EFFECT OF HALLOYSITE NANOTUBES ON THE PERFORMANCE OF SELF-HEALING NATURAL RUBBER

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EFFECT OF HALLOYSITE NANOTUBES ON THE PERFORMANCE OF SELF-HEALING NATURAL RUBBER

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DECLARATION

I hereby declare that I have conducted, completed the research work and written the dissertation entitled ‘effect of halloysite nanotubes on the performance of self-healing natural rubber’. I also declare that it has not been previously submitted for the award of any degree and diploma or other similar title of this for any other examining body or University.

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Witness by

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Date:

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LIST OF SYMBOLS

%	Percentage
°C	Degree Celsius
°C/min	Degree Celsius per minute
C	Compression set
cm^{-1}	Number of wavelengths per centimeter
g	gram
g/cm^3	Gram per centimeter cubic
min	minutes
mm	millimeter
mm/min	Millimeter per minute
MPa	MegaPascal
T_g	Glass transition temperature
t_i	Final specimen thickness
t_n	Spacer bar thickness
t_o	Original specimen thickness
t_{90}	Cure time

LIST OF ABBREVIATIONS

ASTM	American standard testing and materials
CNTs	Carbon nanotubes
DCP	Dicumyl peroxide
DSC	Differential scanning calorimetry
FESEM	Field-emission scanning electron microscopy
FTIR	Fourier-transform infrared spectroscopy
HNTs	Halloysite nanotubes
HRTEM	High resolution transmission electron microscopy
ISO	International organization for standardization
NR	Natural rubber
OM	Optical microscopy
phr	Part per hundred rubber
SEM	Scanning electron microscopy
SMR	Standard Malaysian Rubber
XRD	X-ray diffraction
XRF	X-ray fluorescence
ZDEC	Zinc diethyl dithiocarbamate
ZnO	Zinc oxide

KESAN *HALLOYSITE NANOTUBES* TERHADAP SIFAT MEKANIKAL GETAH ASLI PENYEMBUHAN DIRI

ABSTRAK

Dalam kajian ini, getah asli (NR) penyembuhan diri berasaskan rangkaian ion logam-tiolat telah dibangunkan menggunakan *halloysite nanotube*s (HNT) sebagai pengisi. Sifat mekanikal dan fizikal, morfologi, unsur, sifat haba kedua-dua pengisi HNT dan nanokomposit NR/HNT penyembuhan sendiri telah dinilai. Untuk mempelajari keupayaan penyembuhan diri sampel, mikroskop optik telah membuktikan getah asli penyembuhan diri yang dibangunkan dapat sembuh diri kerana permukaan patah hampir sembuh apabila dua kepingan yang patah bersentuhan antara satu sama lain. Tambahan pula, ujian tegangan menunjukkan kekuatan tegangan meningkat dengan ketara dengan peningkatan masa penyembuhan dan suhu penyembuhan. Untuk penilaian sifat mekanikal, imej mikroskop elektron pengimbas (SEM) mendedahkan bahawa pemulihan lebih baik telah dicapai dalam sebatian nanokomposit dengan pengisi yang lebih rendah kerana tiada jurang yang jelas diperhatikan dalam pengisi yang lebih rendah. Daripada keputusan ujian tegangan dan koyakan pula, keputusan telah membuktikan bahawa pengisi optimum ialah 8 phr. Di samping itu, ujian set mampatan telah menunjukkan bahawa sampel dengan 8 phr HNT mempamerkan set mampatan terendah, bermakna sampel itu dapat mengekalkan sifat keasalannya di bawah daya mampatan. Sementara itu, kekerasan dipertingkatkan daripada 12.67 kepada 18.33 Shore A dengan penambahan HNT dari 0 ke 10 phr. Ketumpatan relatif pula menunjukkan peningkatan daripada 1.01 kepada 1.03 dengan peningkatan pemuatan pengisi daripada 0 ke 10 phr. Dalam pada itu, spektroskopi inframerah fourier transformasi (FTIR) mengesahkan bahawa Si-O dan Al-OH berada dalam HNT serta ikatan C=S dan SCC berada dalam zink tiolat, ikatan ini telah menjustifikasikan kewujudan ikatan ionik boleh balik Zn^{2+} dalam nanokomposit. Hasil daripada kerja ini telah membuktikan bahawa nanokomposit NR/HNT mampu sembuh sendiri pada suhu bilik dan sembuh dengan lebih baik apabila diberikan tekanan. Juga, rangkaian supramolekul ionik boleh balik telah dibentuk dalam nanokomposit dan menyumbang kepada mekanisme penyembuhan diri.

EFFECT OF HALLOYSITE NANOTUBES ON THE PERFORMANCE OF SELF-HEALING NATURAL RUBBER

ABSTRACT

In this study, a self-healing natural rubber (NR) based on metal-thiolate ion network was developed using halloysite nanotubes (HNT) as filler and the corresponding mechanical and physical properties, morphological, elemental, thermal properties of both HNT filler and self-healing NR/HNT nanocomposites were evaluated. The self-healing capability of the samples were proved by optical microscopy by which the fracture surface nearly healed when two broken pieces were brought in contact with each other. The mechanical properties indicated the tensile strength significantly increased with the increasing of healing time and healing temperature. In contrast, for the evaluation of mechanical performance, Scanning Electron Microscopy (SEM) images reveal that better recovery was achieved in nanocomposites compound with lower filler loading as no obvious gap was observed in lower loading. From tensile and tear test, the optimum filler loading was 8 phr. In contrast, for compression set test, sample with 8 phr exhibit lowest compression set, meaning that the sample was able to retain its elastic properties under compressive force. Also, hardness was enhanced from 12.67 to 18.33 Shore A by the addition of 10 phr HNT. The relative density was increased from 1.01 to 1.03 with the increasing of filler loading from 0 to 10 phr. Fourier-transform infrared spectroscopy (FTIR) confirmed the Si-O and Al-OH in HNT as well as C=S and SCC bonding in zinc thiolate, indicates that the reversible ionic bonding of Zn^{2+}. The results proved that NR/HNT nanocomposites was able to self-healed at room temperature and healed more with the applied of pressure. Also, the reversible ionic supramolecular network was formed within the nanocomposites and contributed to self-healing mechanisms.

CHAPTER 1

INTRODUCTION

1.1 Background of Research

Natural rubber has a wide range of technical uses, such as in sports equipment, electronics, transportation vehicles, and civil engineering. Although the product was designed to be as durable as possible, failure could still happen for a number of reasons, such as fatigue or cracks. Besides, during their service, rubber is susceptible to damage induced by mechanical, chemical, thermal, UV radiation or a combination of these factors. Consequently, the formation of microcracks will occur deep within the structure where detection is difficult and most probably impossible to repair. As a result, reduce the performance of the rubber products and thus lower the reliability of the products (Zainol and Shuib, 2020).

In order to prevent catastrophic failure, rubber products require humans to notice, pinpoint, and fix problems. In addition, the possibility of reprocessing and recycling rubber products may be hampered by the irreversible sulphur or peroxide crosslinked networks in vulcanised rubber, resulting in the scrapping of hundreds of thousands of tonnes of rubber products used in the construction and automotive industries. Subsequently, threaten available resources and degrade the environment. Therefore, a viable evolution to the rubber industry is needed to produce more sustainable rubber products (Thajudin et al., 2021).

Hence, researchers discovered the promising characteristic of rubber which is self-healing capability to enhance the quality of rubber (Zainol and Shuib, 2020). This concept refers to the ability of a product to self-healed spontaneously when it is damaged without incurring any structural reliability modifications (Thajudin et al., 2021). Therefore, because of its ability to cure itself, rubber has a wide range of potential application in sensors, intelligent actuators, tyres, artificial skin, and more (Zainol and Shuib, 2020).

In order to improve certain properties like heat resistance, mechanical strength, and impact resistance or to reduce others like electrical conductivity or permeability for gases like oxygen or water vapour, polymer materials have been filled with a variety of inorganic synthetic or/and natural compounds. One of the most rapidly evolving nanocomposites that has been investigated in a variety of disciplines of study is nanoclay loaded rubber. Due to the fact that clay minerals have layers with 1 nm thick planar structures, they could be used as nanoscale additives (Ismail et al., 2013).

1.2 Problem Statement

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 damaged occurred without the need for detection or repair by any kind of manual intervention (Khimi et al., 2019). Nevertheless, the challenge in developing self-healable rubber is to balance the self-healing function and mechanical properties of the products without compromising any of them. This is due to the mechanical performance of rubber depends on the on the rigid and stable covalent crosslink networks, whilst the self-healing behaviour depends on the flexibility of dynamic reversible crosslink networks, making it challenging to accomplish both desirable features simultaneously.

However, only limited research work has been carried out to investigate the capability of natural rubber to be developed as self-healing materials. This is because of natural rubber lacks of functional groups as it is a non-polar rubber. According to

Khimi et al. (2019) study, there are 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 investigated. However, due to the existence of polar oxirane groups that can form reversible hydrogen bonds in the rubber chains, researchers primarily focused on the investigation using epoxidized natural rubber (ENR) (Rahman et al., 2011; Rahman et al., 2013; Imbernon et al., 2015).

As most of the commercial rubbers have no available ionic functional group due to non-polar nature of the natural rubber and thus there is low interest for researchers to investigate the self-healing mechanism in natural rubber. Most of the researchers focused on introducing and improving the self-healing ability of synthetic rubbers. In fact, natural rubber has high potential to be developed as a self-healing material. The reason for this is that the ionic groups can be introduced in rubbers so that a self-healing natural rubber can be developed. The healing process is triggered by the reversibility of ionic crosslinking between rubber molecular chains and thus enable a fractured sample to regain its original properties. Thus, it is clear that generation of ionic associations in rubber molecular chains offer potential to introduce self-healing mechanism in natural rubber (Khimi et al., 2019).

Therefore, in this study, the mechanical performance of self-healing natural rubber based on zinc thiolate network was investigated in order to realize the full potential application and prolong the natural rubber in their service lifetime.

On the other hand, nano-sized fillers receive more attention as revolution from micro-sized filler to nano-sized fillers recently due to several advantages offered by rubber filled with nano-sized filler. Hence, in this study, halloysite nanotubes was selected to be used as nanofiller. The reason of choosing HNTs as filler is due to their unique tubular structure, high surface area, large aspect ratio, nano-scale diameter, good biocompatibility, and low manufacturing cost as well as contrasting chemistry on external and internal surfaces of HNTs (Cao et al., 2012; Liu et al., 2014). Besides, as compared to other nano-sized inorganic fillers, naturally occurring HNTs are readily obtainable and much cheaper than other nanoparticles such as carbon nanotubes (CNTs) (Cao et al., 2012; Ismail et al., 2013). Also, the physical appearance of HNTs which is very similar to CNTs, making HNTs particularly attractive for reinforcing in polymer nanocomposites (Ismail et al., 2013).

Additionally, only small amount of nanofillers is required to improve the mechanical properties of the self-healing natural rubber as compared to conventional filler which require much larger quantities (Rooj et al., 2010). Therefore, HNTs may have the potential to provide cheap alternatives to the expensive CNTs because of their tubular structure in nanoscale and also due to their similarity to the other layered clay minerals such as MMTs (montmorillonites), having the possibility to be further intercalated chemically or physically (Cao et al., 2012). Due to these advantages, naturally occurring multilayered silicate HNT is potential nanofiller for polymer nanocomposite (Kausar, 2018). However, the application of HNTs in rubber composites is very still largely unexplored (Rooj et al., 2010).

Therefore, in this study, halloysite nanotubes (HNTs) were chosen as filler. Halloysite is defined as two layered aluminosilicates. More details on HNT will be discussed in Section 2.5. In this work, healing efficiency of developed self-healable natural rubber filled with different contents of halloysite nanotube filler (0 phr, 2 phr, 4 phr, 6 phr, 8 phr and 10 phr) were investigated. The optimum formulation of HNT filler loading, healing mechanism, and healing efficiencies as well as mechanical, physical, morphological, thermal and elemental properties of the self-healing rubbers with HNT as filler will be discussed in this thesis.

1.3 Research Objectives

The main focus of this research is to investigate the effect of halloysite nanotube as nanofillers on the overall properties of self-healing natural rubbers based on the reversible metal thiolate crosslinks that can self-heal when damaged without manual intervention. The specific research objectives are listed as follows:

1. To characterize halloysite nanotubes (HNT) filler using Field-Emission Scanning Electron Microscopy (FESEM), High Resolution Transmission Electron Microscopy (HRTEM), X-Ray Fluorescence (XRF), X-Ray Diffraction (XRD), Zeta Potential and Particle Size.
2. To access self-healing efficiency of natural rubber based on metal thiolate ionic network by optical microscopy and tensile properties of the control sample.
3. To investigate the reinforcement effect including tensile and tear strength, compression set, hardness as well as relative density of HNT filler loading on self-healing NR/HNTs nanocomposites using Scanning Electron Microscopy (SEM), tensile test, tear test, compression set test, hardness test, relative density test, Fourier-Transform Infrared Spectroscopy (FTIR) and Differential Scanning Calorimetry (DSC).

1.4 Outline of Thesis

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

Chapter 1: Introduced the study of the thesis, which including study background, problem statement and objective of the research.

Chapter 2: Provided literature review related to natural rubber, halloysite nanotubes as well as self-healing mechanism of natural rubber including both extrinsic and intrinsic self-healing mechanism.

Chapter 3: Described the experimental procedure involved in the preparation of self-healing natural rubber nanocomposites. Also, this chapter provide detailed explanation of raw materials and chemicals, as well as equipment and testing procedure including the specification and variables used in the research.

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

Chapter 5: Summarize and conclude on the current work as well as suggestion and recommendation for future work.

1.5 Scope of Study

The first objective of this study focuses on the characterization of HNT filler. The morphology characteristics as well as elemental characteristics of HNT filler were investigated.

For the second objective of study, the self-healing natural rubber without the addition of HNT was prepared as control sample to access the self-healing efficiency of natural rubber using optical microscopy and tensile test. Also, the morphology characteristics, and tensile properties of sample without the addition of filler were studied.

On the other hand, the third stage of study focuses on the mechanical performance of self-healing natural rubber with the use of halloysite nanotubes as filler. The mechanical properties, physical properties, morphology characteristics, elemental characteristics and thermal properties were determined.

CHAPTER 2

LITERATURE REVIEW

2.1 Natural Rubber

Natural rubber, also known as cis-1,4 polyisoprene, is present as latex in a large variety of plants in many regions of the world. As shown in Table 2.1, some plant species from the *Moraceae*, *Euphorbiaceae*, *Apocynaceae*, produce latex that contains appreciable quantities of rubber. The tree *Hevea brasiliensis* is the most significant source because latex from other sources has some disadvantages including low rubber content, high resin content, and difficulties in extraction. Therefore, *Hevea brasiliensis* has become the most widely exploited commercial source of NR (De and White, 2001).

Table 2.1 Major plant sources of natural rubber (De and White, 2001)

Family	**Species**	**Popular Name**
Euphorbiaceae	*Hevea brasiliensis*	Para rubber
Compositae	*Parthenium argentatum*	Guayule rubber
Euphorbiaceae	*Manihot glaziovii*	Ceara rubber
Moracea	*Castilla elastica*	Panama rubber
Moracea	*Ficus elastica*	India rubber
Apocynaceae	*Funtumia elastica*	Lagos silk rubber

Due to the advent of synthetic rubbers which were marketed in compact and uniform as well as medium-sized bales wrapped in plastic film together with technical specifications, NR is also marketed in more attractive forms. As a result to commercialize NR as technically specified rubber in compact bales, NR is covered in polyethylene film and graded according to technical specifications. A technically specified rubbers that are produced and are marketed under different names are shown in Table 2.2, in almost all NR producing countries (De and White, 2001).

Table 2.2 Nomenclature of TSR in different countries (De and White, 2001)

Country	**Nomenclature**
Malaysia	Standard Malaysian Rubber (SMR)
Indonesia	Standard Indonesian Rubber (SIR)
Thailand	Standard Thai Rubber (STR)
India	Indian Standard Natural Rubber (ISNR)
Sri Lanka	Sri Lanka Rubber (SLR)
Singapore	Standard Singapore Rubber (SSR)
Papua New Guinea	Papua New Guinea Classified Rubber (PNGCR)

From Table 2.2, it is clear that the grades of NR are varying from ribbed smoked sheets (RSS) which are made from coagulated field latex, to pale crepe which is made from a latex that has been preserved to prevent enzyme darkening, to technically specified (TSR) grades. These are referred to as Standard Malaysian Rubbers (SMR) grades and were first introduced by the Malaysian rubber industry. Also, there are standard rubber grades from Indonesia (SIR), Thailand (TTR) and Sri Lanka (SLR). These are NR grades which the natural rubber is cleaned and converted to a crumb instead of a sheet rubber. They are further processed to achieve properties such as a constant viscosity (SMR-CV), a light colour (SMR-L) or specified grades of dirt and ash content (SMR 5, 10, 20 and 50). The benefits of TSR grades is that TSR grades offer more consistent properties as compared to that of the conventional rubbers made from coagulated field latex (De and White, 2001).

The structural formula for the molecule of natural rubber is represented by the simple unit C_5H_8 multiplied many thousand times, as illiutrates in Figure 2.1 (Morton, 2013).

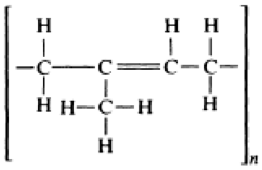

Figure 2.1 Structural formula of natural rubber (Morton, 2013)

As shown in Figure 2.1, n represents a value of about 20,000. The arrangement of carbon and hydrogen atoms obeys the valence rules of 4 for carbon and 1 for hydrogen (Morton 2013). On the other hand, all the possible isomers that can occur in a polyisoprene chain is depicted in Figure 2.2. Natural rubber, *Hevea brasiliensis*, is approximately 96% cis-1,4 polyisoprene, with proteins and lipids making up the remaining 4% (De and White, 2001).

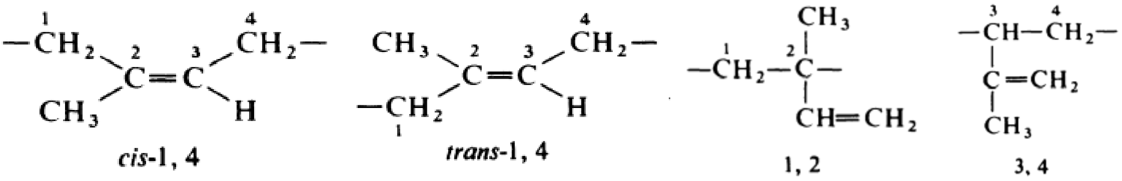

Figure 2.2 Possible isomers of polyisoprene chains (De and White, 2001)

The numbers refer to the particular carbon atoms in each unit that attached to adjacent units. For example, a 1,4 structure means that carbon atoms 1 and 4 are joined in forming the chain. Besides, the terms cis and trans refer to the positions of the various carbon atoms with reference to the carbon-carbon double bond (C=C). Since a double bond is considered to prevent rotation of the attached atoms, it follows that other atoms or groups of atoms may occupy positions on either side of the double bond. It is therefore in the cis-1 ,4 structure, carbon atoms 1 and 4 are both on the same side of the double bond, while in the trans-1 ,4 structure, these two carbon atoms are on opposite sides of the double bond (Morton, 2013).

Also, even in a pure gum or an unreinforced vulcanizate, natural rubber has a high tensile strength and tear resistance as well as high resilience because of its highly regular structure, which causes it to quickly crystallize upon stretching. Besides, NR has an ideal elastic and hysteresis properties (De and White, 2001; Kruželák et al., 2014).

For the applications of natural rubber, NR can be used in many applications especially where high tensile and tear strength is required. Besides, natural rubber is also can be applied in an outsole compound that required flexibility due to the good resistance to flexing, fatigue and heat generation as well as high abrasion resistance of the natural rubber (De and White, 2001). Moreover, NR is an ideal candidate for pressure sealing applications because of its high resilience properties. The excellent elastic recovery or low compression set enables the rubber seals to compensate for any movements of the sealed parts such as the sealing gap growth caused by pressure peaks (Akulichev et al., 2017).

The uniqueness of rubber is it has very high deformability, tough and nervy. This is because natural rubber is made up of extremely high molecular mass molecules that can be crosslinked together to form a network. If the crosslink density is low, the material will retain a memory of its original unstressed state and then return to its original dimensions when external forces are removed even after strains as high as 1000%. This ability to recover to its original dimensions leads natural rubber to be applied in many fields (De and White, 2001). Furthermore, as the chain units in a macromolecule all consist of the same isomer of cis-1,4 structure and thus the polymer is stereoregular. Due to this remarkable regularity, the natural rubber chains can achieve a good regularity, particularly when the rubber is stretched. Since natural rubber crystallizes on stretching, hence leading to higher tensile strength (Morton, 2013).

Also, due to the presence of the reactive double bonds, natural rubber can be chemically crosslinked using a vulcanization (curing) process to form crosslink, which offer high toughness, excellent noise and vibration damping properties, and chemical and thermal stability (Morton, 2013; Kruželák et al., 2014; Wemyss et al., 2020). Vulcanization process will be discussed in detail in Section 2.2.

In this work, SMR L was used as raw rubber matrix used. The standard specification of SMR L according to ASTM D2227 is tabulated in Table 2.3.

Table 2.3 Properties of SMR L rubber (ASTM D2227)

Properties	**SMR L**
Dirt, retained on 45 µm sieve, %	0.05
Ash, %	0.60
Volatile Matter, %	0.80
Nitrogen, %	0.60
Initial plasticity, min	30
Plasticity retention index, min	60.00
Color index, max	6.0

2.2 Vulcanization

For the crosslinks mechanism of rubber macromolecules with peroxides, the first step is a homolytic dissociation of peroxides into radicals at high temperatures, their possible fragmentation and subsequent reactions of peroxide radicals with macromolecules of rubber. Peroxide radicals could potentially react by addition to a double bond or by abstraction of α-methylene hydrogens of unsaturated rubbers. The macromolecular radicals formed consequently undergo recombination reactions, forming a vulcanizate with relatively simple crosslink structure. On the other hand, simultaneously with the main cross-linking process, side reactions including fragmentation reactions, termination of macromolecular radicals by disproportionation, or possible macromolecular chains degradation. These side reactions reduce the yield of vulcanization (Kruželák et al., 2014).

Since the vulcanization by organic dicumyl peroxide is a free radical process, hence carbon-carbon bonds formed between macromolecular chains. The structure of peroxide vulcanizate is relatively simple compared with that of sulphur vulcanizate, as rubber chains are crosslinked by simple carbon-carbon linkages, which are highly stable towards heat. As a result, these vulcanizates possess extremely good thermal ageing characteristics, superior to those of even EV systems, and also lower compression set at elevated temperature (De and White, 2001; Kruželák et al., 2015). Besides, the advantages of peroxide vulcanization are also included simple formulation of rubber compounding, good electrical properties of vulcanizates, good shelf-life stability and no staining of the finished parts (Kruželák et al., 2015).

In contrast, there are also some disadvantages compared to sulfur cured systems, such as low fatigue resistance and low resistance to crystallization temperature low scorch safety, and worse dynamic and elastic properties of vulcanizates (De and White, 2001; Kruželák et al., 2015).

2.3 Rubber Compounding

2.3.1 Zinc Oxide and Stearic Acid

Zinc oxide and stearic acid were used as an activator. In order to fasten the curing process, the combination of zinc oxide and stearic acid is used to activate the accelerator. The mechanism involves of zinc oxide reacts with stearic acid to produce zinc stearate and subsequently reacts with the accelerator to speed up the rate of dicumyl peroxide vulcanization. Thus, the use of zinc oxide and stearic acid reduce the time taken for a complete curing process (Ciesielski, 1999).

2.3.2 Dicumyl Peroxide

Dicumyl peroxide (DCP) is a peroxide vulcanizing agent that induce crosslinks in order to prevent slippage within the rubber chains. Vulcanization by dicumyl peroxide is a free radical process. The rubber chains are crosslinked by simple carbon-carbon linkages, leading to highly heat stable products. As a result, these vulcanizates have better thermal ageing properties than even EV systems, as well as a lower compression set at high temperatures. However, fatigue resistance and resistance to low temperature crystallization are low (De and White, 2001). The chemical structure of DCP is shown in Figure 2.3.

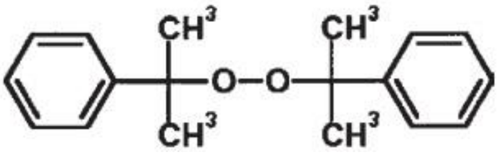

Figure 2.3 Structure of dicumyl peroxide (De and White, 2001)

2.3.3 Zinc Diethyl Dithiocarbamate (ZDEC)

Zinc diethyl dithiocarbamate (ZDEC) is typically used as an accelerator in rubber vulcanization system (De and White, 2001). However, in this work, ZDEC was used as an ionic crosslinker that promotes the healing process in natural rubber. The chemical structure of ZDEC is illustrated in Figure 2.4.

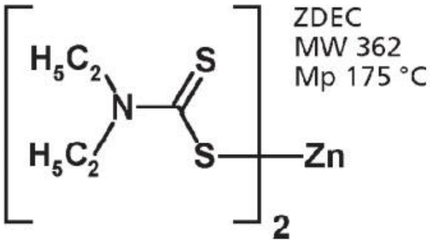

Figure 2.4 Chemical structures of ZDEC (De and White, 2001)

2.3.4 Toluene

In this study, toluene is used as solvent in order to evaluate the total crosslink density of the rubber network. It is an aromatic hydrocarbon with a chemical formula of C_7H_8 as shown in Figure 2.5. Additionally, toluene has a distinctive aromatic odour and is a clear, colourless liquid.

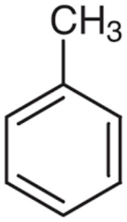

Figure 2.5 Chemical structure of toluene

2.3.5 Chloroacetic Acid

Chloroacetic acid is a halogenated aliphatic carboxylic acid which is mainly used as herbicide and preservative. The chemical structure of chloroacetic acid, with formula $C_lCH_2CO_2H$, is presented in Figure 2.6. It is a colourless crystal with a density of 1.58 g/cm^3 and a melting point of 63°C. In this study, a mixture of chloroacetic acid and toluene in suitable ratio is used to destroyed ionic crosslinks in the rubber network.

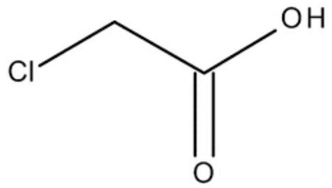

Figure 2.6 Chemical structure of chloroacetic acid

2.4 Overview of Self-Healing Mechanism

Self-healing is one of the most fascinating processes in nature as it has the ability to repair themselves and to recover spontaneously after damaged without any changes of structural reliability (Xu et al., 2016; Thajudin and Shuib, 2020). The advantages of self-healing capability in natural rubber are provide the potential for extending service lifetime and capability of natural rubber by restoring the mechanical damages (Thajudin and Shuib, 2020).

The purpose of self-healing is to reconnect the broken chemical bonds which have been broken during the material fractures in order to avoid catastrophic failure. One of the approaches for self-healing is by introducing ionic bonding in rubber. The concept of introduction of ionic bond in natural rubber is similar to the living polymerisation which forms the growth of rubber chains polymerisation without termination step (Thajudin and Shuib, 2020). Therefore, the natural rubber chains are able to repair mechanical damage such as cut on themselves spontaneously (Xu et al., 2016).

The common approaches of self-healing mechanism are involved noncovalent interactions, such as hydrogen bonding, metal-ligand coordination, ionic interaction and so on, to construct a required network structure. However, noncovalent interactions are relatively weak as compared to that of strong and nonreversible covalent bonds, leading to a reversible association-dissociation characteristic which endows materials with potential self-healing behaviors (Xu et al., 2016). In general, the mechanism can be classified into two categories that are extrinsic and intrinsic. The main difference between these two types of self-healing materials lies in their chemistries (Thakur and Kessler, 2015).

2.4.1 Extrinsic Self-Healing Mechanism

For extrinsic self-healing system, this system is based on the addition of healing agent in the form of capsules or vascular networks and embedded into the materials as the matrix resin itself lacks an intrinsic self-healing mechanism (Zhang and Rong, 2011; Thakur and Kessler, 2015). As soon as the cracks destroy the fragile reservoirs, the discrete micro- or nano-encapsulated healing agents will be released into the crack planes due to capillary effect and covers the damaged site thus restores its function when the material cracks (Bode et al., 2015; Zhang and Rong, 2011).

There are two approaches frequently applied to prepare self-healing materials based on extrinsic mechanism include the (i) microencapsulation and (ii) microvascular network. In both approaches, the self-healing process is initiated by the external/internal damage/rupture in the vascular networks as well as the capsules (Thakur and Kessler, 2015). However, there are some limitations of microencapsulation approach include (i) high cost of the catalyst especially Grubbs catalyst and (ii) the process of self-healing of materials can only occur once since the amount of healing agents is depleted in the healed region (Thakur and Kessler, 2015).

Conventional extrinsic self-healing composites are hard to conduct repeated healing due to rupture of the embedded healant-loaded containers which causes depletion of the healing agent after the first damage. In order to overcome this difficulty, a self-healing system consisting of a three-dimensional microvascular network capable of autonomously repairing repeated damage events was developed (Zhang and Rong, 2011). The healing mechanism of this method used ring-opening metathesis polymerization of dicyclopentadiene (DCPD) monomer by Grubbs' catalyst, benzylidenebis (tricyclohexylphosphine) dichlororuthenium, and this was applied successfully in microencapsulated composites. This mechanism can be explained by in the crack plane, the healing agent interacted with the catalyst particles in the composites to initiate polymerization, rebonding the crack faces autonomically. After a sufficient time period, the cracks were healed, and the structural integrity of the coating was restored. Under subsequent loading, cracks reopened, and the healing cycle was repeated (Zhang and Rong, 2011).

On the other hand, self-healing in terms of healant loaded microcapsules for diene monomers, healing was triggered when damage in the form of a crack ruptured the microcapsules, causing dicyclopentadiene (DCPD) to be released into the crack plane where it came in contact and mixed with the pre-embedded Grubbs' catalyst, as illustrated in Figure 2.7 and Figure 2.8. For increasing catalysis efficiency, the catalyst was capsulated by wax and recrystallized, respectively. It was found that the healing agent was able to effectively repair delamination, low-velocity impact damages and indentation induced interpenetrating crack networks in fiber reinforced epoxy composites. In addition, fatigue crack growth in epoxy can also be retarded by the released fluid. Thus, self-healing composites might be used in practice due to the rapid developed microencapsulation technique and mass production of microcapsules can be easily industrialized (Zhang and Rong, 2011).

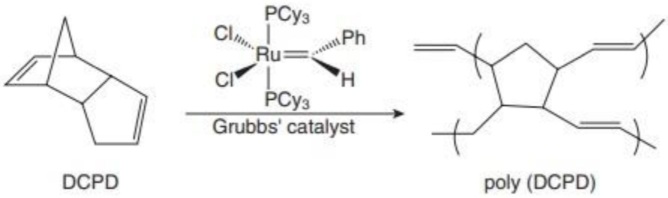

Figure 2.7 Ring opening metathesis polymerization of DCPD (Zhang and Rong, 2011)

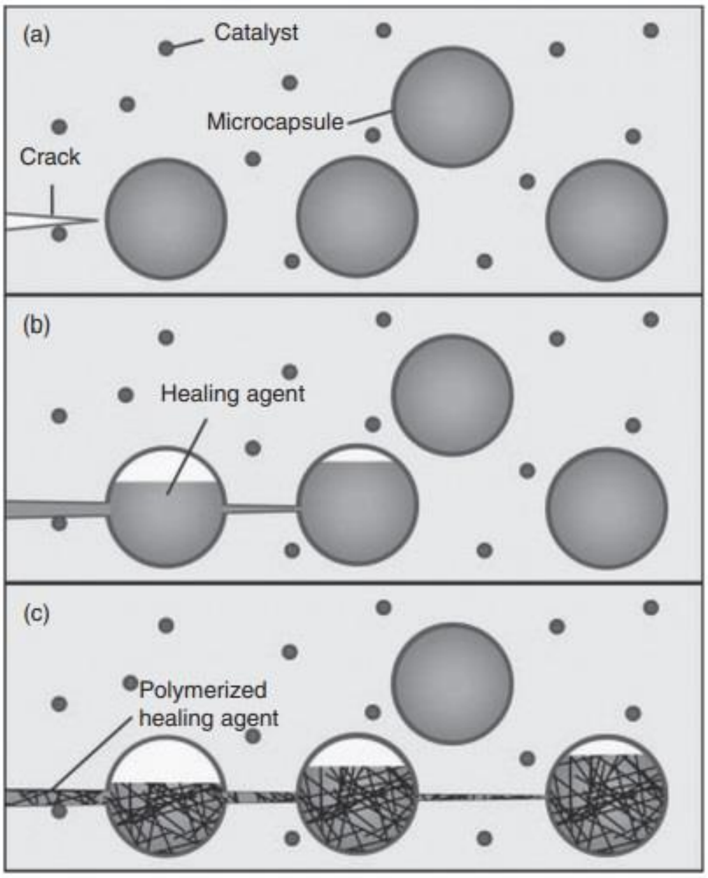

Figure 2.8 The autonomic healing concept. A microencapsulated healing agent is embedded in a structural composite matrix containing a catalyst capable of polymerizing the healing agent: (a) cracks form in the matrix wherever damage occurs; (b) the crack ruptures the microcapsules, releasing the healing agent into the crack plane through capillary action; (c) the healing agent contacts the catalyst, triggering polymerization that bonds the crack faces closed (Zhang and Rong, 2011)

However, the healing of this mechanism is limited to single localized damage. Furthermore, high shear forces during mixing and compounding process could break the capsule down (Thajudin et al., 2020).

2.4.2 Intrinsic Self-Healing Mechanism

In contrast, intrinsic healing is related to chemical modification of the base polymer such that the polymer itself is capable of restoring chemical bonds across a damage site based on either non-covalent chemistries or dynamic covalent chemistries (Bode et al., 2015; Thakur and Kessler, 2015). The non-covalent chemistry approach uses pep stacking, ligandemetal bonding, hydrogen bonding, or hosteguest interaction stacking among other techniques, whereas covalent approaches use DielseAlder reaction, radical exchange, dynamic urea bond, and trans-esterification (Thakur and Kessler, 2015). The mechanism of intrinsic self-healing involves complex reversible chemical bonds within the material which allows multiple healing at the equivalent location. These reversible bonds have created a new way for reconstructing and reshaping the cross-linked rubber (Thajudin et al., 2021).

The most frequently used technique to create self-healing polymers is DielseAlder (DA) reactions to obtain reversible bond formation (Thakur and Kessler, 2015). DA reactions are frequently used due to its fast kinetics and mild reaction conditions. The DA reaction is a [4 + 2] cycloaddition reaction between an electron-rich diene and an electron poor dienophile producing a cyclohexene adduct that could be reverted back via retro-DA reaction (rDA) at elevated temperatures, as depicted in Figure 2.9. For example, the most iconic examples of the DA reaction is between furan and maleimide groups (Tanasi et al., 2019).

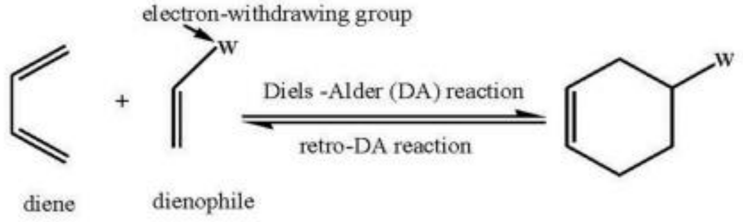

Figure 2.9 Schematic representation of thermally reversible Diels-Alder (DA) reaction of a diene with a dienophile (Tanasi et al., 2019).

Two types of reversible polymer have been fabricated: (i) polymers where the pendant groups cross-link through successive DA coupling reactions and (ii) polymers where the backbone itself is constructed through successive DA coupling reactions involving multifunctional complementary monomers. Both types of polymers can revert to their precursors through the RDA reaction and thus this feature can be applied in recycling and mending (Bergman and Wudl, 2008). For instance, Trovatti et al. (2017) demonstrated the reversible crosslinking of furan-modified natural rubber (NR) via the Diels-Alder. This work presents the concept of binding the furan-modified natural rubber with maleimide-modified nanocellulose in order to generate a covalently crosslinked composite of these two renewable polymers. Thus, this reversible crosslinking in natural rubber opens the way to a straightforward mode of recycling of tires. On the other hand, Tanasi et al. (2019) developed a self-healing natural rubber by chemically modified natural rubber through thermally reversible Diels-Alder process. The results showed that the resulting rubber compound exhibited crosslinking density and mechanical properties comparable to those of a typical vulcanized natural rubber with low sulfur content and the healing efficiency was greater than 80 %, revealing that the damage surface is able to be sealed and thus extend the life cycle while reduce the waste resources.

In contrast, Thajudin et al. (2021) studied the mechanism of self-healing natural rubber based on zinc thiolate reversible ionic network. The possible self-healing mechanism between zinc thiolate and the natural rubber chains in the presence of dicumyl peroxide to produce reversible metallic ion networks is illustrated in Figure 2.10. The results showed that this intrinsic self-healing natural rubber material has good physical and mechanical properties and it is able to restore all its properties at room temperature.

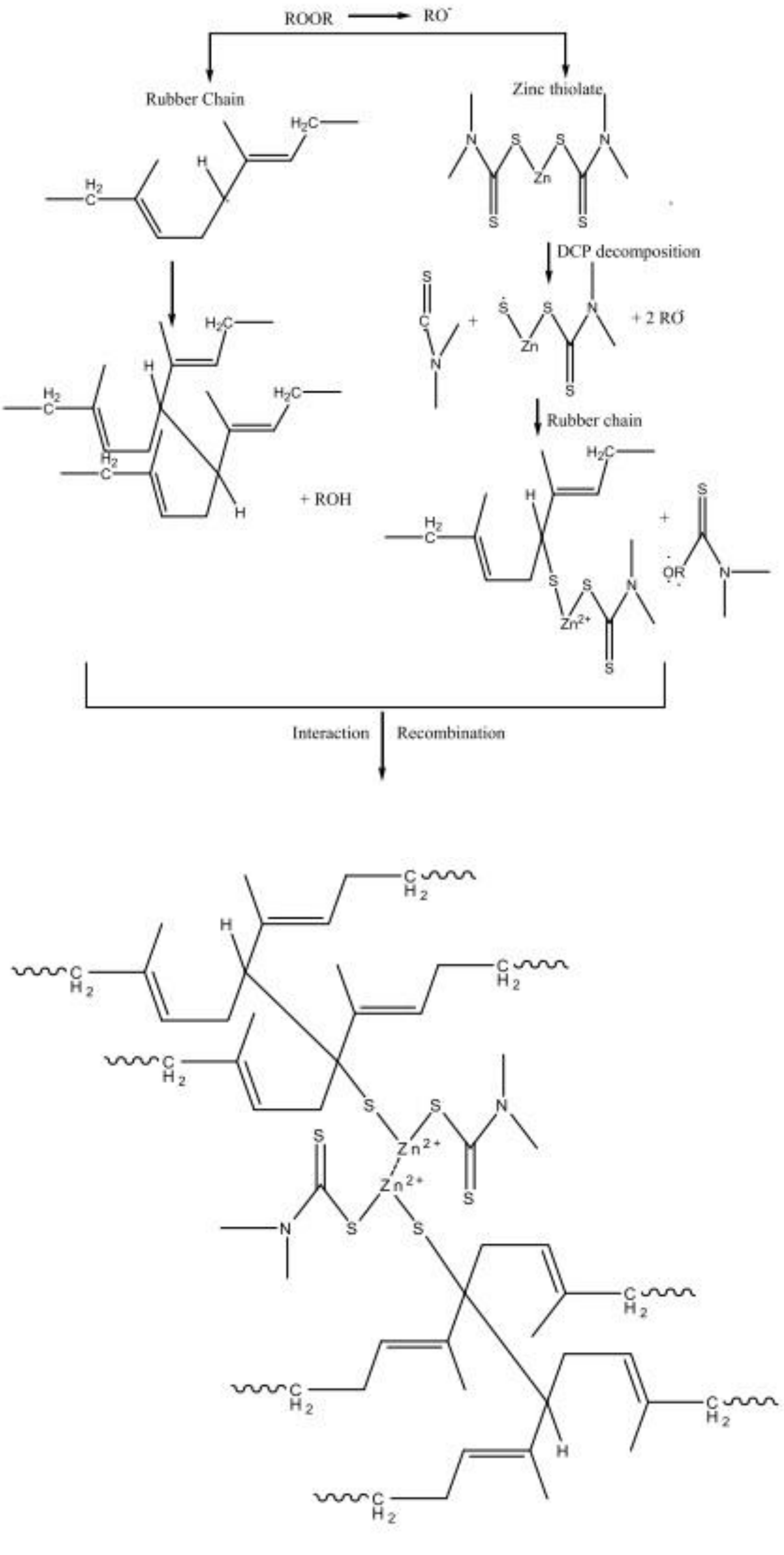

Figure 2.10 Mechanism of self-healing natural rubber through vulcanization by zinc thiolate to produce a reversible ionic network (Thajudin et al., 2021)

From Figure 2.10, the mechanism starts with homolytic dissociation of peroxides into free radicals. Once the peroxide free radical species are formed, the extremely reactive and unstable cleaved peroxide free radical species abstract allylic hydrogens from the natural rubber chains and then recombine to form a crosslink. Due to the sterically hindered in chain double bonds and also the quantum of allylic H-atoms, the addition reactions of peroxide radical species into the double bond of rubber chains are much less pronounced (Thajudin et al., 2021).

Besides react with rubber chains, peroxides free radicals might also react with zinc thiolate to form crosslink precursors. The first step in zinc thiolate vulcanization involves decomposition of zinc thiolate into persulphenyl radicals at vulcanization temperature. Without the formation of true intermediates, the zinc-containing radicals might proceed a concerted reaction between rubber chains and new C-S bonds are formed. In addition to the crosslink formation, the other radicals might react with peroxide free radical species, or with rubber chains or with radical itself. This interactive recombination among radicals and crosslink precursors forming Zn^{2+} ion intermediate and thus crosslinks increase within the material. Due to the lack of a dipole moment in the C-C bonds between rubber chains and the C-S interactions between zinc thiolate and rubber chains, these bonds are categorized as non-polar irreversible covalent bonds. It is believed that the self-healing network construction is due to vulcanized zinc thiolate on rubber chains which consists of ion pair between Zn^{2+} and two S^{-}. Interaction between ion pairs induces strong electrostatic interaction between neighbouring Zn^{2+} ion intermediates, leading to formation of ionic multiplets. This ionic multiplets will then further aggregate to form ion clusters and hence restrict the flexibility and mobility of the natural rubber chains (Thajudin et al., 2021).

Besides, Zainol and Shuib (2020) demonstrated that zinc thiolate can be effortlessly graft-polymerized onto rubber chains when the rubber lattice crosslinked its covalent network during vulcanization. This reveals that zinc thiolate could be a normal ionic compound that readily responds with rubber molecules. At the same time, due to massive ion pairs in polymerized zinc thiolate molecules had solid electrostatic interaction, hence forming multiplets that strongly confined the versatility of adjoining rubber chains. Furthermore, salt-bondings were also introduced into the rubber network by Zn^{2+}, which functions as an adjoiner in the rubber-graft-Zinc thiolate. All these restrictions contributed to the total cross-link network, serving as an unused kind of crosslinking activity which is ionic crosslinks. Thus, it is clear that the ionic cross-links produced from zinc thiolate is to some degree distinctive from the previous specified ionic associations. However, this kind of ionic cross-links have not yet been implemented in self-healing rubbers (Zainol and Shuib, 2020).

2.5 Halloysite Nanotubes (HNTs)

In this study, halloysite nanotube was used as filler. Fillers are generally added to the rubber matrix to enhance the mechanical properties of rubber composites in order to meet industrial requirements (Roy et al., 2019). HNT have been discover as effective reinforcing nanofiller to develop chemical interaction between the rubber and nanoparticles (Kausar, 2018). HNT is quarried naturally from many countries around the world such as Japan, China, America, South Korea, Brazil, France, and Turkey (Gaaz et al., 2016).

Halloysite nanotube was chosen to be used in this study is due to halloysite promising reinforcing material for the development of high performance polymer composites as halloysite nanotube possesses unique combination of properties like