphide metathesis between polysulfides and polybutadiene rubber (BR) with complex catalyst $CuCl_2$ which the rearrangement capability of these polydisulphide networks allowed them to be reprocessed and recycled. Limited work has been carried out to further improve the mechanical properties of the self-healing rubber through disulphide exchanges especially natural rubber.

1.3 Research objectives

The main focus of this research is to develop a new self-healing natural rubbers (NR) based on the reversible dynamic crosslinks that can self-heal when damaged without manual intervention. The specific research objectives are as listed as follows:

I. To develop a self-healing natural rubber (NR) based on reversible metal thiolate ionic networks that able to self-heal without any stimuli

II. To develop a thermo-reversible self-healing natural rubber based on Zn^{2+} salt bonding.

III. To develop a self-healing natural rubber based on thermo-reversible dynamic sulfide exchange.

1.4 Outline of the thesis

This thesis is divided into five chapters. Each chapter covers the research interest as mentioned under the research objectives section:

Chapter 1: Represented the introduction part of the thesis, which offered the background, problem statement and objective of the thesis.

Chapter 2: Provide the literature review related to self-healing natural rubber and extensive review of the methods used to introduce self-healing ability on the materials.

Chapter 3: Represented the experimental procedure involved in the preparation of self-healing rubber. provide detailed explanation of materials and chemicals, as well as equipment and testing procedure including the specification and variables used in the research.

Chapter 4: Discuses the data and results obtained from the research according to the objectives.

Chapter 5: Denoted conclusion on the current work as well as suggest recommendation for future work.

1.5 Scope of study

The first stage of this study focuses on the effect of zinc thiolate which involves reversible ionic networks for the preparation of self-healing natural rubber. In the second stage of study, the self-healing natural rubber was prepared using different content of methacrylic acid in order to assess the formation of thermo-reversible salt bonding in the grafted natural rubber The third stage of study focuses on the reaction between dynamic disulphide networks, bis (4-Aminophenyl) disulphides and natural rubber matrix. The morphology characteristics, mechanical properties and elemental characteristics were investigated for all stages.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction of self-healing in rubber

Rubbers play an imperative role in modern technology which serve as one of the main components for vehicle tires, seals, damping systems, soft robotics, wearable electronics and medical appliances. Raw rubbers need to be chemically crosslinked through the vulcanisation process in constructing persistent shaped components which offer high toughness, excellent vibration damping properties, and chemical and thermal stability (Hernández Santana et al., 2018, Backman, 2018). However, vulcanised rubbers with permanent covalently crosslinked networks cannot be reprocessed, reshaped or recycled (Wemyss et al., 2020). Thus, the self-healing ability can be introduced to the vulcanised rubbers with the capability to arrest crack propagation at an early stage thereby preventing catastrophic failure.

Self-healing rubber materials are a new class of smart materials that capable of repairing themselves and recovering is functionality when the materials are damaged without the need for detection or repair by the manual intervention (Hager et al., 2010). Self-healing capability of the material would also be expected to extend the lifetime of the material as well as restoring the material performance that contributes to the safety and durability of the components. Table 2.1 shows the common self-healing rubber materials. It can be seen that self-healing research has been carried out both natural and synthetic rubber via different approaches. The limitation of these rubber materials stated in Table 2.1 is that they need external stimulus such as temperature and pressure to activates these self-healing mechanisms.

Table 2.1 Common self-healing approaches for rubber materials

Rubber materials	References
NR	(Canadell et al., 2011, Hernández et al., 2016b, Luo et al., 2016, Grande et al., 2015)
PUU elastomer	(Martin et al., 2014, Martin et al., 2016)
ENR	(Rahman et al., 2012, Rahman et al., 2013, Imbernon et al., 2015)
Bromobutyl Rubber (BIIR)	(Le et al., 2017)
PDMS	(Zhang and Rong, 2011a) (Zechel et al., 2017a)
PUU	(Daemi et al., 2016, Comí et al., 2017)
Carboxylated Styrene Butadiene Rubber (XSBR)	(Xu et al., 2016c, Xu et al., 2019)

2.2 Classification of self-healing methods in rubbers

Self-healing rubbers are always on the top of the wish list of researchers. A rubber displaying self-healing properties needs the ability to transform physical energy into a chemical and physical response which able to heal the damage. To date, the self-healing materials for rubber can be classified broadly into two groups: extrinsic and intrinsic systems as illustrated in Figure 2.1. Intrinsic self-healing process occurs through a chemical mechanism which is built inside the material. These chemical mechanisms included covalent bond, ionic bond, intermolecular force and supramolecular interaction which can be dynamically re-bond when there is damaged (Billiet et al., 2013). Extrinsic self-healing process involved the addition of a structure such as microcapsule-based materials into the rubber matrix. Damage in the form of a crack is the external trigger which initiates healing for both intrinsic and extrinsic healing mechanisms. The materials regain their initial properties after the healing process finished (Keller and Crall, 2018).

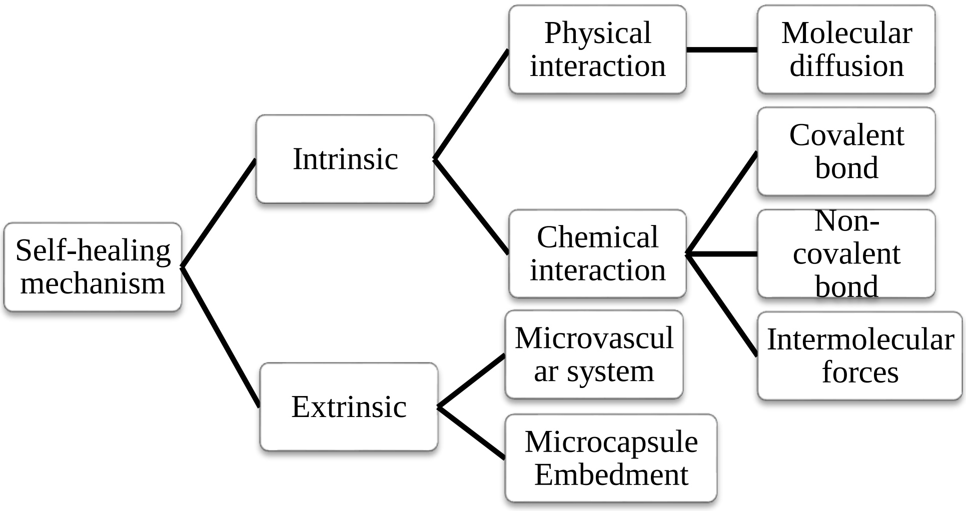

Figure 2.1 Categories of self-healing approaches (Subramanian and Varade, 2017)

2.3 Extrinsic self-healing

An extrinsic self-healing system is a system where the self-healing property is obtained by adding healing agents to the material to be repaired either in the form of a capsule, hollow fiber or vascular network (Blaiszik et al., 2010). Either in a capsule or a vascular-based system, upon a damage-induced cracking, the self-healing mechanism is triggered by the rupture of capsules or vascular network and subsequent release of the healing agent in the affected region (Billiet et al., 2013). The damaged area is considered to heal after the healing agent solidified through physical and chemical interaction between the healing agent and rubber matrix as shown in Figure

2.2. As a result of this mechanism, the crack development can be reduced and allowing a longer service life of the product which halts catastrophic failure that occurred to structure. Advantage of extrinsic self-healing is that it does not require any intimate contact on the region of the crack which is suitable for healing a broader range of damage volumes. On the other hands, the main drawbacks of extrinsic healing mechanism include expensive catalyst and the self-healing process can occur only once due to the concentration of healing agents were reduced in the healed region (Thakur and Kessler, 2015).

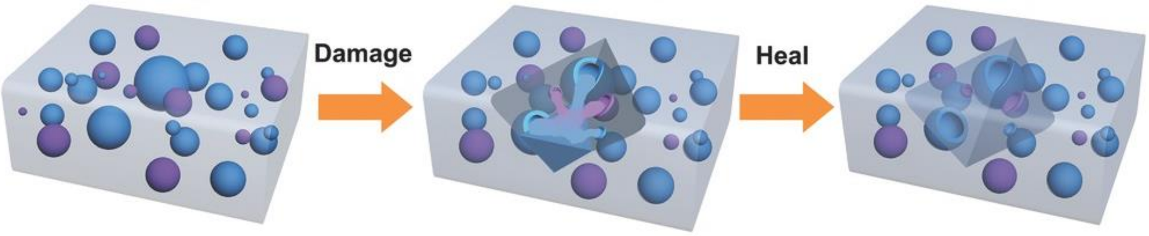

Figure 2.2 Schematic illustrated mechanism of self-healing material based healing agent (Chen et al., 2017)

2.3.1 Microcapsule –based self-healing materials

Microcapsule embedment approach is one of the successful techniques for extrinsic self-healing. Microcapsules consist of two parts which are core and shell, chemically unreactive to each other. Microcapsules can be either in spherical or irregular shapes and may be varied in size from nano to microscale. The healing agent can be stored in an encapsulated reservoir such as reactive chemical, suspension, solvent or low melting point metal (Zhu et al., 2015). The capsules filled with a healing agent will cracks when the material breaks and the resins solidify in the cracks allowing the material to self-heal. The crack or damage acts as an external trigger which initiates the healing process to take place. During damage, microcapsules released the healing agent and reacted with the embedded catalyst. This terminates further growth of crack or damage and recovers property of the system. After the capsules are incorporated in the rubber material, the mechanical properties, triggering mechanism and healing performance can be characterized. In obtaining an excellent self-healing efficiency using microcapsule, few parameters should be considered such as wall thickness, stiffness and the interface with polymer matrix (Awaja et al., 2016). However, this encapsulation method is limit to only a singular local healing event (Blaiszik et al., 2010) as shown in Figure 2.3.

Keller et al. (2007) used two different types of microcapsules which are resin capsule and initiator capsule to develop polydimethylsiloxane (PDMS)-based elastomers with self-healing capability. In this system, the healing reaction is carried out by hydrosilylation of PDMS resin in the presence of platinum as a catalyst. The self-healing PDMS was able to recover almost 70-100% of its original tear strength. It was found that addition of microcapsules resulted in the increasing tear strength of PDMS. The effect of microcapsules size on the self-healing efficiency was further investigated. Xiu Liu et al. (2012) prepared a smart self-healing coating consisted of an epoxy resin (diglycidyl ether of bisphenol A) as matrix and microcapsules filled with the same polymer as curing agent. Capsules were synthesized by interfacial polymerization of epoxy droplets with ethylenediamine (EDA). These microcapsules exhibited high shell strength while they could rupture under external force, releasing the healing agent to the damaged area. The encapsulation technique must be ideal and user friendly which the healing agent should chemically inert. These capsules must have good compatibility with the surrounding polymer matrix to promote good adhesion and maximize the healing process(Liu et al., 2012).

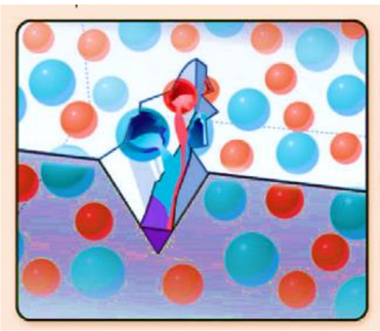

Figure 2.3 Schematic diagram of capsule-based self-healing for singular local healing event (Blaiszik et al., 2010)

2.3.2 Vascular network

Vascular self-healing approach is gaining attention in engineered self-healing materials since Dry et al. (1996) introduced a hollow-tube-based self-healing technique in the 1990s. The idea of self-healing system based on the microvascular method is originated from the respiratory system of livings. The vascular network is capable of supplying a larger volume of a healing agent into the polymer network either in the form of capillaries or hollow channels after the network has been integrated into the matrix (Hansen et al., 2009). After the vascular network is damaged and the first delivery of a healing agent occurs, the network may be refilled by an external source or from an undamaged as shown in Figure 2.4. This refilling action allows for multiple local healing events. Vascular-based healing system can exhibit numerous healing events, but to maintain high healing efficiency at higher healing cycles is still a challenge. The vascular system required a precise selection of healing agents in terms of surface wettability, chemical reactivity and viscosity in permitting efficient filling of the network since the network has been integrated into the matrix (Toohey et al., 2009). Everitt et al. (2015) prepared an epoxy blend as healing agents for the extrinsic self-healing fibre-reinforced composites. Optimised epoxy blends can provide recoveries in fracture toughness of up to 269 %. The infusion of the damage via epoxies embedded vascular which capable of offering complete recovery of stiffness.

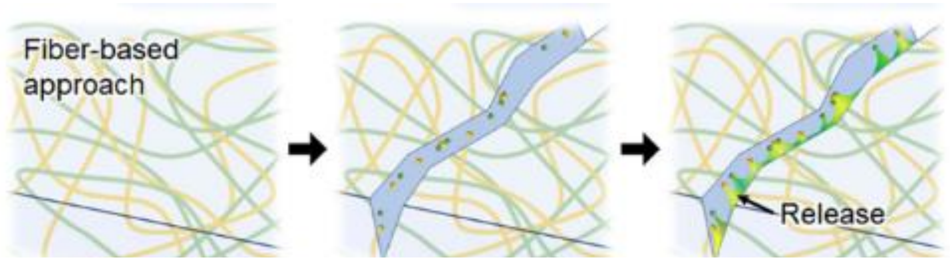

Figure 2.4 Schematic diagram of a vascular network for refilling multiple local healing events (Adriaensens et al., 2000)

2.4 Intrinsic self-healing

Intrinsic self-healing system capable of repairing the damage or fracture due to the ability of material to reflow in the damaged region through a temporary increase in mobility. This is due to inter-chain mobility upon the supply of energy followed by process of restoration of the chemical or physical bond strength upon stimulus removal (Garcia, 2014). Generally, intrinsic healing requires external triggers such as heat, pH or UV light, electrical, or moisture to allow the healing process to occur as shown in Figure 2.5 (Hager et al., 2010, Peponi et al., 2016). Intrinsic self-healing requires no separate healing agents, which is to be preferred but, depending on the material class and healing mechanism, not always feasible. Several concepts of intrinsic self-healing approaches by utilizing ionic interaction, hydrogen bonding, disulphide, Diels-Alder reaction and metal ligands have been reported in the literature (Hernández Santana et al., 2018).

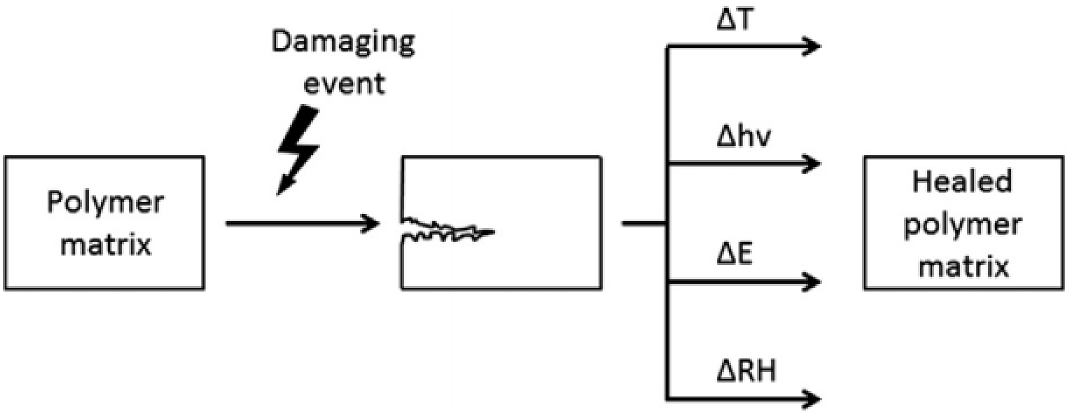

Figure 2.5 Schematic representation of intrinsic self- healing polymer by the presence of external stimuli (Zhong and Post, 2015a)

2.4.1 Heat-induced self-healing

Heat-induced self-healing is initiated on the notion of molecular chain bonds that break into reversible bonds when the heat is introduced. When the material is heated at an elevated temperature, the material turn to a gel-like structure and the cracks on the material disappear by the mobility formed within the material bond. After the healing process, the material is cooled back to room temperature and the broken reversible bonds recovered back to give the material a stable structure under normal conditions. A conventional self-healing mechanism using heat as stimuli is shown in Figure 2.6 (Terryn et al., 2017). Firstly, the material is heated up to allowed the bonds breaking during the heating. The mobility of the material increases permitting the microscopic and macroscopic gaps in contact during the isothermal process. The cooling is performed at a slow rate leading to the recovery of the mechanical properties of the material. Self-healing induced by heat stimuli can be accomplished with reversible chemical crosslink bonds such as dynamic covalent bond and supramolecular interaction. The major pitfall of the heat-induced self-healing system is that it is not an autonomous self-healing (Syrett et al., 2010). Terryn et al. (2017) perform a heat stimulated self-healing rubber composed of a reversible Diels-Alder reaction. It was found that at the point of rupture differ which the mechanical properties of the material almost completely recovered after self-healing.

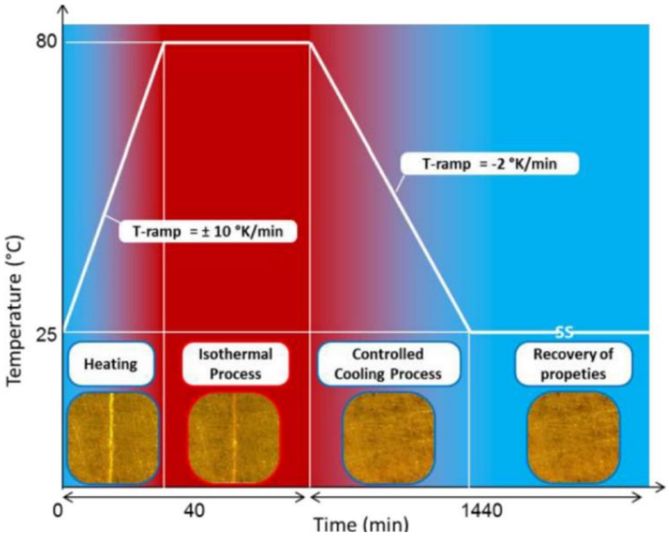

Figure 2.6 Steps occur in the temperature profile of the heat stimulated self-healing process (Terryn et al., 2017)

2.4.2 Light-induced self-healing

Light-induced self-healing is an idea based on the bonds break and reform when a reactive rubber in contact with light stimulus. When the cracks formed in the rubber structure, the capsules located on the path of crack propagation could be ruptured followed by the release of the healing agent into the crack. When the UV light was projected to the crack or the cracked area was exposed to long-term solar light radiation, the self-healing is realized through the crosslinking of the repairing chemicals in the region of damage (Lv et al., 2020). Light mediated self-healing can be accomplished using three different approaches such as cycloaddition, reshuffling of covalent bonds and photothermal effect (Backman, 2018). Cycloaddition involves photo crosslinking reaction between molecular parts that are photoreactive forms the reversible bonds during light treatment. The UV-light breaks the covalent bonds leading to a combination of new bonds or reshuffling of the covalent bonds which heals the crack on the material. The photothermal effect uses a metal-supramolecular rubber that absorbs UV light. When the rubber heats up over its glass transition temperature while absorbing the UV light, the surface becomes a gel-like substance which fills the crack leading to self-healing mechanism (Habault et al., 2013).

Chung et al. (2004) were the first to develop light-induced self-healing polymer using cycloaddition of cinnamoyl groups. The recovery and healing efficiency of the specimens was up to 19% at higher temperatures. Ghosh et al. (2009, 2011) implemented polyurethane (PU) self-healing networks upon exposure to UV light. The self-healing potential of the PU was tested by making a scratch on the surface and the healing of the scratch was found to be enhanced with increasing UV light intensity. Self-healing with sunlight as a stimulus is desirable, but sunlight is unable to infiltrate the materials deeply, so it only applies to scratches on material surfaces (Mauldin and Kessler, 2010).

2.4.3 Electrical-induced self-healing

The electrically triggered self-healing functions as the electric field appearing in the materials carrying interconnect polarizes, the particles become conductive and chains them up to create a healable material (Parab et al., 2019). This new method involving electrically triggered self-healing was promising for the rubber materials. Although the studies related to electrical-induced is limited, self-healing based on electrical stimuli has excellent potential in electronic application (Zhong and Post, 2015a). Self-healing induced by electrical has already done for polymer as David et al introduced a study of self-healing upon electrical stimulus based on the colloidal aggregation between polystyrene (David L. Milius, 2020). This technology contains two concentric cylinders with an electrical field applied to the system as shown in the following Figure 2.7 which use electrohydrodynamic to close the defect occurred. The colloidal dispersion of polystyrene or silica particles is between the two cylinders which used to repair defects that occur in the inner cylinder when high stress is applied. When a defect occurs in the insulating coating, underneath metal allows the colloidal particles to coagulate around the defect. This process produces a coating at the site of the initial defect which able the material to self-heal.

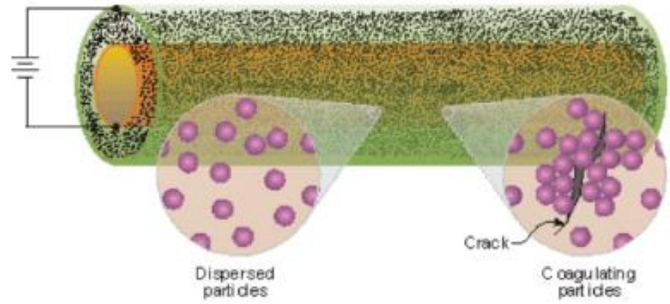

Figure 2.7 A schematic for a self-healing system that uses the electrohydrodynamic coagulation of particles to close a defect (David L. Milius, 2020)

2.4.4 Moisture-induced self-healing

Moisture-induced self-healing is based on a zipper-like healing mechanism which both sides of the crack within the functional contact areas are coupled by reacting with moisture. This process can be extended to the ineffectively contacted regions which result in healing of the crack (Zhong and Post, 2015a). Moisture stimulus that triggers self-healing in polyurethanes urea-based material was reported by Wittmer et al. (2018). FTIR analysis revealed that moisture able to act as a plasticizer interrupting hydrogen bonding interactions within the polymer network leading to possible self-healing materials.

2.5 Mechanisms of self-healing in rubbers

2.5.1 Entanglements

There is no denying that rubbers molecular entanglement and chain mobility are a key factor to facilitate self-healing (Irigoyen et al., 2019). Most of the present intrinsic self-healing rubbers heal the fracture or cut based on physical nature. The fractured of a long rubbers chain re-entangled with other self-healing crosslinkers when the surface is bought in contact to form new molecular entanglements. The rearrangement of rubber chains and the self-healing crosslinker formed a large-scale intermolecular diffusion between the chains over some time leading to the recovery of its initial mechanical properties. The healing mechanism of rubbers introduced by Wool and O'Connor (1982) are presented in Figure 2.8. Throughout the healing period, the molecular chains on the surface rearranged and advanced into random and complete diffusion on a low level making the fracture surface into the original state.

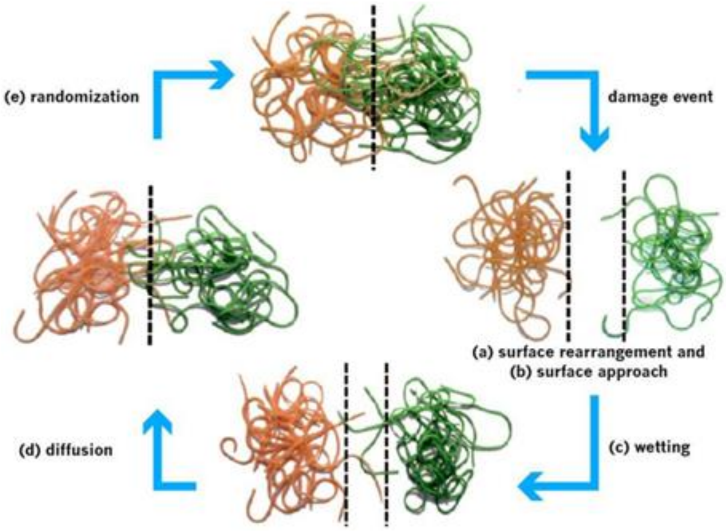

Figure 2.8 Stage of self-healing mechanism (Wool and O'Connor,1982)

2.5.2 Dangling chains and brushes

The dangling chains in the rubber chain are found applicable in designing a self-repairing rubber. The dangling chains of rubber are described as diffusion that utilises the interaction between dangling chains of rubber and branching of the main rubber backbone (Yamaguchi et al., 2012). After diffusion, the dangling chains manage to heal the rubber either by mechanical interlocking or chemical interaction. The dangling chain facilitated the healing process mechanically leading to higher healing efficiency at room temperature. The dangling and bushed of polymeric material undergoes a three-step healing mechanism as shown in Figure 2.9. Firstly, the adhesion between surfaces was initiated based on the Van Der Waals forces followed by chain repetition which results in a broad scale of diffusion. Eventually, randomization occurs with fully restoring the adhesion between the cuts and its mechanical properties in a short time without any manual intervention(Hernández Santana et al., 2018).

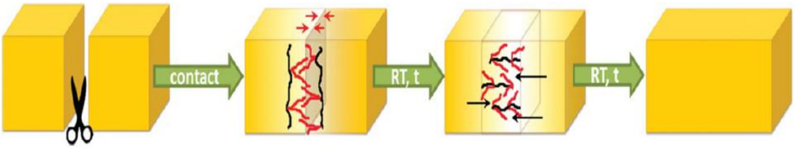

Figure 2.9	Three-step healing mechanism regarding dangling chains (Hernández Santana et al., 2018)

2.5.3 Diels-Alder chemistry

Thermoreversible Diels-Alder (DA) reaction is the most commonly used mechanism to fabricate reversible network in rubbers. Diels–Alder initially synthesized from a chemical reaction between a conjugated diene and a substituted alkene, commonly termed the dienophile which responsible for the reversible chemical bonds (Bose et al., 2014). Diels-Alder chemistry was first introduced by Otto Diels and Kurt Alder by using a six-membered DA adduct on a broad range of organic substrates which controlled by reactive functional groups, such as epoxies, acrylates, amines, isocyanates, and hydroxyls (Kloetzel, 2004). Thermally reversible properties of Diels-Alder allowing the Diels – Alder moieties be applied to existing polymeric networks without significant disrupt the properties of the materials which lead to excellent self-healing capabilities. Trovatti et al. (2015) and Bai et al. (2015) reported thermally polybutadiene rubber with DA crosslinked networks in recyclable tire application. They found that the obtained polybutadiene vulcanizate recover at 60 ^{0}C and the mechanical properties of polybutadiene elastomer can be modified by the number of maleimide crosslinkers. Chen et al. (2003) reacted four furan moieties with three maleimide moieties to form a highly crosslink polymer via DA reactions. This highly crosslink polymer is a tough transparent solid that able to re-mend under mild conditions with mechanical strength recovery of about 83%. Intermonomer linkages were disconnect at temperature above 120 ^{0}C, but they reconnect back once cooling. It is a fully reversible process which can used to restore material integrity without any catalyst, monomer or special surface treatment of the damaged surface.

Figure 2.10 below illustrated the DA reaction between furan and maleimide (Chen et al., 2003). Peng et al. (2018) designed a strong and tough self-healing elastomer by combining ionic interactions and Diels-Alder (DA) crosslinks to form double reversible networks. One-pot copolymerization is used to synthesis this self-healing elastomer by the reaction between oppositely charged monomers and furan functionalized methacrylate (FMS), followed by crosslinking via DA reaction with 1,1’-(Methylenebis(4,1-phenylene)) bis(1H-pyrrole-2,5-dione) (BMI). Ionic bonds formed in this system tend to aggregate together which in turn act as a strong sacrificial bond to toughen the material. Besides, the ionic bond also responsible for self-healing property of elastomer at room temperature. DA reaction may be possible to apply on the natural rubber materials without any interferences which can produce self-healing rubber but the work remains a challenge.

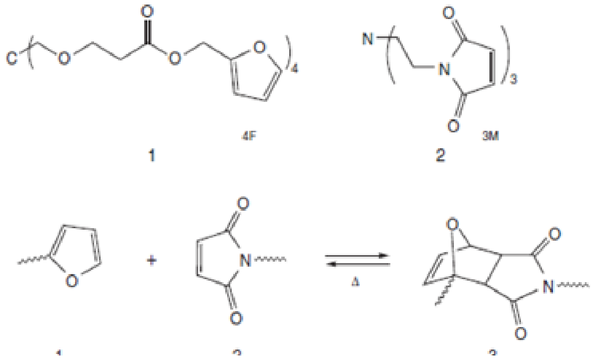

Figure 2.10 DA reaction between furan and malaimide (Kloetzel, 2004)

2.5.4 Sulfur-based chemistry

The potential of disulphide groups in incorporating self-healing properties into rubber materials has been widely explored due to the important role of sulfur that has been playing as a crosslinking agent in the rubber vulcanization process (Hernández Santana et al., 2018). Disulphide groups can undergo dynamic rearrangement process via disulphide exchange or thiol-disulphide exchange reaction and the exchange reactions usually occur in response to external factors such as heat, light and pH. Figure 2.11 shows a general reaction of disulphide exchange reaction (Martin et al., 2016). When the damage is detected, the disulphide bonds undergo homolytic cleavage to form free radicals due to the lowest bond energy dissociation. The sulfides were then rearranged to create a new disulphide group with adjacent chains. The presence of dynamic crosslink promoted an interfacial reshuffling of disulfiide and healed the fracture at the equilibrium condition. The disulphide exchange was first applied in poly(urea-urethane) (PUU) due to its simplicity (Belenguer et al., 2011). The chemistry of the disulphide concept has been incorporated with rubber-based materials for a wide range of applications, such as advanced drug delivery vehicles, bio-artificial implants and self-healing and shape-imprinting polymers (Canadell et al., 2011, Yang et al., 2014, Montarnal et al., 2011, Pire et al., 2014).

A self-healing vulcanized chloroprene rubber (CR) was designed by Xiang et al. (2015) by incorporating disulphide metathesis with the presence of organic complex copper (II) methacrylate (MA-Cu) as catalyst. The apparent shear strength of CR shows excellent healing efficiency up to 92 %. The recovery of shear strength after 3rd healing cycle able to achieve up to 78.2 %, indicating that the dynamic rearrangement of disulphide metathesis had remarkably contributed to the excellent self-healing performance. Martin et al (2016) has experimentally investigated on the silicone rubber where the crosslinked network is built between thiol-functionalized polydimethylsiloxane (PDMS) and silver nanoparticles (AgNPs) through synthesis. The silver(I)-thiolate species rearranged and bonded with nearby AgNPs when the damaged surface in contact and give full recovery of the network within 24 hours after the material damage shown in Figure 2.12 (Binder, 2013b).

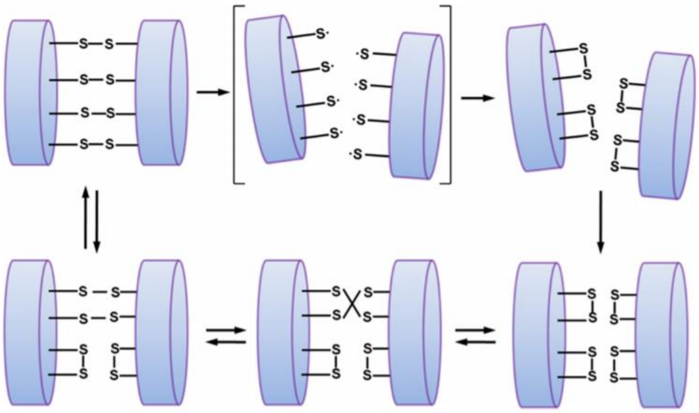

Figure 2.11 Simplified representation of network healing through disulphide exchange reactions (Martin et al., 2016)

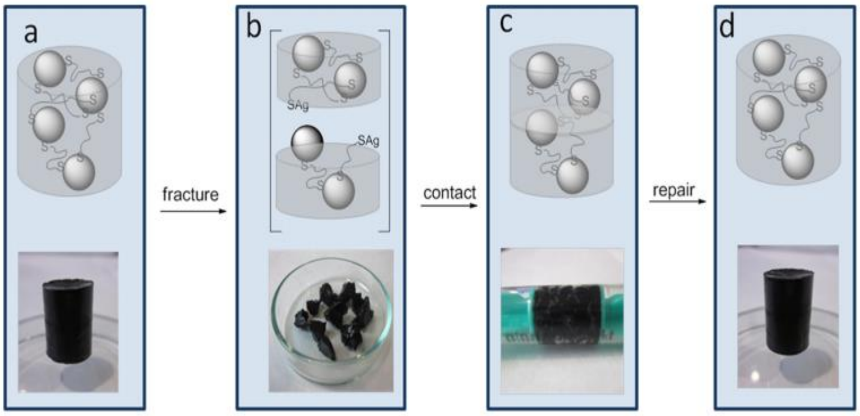

Figure 2.12 Thiolate/nanoparticles exchange network performed during the healing process (Binder, 2013b)

2.5.5 Vitrimers chemistry

Vitrimer is a new class of material in which the crosslink network is formed by exchangeable covalent bonds that are associative in nature. The network topology changes in response to high temperature via exchange reaction and the covalent bonds only break after they have reformed, hence remaining the network integrity and keeping the number of bonds constant during the exchange process (Yang et al., 2014). Vitrimers have glass transition temperature like other conventional polymers but they also exhibit topology transition temperature (Tv) which shows the transition of viscoelastic solid to viscoelastic liquid. Below Tv, the material behaves like a classic thermoset due to limited exchange mechanism between the covalent bonds. When the vitrimer is heated above Tv, the bond exchange reaction becomes rapid, allowing the network to flow like thermoplastic which contributes to the ability of material to self-heal, reshape and reprocess (Wemyss et al., 2020).

The use of vitrimers to induce self-healing was introduced by Leiber et al, which can overcome multiple problems of traditional polymer networks and coalesce the advantageous properties from different polymer classes (Montarnal et al., 2011). Epoxidized natural rubber (ENR) has been often used as a raw rubber to introduce vitrimer-like behaviour in elastomeric materials due to the presence of epoxide groups because an epoxy-acid system can undergo transesterification to form vitrimer material easily (Pire et al., 2014, de Luzuriaga et al., 2016). Generally, most of the vitrimer exchange reactions require catalyst in order to function effectively and the most common catalyst used is zinc acetate, $Zn(Ac)_2$ (Tang et al., 2016, Imbernon et al., 2015). However, it was observed that when $Zn(Ac)_2$ was introduced to ENR as catalyst, it slowly migrated to the surface over time and potentially contribute to environmental pollution. For rubber material, vitrimers chemistry appears to be a perfect solution in combining the strong mechanical properties of covalently crosslinked elastomers with total repairability. Most of the works studied the vitrimer-like behaviour in rubber material using ENR and there was limited amount of works that involved other natural or synthetic rubbers (Feng et al., 2017, Qiu et al., 2018, Xu et al., 2018). Even though Lu et al.(2012) had reported a vitrimer-like BR network with the addition of Grubbs catalyst to perform olefin metathesis, the cost of Grubbs catalyst was considered high to be used in industrial applications. The approach is potentially applicable to other rubbers, but it may affect the cis-configuration of rubber structure such as NR that results in poor functional properties of the final rubber product (Imbernon et al., 2015).

2.5.6 Ionic Interaction

Ionic interaction can be formed between anions of an ionomer and a metal cation from Group 1A, Group 2A or transitional metal cations as shown in Figure 2.13. Ionomers are usually synthesis by two methods which is either direct synthesis or post-functionalization of saturated polymer. Electrostatic interactions can be created through ionomer where the polymeric systems containing a hydrogen backbone and pendent acid groups, the acid groups are neutralized partially or fully to form ionic metal salts. Electrostatic interaction caused the polar ionic groups tend to aggregate together forming an ion cluster. The ion clusters will restrict the mobility of rubber chains and lead to the formation of new crosslinks that are reversible in nature and allowed self-healing process to occur. Besides that, addition of ionic group in a small proportion resulted in an increase of mechanical properties such as tear resistance, tensile strength and impact strength (Ghosh, 2009, Xu et al., 2016a). Figure 2.14 represent the formation of ionomer morphology from ion pair to a crosslinked network while Figure 2.15 shows the healing process through ionic interaction.

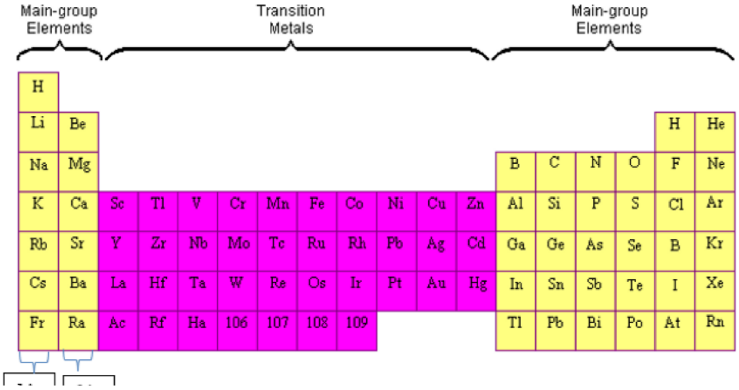

Figure 2.13 Periodic Table showing Group 1A, Group 2A and transition metal

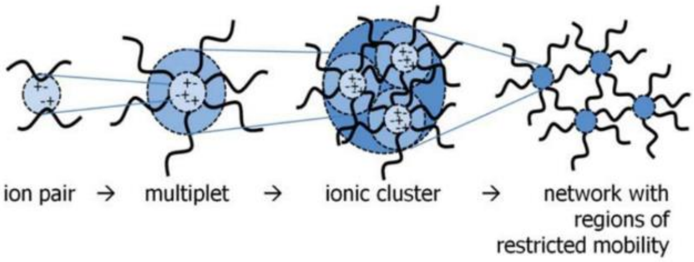

Figure 2.14 The formation of ionomer morphology from ion pair to a crosslinked network (Hernández et al., 2016b)